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Exploring and Expanding the Structural Diversity of Self-Assembling Dendrons through Combinations of AB, Constitutional Isomeric AB_2, and AB_3 Biphenyl-4-Methyl Ether Building Blocks

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Abstract: General, efficient and inexpensive methods for the synthesis of dendritic building blocks methyl 3′,4′-dihydroxybiphenyl-4-carboxylate, 3′,5′-dihydroxybiphenyl-4-carboxylate, and methyl 3′,4′,5′-trihydroxybiphenyl-4-carboxylate were elaborated. In all syntheses the major step involved an inexpensive Ni^{II}-catalyzed Suzuki cross-coupling reaction. These three building blocks were employed together with methyl 4′-hydroxybiphenyl-4-carboxylate in a convergent iterative strategy to synthesize seven libraries containing up to three generations of 3′,4′-, 3′,5′-, and 3′,4′,5′-substituted biphenyl-4-methyl ether based amphiphilic dendrons. These dendrons self-assemble into supramolecular dendrimers that self-organize into periodic assemblies. Structural and retrostructural analysis of their assemblies demonstrated that these dendrons self-assemble into hollow and non-hollow supramolecular dendrimers exhibiting dimensions of up to twice those reported for architecturally related dendrons based on benzyl ether repeat units. These new dendrons expand the structural diversity and demonstrate the generality of the concept of self-assembling dendrons based on amphiphilic arylmethyl ethers.

Keywords: dendrons • liquid crystals • porous columns • self-assembly • supramolecular chemistry

Introduction

Self-assembling dendrons and dendrimers accessed by divergent[1] and convergent[2] synthetic methods provide some of the most powerful monodisperse nonbiological architectures[3–5] available to investigate the principles by which primary structure determines the formation of three-dimensional structure in macromolecules.[6] Current architectures that enable the elaboration of self-assembling dendrons that provide supramolecular dendrimers able to self-organize in periodic arrays[5] are elaborated from dendrons containing anisotropic mesogenic repeat units,[7a–f,r] mesogenic dendrons and dendrimers,[7g,k] amorphous or liquid dendrimers containing mesogenic groups on their periphery,[7a,g] amphiphilic dendrons based on benzyl ether[8–12] and phenylpropyl ether units,[13] other amphiphilic dendrons,[14] and from polymer backbones dendronized with self-assembling dendrons.[15,16] A diversity of new periodic[8d,11,12a,b] and quasiperiodic[12b] lattices were discovered by the structural and retrostructural analysis of ordered arrays generated from self-assembling dendrons. Our laboratory explores functionalized benzyl ether[8–12] and phenylpropyl ether[13] based dendrons to assess the structural origin of functions,[6] according to biological principles, by studying their three-dimensional tertiary and quaternary assemblies. The dimensions of current three-dimensional structures generated from self-assembling dendrons are limited both by the dendritic architecture and by the chemical structure of their repeat unit. The transition from benzyl ether[9b] to phenylpropyl ether[13] and to more-complex hybrid dendrons generated from combinations of $(AB)_y$–AB_3 and $(AB)_y$–AB_2 building blocks[10] increased the

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dimensions of supramolecular structures from less than 70 Å to up to 217 Å. Here we report the replacement of 4-, 3,4-, 3,5-, and 3,4,5-substituted benzyl ether repeat units from amphiphilic self-assembling dendrons with the architecturally related biphenyl-4-methyl ether to explore the scope and limitations of these new dendritic architectural motifs.

Results and Discussion

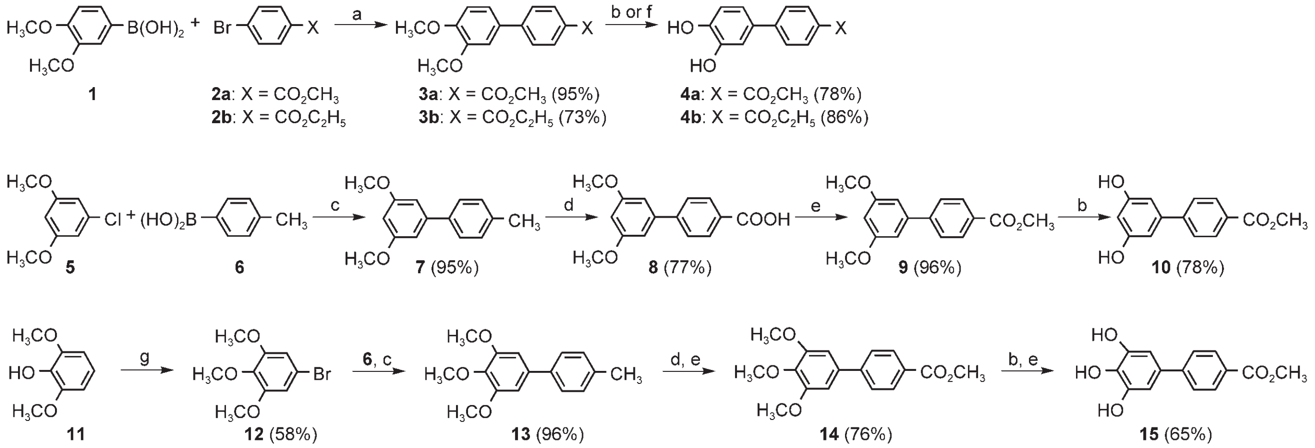
Synthesis: The esters of the constitutional isomeric 3′,4′- and 3′,5′-dihydroxybiphenyl-4-carboxylic acids (**4a**,**b** and **10**) and of 3′,4′,5′-trihydroxybiphenyl-4-carboxylic acid (**15**) were selected as starting building blocks for the synthesis of the novel library of self-assembling dendrons. They are architecturally related to the benzyl ether and phenylpropyl ether dendrons reported previously by us. Scheme 1 outlines the synthesis of these building blocks.

The synthesis of 3,4-(dimethoxy)phenyl-1-boronic acid **1** was accomplished according to a literature procedure.[17] The lithiation of 1-bromo-3,4-dimethoxybenzene with *n*BuLi at −78 °C was performed in THF under N_2 for 2.5 h. Subsequently, $B(OMe)_3$ was added as the reaction mixture was allowed to warm to 22 °C over 14 h. Finally, the reaction mixture was treated with 15% HCl at 22 °C to afford the boronic acid **1** in 64.9% yield. 1-Bromo-3,4-dimethoxybenzene was synthesized by the electrophilic bromination of 1,2-dimethoxybenzene with *n*-bromosuccinimide in acetone.[18a] Methyl and ethyl 4-bromobenzoate (**2a**,**b**) were synthesized from the corresponding commercially available acid by esterification with MeOH (EtOH) using H_2SO_4 as catalyst at reflux for 18 h. The Suzuki coupling of **1** with **2a**,**b**, catalyzed by freshly prepared $[Pd(PPh_3)_4]$,[18b] produced methyl and ethyl 3′,4′-dimethoxybiphenyl-4-carboxylates (**3a**,**b**) in 95 and 73% yields, respectively. This Suzuki reaction can also be catalyzed by $[NiCl_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane).[19] Compound **3a** was subsequently deprotected with BBr_3[20] to give **4a** (78%). Compound **3b** was treated with pyridinium hydrochloride[21] (PyHCl) to yield a mixture of **4b** and the corresponding acid was subsequently esterified by using a saturated solution of dry HCl in EtOH to give **4b** in 86% overall yield.

The 3′,5′-dihydroxybiphenyl building block was prepared in a similar way. 4-Methylphenylboronic acid (**6**)[22] was cross-coupled with the commercially available 1-chloro-3,5-dimethoxybenzene (**5**) by using an in situ prepared Pd complex with 2-(di-*tert*-butylphosphino)biphenyl as catalyst[23] to give the desired 3′,5′-dimethoxy-4-methylbiphenyl **7** in 95% yield. When this cross-coupling was catalyzed by $[NiCl_2(dppe)]/PPh_3$, **7** was obtained in 86% yield.[19] Previously, the synthesis of **7** was accomplished by the Pd-catalyzed cross-coupling of 1-iodo-3,5-dimethoxybenzene, which was prepared in several steps from 1-chloro-3,5-dimethoxybenzene, with **6**.[24] After oxidation of **7** with $KMnO_4$ to acid **8** (77%) and esterification with $MeOH/H_2SO_4$ (96%), the methoxy groups were deprotected with BBr_3 to afford methyl 3′,5′-dihydroxybiphenyl-4-carboxylate (**10**) in 78% yield.

The 3′,4′,5′-trihydroxy derivative **15** was synthesized by a related sequence of reactions. 2,6-Dimethoxyphenol (**11**) was deprotonated with NaH in a mixture of $CHCl_3$ and MeOH and brominated with *N*-bromosuccinimide (NBS) at −60 °C for 2 h, then warmed to 22 °C and heated to reflux for 1 h to give 4-bromo-2,6-dimethoxyphenol.[25] The methylation of 4-bromo-2,6-dimethylphenol with Me_2SO_4 produced 1-bromo-3,4,5-trimethoxybenzene (**12**) in 58% overall yield starting from **11**. $[NiCl_2(dppe)]/PPh_3$-catalyzed[19] cross-coupling of **12** with **6** produced **13** in 96% yield. Oxidation of **13** with $KMnO_4$ followed by acid-catalyzed esterification with MeOH generated **14** in 76% yield. Compound **14** was demethylated with BBr_3 and subsequently esterified at reflux with MeOH by using H_2SO_4 as catalyst to produce **15** in 65% yield.

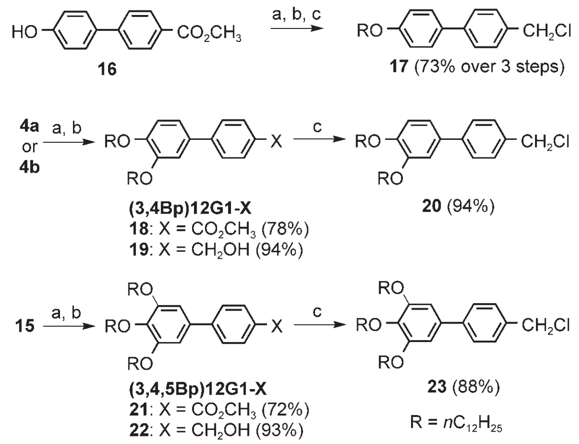
These three new building blocks, together with 4-[4′-(*n*-dodecan-1-yloxy)phenyl]benzyl chloride (**11**), prepared as previously reported,[26] were employed in the synthesis of seven libraries of dendrons. The synthesis of the dendrons



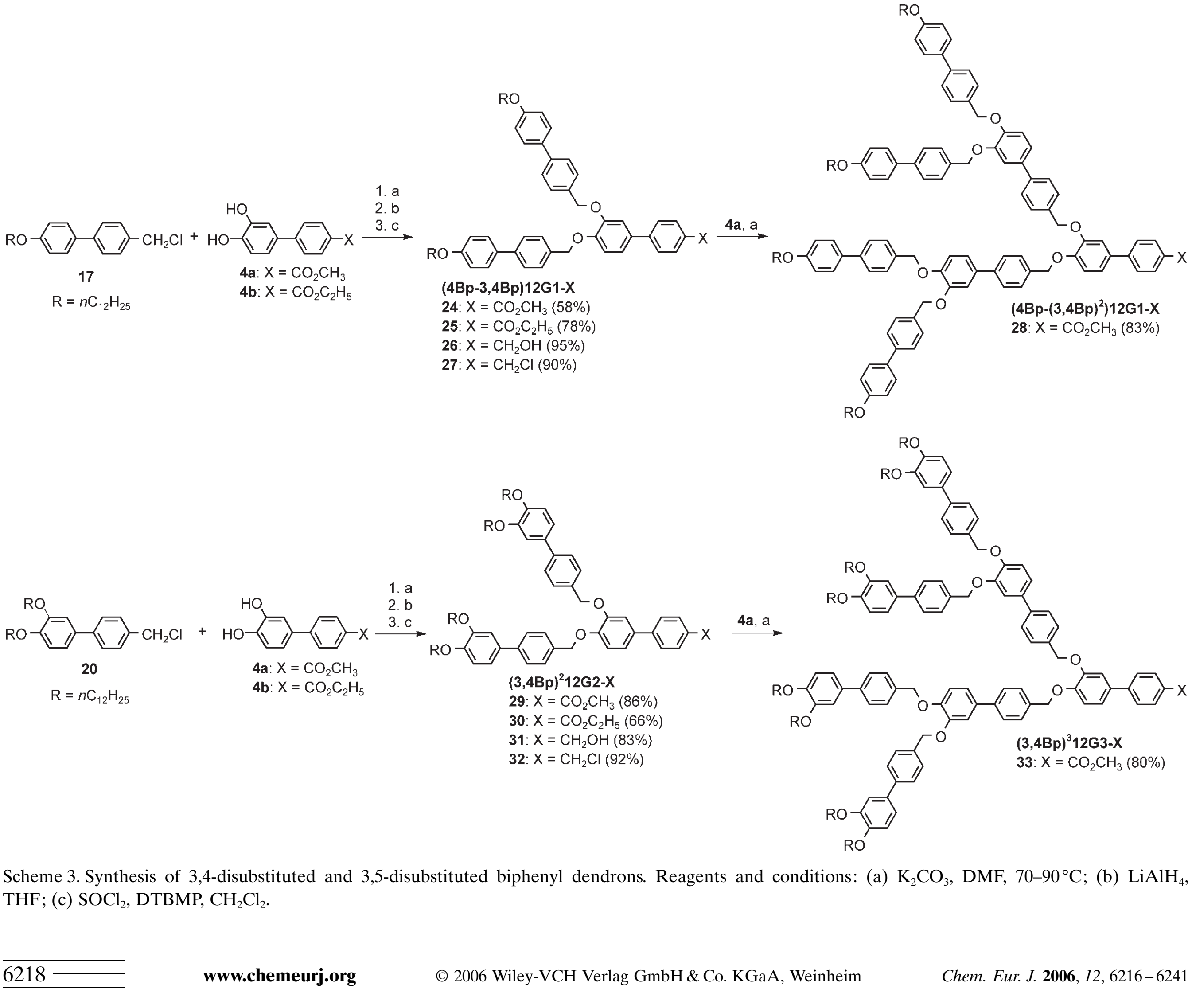
Scheme 1. Synthesis of biphenyl building blocks. Reagents and conditions: (a) $[Pd(PPh_3)_4]$, Na_2CO_3, H_2O, toluene, EtOH, reflux; (b) BBr_3, CH_2Cl_2, 0–20 °C; (c) $[NiCl_2(dppe)]/PPh_3$, K_3PO_4, toluene, 80 °C; (d) $KMnO_4$, pyridine/H_2O (1:1); (e) MeOH, H_2SO_4 (cat.), reflux; (f) (i) PyHCl, 190 °C; (ii) EtOH, HCl; (g) (i) NBS, NaH, $CHCl_3$; (ii) Me_2SO_4, K_2CO_3.

was accomplished by using the convergent strategy[2] developed in our laboratory for the synthesis of dendritic benzyl ethers.[8d]

The building blocks **16**, **4a**, **4b**, and **15** were etherified with 1-bromododecane. The resulting ethers were reduced with $LiAlH_4$ and chlorinated with $SOCl_2$ to generate **17**, **20**, and **23** (Scheme 2). For simplicity, the nomenclature of biphenyl derivatives employs, for example, 3,4,5- rather than 3′,4′,5′-. This facilitates an easy comparison with the corresponding benzyl ether dendrons. These compounds were used to functionalize the periphery of all dendrons. The synthesis of the first two libraries of dendrons based entirely on 3′,4′-disubstituted biphenyl-4-methyl ether internal repeat units is outlined in Scheme 3. Etherification of **4a**,**b** with **17** in DMF at 70 °C for 15 h in the presence of K_2CO_3 as base produced the first generation of biphenyl-based dendrimers **(4Bp-3,4Bp)12G1-CO$_2$CH$_3$** (**24**) and **(4Bp-3,4Bp)12G1-CO$_2$C$_2$H$_5$** (**25**) in 58 and 78 % yields, respectively. The reduction of **24** with $LiAlH_4$ in THF at 0–50 °C produced 95 % of **(4Bp-3,4Bp)12G1-CH$_2$OH** (**26**) after 4 h reaction time. Chlorination of **26** with $SOCl_2$ in CH_2Cl_2 at 40 °C for 4 h in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) proton trap[27] afforded **27** in 90 % yield. The second generation, **(4Bp-(3,4Bp)^2)12G2-CO$_2$CH$_3$** (**28**), was prepared by the etherification of **4a** with **27** in DMF at 70 °C for 48 h under N_2 in 83 % yield. At this generation, the lower solubility of both **27** and of the product **28** limited the synthesis of



Scheme 2. Synthesis of the building blocks from the periphery of dendrons. Reagents and conditions: (a) $C_{12}H_{25}Br$, K_2CO_3, DMF, 90 °C; (b) $LiAlH_4$, THF, 0 °C; (c) $SOCl_2$, DMF (cat.), CH_2Cl_2.



Scheme 3. Synthesis of 3,4-disubstituted and 3,5-disubstituted biphenyl dendrons. Reagents and conditions: (a) K_2CO_3, DMF, 70–90 °C; (b) $LiAlH_4$, THF; (c) $SOCl_2$, DTBMP, CH_2Cl_2.

higher generations from this library. Compound **28** was almost insoluble in all organic solvents, except for hot chloroform. Column chromatography and recrystallization from chloroform yielded white crystalline **28**.

The second library from the 3′,4′-series contains 3′,4′-disubstituted biphenyl also on the periphery. These dendrons bear more aliphatic tails and, therefore, were expected to be more soluble in organic solvents than those with 4′-3′,4′-substitution pattern on the periphery of the aromatic region. The bottom part of Scheme 3 outlines the synthesis of the first three generations of the **(3,4Bp)*ⁿ*12G*n*-X** dendrons. The first-generation dendron **(3,4Bp)12G1-CO_2CH_3 (18)** was prepared by etherification of **4a** with 1-bromododecane under the usual conditions in 78% yield (Scheme 2). Compound **18** was reduced with $LiAlH_4$ (94%) and subsequently chlorinated with $SOCl_2$ (94%) to give **20**. The etherification of **4a**,**b** with **20** in DMF at 70°C under N_2 for 15 h in the presence of K_2CO_3 afforded **$(3,4Bp)^2$12G2-CO_2CH_3** (**29**) and **$(3,4Bp)^2$12G2-$CO_2C_2H_5$** (**30**) in 86 and 66% yields, respectively. The esters **29** and **30** were purified by column chromatography with $CHCl_3$ as eluent followed by recrystallization from EtOAc. The synthesis of the third generation of this series involved the reduction of **29** with $LiAlH_4$ to produce alcohol **31** (83%). Compound **31** was chlorinated to **$(3,4Bp)^2$12G2-CH_2Cl** (**32**) (92%). Etherification of **4a** with **32** in DMF at 80°C for 15 h under N_2 with K_2CO_3 as base afforded **$(3,4Bp)^3$12G3-CO_2CH_3** (**33**) in 80% yield. Compound **33** was more soluble than **28** and, therefore, was purified by recrystallization from EtOH.

The following three libraries consist of dendrons containing biphenyl building blocks with the substitution pattern **(4Bp-3,4Bp-3,5Bp)12G2-X** and **($(3,4Bp)^a$-$(3,5Bp)^b$)12G*n*X** ($n=a+b$; $a=1$, 2; $b=0$, 1). Their synthesis is outlined in Scheme 4.

Similarly, **(4Bp-3,4Bp-3,5Bp)12G1-CO_2CH_3** (**34**) was prepared by etherification of **10** and **27**. The limited solubility of **34** allowed purification only by column chromatography with $CHCl_3$/hexanes as eluent. Reduction of **34** with $LiAlH_4$ generated **35** in 77% yield. Compound **($(3,4Bp)^2$-3,5Bp)12G3-CO_2CH_3** (**36**) was prepared by the etherification of **10** with **32** in 74% yield. Dendron **36** was soluble in hexanes. The dramatic increase in solubility of **36** versus **28**, **34**, and **35** provides a remarkable example of the dendritic-architecture effect. The second-generation dendron **(3,4Bp-3,5Bp)12G2-CO_2CH_3** (**37**) was prepared by etherification of **10** with the chloride **20** under the standard conditions in 69% yield. Reduction of **37** with $LiAlH_4$ produced **38** in 85% yield. Chlorination of **38** with $SOCl_2$ generated **39** in 87% yield. Etherification of **10** with **39** afforded the third-generation dendron **(3,4Bp-$(3,5Bp)^2$)12G3-CO_2CH_3** (**40**) (85%).

The synthesis of the last two libraries of dendrons is outlined in Scheme 5. Both libraries are based on 3′,4′,5′-trisubstituted and 3′,5′-disubstituted biphenyl-4-methyl ether repeat units. Etherification of **17** with **15** produced first-generation **(4Bp-3,4,5Bp)12G1-CO_2CH_3** (**41**) in 83% yield. Compound **41** was reduced with $LiAlH_4$ to generate **42** (87%), whose chlorination with $SOCl_2$ produced **43** in 94% yield. The etherification of **10** with **43** yielded 83% of **(4Bp-3,4,5Bp-3,5Bp)12G2-CO_2CH_3** (**44**). Reduction of **44** with $LiAlH_4$ produced **45**. The final library contains 3′,4′,5′-biphenyl repeat units both on the periphery and in the inner part of the dendron. Compound **$(3,4,5Bp)^2$12G2-CO_2CH_3** (**46**) (82%) was obtained by the etherification of **15** with **23**. Compound **46** was reduced with $LiAlH_4$ to produce **47** (95%). The chlorination of **47** with $SOCl_2$ in the presence of DTBMP yielded **48** (95%). Dendron **$(3,4,5Bp)^3$12G3-CO_2CH_3** was obtained in 59% yield by the etherification of **15** with **48**. The structure and >99% purity of all dendrons were demonstrated by a combination of ^1H and ^{13}C NMR, HPLC, and MALDI-TOF analyses.

Structural and retrostructural analysis: The phase behavior of all dendrons was analyzed by a combination of differential scanning calorimetry (DSC), thermal optical polarized microscopy (TOPM), and small- and wide-angle X-ray diffraction (XRD) analysis carried out on powder and aligned fibers.[6,8c,d,9b,10]

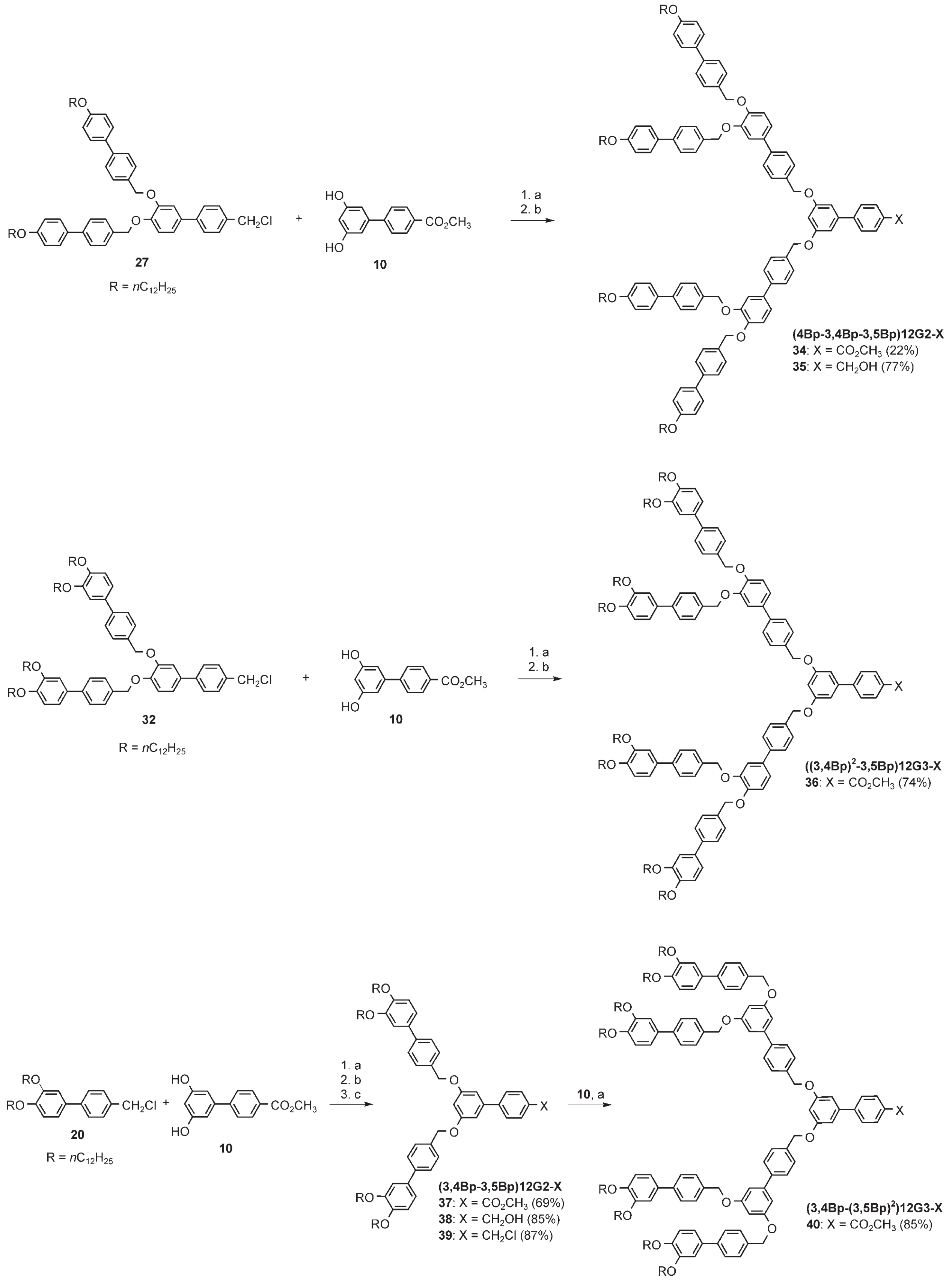
Figure 1 shows the DSC traces obtained from the first and second heating and from the first cooling scans. Crystalline phases were not determined. However, all smectic, columnar and cubic phases were analyzed.

Table 1 summarizes the phase behavior of all dendrons that exhibit, in addition to crystalline phases, various liquid-crystal (LC) phases with lattices of different symmetries. The *d* spacings and lattice symmetries are summarized in Table 2.

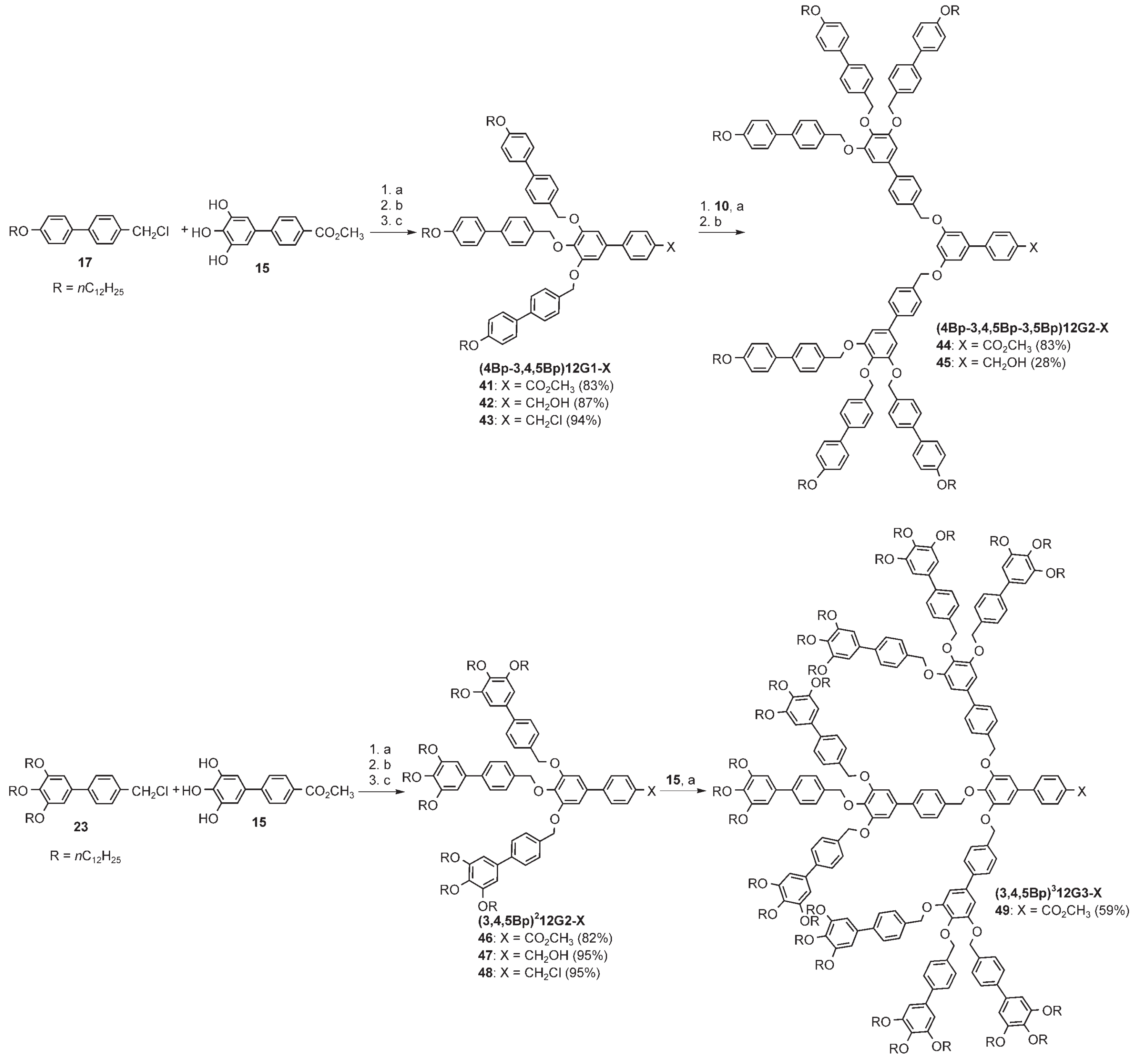
Table 3 reports the lattices dimensions (*a*,*b*), the experimental densities (ρ_{20}), the diameters of supramolecular dendrimers (D_{exp}), the number of dendrons in the supramolecular sphere or in the 4.7-Å[9b,10,13] cross-section of a supramolecular column (μ), and the projection of the solid angle of the dendron (α').

All three first-generation dendrons of the (4-3,4) or (4-3,5) series with ester groups in their apex, that is, **(4Bp-3,4Bp)12G1-CO_2CH_3**, **(4Bp-3,4Bp)12G1-$CO_2C_2H_5$**, and **(4Bp-3,5Bp)12G1-CO_2CH_3**, show one or two crystalline and one smectic (S) LC mesophases with isotropization temperatures of 209.7, 204.3, and 147.2°C, respectively (Scheme 6).

These smectic phases have interlayer separations of $a=$ 39.7–40.6 Å. The molecular-model length of a dimerlike arrangement of these dendrons in their all-*trans* configuration is 74.2 Å. This suggests that the molecules are paired up in a parallel fashion forming an interdigitated bilayer structure. Such an arrangement is known for rodlike molecules, such as unbranched biphenyls.[28] In the case of **(4Bp-3,4Bp)12G1-CH_2OH**, the smectic phase is replaced by a simple rectangular columnar (*p*2*mm*, $\Phi_{r\text{-}s}$) phase whose lattice parameters are $a=70.9$ and $b=89.3$ Å at 160°C. As expected, the lattice parameter *a* is slightly smaller than twice the interlayer distance of the highly interdigitated smectic systems, such as those found in **(3,4Bp)12G1-CO_2CH_3**. This corresponds to $D_a=70.9$ Å and $D_b=89.3$ Å, respectively. Therefore, the hydroxyl groups present in **(4Bp-**



Scheme 4. Synthesis 3,5-disubstituted biphenyl dendrons. Reagents and conditions: (a) K$_2$CO$_3$, DMF, 70–90°C; (b) LiAlH$_4$, THF; (c) SOCl$_2$, DTBMP, CH$_2$Cl$_2$.



Scheme 5. Synthesis 3,4,5-trisubstituted biphenyl dendrons. Reagents and conditions: (a) K_2CO_3, DMF, 70–90 °C; (b) $LiAlH_4$, THF; (c) $SOCl_2$, DTBMP, CH_2Cl_2.

3,4Bp)12G1-CH$_2$OH are inducing the formation of hydrogen bonds that prevent a parallel arrangement, such as that in the smectic examples mentioned above.

The second-generation dendron **(4Bp-(3,4Bp)^2)12G2-CO$_2$CH$_3$** also forms a simple rectangular LC phase (*p*2*mm*, $\Phi_{r\text{-}s}$) at temperatures above 90.9 °C. The lattice dimensions and column diameters are $a = 83.5$ Å, $b = 132.9$ Å, and $D_{col} =$ 83.5 and 132.9 Å. This is one of the largest D_{col} diameters of a supramolecular dendrimer reported so far. Results of DSC indicates decomposition at the isotropization temperature of ~285 °C (Figure 1). However, TOPM analysis revealed that slow decomposition already begins at lower temperatures and, therefore, XRD studies at higher temperatures were not possible.

The replacement of the inner 3′,4′-disubstituted biphenyl repeat unit by a 3′,5′-disubstituted biphenyl repeat unit gives the dendron **(4Bp-3,4Bp-3,5Bp)12G2-CO$_2$CH$_3$** (Scheme 6, right column). The introduction of this 3′,5′-disubstituted biphenyl repeat unit decreases the isotropization temperature by ~80 °C. Dendron **(4Bp-3,4Bp-3,5Bp)12G2-CO$_2$CH$_3$** forms a smectic phase at low temperatures and self-assembles into a columnar hexagonal (*p*6*mm*, Φ_h) lattice, with a column diameter of 85.7 Å at higher temperatures. The X-ray plot shows slightly enhanced d_{110} and d_{200} peaks. The detailed structure of this supramolecular column will be discussed later. At 210 °C, **(4Bp-3,4Bp-3,5Bp)12G2-CO$_2$CH$_3$** self-assembles into supramolecular spheres forming a cubic phase (Scheme 6). The molecular weight (MW = 533 583.5) and di-

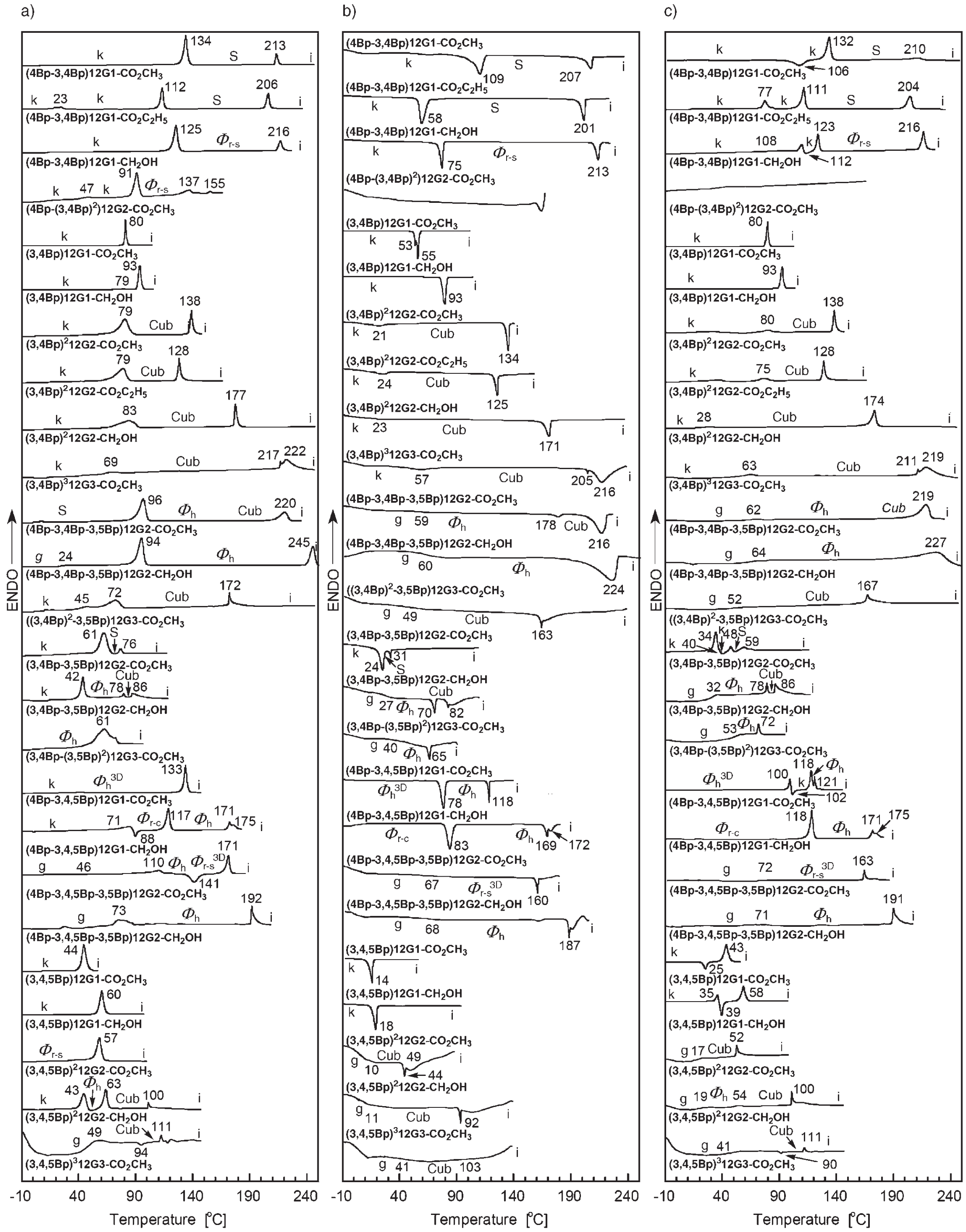


Figure 1. DSC traces [10 °C min^{-1}] of biphenyl-based dendrons. Transition temperatures [°C] are marked on each trace: (a) first heating scan; (b) first cooling scan; (c) second heating scan. Peak intensities are not scaled.

ameter (117.6 Å) of this supramolecular sphere reveal the largest dendritic supramolecular sphere achieved so far.[9b,10,13] This sphere is generated by the assembly of 261 dendrons. The replacement of the methyl ester from the apex of **(4Bp-3,4Bp-3,5Bp)12G2-CO$_2$CH$_3$** with CH$_2$OH provides **(4Bp-3,4Bp-3,5Bp)12G2-CH$_2$OH** that self-assembles in a Φ_h phase.

The second series of dendrons based on biphenyl building blocks reported here contains only 3,4-disubstituted biphenyl repeat units on their periphery (Scheme 7). The first-generation dendron from this series, that is, **(3,4Bp)12G1-X** (X = CO$_2$CH$_3$, CH$_2$OH), does not exhibit a mesophase. However, all dendrons of the second and third generations, that is, **(3,4Bp)^{2}12G2-X** (X = CO$_2$CH$_3$, CO$_2$C$_2$H$_5$, and

Table 1. Thermal transitions of supramolecular dendrimers self-assembled from dendrons containing biphenyl building blocks, determined by DSC.

Dendron	Thermal transitions [°C] and corresponding enthalpy changes [kcal mol^{-1}][a]	
	heating	cooling
(4Bp-3,4Bp)12G1-CO$_2$CH$_3$	k[b] 133.7 (19.37) S[c] 213.4 (3.55) i[d]	i 206.9 (2.70) S 109.4 (7.25) k
	k 105.9 (−8.82) k 132.2 (17.88) S 209.7 (2.73) i	
(4Bp-3,4Bp)12G1-CO$_2$C$_2$H$_5$	k 23.4 (1.17) k 112.3 (5.87) S 205.6 (4.00) i	i 200.8 (3.84) S 58.1 (7.57) k
	k 76.9 (2.38) k 111.0 (5.29) S 204.3 (3.93) i	
(4Bp-3,4Bp)12G1-CH$_2$OH	k 124.5 (20.44) $\Phi_{\text{r-s}}$[e] 216.1 (5.77) i	i 212.6 (5.62) $\Phi_{\text{r-s}}$ 75.4 (7.66) k
	k 108.0 (1.79) 112.6 (−0.76) k 122.8 (3.83) $\Phi_{\text{r-s}}$ 215.5 (5.72) i	
(4Bp-(3,4Bp)^2)12G2-CO$_2$CH$_3$	k 47.1 (0.56) k 90.7 (6.17) $\Phi_{\text{r-s}}$ 136.9 (1.21) 155.2 (0.25)[i]	–
(3,4Bp)12G2-CO$_2$CH$_3$	k 80.2 (17.93) i	i 55.4 (7.91)[k] 52.7[j] k
	k 79.9 (16.96) i	
(3,4Bp)12G2-CH$_2$OH	k 78.8 (0.15) 92.8 (16.32) i	i 92.8 (10.48) k
	k 92.7 (16.32) i	
(3,4Bp)^{2}12G2-CO$_2$CH$_3$	k 79.1 (9.25) Cub[h] 137.9 (4.30) i	i 134.2 (4.09) Cub 20.8 (0.57) k
	k 79.5 (1.67) Cub 137.7 (4.34) i	
(3,4Bp)^{2}12G2-CO$_2$C$_2$H$_5$	k 78.6 (9.20) Cub 128.0 (4.52) i	i 124.5 (4.67) Cub 23.6 (1.28) k
	k 74.5 (1.66) Cub 127.8 (4.49) i	
(3,4Bp)^{2}12G2-CH$_2$OH	k 83.0 (9.21) Cub 176.7 (5.22) i	i 170.7 (5.24) Cub 23.0 (0.14) k
	k 28.2 (0.60) Cub 174.0 (5.46) i	
(3,4Bp)^{3}12G3-CO$_2$CH$_3$	k 68.7 (1.24) Cub 217.0 222.1[j] (6.62)[k] i	i 216.5 (6.17)[k] 203.8[j] Cub 57.4 (0.88) k
	k 63.3 (1.04) Cub 211.2 219.0[j] (6.46)[k] i	
(4Bp-3,4Bp-3,5Bp)12G2-CO$_2$CH$_3$	S 96.3 (27.10) Φ_{h}[f] Cub 220.3 (11.76) i	i 216.2 (11.47) Cub 178.0 (0.93) Φ_{h} 59.1 g
	g[l] 61.7 Φ_{h} Cub 218.8 (11.40) i	
(4Bp-3,4Bp-3,5Bp)12G2-CH$_2$OH	g 24.9 94.0 (17.09) Φ_{h} 244.6 (9.52) i	i 224.1 (5.44) Φ_{h} 60.5 g
	g 63.6 Φ_{h} 226.8 (4.35) i	
((3,4Bp)^2-(3,5Bp))12G3-CO$_2$CH$_3$	k 45.4 (1.06) 71.6 (7.17) Cub 171.6 (4.12) i	i 163.2 Cub 48.9 g
	g 51.7 Cub 166.7 (4.10) i	
(3,4Bp-3,5Bp)12G2-CO$_2$CH$_3$	k 61.3 (13.85) S 75.9 (1.24) i	i 31.3 (0.62) S 24.0 (4.33) k
	k 34.5 (6.15) k 40.4 (−1.92) k 47.6 (0.90) S 59.4 (2.11) i	
(3,4Bp-3,5Bp)12G2-CH$_2$OH	k 42.2 (4.15) Φ_{h} 78.1 (0.41) Cub 86.0 (0.96) i	i 81.7 (1.13) Cub 69.9 (0.74) Φ_{h} 27.0 g
	g 31.7 Φ_{h} 78.1 (0.46) Cub 85.6 (0.93) i	
(3,4Bp-(3,5Bp)^2)12G3-CO$_2$CH$_3$	Φ_{h} 61.4 (21.25) i	i 65.3 (0.94) Φ_{h} 39.8 g
	g 53.4 Φ_{h} 72.2 (0.83) i	
(4Bp-3,4,5Bp)12G1-CO$_2$CH$_3$	$\Phi_{\text{h}}^{\text{3D}}$ 133.0 (20.4) i	i 118.4 (2.32) Φ_{h} 78.1 (9.22) $\Phi_{\text{h}}^{\text{3D}}$
	$\Phi_{\text{h}}^{\text{3D}}$ 99.6 (3.98) 101.8 (−1.12) k 118.2 (3.99) Φ_{h} 121.1 (1.38) i	
(4Bp-3,4,5Bp)12G1-CH$_2$OH	k 71.5 (2.96) 88.4 (−1.47) $\Phi_{\text{r-c}}$[g] 117.2 (8.41) Φ_{h} 171.2 174.6[j] (3.44)[k] i	i 172.2 168.7[j] (3.73)[k] Φ_{h} 83.1 (7.02) $\Phi_{\text{r-c}}$
	$\Phi_{\text{r-c}}$ 117.6 (8.61) Φ_{h} 171.0 174.5[j] (3.39) i	
(4Bp-3,4,5Bp-3,5Bp)12G2-CO$_2$CH$_3$	g 46.1 109.9 (7.32) Φ_{h} 141 (−13.84) $\Phi_{\text{r-s}}^{\text{3D}}$ 170.9 (19.76) i	i 160.25 (1.43) $\Phi_{\text{r-s}}^{\text{3D}}$ 66.9 g
	g 72.3 $\Phi_{\text{r-s}}^{\text{3D}}$ 163.2 (1.72) i	
(4Bp-3,4,5Bp-3,5Bp)12G2-CH$_2$OH	g 73.2 Φ_{h} 191.9 (4.18) i	i 186.9 (3.69) Φ_{h} 67.7 g
	g 70.7 Φ_{h} 190.8 (3.99) i	
(3,4,5Bp)12G2-CO$_2$CH$_3$	k 43.7 (22.12) i	i 13.7 (13.54) k
	k 24.8 (−5.86) 43.0 (21.41) i	
(3,4,5Bp)12G2-CH$_2$OH	k 59.9 (18.32) i	i 17.7 (8.45) k
	k 35.1 (3.52) 38.9 (−9.68) 58.0 (16.35) i	
(3,4,5Bp)^{2}12G2-CO$_2$CH$_3$	$\Phi_{\text{r-s}}$ 56.5 (18.34) i	i 49.4 (0.29) Cub 43.8 (0.16) 10.0 g
	g 17.1 Cub 51.8 (1.06) i	
(3,4,5Bp)^{2}12G2-CH$_2$OH	k 43.5 (7.91) Φ_{h} 62.8 (8.65) Cub 100.2 (0.73) i	i 92.4 (0.25) Cub 11.0 g
	g 19.5 Φ_{h} 53.9 (0.30) Cub 100.2 (0.65) i	
(3,4,5Bp)^{3}12G3BpCO$_2$CH$_3$	g 49.3 k 94.0 (−0.20) Cub 111.4 (0.34) i	i 103.4 (0.16) Cub 41.4 g
	g 40.5 k 90.1 (−0.20) Cub 110.9 i	

[a] Data from the first heating and cooling scans are on the first line and data from the second heating are on the second line. [b] k = Crystalline. [c] S = Smectic phase. [d] i = Isotropic. [e] $\Phi_{\text{r-s}} = p2mm$ simple rectangular columnar lattice. [f] $\Phi_{\text{h}} = p6mm$ hexagonal columnar lattice. [g] $\Phi_{\text{r-c}} = c2mm$ centered rectangular columnar lattice. [h] Cub = $Pm\bar{3}n$ cubic lattice. [i] Sample starts to decompose. [j] Peaks of phase transition are not fully resolved. [k] Enthalpy based on two overlapped peaks. [l] g = Glassy.

CH$_2$OH) and **(3,4Bp)^{3}12G3-CO$_2$CH$_3$** self-assemble into spherical dendrimers that self-organize in a $Pm\bar{3}n$ cubic lattice (Scheme 7). The number of dendrons per single sphere (μ), calculated according to results of density measurements by using the formula $\mu = N_A abt\rho/2M$ (in which $N_A = 6.022045 \times 10^{23}$; a,b = lattice dimensions; t = average thickness of a stratum; ρ = density; M = molecular weight) is extremely high (X = CO$_2$CH$_3$: $\mu = 171$; X = CO$_2$C$_2$H$_5$: $\mu = 166$; X = CO$_2$C$_4$H$_9$: $\mu = 243$; X = CH$_2$OH: $\mu = 140$; see Table 3 and Scheme 7). This can be explained by the long and sharp shape of the conical dendrons. Consequently, the molecular weights of the formed spheres (MW) are some of the highest reported so far.

Interestingly, the diameters of the spheres formed by the esters of the second generation for **(3,4Bp)^{2}12G2-CO$_2$CH$_3$** at 125 °C is 88.6 Å, and for **(3,4Bp)^{2}12G2-CO$_2$C$_2$H$_5$** at 118 °C

Table 2. Measured *d* spacing [Å] of the smectic (S_{Ad}), *p2mm* simple rectangular columnar ($\Phi_{r\text{-}s}$), *c2mm* centered rectangular columnar ($\Phi_{r\text{-}c}$), *p6mm* hexagonal columnar (Φ_h), and $Pm\bar{3}n$ cubic (Cub) lattices generated by dendrons based on biphenyl building blocks.

Dendron	*T* [°C]	lattice	*d* Spacings and their indices												
			$d_{100}^{[a]}$	d_{200}	d_{300}										
			$d_{100}^{[b]}$	d_{110}	d_{120}	d_{030}	d_{200}	d_{220}	d_{050}	d_{330}	d_{260}	d_{010}	d_{210}	d_{020}	
			$d_{200}^{[c]}$	d_{210}	d_{211}	d_{220}	d_{222}	d_{310}	d_{320}	d_{321}	d_{400}	d_{420}	d_{421}	d_{422}	d_{520}
			$d_{100}^{[d]}$	d_{110}	d_{200}	d_{210}									
			$d_{100}^{[e]}$	d_{110}	d_{200}	d_{020}	d_{220}								
(4Bp-3,4Bp)12G1-CO$_2$CH$_3$	160	S_{Ad}	40.5[a]												
(4Bp-3,4Bp)12G1-CO$_2$C$_2$H$_5$	120	S_{Ad}	39.7[a]	19.8											
(4Bp-3,4Bp)12G1-CH$_2$OH	160	*p2mm*	70.6[b]	55.6	37.2	29.9	35.7	27.7							
(4Bp-(3,4Bp)^2)12G2-CO$_2$CH$_3$	104	*p2mm*	83.8[b]	72.2			40.8	35.5	26.4	23.4	19.5				
(3,4Bp)^{2}12G2-CO$_2$CH$_3$	125	$Pm\bar{3}n$	71.4[c]	63.5	58.3	49.9		45.2	39.8	38.1	35.5	32.2	31.4	29.1	
(3,4Bp)^{2}12G2-CO$_2$C$_2$H$_5$	118	$Pm\bar{3}n$	70.6[c]	64.1	58.7					37.9	35.5		34.1		
(3,4Bp)^{2}12G2-CO$_2$C$_4$H$_9$	93	$Pm\bar{3}n$	78.5[c]	72.2	64.8	57.1		49.5	44.9	42.5	39.5	35.9	35.1	32.7	29.6
(3,4Bp)^{2}12G2-CH$_2$OH	190	$Pm\bar{3}n$	64.1[c]	57.6	52.8	45.5	37.0			34.7	32.4		28.3	26.2	
(3,4Bp)^{3}12G3-CO$_2$CH$_3$	178	$Pm\bar{3}n$	76.4[c]	67.7	62.3					40.3	37.2		32.8		
(4Bp-3,4Bp-3,5Bp)12G2-CO$_2$CH$_3$	25	S_{Ad}	72.5[a]	36.2	24.5										
	80	*p6mm*	74.3[d]	42.6	36.7	27.5									
	210	$Pm\bar{3}n$	95.2[c]	84.6	77.3		55.6	61.4	53.2	51.6	47.6				
(4Bp-3,4Bp-3,5Bp)12G2-CH$_2$OH	120	*p6mm*	75.4[d]	41.1	35.9	26.6									
((3,4Bp)^2-3,5Bp)12G3-CO$_2$CH$_3$	110	$Pm\bar{3}n$	74.8[c]	67.7	62.1					40.0	37.5		33.0		
(3,4Bp-3,5Bp)12G2-CO$_2$CH$_3$	70	S_{Ad}	40.0[a]	19.8											
(3,4Bp-3,5Bp)12G2-CH$_2$OH	58	*p6mm*	51.9[d]	29.4	25.3										
	80	$Pm\bar{3}n$	54.7[c]	49.0	44.8					29.0	27.1		24.1		
(3,4Bp-(3,5Bp)^2)12G3-CO$_2$CH$_3$	58	*p6mm*	50.5[d]	29.0	25.1										
(4Bp-3,4,5Bp)12G1-CO$_2$CH$_3$	115	*p6mm*	57.1[d]	32.1	28.6										
(4Bp-3,4,5Bp)12G1-CH$_2$OH	110	*c2mm*		43.4[e]	55.2	23.4	21.5								
	150	*p6mm*	54.4[d]	31.1	26.9										
(4Bp-3,4,5Bp-3,5Bp)12G2-CO$_2$CH$_3$	120	*p6mm*	58.9[d]	33.7	29.2	22.1									
	168	*p2mm*	54.0[b]									38.1	22.2	19.4	
(4Bp-3,4,5Bp-3,5Bp)12G2-CH$_2$OH	150	*p6mm*	56.1[d]	32.4	28.2										
(3,4,5Bp)^{2}12G2-CO$_2$CH$_3$	25	*p2mm*	47.9[b]	37.5								27.7			
	50	$Pm\bar{3}n$	51.9[c]	46.5	43.0		33.2	28.7	27.8	26.1	23.1				
(3,4,5Bp)^{2}12G2-CH$_2$OH	43	*p6mm*	44.3[d]	25.4	22.0										
	81	$Pm\bar{3}n$	49.8[c]	44.6	40.3	35.5		31.4	27.3	26.3	24.6	22.0	21.5		
(3,4,5Bp)^{3}12G3-CO$_2$CH$_3$	100	$Pm\bar{3}n$	51.1[c]	45.9	41.9	36.7		32.5	28.4	27.4	25.6				

[a] Smectic lattice (S_{Ad}). [b] Simple rectangular columnar lattice *p2mm* ($\Phi_{r\text{-}s}$). [c] Cubic lattice $Pm\bar{3}n$ (Cub). [d] Hexagonal columnar lattice *p6mm* (Φ_h). [e] Centered rectangular columnar lattice *c2mm* ($\Phi_{r\text{-}c}$).

is 88.5 Å. These are almost the same as that of spheres formed by the third-generation dendron of this series (93.9 Å for **(3,4Bp)^{3}12G3-CO$_2$CH$_3$** at 110 °C). The length of a dimerlike arrangement of **(3,4Bp)^{2}12G2-CO$_2$CH$_3$** molecules in the all-*trans* configuration calculated from the molecular model is 72 Å and, thus, is ~20 Å smaller than the diameter of the sphere formed by these supramolecular dendrimers. However, the length of the same type of dimerlike arrangement of **(3,4Bp)^{3}12G3-CO$_2$CH$_3$** molecules is only ~94 Å (from molecular models), which is very close to the experimental diameter of the supramolecular spherical object formed by this dendron. These observations suggest some unusual structural features in the cubic phase formed by (3,4)^2 dendrons. The nature of these features will be discussed later.

The replacement of the 3,4-biphenyl repeat unit(s) closest to the apex by 3,5-biphenyl repeat units leads to dendrons that tend to self-assemble into columns that subsequently self-organize into columnar lattices, rather than form spheres, as found for the series of dendrons based on 3,4-biphenyl repeat units only (Scheme 7 middle and right columns and Scheme 6). Moreover, the isotropization temperatures of their periodic arrays decrease as the number of 3,5-biphenyl building blocks introduced rises. This behavior is similar to that observed for the corresponding dendrons based on benzyl ether repeat units.[9a]

Similar to the first-generation dendron **(4Bp-3,4Bp)12G1-CO$_2$CH$_3$**, the second-generation ester **(3,4Bp-3,5Bp)12G2-CO$_2$CH$_3$** forms a smectic mesophase with an interlayer distance of $a = 40.0$ Å at 70 °C. In the same fashion, the enhanced hydrogen-bonding interactions of the corresponding alcohol **(3,4Bp-3,5Bp)12G2-CH$_2$OH** leads to a replacement of the smectic mesophase by a columnar or cubic mesophase. Between ~30 and ~72 °C, **(3,4Bp-3,5Bp)12G2-CH$_2$OH** forms a hexagonal columnar mesophase with only 6.3 dendrons per column stratum. Between ~72 and ~85 °C, this compound self-assembles into spherical objects, which subsequently self-organize into a $Pm\bar{3}n$ cubic lattice. The number of conical dendrons per sphere, μ, is 72.7. The third-generation dendron **(3,4Bp-(3,5Bp)^2)12G3-CO$_2$CH$_3$** forms only a hexagonal columnar phase ($\mu = 3$). It is striking that the number of dendrons μ for the **(3,4Bp-(3,5Bp)$^{n-1}$)12G*n*-**

Table 3. Structural characterization of supramolecular dendrimers self-assembled from dendrons based on biphenyl building blocks.

Dendron	T [°C]	Lattice	$a(a,b)$ [Å]	ρ_{20}[f] [$g\,cm^{-3}$]	D_{exp} [Å]	μ	α'[o] [°]
(4Bp-3,4Bp)12G1-CO_2CH_3	160	S_{Ad}	40.5[a]	1.04			
(4Bp-3,4Bp)12G1-$CO_2C_2H_5$	120	S_{Ad}	39.7[a]	1.02			
(4Bp-3,4Bp)12G1-CH_2OH	160	$p2mm$	70.9; 89.3[b]	0.98	70.9; 89.3[g]	19.1[k]	18.8
(4Bp-(3,4Bp)^2)12G2-CO_2CH_3	104	$p2mm$	83.5; 132.9[b]	1.02	83.5; 132.9[g]	15.7[k]	23.0
(3,4Bp)^{2}12G2-CO_2CH_3	125	$Pm\bar{3}n$	142.7[c]	1.03	88.6[h]	171.0[l]	2.1
(3,4Bp)^{2}12G2-$CO_2C_2H_5$	118	$Pm\bar{3}n$	142.1[c]	1.02	88.5[h]	166.0[l]	2.2
(3,4Bp)^{2}12G2-$CO_2C_4H_9$	93	$Pm\bar{3}n$	162.1[c]	1.02	100.6[h]	243.4[l]	1.5
(3,4Bp)^{2}12G2-CH_2OH	190	$Pm\bar{3}n$	132.4[c]	1.02	82.2[h]	140.0[l]	2.6
(3,4Bp)^{3}12G3-CO_2CH_3	178	$Pm\bar{3}n$	151.3[c]	1.04	93.9[h]	98.3[l]	3.7
(4Bp-3,4Bp-3,5Bp)12G2-CO_2CH_3	25	S_{Ad}	72.5[a]				
	80	$p6mm$	85.7[d]	1.04	85.7[i]	8.8[m]	40.8
	210	$Pm\bar{3}n$	189.6[c]		117.6[h]	261.2[l]	1.4
(4Bp-3,4Bp-3,5Bp)12G2-CH_2OH	120	$p6mm$	80.6[d]	1.10	80.6[i]	7.7[m]	46.7
((3,4Bp)^2-3,5Bp)12G3-CO_2CH_3	110	$Pm\bar{3}n$	150.6[c]	1.02	93.4[h]	94.6[l]	3.8
(3,4Bp-3,5Bp)12G2-CO_2CH_3	70	S_{Ad}	40.0[a]	1.02			
(3,4Bp-3,5Bp)12G2-CH_2OH	58	$p6mm$	59.1[d]	1.01	59.1[i]	6.3[m]	57.0
	80	$Pm\bar{3}n$	109.1[c]		67.7[h]	72.7[l]	4.9
(3,4Bp-(3,5Bp)^2)12G3-CO_2CH_3	58	$p6mm$	58.1[d]	1.03	58.1[i]	3.0[m]	120.0
(4Bp-3,4,5Bp)12G1-CO_2CH_3	115	$p6mm$	65.4[d]	1.02	65.4[i]	7.8[m]	46.1
(4Bp-3,4,5Bp)12G1-CH_2OH	110	$c2mm$	109.5; 46.8[e]	1.08	63.2; 46.8[j]	6.1[n]	59.0
	150	$p6mm$	62.4[d]		62.4[i]	7.7[m]	46.9
(4Bp-3,4,5Bp-3,5Bp)12G2-CO_2CH_3	120	$p6mm$	67.6[d]	1.00	67.6[i]	4.0[m]	90.0
	168	$p2mm$	54.2; 38.8[b]		54.2; 38.8[g]	2.1[k]	167.9
(4Bp-3,4,5Bp-3,5Bp)12G2-CH_2OH	150	$p6mm$	45.4[d]	1.02	45.4[i]	3.6[m]	100.0
(3,4,5Bp)^{2}12G2-CO_2CH_3	25	$p2mm$	49.3; 55.6[b]	0.97	49.3; 55.6[g]	3.1[k]	115.6
	50	$Pm\bar{3}n$	104.2[c]		64.6[h]	35.9[l]	10.0
(3,4,5Bp)^{2}12G2-CH_2OH	43	$p6mm$	50.9[d]	1.02	50.9[i]	2.7[m]	131.0
	81	$Pm\bar{3}n$	99.0[c]		61.4[h]	31.2[l]	11.5
(3,4,5Bp)^{3}12G3-CO_2CH_3	100	$Pm\bar{3}n$	102.5[c]	0.99	63.6[h]	11.3[l]	31.9

[a] Smectic lattice parameter (=layer separation) $a=(d_{10}+2d_{20}+3d_{30}+4d_{40})/4$. [b] $p2mm$ simple rectangular columnar lattice parameters a and b; $a=hd$, $b=kd$; (h0) and (k0) from diffractions. [c] $Pm\bar{3}n$ cubic lattice parameter $a=(\sqrt{3}d_{110}+\sqrt{4}d_{200}+\sqrt{5}d_{210}+\sqrt{6}d_{211}+\sqrt{8}d_{220}+\sqrt{10}d_{310}+\sqrt{14}d_{321}+\sqrt{16}d_{400})/8$. [d] Hexagonal columnar lattice parameter $a=2\langle d_{100}\rangle/\sqrt{3}$; $\langle d_{100}\rangle=(d_{100}+\sqrt{3}d_{110}+\sqrt{4}d_{200}+\sqrt{7}d_{210})/4$. [e] $c2mm$ centered rectangular columnar lattice parameters a and b; $a=hd$, $b=kd$; (h0) and (k0) from diffractions. [f] ρ_{20}=experimental density at 20 °C. In cases for which ρ is not measured, it is assumed to be 1.02 $G\,cm^{-3}$. [g] Experimental elliptical column diameters of $p2mm$ simple rectangular columnar lattice $D_a=a$ and $D_b=b$. [h] Experimental $Pm\bar{3}n$ cubic spherical diameter $D=2\sqrt[3]{3a^3/32\pi}$. [i] Experimental column diameter of $p6mm$ hexagonal columnar lattice $D=2\langle d_{100}\rangle/\sqrt{3}$. [j] Experimental elliptical column diameters of $c2mm$ centered rectangular columnar lattice $D_a=a/\sqrt{3}$ and $D_b=b$. [k] Number of dendrons per elliptical $p2mm$ simple rectangular column stratum $\mu=(N_A abt\rho)/M$. [l] Number of dendrons per $Pm\bar{3}n$ spherical dendrimer $\mu=\mu'/8$, $\mu'=(a^3N_A\rho)/M$. [m] Number of dendrons per $p6mm$ hexagonal column stratum $\mu=(\sqrt{3}N_A D^2 t\rho)/2M$. [n] Number of dendrons per elliptical $c2mm$ centered rectangular column stratum $\mu=(N_A abt\rho)/2M$. [o] Projection of the solid angle for tapered and conical dendron $\alpha'=2\pi/\mu$ [°]. Avogadro's number $N_A=6.0220455\times10^{23}\,mol^{-1}$, the average height of the column stratum $t=4.7$ Å,[9b,10] M=molecular weight of dendron.

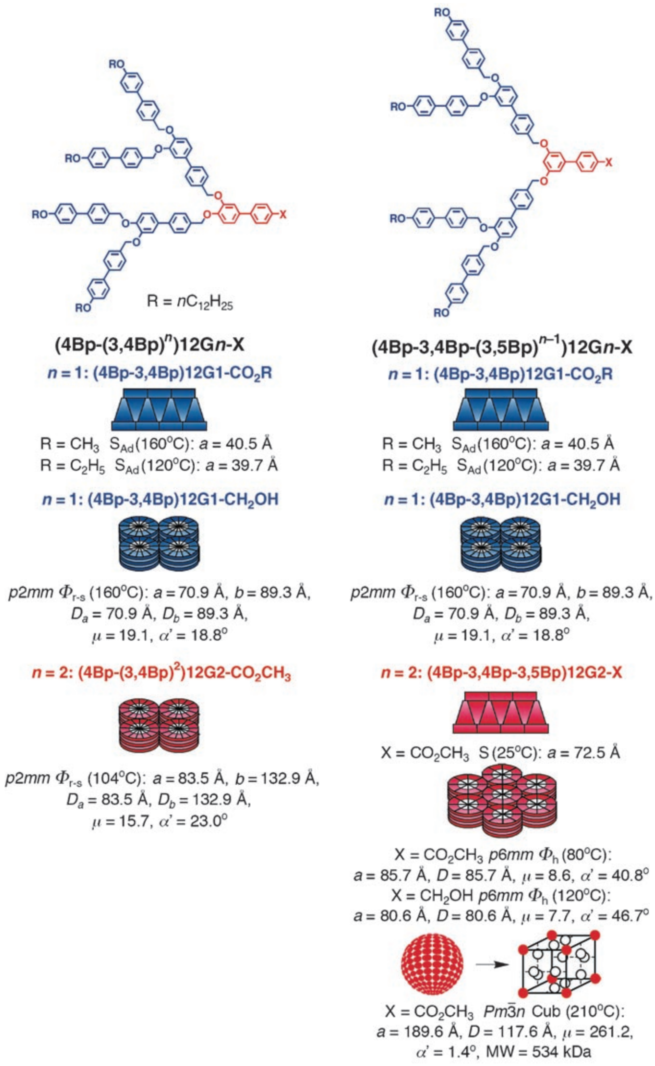
CO_2CH_3 assemblies is much lower than the μ values for the corresponding dendrons with only 3′,4′-biphenyl repeat units. This can arise from the steric hindrance due to the relatively wider 3′,5′-biphenyl repeat units. The column diameter and the lattice dimension of **(3,4Bp-(3,5Bp)^2)12G3-CO_2CH_3** are remarkably small ($D=a=58.1$ Å). This suggests a large dendron-tilt in the supramolecular column.

The dendron **((3,4Bp)^2-3,5Bp)12G3-CO_2CH_3**, which contains only one 3′,5′-biphenyl repeat unit (Scheme 7), behaves similarly to **(3,4Bp)^{3}12G3-CO_2CH_3**. The dendron **((3,4Bp)^2-3,5Bp)12G3-CO_2CH_3** forms a cubic $Pm\bar{3}n$ lattice with $\mu=94.6$ and MW = 262 997.5, which are close to the values observed for **(3,4Bp)^{3}12G3-CO_2CH_3** ($\mu=98.3$; MW = 273 283.8). The diameters of the two supramolecular spheres are also equal (93.4 versus 93.9 Å).

Scheme 8 summarizes the structural and retrostructural analysis of the libraries generated with 3′,4′,5′-trisubstituted and 3′,5′-disubstituted biphenyl dendrons. Dendrons **(4Bp-3,4,5Bp)12G1-CO_2CH_3** self-assemble into supramolecular columns that self-organize into hexagonal columnar periodic arrays. The corresponding benzyl ether requires a carboxylic or ester group at its apex to self-assemble into a supramolecular column.[9b] Interestingly, the diameter of the supramolecular column self-assembled from **(4Bp-3,4,5Bp)12G1-CO_2CH_3**, 25 Å, is larger than that self-assembled from the corresponding benzyl ether dendron containing the −COOH group at the apex. Therefore, **(4Bp-3,4,5Bp)12G1-CO_2CH_3** does not require a hydrogen-bonding group at the apex to mediate its self-assembly. This makes this self-assembling dendron a very interesting building block to mediate the self-assembly of a large diversity of functional groups in the core of its supramolecular column. Dendron **(4Bp-3,4,5Bp)12G1-CH_2OH** also self-assembles in ovoidal columns that self-organize in a centered rectangular lattice ($\Phi_{r\text{-}c}$).

The second-generation **(4Bp-3,4,5Bp-3,5Bp)12G2-X** also self-assemble into supramolecular columns. If X = CO_2CH_3, they form circular columns that self-organize in a Φ_h lattice at 120 °C and ovoidal columns that form a simple rectangular lattice ($\Phi_{r\text{-}s}$). If X = CH_2OH, the dendrons self-assemble only in circular columns forming a Φ_h lattice. Therefore, **(4Bp-3,4,5Bp)12G1-X** and **(4Bp-3,4,5Bp-3,5Bp)12G2-X** expand considerably the limited number of dendrons that self-assemble into supramolecular columns.

The final library investigated contains only 3′,4′,5′-biphenyl based dendrons. As in the case of the corresponding benzyl ether dendrons, with the exception of the first generation that is crystalline, all other generations self-assemble



Scheme 6. Retrostructural analysis of supramolecular dendrimers self-assembled from 3,4- and 3,5-disubstituted AB_2 biphenyl-based dendrons.

into spherical dendrimers that self-organize in cubic phases (Scheme 8, right column). It is, however, remarkable that **(3,4,5Bp)^{2}12G2-X** self-assemble into supramolecular columns.

Comparison of the supramolecular dendrimers based on biphenyl building blocks with that based on benzyl ether: Table 4 compares the LC phases and dimensions of the supramolecular dendrimers generated by the self-assembly of dendrons based on benzyl and biphenyl building blocks.

The abbreviated short nomenclature of the dendrons is given in the first column of Table 4: only the branching units and apex groups are given, for example, "(4-3,4)-CO_2Me" stands for **(4-3,4)12G1-CO_2CH_3** in the case of benzyl ether repeat units and for **(4Bp-3,4Bp)12G1-CO_2CH_3** in the case of biphenyl methyl ether repeat units.

In general, more LC phases are found for biphenyl-based dendrons than are reported for the corresponding benzyl ether dendrons. This can be explained by the larger functional contribution to the aromatic region by the biphenyl systems, which also increases the interactions of the aromatic part of the supramolecule. Moreover, smaller biphenyl dendrons tend to form smectic rather than hexagonal columnar LC mesophases, such as for the examples (4-3,4)-CO_2CH_3 and (3,4-3,5)-CO_2CH_3. This is not surprising as biphenyl dendrons have a rodlike architecture and, therefore, behave more like "conventional" rodlike molecules and form smectic LCs as long as other groups that provide a strong interaction (e.g., $-CH_2OH$ instead of $-CO_2H$) are not present at the apex. The longer shape of the biphenyl methyl ether repeat unit relative to that of the benzyl ether repeat unit is also responsible for the fact that **(4Bp-(3,4Bp)^2)12G2-CO_2CH_3** self-organizes into a simple rectangular columnar structure, whereas **(4-(3,4)^2)12G2-CO_2CH_3** forms a cubic ($Pm\bar{3}n$) structure.

As expected, the supramolecular objects formed by biphenyl dendrons are larger than those formed by benzyl ether dendrons. The elliptical columns formed by **(4Bp-(3,4Bp)^2)12G2-CO_2CH_3** are the largest reported so far for supramolecular dendrimers ($D_a = 83.5$, $D_b = 132.9$ Å). The largest sphere diameter ($D = 117.6$ Å) is found for the supramolecular objects formed by **(4Bp-3,4Bp-3,5Bp)12G2-CO_2CH_3**. As a comparison, the largest column diameter for benzyl ether systems found so far is 57.9 Å **(4-3,4-(3,5)^2)12G3-CO_2CH_3**, whereas the largest sphere diameter for benzyl ether systems is $D = 75.0$ Å **(4-(3,4)^3)12G3-CO_2CH_3**.[9b]

Wide-angle XRD analysis of oriented fibers: The columnar supramolecular dendrimers were also investigated by wide-angle XRD analysis on oriented fibers. A representative XRD result is shown in Figure 2.

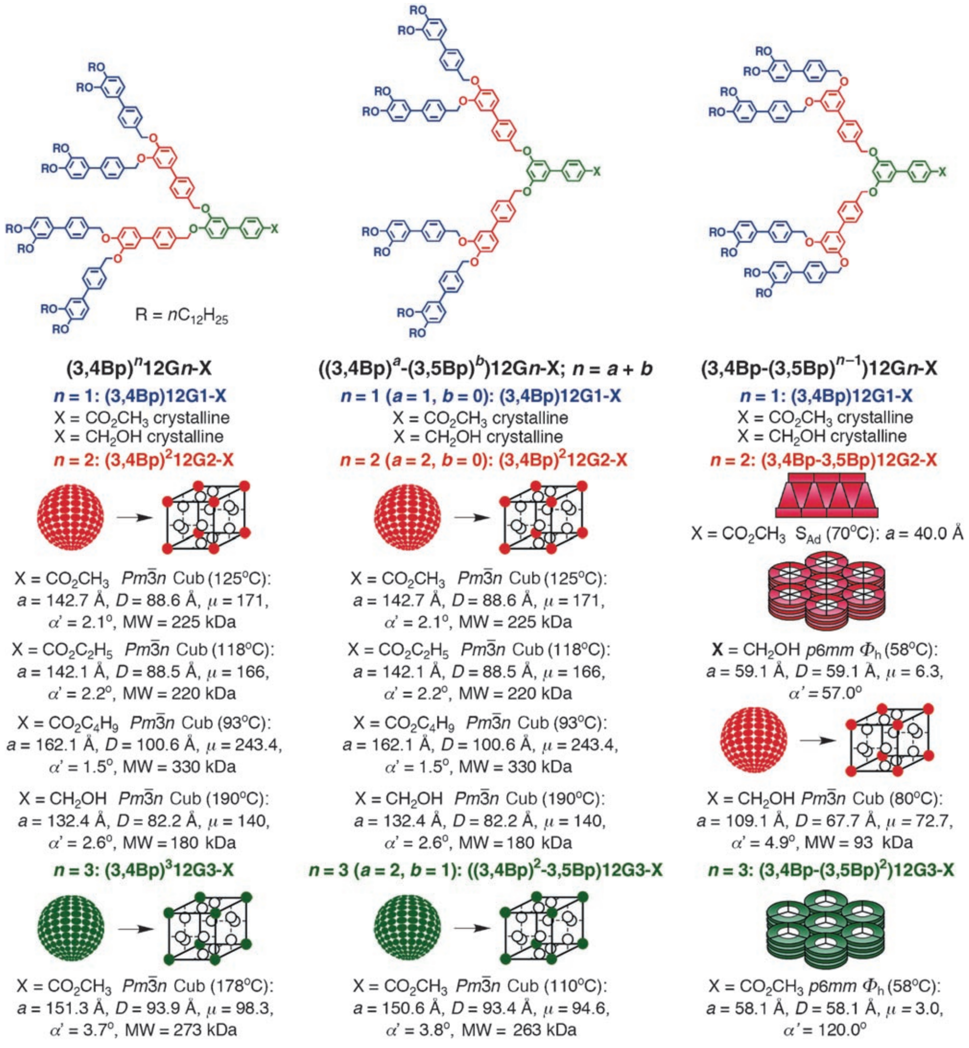
This XRD pattern demonstrates that both circular and elliptical supramolecular columns[29e] are assembled from tilted dendrons arranged in a helical arrangement.[6] Therefore, the supramolecular columns are chiral structures self-assembled from achiral building blocks. This helical arrangement was also supported by results of circular dichroism experiments.[6b]

The helical pitch i and tilt angle t (Figure 2) of the supramolecular columns were determined from oriented fiber XRD experiments as reported previously,[6] and are summarized in Table 5. The tilt of the dendron increases as the number of 3,5Bp repeat units from the inner part of the dendron increases.

Hollow supramolecular dendrons: Inspection of the intensity of the higher-order diffraction peaks of the powder wide-angle diffractograms revealed that some of the supramolecular columns exhibit a porous structure.[6b,29] Representative examples of porous columns are shown in Figures 3 and 4. The electron-density maps from Figure 3b,c were calculated from four diffraction peaks. If more diffraction peaks had been used, the minimum density of the pore would have been below that of the alkyl groups from the column[29e] periphery. The diameter of the pore (D_{pore}) of the porous columns was calculated by using the method elaborated previously[6b,e] and the results are summarized in Table 6.

The results in Table 6 indicate that the presence of the 3′,5′- and even 3′,4′,5′-biphenyl repeat units at the apex of the self-assembling dendron favor the assembly of hollow supramolecular columns.

The intensity of the XRD pattern of spherical supramolecular dendrimers was also inspected. The structures reported in Table 7 exhibit enhanced intensity of their higher-order diffraction peaks. This indicates the possible assembly of hollow supramolecular spheres. This hypothesis is also supported by the larger-than-expected diameter for the supramolecular sphere assembled from **(3,4Bp)^{2}12G2-X** building blocks (Scheme 7). A representative XRD result indicating a potential hollow sphere is shown in Figure 4b.



Scheme 7. Retrostructural analysis of supramolecular dendrimers self-assembled from 3,4- and 3,5-disubstituted AB_2 biphenyl-based dendrons.

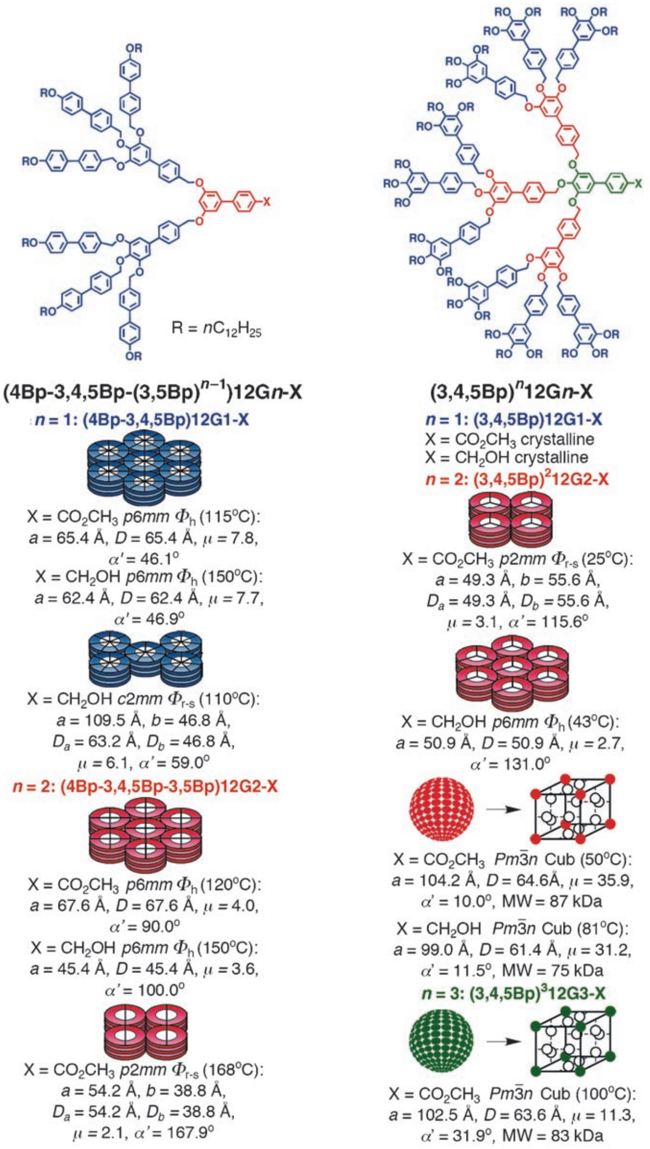
Table 4. Comparison of dimensions of columns, spheres, or interlayer distances formed by the self-organization of supramolecular dendrimers based on benzyl and biphenyl building blocks.

Branching units and apex group	Supramolecular dendrimers based on benzyl building blocks		Supramolecular dendrimers based on biphenyl building blocks	
	lattice type	D [Å][a] (T [°C])	lattice type	D [Å][a] (T [°C])
(4-3,4)-CO_2Me	Φ_h[9b]	57.6 (57)	S	40.5 (160)
(4-3,4)-CH_2OH	no LC phase[8i]	n/a	$\Phi_{r\text{-}s}$	70.9; 89.3 (160)
(4-(3,4)^2)-CO_2Me	$Pm\bar{3}n$[9b]	72.8 (89)	$\Phi_{r\text{-}s}$	83.5; 132.9 (104)
(4-3,4-3,5)-CO_2Me	Φ_h[9b]	56.7	Φ_h	84.9 (80)
			Cub	117.6 (210)
(4-3,5)-CO_2Me	no LC phase[15d]	n/a	S	40.6 (135)
(3,4)^2-CO_2R[b]	$Pm\bar{3}n$[32]	51.8 (112)	$Pm\bar{3}n$	89.6 (125)
(3,4)^2-CH_2OH	no LC phase[9b]	n/a	$Pm\bar{3}n$	81.3 (160)
(3,4)^3-CO_2R[b]	$Pm\bar{3}n$[9b]	59.6 (145)	$Pm\bar{3}n$	93.9 (178)
((3,4)^2-3,5)-CO_2Me	n/a	n/a	$Pm\bar{3}n$	93.6 (110)
(3,4-3,5)-CO_2R[b]	Φ_h[9b]	43.3 (66)	S	40.0 (70)
(3,4-3,5)-CH_2OH	Φ_h[9b]	42.6 (49)	Φ_h $Pm\bar{3}n$	59.1 (58) 67.7 (80)
(3,4-(3,5)^2)-CO_2Me	Φ_h[9b]	53.1 (36)	Φ_h	58.1 (58)
(4-3,4,5-3,5)-CO_2Me	Φ_h[9b]	47.0 (60)	Φ_h	67.6 (120)
	Φ_h[9b]	46.1 (70)	$\Phi_{r\text{-}s}$	54.2; 38.3 (168)

[a] Column or sphere diameter. [b] For the 12Gn systems, R = H; for the 12GnBp systems, R = Me. Interestingly, the corresponding esters, that is, 12Gn-CO_2Me, do not form an LC phase.

Conclusion

The design, synthesis, and self-assembly of dendrons based on AB, constitutional isomeric AB_2, and AB_3 biphenyl-4-methyl ether building blocks was described. The retrostructural analysis of the lattices self-organized from libraries of their supramolecular dendrimers revealed supramolecular structures up to twice as large as those reported previously for the architecturally related benzyl ether,[9b] and which were comparable with some of the phenylpropyl ether dendrons.[13] The lower solubility and the high transition temperatures of these biphenyl dendrons have, however, limited the number of generations accessible from these building blocks. Nevertheless, the architectures reported here com-



Scheme 8. Retrostructural analysis of supramolecular dendrimers self-assembled from 3,5-disubstituted AB_2 and 3,4,5-trisubstituted AB_3 biphenyl based dendrons.

Table 5. Data from XRD experiments on oriented fibers.

Dendron	T [°C]	Tilt angle [°]	Short-range helical pitch [Å]
(4Bp-3,4Bp)12G1-CH$_2$OH	160	0	4.5
(4Bp-3,4Bp-3,5Bp)12G2-CO$_2$CH$_3$	125	9.5	4.0
(4Bp-3,4Bp-3,5Bp)12G2-CH$_2$OH	122	10	4.6
(3,4Bp-3,5Bp)12G2-CH$_2$OH	58	20	4.4
(3,4Bp-(3,5Bp)^2)12G3-CO$_2$CH$_3$	60	29	4.0
(4Bp-3,4,5Bp-3,5Bp)12G2-CO$_2$CH$_3$	80	20	4.5

bined with concepts reported in previous publications[10,13] indicate pathways to enhance solubility, reduce thermal transitions, and access higher generations most probably via biphenylpropyl ether based dendrons.[13] It is expected that biphenylpropyl ethers together with dendritic architectural motifs based on combinations of $(AB)_y$–AB_2 and $(AB)_y$–AB_3 dendrons[10] will provide access to the design of highly dynamic[13] supramolecular structures with dimensions approaching the range required to manipulate light. These biphenyl-4-methyl ether dendrons also demonstrated that dendritic building blocks based on 3′,5′- and 3′,4′,5′-biphenyl groups at the apex allowed the discovery of, and will facilitate a new and rational strategy to design, hollow columnar and spherical supramolecular structures that were previously accessible from self-assembling dendritic dipeptides only,[6b,29] and from few examples of amphiphilic dendrons.[13] Finally, these experiments demonstrate the generality of the concept of self-assembling dendrons based on amphiphilic arylmethyl ether repeat units by transplanting them from benzyl- to biphenyl methyl ethers, thereby expanding the diversity of self-assembling amphiphilic dendrons.[9b,10,13]

Experimental Section

Materials: Al_2O_3 (activated, basic, Brokmann I, standard grade, ~150 mesh, 58 Å) and silica gel (ICN EcoChrom SiliTech 23–63 D 60 Å) were used as received. THF, dioxane, and Et_2O (Fisher, A.C.S. reagents) were refluxed over sodium ketyl and were freshly distilled before use. CH_2Cl_2 (Fisher, A.C.S. reagent) was refluxed over CaH_2 and was freshly distilled before use. MeOH, EtOH, DMSO, $CHCl_3$, HNO_3, H_2SO_4, HCl, DMF, toluene, $Na_2S_2O_3$, KOH, $MgSO_4$, K_2CO_3, Na_2CO_3, and $NaHCO_3$ (all Fisher, A.C.S. reagents) were used as received. KF (B & A), 5-chloro-1,3-dimethoxybenzene (Acros), 2-(di-*tert*-butylphosphino)biphenyl (99 %, Strem), $KMnO_4$, trimethyl borate (98 %), 1-bromododecane (98+ %), 4-bromobenzoic acid (98 %), pyridine, 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) (97 %), $Pd(OAc)_2$, and $PdCl_2$ (all from Lancaster) were used as received. *n*-Butyl lithium (2.5 or 1.6 M solution in hexanes), PPh_3 (99 %), dimethyl sulfide (anhydrous, 99 %), 4-bromobenzoic acid (98 %), neutral chromatographic Al_2O_3, $SOCl_2$ (97 %), 4-hydroxybenzoic acid (98 %), 3,4-dihydroxybenzoic acid (98 %), $LiAlH_4$ (95+ %), BBr_3 (99+ %) (all from Aldrich) were used as received.

Techniques: ^1H (200, 250, and 500 MHz) NMR spectra were recorded by using Bruker AC-200, AC-360, and DRX500 instruments. ^{13}C (90, 125 MHz) NMR spectra were recorded by using Bruker AC-360 and DRX 500 spectrometers. Melting points were measured by using a unimelt capillary melting-point apparatus (Arthur H. Thomas Company, Philadelphia, USA) and are uncorrected. Thin layer chromatography (TLC) was performed by using precoated TLC plates (silica gel with F_{254} indicator; layer thickness, 200 μm; particle size, 5–25 μm; pore size, 60 Å, SIGMA–Aldrich). HPLC analyses were performed by using a Shimadzu LC-10AT high-pressure liquid chromatograph equipped with CTO-10A column oven (40 °C), PE Nelson Analytical 900 Series integrator data station, Shimadzu RID-10A RI detector, SPD-10A UV/Vis detector (254 nm), and a PL gel column (5 μm, 100 Å). THF (Fisher, HPLC grade) was used as eluent at a flow rate of $4\,mL\,min^{-1}$. GC analysis was performed by using a Hewlett–Packard HP68 gas chromatograph. Thermal transitions were measured by using a TA Instruments 2920 modulated differential scanning calorimeter (DSC). In all cases, heating and cooling rates were $10\,°C\,min^{-1}$. Transition temperatures were reported as the maxima and minima of their endothermic and exothermic peaks. Indium was used as calibration standard. An Olympus BX-40 optical polarized microscope (100X magnification) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to verify thermal transitions. X-ray diffraction (XRD) measurements were performed by using $Cu_{K\alpha 1}$ radiation ($\lambda = 1.54178$ Å) from a Bruker–Nonius FR-591 rotating anode X-ray source equipped with a $0.2 \times 0.2\,mm^2$ filament operated at 3.4 kW. The Cu radiation beam was collimated and focused by a

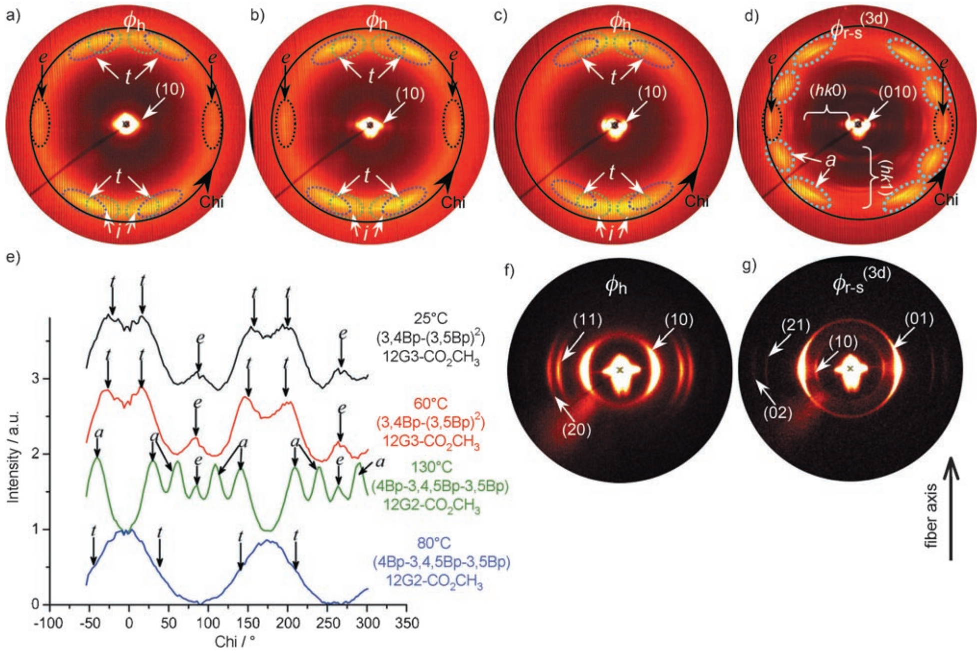


Figure 2. Wide-angle XRD patterns of aligned samples: (a) and (b) **(3,4Bp-(3,5Bp)^2)12G3-CO$_2$CH$_3$** at 25 and 60 °C, respectively; (c) and (d) **(4Bp-3,4,5Bp-3,5Bp)12G2-CO$_2$CH$_3$** at 80 and 130 °C, respectively; (e) azimuthal chi plots of the 4.5-Å alkyl-tail correlation regions for the patterns in (a–d); (f) and (g) the small-angle XRD patterns in (c) and (d), respectively; (*hk*), (*hk*0), (*hkl*): lattice reflections; *e*: equatorial features positioned at the 4.5-Å average alkyl-tail separation; *a*: sharp correlation features positioned at the 4.5-Å average alkyl-tail separation; *i*: short-range helical feature; *t*: dendron-tilt feature.

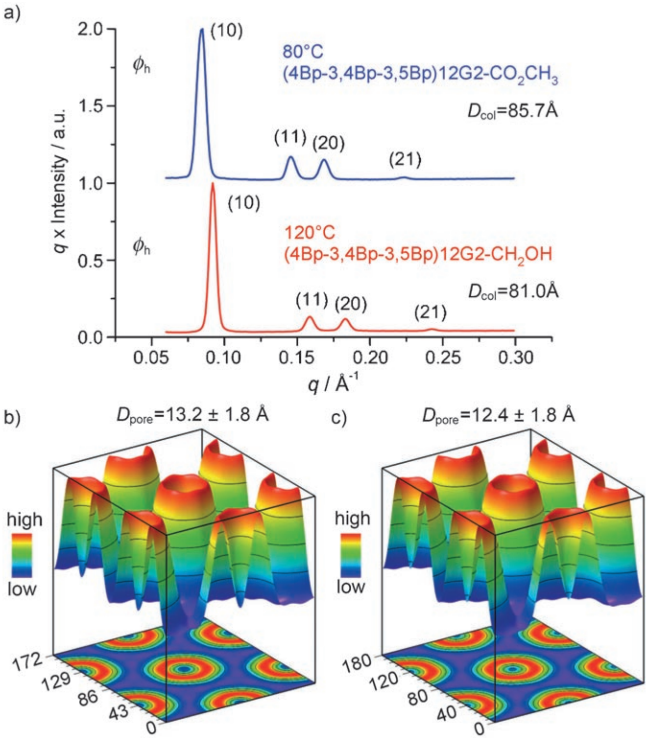


Figure 3. Small-angle powder XRD stack plots for supramolecular dendrimers with enhanced intensities of higher-order diffractions (a), and the reconstructed two-dimensional electron-density maps of the **(4Bp-3,4Bp-3,5Bp)12G2-CO$_2$CH$_3$** (b) and **(4Bp-3,4Bp-3,5Bp)12G2-CH$_2$OH** (c).

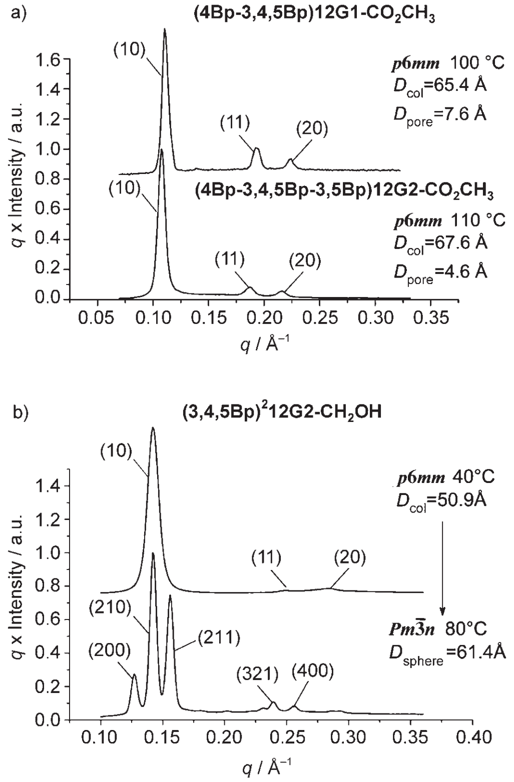


Figure 4. Representative small-angle X-ray powder diffraction plots: (a) comparison of the Φ_h phases of **(4Bp-3,4,5Bp)12G1-CO$_2$CH$_3$** and **(4Bp-3,4,5Bp-3,5Bp)12G2-CO$_2$CH$_3$**; (b) the first (3,4,5)-substituted dendron with hydrogenated tails that exhibit Φ_h and $Pm\bar{3}n$ cubic phases.

Table 6. XRD data and D_{pore} for selected supramolecular porous columns.

Dendron	T [°C]	d_{10}[a] [Å] (A_{10}[b][a.u.])	d_{11}[a] [Å] (A_{11}[b][a.u.])	d_{20}[a] [Å] (A_{20}[b][a.u.])	d_{21}[a] [Å] (A_{21}[b][a.u.])	$a=D_{col}$ [Å]	D_{pore} [Å]	μ	α [°]
(4Bp-3,4Bp-3,5Bp)12G2-CO_2CH_3	80	74.3 (44.3)	42.6 (23.4)	36.7 (24.0)	27.5 (8.3)	85.7	13.2	8.6	41.9
(4Bp-3,4Bp-3,5Bp)12G2-CH_2OH	120	75.4 (45.4)	41.1 (22.9)	35.9 (23.0)	26.6 (7.6)	80.6	12.4	7.7	46.8
(4Bp-3,4,5Bp)12G1-CO_2CH_3	100	56.6 (53.3)	32.5 (27.8)	28.1 (18.9)		65.1	7.6	7.0	51.4
(4Bp-3,4,5Bp-3,5Bp)12G2-CO_2CH_3	110	58.6 (60.3)	33.8 (20.8)	29.3 (16.1)	22.1 (2.8)	67.6	4.6	3.7	97.3

[a] d Spacings of the Φ_h phase. [b] Peak amplitude scaled to the sum of the observed diffraction peaks is given in parenthesis (a.u. = arbitrary units).

Table 7. XRD data for selected examples of supramolecular spheres with enhanced higher-order diffractions.

Dendron	T [°C]	d_{200}[a] [Å]	d_{210}[a] [Å]	d_{211}[a] [Å]	d_{220}[a] [Å]	d_{222}[a] [Å]	d_{310}[a] [Å]	d_{320}[a] [Å]	d_{321}[a] [Å]	d_{400}[a] [Å]	d_{420}[a] [Å]	d_{421}[a] [Å]	d_{422}[a] [Å]	d_{520}[a] [Å]	D [Å]	μ
$(3,4Bp)^2$12G2-CO_2CH_3	125	71.4	63.5	58.3	49.9		45.2	39.8	38.1	35.5	32.2	31.4	29.1		88.6	171
$(3,4Bp)^2$12G2-$CO_2C_2H_5$	118	70.6	64.1	58.7					37.9	35.5		34.1			2	166
$(3,4Bp)^2$12G2-$CO_2C_4H_9$	93	78.5	72.2	64.8	57.1		49.5	44.9	42.5	39.5	35.9	35.1	32.7	29.6	100.6	243.4
$(3,4Bp)^2$12G2-CH_2OH	190	64.1	57.6	52.8	45.5	37.0			34.7	32.4		28.3	26.2		82.2	140

[a] d Spacings of the Cub phase.

single bent mirror and sagittally focused through a Si(111) monochromator, to generate a 0.3 × 0.4 mm^2 spot on a Bruker-AXS Hi-Star multiwire area detector. To minimize attenuation and background scattering, an integral vacuum was maintained along the length of the flight tube and within the sample chamber. Samples were held in quartz capillaries (0.7–1.0 mm in diameter), mounted in a temperature-controlled oven (temperature precision: ±0.1 °C, temperature range from −120 to 270 °C). The distance between the sample and the detector was 12.0 cm for wide-angle diffraction experiments and 54.0 cm for intermediate-angle diffraction experiments, respectively. Aligned samples for fiber XRD experiments were prepared by using a custom-made extrusion device. The powdered sample (~10 mg) was heated inside the extrusion device above isotropization temperature. After slow cooling from the isotropic phase, the fiber was extruded in the liquid-crystal phase and cooled to 22 °C. Typically, the aligned samples have a thickness of ~0.3–0.7 mm and a length of ~3–7 mm. All XRD measurements were performed with the aligned sample axis perpendicular to the beam direction. XRD peaks position and intensity analysis was performed by using Datasqueeze Software (version 2.01) that allows background elimination and Gaussian, Lorentzian, Lorentzian squared, or Voigt peak-shape fitting.

MALDI-TOF mass spectra were recorded by using a PerSpective Biosystems Voyager DE using 2-(4-hydroxyphenylazo)benzoic acid as matrix. Angiotensin I and des-Arg1-Bradykinin were used as standards. Sample preparation was as follows: The matrix (ca. 10 mg) was dissolved in 1 mL of THF. The sample (ca. 10 mg) was also dissolved in 1 mL of THF. The matrix solution (50 μL) and the sample solution (10 μL) were mixed, then 10 μL of the THF solution of AgTFA (1 $mg\,mL^{-1}$) was added. The mixture was mixed well and an amount (5 mL) was loaded onto a MALDI plate and air dried before inserting into the vacuum chamber of the MALDI instrument. Mass spectra were recorded by direct sample introduction onto a LCMS (Micromass) platform (electron spray ionizer, electron energy 70 eV). Elemental analyses of all new compounds (M-H-W Laboratories, Phoenix, AZ) agree with the calculated values to within ±0.4%.

Synthesis: The synthesis of 1-bromo-3,4-dimethoxybenzene,[18a] 3,4-(dimethoxy)phenyl-1-boronic acid[17] (**1**), 4-methylphenylboronic acid[22] (**6**), and $[Pd(PPh_3)_4]$[18b] followed literature procedures. Methyl and ethyl 4-bromobenzoate (**2a**,**b**) were prepared by acid-catalyzed esterification of 4-bromobenzoic acid with MeOH or EtOH, respectively. The synthesis of (4′-(*n*-dodecane-1-yloxy)biphenyl-4-methyl chloride (**17**) was performed as reported previously.[26] Pyridinium hydrochloride was prepared by the dropwise addition of HCl to pyridine until pH 4–5 was reached, followed by evaporation of water.

Methyl 3′,4′-dimethoxybiphenyl-4-carboxylate (3a): Compound **3a** was prepared by using a modified literature procedure.[18c] To a thoroughly degassed mixture of **1** (35.3 G, 194 mmol) in EtOH (143 mL), Na_2CO_3 (30 G, 283 mmol) in H_2O (143 mL), and **2a** (36.0 G, 168.4 mmol) in toluene (840 mL) were added under Ar. $[Pd(Ph_3P)_4]$ (7.0 G, 6.7 mmol) was added against an Ar flow. The mixture was heated to reflux overnight, after which TLC (CH_2Cl_2) indicated complete reaction. The mixture was cooled to 22 °C, H_2O and Et_2O were added, and the organic phase was separated. The aqueous layer was then extracted twice with Et_2O, the ethereal portion was washed twice with NaOH solution (2 M), dried over Na_2SO_4, and concentrated. Purification by column chromatography (silica gel, CH_2Cl_2) gave the product as a white solid (43.4 G, 95%). R_f = 0.51 (CH_2Cl_2); m.p. 122–123 °C (ref. [18d] 130–131.5 °C); ^1H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 3.94$, 3.96 (3s, overlapped, 9H; 3′,4′ ArOC*H*$_3$, CO$_2$C*H*$_3$), 6.96 (d, $J = 8.3$ Hz, 1H; 2′ Ar*H*), 7.13 (d, $J = 2.0$ Hz, 1H; 5′ Ar*H*), 7.20 (dd, $J = 2.0$, 8.3 Hz, 1H; 6′ Ar*H*), 7.62 (d, $J = 8.4$ Hz, 2H; 2,6 Ar*H*), 8.07 ppm (d, $J = 8.4$ Hz, 2H; 3,5 Ar*H*). The NMR data was consistent with the literature.[18d]

Ethyl 3′,4′-dimethoxybiphenyl-4-carboxylate (3b): Compound **3b** was prepared by using a modified literature procedure.[18c] To a two-necked 500-mL flask containing a degassed mixture of **1** (10 G, 0.055 mol in 35 mL EtOH), Na_2CO_3 (2 M, in 40 mL H_2O), and **2b** (8.00 G, 50 mmol, in 80 mL toluene), $[Pd(PPh_3)_4]$ (1.43 G, 1.5 mmol) was added after 20 min and the mixture was heated to 115 °C for 12 h under stirring. The mixture was concentrated and the residue was extracted with Et_2O. The organic phase was washed with NaOH solution (1 M) and brine, then dried over $MgSO_4$ and passed through a plug of basic Al_2O_3 by using CH_2Cl_2. The solvent was removed under vacuum and the solid was recrystallized twice from a hexanes/acetone mixture to yield 10.4 G (72.5%) of a white powder. R_f = 0.50 (hexanes/EtOAc 2:1); m.p. 90–92 °C; purity (HPLC): 99+%; ^1H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 1.41$ (t, $J = 6.9$ Hz, 3H; CH$_2$C*H*$_3$), 3.93, 3.96 (2s, 6H; 3′,4′ ArOC*H*$_3$), 4.40 (q, $J = 7.2$ Hz, 2H; ArOC*H*$_2$CH$_3$), 6.96 (d, $J = 8.4$ Hz, 1H; 5′ Ar*H*), 7.13 (d, $J = 2.2$ Hz, 1H; 2′ Ar*H*), 7.19 (dd, $J = 2.2$, 8.3 Hz, 1H; 6′ Ar*H*), 7.61 (d, $J = 8.4$ Hz, 2H; 2,6 Ar*H*), 8.07 ppm (d, $J = 8.4$ Hz, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz,

$\mathrm{CDCl_3}$, 20 °C): $\delta = 14.35$ ($\mathrm{CH_2CH_3}$), 56.01, 56.03 (ArO*C*$\mathrm{H_3}$, 3′,4′ positions), 60.90 ($\mathrm{CO_2CH_2CH_3}$), 110.50 (Ar*C*H, 2′ position), 111.59 (Ar*C*H, 5′ position), 119.78 (Ar*C*H, 6′ position), 126.57 (ArCH, 2,6 positions), 128.80 (Ar*C*$\mathrm{CO_2CH_3}$), 130.04 (Ar*C*H, 3,5 positions), 132.97 (Ar*C*, 1′ position), 145.32 (Ar*C*, 1 position), 149.35 (overlapped Ar*C*, 3′,4′ positions), 166.52 ppm (*C*$\mathrm{O_2CH_3}$); MS (ESI-TOF): *m*/*z*: 309.1 $[M+\mathrm{Na}]^+$; elemental analysis calcd (%) for $\mathrm{C_{17}H_{18}O_4}$ (286.32): C 71.31, H 6.34; found: C 71.16, H 6.25.

Methyl 3′,4′-dihydroxybiphenyl-4-carboxylate (4a): Compound **4a** was prepared by using a modified literature procedure.[24] Compound **3a** (4.35 G, 16.7 mmol) was dissolved and degassed in dry $\mathrm{CH_2Cl_2}$ (100 mL) and cooled over ice under Ar. $\mathrm{BBr_3}$ (4.72 mL. 50 mmol) was dissolved in degassed dry $\mathrm{CH_2Cl_2}$ (50 mL) to produce a 4 M solution. After about half of the $\mathrm{BBr_3}$ had been added by using a syringe, the mixture cleared to a bright-yellow solution. The mixture was left to stir over ice, gradually warming to 22 °C overnight. The reaction was then quenched by cautious addition of MeOH. The mixture was slowly added to $\mathrm{Na_2S_2O_3}$ (0.2 M, 150 mL) solution with stirring. The organic phase was extracted with EtOAc. The aqueous layer was extracted with $\mathrm{CH_2Cl_2}$ and the combined organic layer was dried over $\mathrm{MgSO_4}$. The solvent was removed under vacuum and the product was recrystallized from acetone to yield 3.00 G (78.0%) of white crystals. $R_f = 0.35$ (hexanes/EtOAc 1:1); m.p. 188–190 °C; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 20 °C): $\delta = 3.89$ (s, 3H; $\mathrm{CO_2C}H_3$), 6.89 (d, $J = 8.3$ Hz, 1H; 5′ Ar*H*), 7.07 (dd, $J = 2.0$, 8.3 Hz, 1H; 6′ Ar*H*), 7.16 (d, $J = 2.0$ Hz, 1H; 2′ Ar*H*), 7.71 (d, $J = 8.4$ Hz, 2H; 2,6 Ar*H*), 8.01 (d, $J = 8.4$ Hz, 2H; 3,5 Ar*H*), 9.25 ppm (brs, 2H; 2×O*H*); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 20 °C): $\delta = 53.00$ ($\mathrm{CO_2}C\mathrm{H_3}$), 115.07 (Ar*C*H, 2′ position), 117.13 (Ar*C*H, 5′ position), 119.16 (Ar*C*H, 6′ position), 126.93 (ArCH, 2,6 positions), 128.22 (Ar*C*$\mathrm{CO_2CH_3}$), 130.74 (Ar*C*H, 3,5 positions), 130.96 (Ar*C*, 1′ position), 145.93 (Ar*C*, 4′ position), 146.76 (Ar*C*, 3′ position), 147.18 (Ar*C*, 1 position), 167.13 ppm (*C*$\mathrm{O_2CH_3}$); MS (ESI-TOF): *m*/*z*: 244.7 $[M-\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{14}H_{12}O_4}$ (245.24): C 68.85, H 4.95; found: C 68.61, H 4.98.

Ethyl 3′,4′-dihydroxybiphenyl-4-carboxylate (4b): Compound **3b** (2.86 G, 10 mmol) was placed in a round-bottomed flask containing a large excess of pyridinium chloride (PyHCl) under Ar. The solid mixture was heated to 190 °C, forming a clear, yellow melt, which was stirred for 3 h, then allowed to cool to 110 °C. Subsequently, $\mathrm{H_2O}$ (50 mL) was added and the mixture was cooled to 0 °C. The precipitate was filtered and the supernatant was extracted twice with $\mathrm{Et_2O}$ (50 mL). The solvent was removed under vacuum. NMR and TLC analysis of the resulting solid revealed that the ester group was partially cleaved. Consequently, esterification was performed on the mixture by using a saturated solution of HCl in dry EtOH at 70 °C for 12 h. The solvent was removed under vacuum and the product was further purified by column chromatography (silica gel, hexanes/EtOAc 1:1). Recrystallization from toluene yielded 2.22 G (86.0%) of white crystals. $R_f = 0.5$ (hexanes/EtOAc 1:1); m.p. 163 °C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 20 °C): $\delta = 1.33$ (t, $J = 7.0$ Hz, 3H; $\mathrm{CO_2CH_2C}H_3$), 4.32 (q, $J = 7.0$ Hz, 2H; $\mathrm{CO_2C}H_2\mathrm{CH_3}$), 6.85 (d, $J = 8.3$ Hz, 1H; 5′ Ar*H*), 7.03 (m, 1H; 6′ Ar*H*), 7.13 (m, 1H; 2′ Ar*H*), 7.66 (d, $J = 8.4$ Hz, 2H; 2,6 Ar*H*), 7.96 (d, $J = 8.4$ Hz, 2H; 3,5 Ar*H*), 9.30 ppm (brs, 2H; 2×O*H*); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 20 °C): $\delta = 14.08$ ($\mathrm{CO_2CH_2}C\mathrm{H_3}$), 60.45 ($\mathrm{CO_2}C\mathrm{H_2CH_3}$), 114.02 (Ar*C*H, 2′ position), 116.07 (Ar*C*H, 5′ position), 118.06 (Ar*C*H, 6′ position), 125.81 (ArCH, 2,6 positions), 127.45 (Ar*C*$\mathrm{CO_2CH_3}$), 129.59 (Ar*C*H, 3,5 positions), 129.93 (Ar*C*, 1′ position), 144.81 (Ar*C*, 4′ position), 145.68 (Ar*C*, 3′ position), 146.08 (Ar*C*, 1 position), 165.53 ppm (*C*$\mathrm{O_2CH_2CH_3}$); MS (ESI-TOF): *m*/*z*: 257.6 $[M-\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{15}H_{14}O_4}$ (258.27): C 69.76, H 5.46; found: C 69.68, H 5.36.

3′,5′-Dimethoxy-4-methylbiphenyl (7): Compound **7** was synthesized according to a modified literature procedure.[23] A Schlenk tube was evacuated and backfilled with Ar and charged with *p*-tolylboronic acid (**6**) (6.00 G, 44.1 mmol), KF (5.12 G, 88.1 mmol), 5-chloro-1,3-dimethoxybenzene (**5**) (5.08 G, 29.4 mmol), $\mathrm{Pd(OAc)_2}$ (66 mg, 0.29 mmol, 1.0 mol%), and 2-(di-*tert*-butylphosphino)biphenyl (175 mg, 0.588 mmol, 2.0 mol%). The flask was sealed with a teflon screwcap and evacuated/backfilled several times. Dry, degassed THF (40 mL) was added by using a syringe and the reaction mixture was stirred at 22 °C until the aryl chloride had been consumed (GC analysis, 4 h). The mixture was diluted with $\mathrm{Et_2O}$ (250 mL), filtered, and washed with NaOH solution (1 M, 200 mL). The aqueous layer was extracted with $\mathrm{Et_2O}$ (2×150 mL), the combined organic layer was washed with brine (150 mL) and dried over $\mathrm{MgSO_4}$. After evaporation the crude material was passed through a short column of silica by using $\mathrm{CH_2Cl_2}$ as eluent. The solvent was evaporated and the product was recrystallized from EtOH to yield 6.40 G (95.0%) of white crystals. $R_f = 0.66$ (hexanes/EtOAc 1:1); m.p. 56–57 °C (ref. [24] 57.3–57.5 °C); purity (GC): 99+ %.

3′,5′-Dimethoxybiphenyl-4-carboxylic acid (8): Compound **7** was oxidized according to modified literature procedures.[30] Compound **7** (11.7 G, 51.3 mmol) was dissolved in pyridine (300 mL) and $\mathrm{H_2O}$ (300 mL) at 50 °C. Then 5 equivalents of $\mathrm{KMnO_4}$ (41.0 G, 259.4 mmol) were added in one portion. The temperature was raised to 100 °C and the mixture was stirred for 2 h. An additional portion of $\mathrm{KMnO_4}$ (40.0 G, 253 mmol) was added and stirring was continued for 1 h. The excess of $\mathrm{KMnO_4}$ was quenched with EtOH, the solid was filtered and washed with hot $\mathrm{H_2O}$. The colorless filtrate was concentrated and acidified with 10% HCl. The precipitate was collected by filtration, washed with $\mathrm{H_2O}$, and dried in vacuo to yield 10.2 G (77.0%) of a white crystalline solid. $R_f = 0.41$ (hexanes/EtOAc 1:1); m.p. 185.0–186.5 °C; purity (HPLC): 99%; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta = 3.87$ (s, 6H; $\mathrm{ArCOC}H_3$), 6.53 (t, $J = 2.2$ Hz, 1H; 4′ Ar*H*), 6.76 (d, $J = 2.2$ Hz, 1H; 2′,6′ Ar*H*), 7.67 (d, $J = 8.4$ Hz, 2H; 2,6 Ar*H*), 8.17 ppm (d, $J = 8.4$ Hz, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta = 100.21$ (Ar*C*, 4′ position), 105.68 (Ar*C*H, 2′,6′ positions), 127.26 (ArCH, 2,6 positions), 128.22 (Ar*C*$\mathrm{CO_2CH_3}$), 130.67 (Ar*C*H, 3,5 positions), 142.10 (Ar*C*, 1′ position), 146.50 (Ar*C*, 1 position), 161.23 (Ar*C*, 3′,5′ positions), 170.98 ppm (*C*$\mathrm{O_2H}$); MS (ESI-TOF): *m*/*z*: 259.1 $[M+\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{15}H_{14}O_4}$ (258.27): C 69.76, H 5.46; found: C 70.13, H 5.35.

Methyl 3′,5′-dimethoxybiphenyl-4-carboxylate (9): Compound **8** (15.50 G, 60.0 mmol) was dissolved in MeOH (300 mL) and conc. $\mathrm{H_2SO_4}$ (15 mL). The solution was stirred under reflux for 16 h and then allowed to cool to 22 °C. $\mathrm{H_2O}$ (600 mL) was added and the mixture was stirred for 10 min. The precipitate was collected by filtration, washed with $\mathrm{H_2O}$, and dried in vacuo to yield 12.7 G (96.0%) of ester **9** as a white crystalline solid. $R_f = 0.73$ (hexanes/EtOAc 1:1); m.p. 80.5–81.5 °C; purity (GC): 99+ %; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta = 3.86$ (s, 6H; $\mathrm{ArCOC}H_3$), 3.94 (s, 3H; $\mathrm{CO_2C}H_3$), 6.50 (t, $J = 2.1$ Hz, 1H; 4′ Ar*H*), 6.75 (d, $J = 2.1$ Hz, 1H; 2′,6′ Ar*H*), 7.63 (d, $J = 8.4$ Hz, 2H; 2,6 Ar*H*), 8.07 ppm (d, $J = 8.4$ Hz, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta = 52.13$ ($\mathrm{CO_2}C\mathrm{H_3}$), 55.45 ($\mathrm{ArCO}C\mathrm{H_3}$), 99.96 (Ar*C*H, 4′ position), 105.54 (Ar*C*H, 2′,6′ positions), 127.09 (Ar*C*H, 2,6 positions), 129.11 (Ar*C*$\mathrm{CO_2CH_3}$), 130.01 (ArCH, 3,5 positions), 142.17 (Ar*C*, 1′ position), 145.56 (Ar*C*, 1 position), 161.12 (Ar*C*, 3′,5′ positions), 166.93 ppm (*C*$\mathrm{O_2CH_3}$); MS (ESI-TOF): *m*/*z*: 273.1 $[M+\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{16}H_{16}O_4}$ (272.30): C 70.57, H 5.92; found: C 70.47, H 5.79.

Methyl 3′,5′-dihydroxybiphenyl-4-carboxylate (10): Compound **10** was synthesized according to a modified literature procedure.[24] The ester **9** (10.0 G, 36.7 mmol) was dissolved in dry $\mathrm{CH_2Cl_2}$ (250 mL) under $\mathrm{N_2}$ at 22 °C and purged with $\mathrm{N_2}$ for 15 min. The solution was cooled to 0 °C and a solution of $\mathrm{BBr_3}$ (10.6 mL, 110.2 mmol) in dry $\mathrm{CH_2Cl_2}$ (110 mL) was added by using a syringe over the period of 15 min. The solution was kept at 0 °C for 4 h and then allowed to warm up to 22 °C overnight under $\mathrm{N_2}$. The reaction was carefully quenched with MeOH and stirred for 5 min. The excess of $\mathrm{BBr_3}$ was eliminated by adding $\mathrm{Na_2S_2O_3}$ solution (200 mL, 0.2 M). EtOAc (300 mL) was added. The organic layer was separated and washed with $\mathrm{H_2O}$. After the evaporation of the solvents, the crude product was purified by column chromatography (silica gel, hexanes/EtOAc 1:1) to give 6.97 G (78%) of creamy solid. $R_f = 0.54$ (hexanes/EtOAc 1:1); m.p. 213.5–214.5 °C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 20 °C): $\delta = 3.90$ (s, 3H; $\mathrm{CO_2C}H_3$), 6.31 (t, $J = 2.1$ Hz, 1H; 4′ Ar*H*), 6.56 (d, $J = 2.1$ Hz, 1H; 2′,6′ Ar*H*), 7.71 (d, $J = 8.4$ Hz, 2H; 2,6 Ar*H*), 8.03 (d, $J = 8.4$ Hz, 2H; 3,5 Ar*H*), 9.51 ppm (brs, 2H; 2×O*H*); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 20 °C) $\delta = 53.10$ ($\mathrm{CO_2}C\mathrm{H_3}$), 103.53 (Ar*C*H, 4′ position), 106.04 (Ar*C*H, 2′,6′ positions), 127.70 (Ar*C*H, 2,6 positions), 129.29 (Ar*C*$\mathrm{CO_2CH_3}$), 130.70 (Ar*C*H, 3,5 positions), 141.76 (Ar*C*, 1′ position), 146.09 (Ar*C*, 1 position), 159.91

(Ar*C*, 3′,5′ positions), 167.03 ppm ($\mathit{C}O_2CH_3$); MS (ESI-TOF): *m*/*z*: 244.1 $[M]^+$; elemental analysis calcd (%) for $C_{14}H_{12}O_4$ (244.24): C 68.85, H 4.95; found: C 69.85, H 4.73.

1-Bromo-3,4,5-trimethoxybenzene (12):[25] 2,6-Dimethoxyphenol **11** (15.2 G, 98.6 mmol) was dissolved in dry $CHCl_3$ (150 mL). MeOH (1.5 mL) and NaH (0.2 G, 5 mmol) were added under Ar. The blue solution was cooled to −60°C and stirred for 20 min. *N*-Bromosuccinimide (NBS) (17.6 G, 98.6 mmol) was added rapidly. The reaction mixture was stirred at −60°C for 2 h and then allowed to warm to 22°C, refluxed for 1 h, and evaporated to dryness. The brown solid was suspended in Et_2O (200 mL) and succinimide was filtered off. The filtrate was evaporated to yield a cream-colored solid. The solid was dissolved in boiling heptane (650 mL). The hot solution was decanted from brown oil and filtered through Celite into a preheated flask. A brown oil precipitated at ~22°C. The solution was decanted and filtered again. A white precipitate appeared in a cold receiving flask. 15.8 G of white woolly crystals of 4-bromo-2,6-dimethoxyphenol in 95 % purity was obtained after filtration and drying. The crude product was dissolved in acetone (200 mL). K_2CO_3 (9.65 G, 69.8 mmol) was added followed by dimethyl sulfate (8.7 G, 69.8 mmol). The reaction mixture was heated to reflux for 4 h. Then an additional amount of dimethyl sulfate (4.3 G, 34.9 mmol) was added. 100 % conversion was detected by TLC (hexane/EtOAc 6:1) after another 14 h of heating. The reaction mixture was allowed to cool to 22°C. Inorganic solids were filtered and washed with acetone. 14.2 G (58 % over two steps) of white crystals was obtained after two recrystallizations from MeOH. $R_f = 0.4$ (hexane/EtOAc 6:1); m.p. 74°C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20°C): $\delta = 3.82$ (s, 3H; 4 ArOC*H*$_3$), 3.85 (s, 6H; 3,5 ArOC*H*$_3$), 6.73 ppm (s, 2H; Ar*H*). Melting point and ^{1}H NMR were consistent with literature data.[31]

3′,4′,5′-Trimethoxy-4-methylbiphenyl (13):[25] A 250 mL flask was loaded with **12** (8.0 G, 34.3 mmol), 4-methylphenylboronic acid (6.1 G, 44.6 mmol), [NiCl(dppe)] catalyst (0.91 G, 1.7 mmol), dppe (0.68 G, 1.7 mmol), K_3PO_4 (21.9 G, 103.0 mmol), and thoroughly flushed with Ar. Toluene (160 mL) was added and the reaction mixture was heated to 80°C under Ar. 100 % conversion was detected by TLC (CH_2Cl_2) in 14 h. The reaction mixture was allowed to cool to ~22°C and quenched with CH_2Cl_2 (200 mL). Inorganic solids were removed by filtration through silica gel. The filtrate was evaporated to dryness. 8.5 G (96 %) of white crystals were obtained by crystallization from hexane. $R_f = 0.2$ (CH_2Cl_2); m.p. 65°C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20°C): $\delta = 2.41$ (s, 3H; ArC*H*$_3$), 3.89 (s, 3H; 4′ ArOC*H*$_3$), 3.93 (s, 6H; 3′,5′ ArOC*H*$_3$), 6.78 (s, 2H; 2′,6′ Ar*H*), 7.25 (d, *J* = 8.0 Hz, 2H; 2,6 Ar*H*), 7.46 ppm (d, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta = 21.28$ (Ar*C*H$_3$), 56.46 (3′,5′ ArO*C*H$_3$), 61.17 (4′ ArO*C*H$_3$), 104.68 (2′ Ar*C*), 127.15 (2 Ar*C*), 129.66 (3 Ar*C*), 137.31 (4 Ar*C*), 137.41 (4′ Ar*C*), 137.51 (1′ Ar*C*), 138.71 (1 Ar*C*), 153.69 ppm (3′ Ar*C*); MS (ESI-TOF): *m*/*z*: 258.3 $[M^+]$; elemental analysis calcd (%) for $C_{16}H_{18}O_3$ (258.31): C 74.39, H 7.02; found: C 74.16, H 7.08.

Methyl 3′,4′,5′-trimethoxybiphenyl-4-carboxylate (14): Compound **13** (1.0 G, 3.9 mmol) was dissolved in a pyridine/water mixture (1:1, 50 mL) and heated to 100°C. $KMnO_4$ (6.1 G, 38.7 mmol) was added in two portions over 4 h. 100 % conversion was detected by TLC (CH_2Cl_2/MeOH 15:1). The reaction was allowed to cool to ~22°C and EtOH (100 mL) was added. The mixture was filtered and washed with hot EtOH. The filtrate was evaporated to dryness, dissolved in H_2O, and acidified to pH 2 with HCl (2 M). The white precipitate was filtered, dried, and dissolved in dry MeOH (50 mL). H_2SO_4 (0.5 mL) was added and the reaction mixture was heated to reflux for 24 h, concentrated, dissolved in CH_2Cl_2 (50 mL), washed with H_2O, and evaporated to dryness. Residual **13** was removed by washing the product with hexane (50 mL). 0.9 G (76 %) of ester **14** was obtained as white crystals. $R_f = 0.95$ (CH_2Cl_2/MeOH 15:1); m.p. 99°C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20°C): $\delta = 3.91$ (s, 3H; 4′ ArOC*H*$_3$), 3.95 (s, 6H; 3′,5′ ArOC*H*$_3$), 3.96 (s, 3H; CO$_2$C*H*$_3$), 6.82 (s, 2H; 2′,6′ Ar*H*), 7.63 (d, *J* = 8.5 Hz, 2H; 2,6 Ar*H*), 8.10 ppm (d, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta = 52.17$ (CO$_2$*C*H$_3$), 56.53 (3′,5′ ArO*C*H$_3$), 61.17 (4′ ArO*C*H$_3$), 105.00 (2′ Ar*C*), 127.16 (3 Ar*C*), 129.16 (1 Ar*C*), 130.29 (2 Ar*C*), 136.07 (1′ Ar*C*), 138.77 (4′ Ar*C*), 145.94 (4 Ar*C*), 153.85 (3′ Ar*C*), 167.12 ppm ($\mathit{C}O_2CH_3$); MS (ESI-TOF): *m*/*z*: 302.2 $[M^+]$; elemental analysis calcd (%) for $C_{17}H_{18}O_5$ (302.32): C 67.54, H 6.00; found: C 67.4, H 6.06.

Methyl 3′,4′,5′-trihydroxybiphenyl-4-carboxylate (15): BBr_3 (1.4 mL, 14.9 mmol) was dissolved in dry CH_2Cl_2 (20 mL) under Ar at −78°C. Compound **14** (0.9 G, 3.0 mmol) was added. The reaction mixture was allowed to warm to ~22°C and stirred for 19 h. H_2O (3 mL) was added to quench the excess of BBr_3. The precipitated 3′,4′,5′-trihydroxybiphenyl-4-carboxylic acid was filtered and dissolved in dry MeOH (40 mL). Then H_2SO_4 (0.5 mL) was added, the solution was heated to reflux for 20 h and evaporated to dryness. 0.5 G (65 %) of **15** was obtained by crystallization from acetonitrile. $R_f = 0.4$ (CH_2Cl_2/MeOH 15:1); m.p. 205°C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, [D$_6$]DMSO, 20°C): $\delta = 3.85$ (s, 3H; CO$_2$C*H*$_3$), 6.65 (s, 2H; 2′,6′ Ar*H*), 7.61 (d, *J* = 8.7 Hz, 2H; 2,6 Ar*H*), 7.96 (d, 2H; 3,5 Ar*H*), 8.42 (brs, 4′ ArO*H*), 9.05 ppm (brs, 2H; 3′,5′ ArO*H*); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 20°C): $\delta = 52.00$ (CO$_2$*C*H$_3$), 105.79 (2′ Ar*C*), 125.92 (2 Ar*C*), 127.24, 129.08, 129.72 (3 Ar*C*), 134.04, 145.22, 146.55, 166.13 ppm ($\mathit{C}O_2CH_3$); elemental analysis calcd (%) for $C_{14}H_{12}O_5$ (260.24): C 64.61, H 4.65; found: C 64.43, H 4.68.

Methyl 3′,4′-bisdodecyloxybiphenyl-4-carboxylate [(3,4Bp)12G1-CO$_2$CH$_3$] (18): Compound **4a** (1.86 G, 7.6 mmol) was stirred and degassed under Ar in a suspension of K_2CO_3 (4.42 G, 32 mmol) in DMF (120 mL) at 70°C. 1-Bromododecane **18** (3.85 mL, 16.0 mmol) was added slowly by using a syringe. The mixture was maintained at 90°C for 15 h, after which TLC indicated complete reaction. The mixture was poured into HCl (10 %, 300 mL + ~50 G ice) under vigorous stirring. The product was extracted with Et_2O (3×150 mL), washed with H_2O, brine, and dried over $MgSO_4$. The solvent was evaporated and the solid was dissolved in hot EtOH and decanted to remove oily, brown solid impurities. A further recrystallization from EtOH yielded 3.44 G (78 %) of bright-white flaky crystals. $R_f = 0.65$ (hexanes/CH_2Cl_2 1:1); m.p. 77.5–78.5°C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20°C): $\delta = 0.88$ (m, 6H; CH$_2$C*H*$_3$), 1.27 (m, 32H; CH$_3$(C*H*$_2$)$_8$), 1.48 (m, 4H; ArOCH$_2$CH$_2$C*H*$_2$), 1.84 (qi, *J* = 6.3 Hz, 4H; ArOCH$_2$C*H*$_2$), 3.93 (s, 3H; CO$_2$C*H*$_3$), 4.04 (2t, overlapped, *J* = 6.7 Hz, 4H; ArOC*H*$_2$), 6.95 (d, *J* = 8.1 Hz, 1H; 5′ Ar*H*), 7.16 (m, 2H; 2′,6′ Ar*H*), 7.61 (d, *J* = 8.3 Hz, 2H; 2,6 Ar*H*), 8.06 ppm (d, *J* = 8.8 Hz, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta = 14.11$ (*C*H$_3$), 22.68 (*C*H$_2$CH$_3$), 26.05 (*C*H$_2$CH$_2$CH$_2$OAr), 29.28–29.70 (ArOCH$_2$*C*H$_2$, CH$_3$CH$_2$CH$_2$(*C*H$_2$)$_6$), 31.92 (CH$_3$CH$_2$*C*H$_2$), 52.05 (CO$_2$*C*H$_3$), 69.29, 69.54 (ArO*C*H$_2$CH$_2$, 3′,4′ positions), 113.13 (Ar*C*H, 2′ position), 113.91 (Ar*C*H, 5′ position), 119.95 (Ar*C*H, 6′ position), 126.54 (ArCH, 2,6 positions), 128.24 (Ar*C*CO$_2$CH$_3$, 4 position), 130.04 (Ar*C*H, 3,5 positions), 133.78 (Ar*C*, 1′ position), 145.50 (Ar*C*, 1 position), 149.40, 149.62 (Ar*C*, 3′,4′ positions), 167.05 ppm ($\mathit{C}O_2CH_3$); MS (ESI-TOF): *m*/*z*: 1184.7 $[M+Na]^{2+}$; elemental analysis calcd (%) for $C_{38}H_{60}O_4$ (580.88): C 78.57, H 10.41; found: C 78.70, H 10.62.

(3′,4′-Bisdodecyloxybiphenyl-4-yl)methanol [(3,4Bp)12G1-CH$_2$OH] (19): Compound **18** (3.80 G, 6.7 mmol) was dissolved in dry THF (50 mL) and added to an ice-cooled stirred suspension of $LiAlH_4$ (0.38 G, 10 mmol) in THF (150 mL) under Ar. After 30 min all starting material was consumed (TLC) and the reaction was quenched by the dropwise addition of NaOH (2 M) until gas evolution ceased. The product was filtered through Celite, washed with THF, dissolved in refluxing acetone, and filtered from the solid residue. The solution was concentrated to about 80 mL to yield a white powder precipitate that was filtered and recrystallized from acetone to give 3.46 G (94 %) of fine white platelets. $R_f = 0.59$ (hexanes/EtOAc 1:1); m.p. 88.5–89°C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20°C): $\delta = 0.88$ (m, 6H; CH$_2$C*H*$_3$), 1.27 (m, 32H; CH$_3$(C*H*$_2$)$_8$), 1.49 (qi, *J* = 7.3 Hz, 4H; ArOCH$_2$CH$_2$C*H*$_2$), 1,70 (brs, 1H; CH$_2$O*H*), 1.84 (m, 4H; ArOCH$_2$C*H*$_2$), 3.93 (s, 3H; CO$_2$C*H*$_3$), 4.05 (2t, overlapped, *J* = 6.6 Hz, 4H; ArOC*H*$_2$), 4.72 (d, *J* = 5.9 Hz, 1H; CH$_2$O*H*), 6.94 (d, *J* = 8.8 Hz, 1H; 5′ Ar*H*), 7.11 (m, 2H; 2′,6′ Ar*H*), 7.41 (d, *J* = 8.6 Hz, 2H; 2,6 Ar*H*), 7.55 ppm (d, *J* = 8.3 Hz, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta = 14.10$ (*C*H$_3$), 22.68 (*C*H$_2$CH$_3$), 26.05 (*C*H$_2$CH$_2$CH$_2$OAr), 29.31–29.70 (ArOCH$_2$*C*H$_2$, CH$_3$CH$_2$CH$_2$(*C*H$_2$)$_6$), 31.92 (CH$_3$CH$_2$*C*H$_2$), 65.15 (*C*H$_2$OH), 69.37, 69.48 (ArO*C*H$_2$CH$_2$, 3′,4′ positions), 113.14 (Ar*C*H, 2′ position), 114.09 (Ar*C*H, 5′ position), 119.56 (Ar*C*H, 6′ position), 126.96 (ArCH, 2,6 positions), 127.42 (Ar*C*H, 3,5 positions), 133.82 (Ar*C*, 1′ position), 139.29 (Ar*C*, 1 position), 140.55

(ArCCH$_2$Cl, 4 position), 148.91, 149.33 ppm (ArC, 3′,4′ positions); MS (ESI-TOF): m/z: 1128.6 $[M+Na]^{2+}$; elemental analysis calcd (%) for $C_{37}H_{60}O_3$ (552.87): C 80.38, H 10.94; found: C 80.51, H 10.93.

4-Chloromethyl-3′,4′-bisdodecyloxybiphenyl [(3,4Bp)12G1-CH$_2$Cl] (20): Compound **19** (3.2 G, 5.7 mmol), $SOCl_2$ (3.86 mL, 6.3 mmol), and DMF (0.5 mL) were stirred for 1 h at 40 °C in degassed CH_2Cl_2 (150 mL) under Ar. Additional CH_2Cl_2 (150 mL) was added, the solution was washed with H_2O (2×100 mL) followed by brine, and dried over $MgSO_4$. The solvent was evaporated to give a pale-yellow solid, which was recrystallized from EtOH to yield fine white platelets (3.13 G, 94 %). $R_f=0.73$ (hexanes/EtOAc 5:1); m.p. 67–68 °C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=0.88$ (m, 6H; CH_2CH_3), 1.27 (m, 32H; $CH_3(CH_2)_8$), 1.47 (qi, $J=7.3$ Hz, 4H; $ArOCH_2CH_2CH_2$), 1.84 (m, 4H; $ArOCH_2CH_2$), 4.05 (2t, overlapped, $J=6.6$ Hz, 4H; $ArOCH_2$), 4.62 (s, 2H; CH_2Cl), 6.94 (d, $J=8.8$ Hz, 1H; 5′ ArH), 7.11 (m, 2H; 2′,6′ ArH), 7.43 (d, $J=8.6$ Hz, 2H; 2,6 ArH), 7.54 ppm (d, $J=8.4$ Hz, 2H; 3,5 ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=14.10$ (CH_3), 22.68 (CH_2CH_3), 26.05 ($CH_2CH_2CH_2OAr$), 29.31–29.70 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.92 ($CH_3CH_2CH_2$), 46.10 (CH_2Cl), 69.32, 69.47 ($ArOCH_2CH_2$, 3′,4′ positions), 113.12 (ArCH, 2′ position), 114.01 (ArCH, 5′ position), 119.62 (ArCH, 6′ position), 127.09 (ArCH, 2,6 positions), 128.98 (ArCH, 3,5 positions), 133.44 (ArC, 1′ position), 135.83 (ArCCH$_2$Cl, 4 position), 141.29 (ArC, 1 position), 149.08, 149.34 ppm (ArC, 3′,4′ positions); MS (ESI-TOF): m/z: 1165.3 $[M+Na]^{2+}$; elemental analysis calcd (%) for $C_{37}H_{59}ClO_2$ (571.32): C 77.78, H 10.41; found: C 77.57, H 10.39.

Methyl 3′,4′,5′-tridodecyloxybiphenyl-4-carboxylate [(3,4,5Bp)12G1-CO$_2$CH$_3$] (21): K_2CO_3 (249 mg, 1.80 mmol) was suspended in thoroughly degassed DMF (50 mL) under Ar. Trihydroxy compound **15** (52 mg, 0.20 mmol) was added. The reaction mixture was heated to 70°C. Dodecyl bromide (155 mg, 0.62 mmol) was dissolved in DMF (1 mL) and added to the reaction mixture. Heating was continued for 10 h. The reaction mixture was allowed to cool to ~22 °C, then poured into H_2O (250 mL) and extracted with Et_2O (3×100 mL). The extract was washed with H_2O, dried over Na_2SO_4, evaporated to dryness, and dissolved in CH_2Cl_2 (3 mL). 110 mg (72 %) of **21** was obtained by precipitation with MeOH. $R_f=0.95$ (CH_2Cl_2); m.p. 44°C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20°C): $\delta=0.89$ (t, 9H; CH_2CH_3), 1.28 (m, 42H; $(CH_2)_7CH_3$), 1.37 (m, 6H; $ArOCH_2CH_2CH_2CH_2$), 1.50 (m, 6H; $ArOCH_2CH_2CH_2$), 1.78 (m, 2H; 4′ $ArOCH_2CH_2$), 1.84 (m, 4H; 3′,5′ $ArOCH_2CH_2$), 3.95 (s, 3H; CO_2CH_3), 4.01 (t, $J=6.6$ Hz, 2H; 4′ $ArOCH_2$), 4.05 (t, $J=6.3$ Hz, 4H; 3′,5′ $ArOCH_2$), 6.79 (s, 2H; 2′,6′ ArH), 7.61 (d, $J=8.6$ Hz, 2H; 2,6 ArH), 8.08 ppm (d, $J=8.6$ Hz, 2H; 3,5 ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta=14.31$ (CH_3), 22.91 (CH_2CH_3), 26.36 (CH_2), 29.58 (CH_2), 29.70–30.61 (CH_2), 32.15 ($ArOCH_2CH_2$), 52.30 (CO_2CH_3), 69.67 (3′,5′ $ArOCH_2$), 73.83 (4′ $ArOCH_2$), 106.54 (2′,6′ ArC), 127.10 (2,6 ArCH), 128.92 (1 ArC), 130.24 (3,5 ArCH), 135.45 (1′ ArC), 139.10 (4′ ArC), 146.13 (4 ArC), 153.76 (3′,5′ ArC), 167.23 ppm (CO_2CH_3); MS (ESI-TOF): m/z: 765.4 $[M^+]$; elemental analysis calcd (%) for $C_{50}H_{84}O_5$ (765.20): C 78.48, H 11.06; found: C 77.93, H 10.85.

(3′,4′,5′-Tridodecyloxybiphenyl-4-yl)methanol [(3,4,5Bp)12G1-CH$_2$OH] (22): Ester **21** (1.96 G, 2.55 mmol) was dissolved in dry THF (50 mL) and added into a suspension of $LiAlH_4$ (0.18 G, 4.51 mmol) in dry THF (50 mL) at 0°C. The reaction mixture was allowed to warm up to ~23°C, stirred for 1.5 h, and quenched with H_2O (3 mL). Precipitation was removed by filtration through Celite. Filtrate was evaporated to dryness, dissolved in CH_2Cl_2, and precipitated with MeOH. 1.78 G (93 %) of **22** was obtained as white crystals. $R_f=0.45$ (CH_2Cl_2); m.p. 50°C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20°C): $\delta=0.90$ (t, 9H; CH_2CH_3), 1.28 (m, 48H; $(CH_2)_8CH_3$), 1.50 (m, 6H; $ArOCH_2CH_2CH_2$), 1.66 (t, 1H; CH_2OH), 1.78 (m, 2H; 4′ $ArOCH_2CH_2$), 1.83 (m, 4H; 3′,5′ $ArOCH_2CH_2$), 4.01 (t, $J=6.6$ Hz, 2H; 4′ $ArOCH_2$), 4.05 (t, $J=6.3$ Hz, 4H; 3′,5′ $ArOCH_2$), 4.74 (d, $J=4.5$ Hz, 2H; CH_2OH), 6.76 (s, 2H; 2′,6′ ArH), 7.42 (d, $J=8.6$ Hz, 2H; 2,6 ArH), 7.55 ppm (d, $J=8.6$ Hz, 2H; 3,5 ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta=14.31$ (CH_3), 22.90 (CH_2CH_3), 26.39 (CH_2), 29.58 (CH_2), 29.65–30.62 (CH_2), 32.15 ($ArOCH_2CH_2$), 65.36 (CH_2OH), 69.61 (3′,5′ $ArOCH_2$), 73.80 (4′ $ArOCH_2$), 106.39 (2′,6′ ArCH), 127.42 (2,6 ArCH), 127.58 (3,5 ArCH), 136.36 (1 ArC), 138.40 (4′ ArC), 139.94 (4 ArC), 141.18 (1′ ArC), 153.64 ppm (3′ ArC); MS (ESI-TOF): m/z: 736.8 $[M^+]$; elemental analysis calcd (%) for $C_{49}H_{84}O_4$ (737.19): C 79.83, H 11.49; found: C 80.03, H 11.44.

4-Chloromethyl-3′,4′,5′-trisdodecyloxybiphenyl [(3,4,5Bp)12G1-CH$_2$Cl] (23): Alcohol **22** (1.50 G, 2.04 mmol) was dissolved in dry CH_2Cl_2 (100 mL) under Ar. DMF (1 mL) and $SOCl_2$ (0.18 mL, 2.44 mmol) were added and the reaction mixture was stirred at 22°C for 1 h, washed with H_2O (4×25 mL) and brine (25 mL), dried over $MgSO_4$, and evaporated to dryness yielding 1.35 G (88 %) of **23**. $R_f=0.9$ (CH_2Cl_2); m.p. 37–39°C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 23°C): $\delta=0.89$ (t, 9H; CH_2CH_3), 1.28 (m, 48H; $(CH_2)_8CH_3$), 1.49 (m, 6H; $ArOCH_2CH_2CH_2$), 1.78 (m, 2H; 4′ $ArOCH_2CH_2$), 1.83 (m, 4H; 3′,5′ $ArOCH_2CH_2$), 4.00 (t, $J=6.0$ Hz, 2H; 4′ $ArOCH_2$), 4.04 (t, $J=6.5$ Hz, 4H; 3′,5′ $ArOCH_2$), 4.64 (s, 2H; CH_2Cl), 6.75 (s, 2H; 2′,6′ ArH), 7.44 (d, $J=7.9$ Hz, 2H; 2,6 ArH), 7.54 ppm (d, $J=7.9$ Hz, 2H; 3,5 ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta=14.31$ (CH_3), 22.90 (CH_2CH_3), 26.38 (CH_2), 29.57 (CH_2), 29.21–30.12 (CH_2), 32.16 ($ArOCH_2CH_2$), 45.91 (CH_2Cl), 69.13 (3′,5′ $ArOCH_2$), 73.21 (4′ $ArOCH_2$), 105.88 (2′,6′ ArCH), 127.34 (2,6 ArCH), 127.49 (3,5 ArCH), 138.41 (4′ ArC), 139.92 (4 ArC), 141.17 (1′ ArC), 153.61 ppm (3′ ArC).

Methyl 3′,4′-bis(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-carboxylate [(4Bp-3,4Bp)12G1-CO$_2$CH$_3$] (24): A suspension of K_2CO_3 (4.83 G, 25 mmol) and **4a** (1.63 G, 7 mmol) in DMF (110 mL) was degassed and stirred for 1 h at 70 °C under Ar. Compound **17** (4.52 G, 13.4 mmol) was added in small portions against a flow of Ar. The mixture was maintained at 90 °C for 15 h. Additional DMF (300 mL) was added and the mixture was carefully poured into HCl (10 %, 400 mL) under vigorous stirring (care, much frothing was involved). The solid product was filtered, washed with H_2O, and recrystallized twice from CH_2Cl_2 to yield 3.85 G (58.4 %) of white crystals. $R_f=0.58$ ($CHCl_3$); m.p. 133.7 °C; purity (HPLC) 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=0.89$ (t, $J=6.9$ Hz, 6H; CH_2CH_3), 1.28 (m, 32H; $CH_3(CH_2)_8$), 1.48 (qi, $J=7.3$ Hz, 4H; $ArOCH_2CH_2CH_2$), 1.81 (qi, $J=7.1$ Hz, 4H; $ArOCH_2CH_2$), 3.93 (s, 3H; CO_2CH_3), 4.00 (t, $J=6.6$ Hz, 4H; $ArOCH_2$), 5.25, 5.27 (2s, 4H; 3′,4′ $ArOCH_2$), 6.96 (d, $J=8.5$ Hz, 4H; G1, 3′,5′ ArH), 7.05 (d, $J=8.3$ Hz, 1H; 5′ ArH), 7.22 (dd, $J=2.0$, 8.3 Hz, 1H; 6′ ArH), 7.26 (d, $J=2.0$ Hz, 1H; 2′ ArH), 7.70 (m, 14H), 8.06 ppm (d, $J=8.3$ Hz, 2H; 3,5 ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=14.12$ (CH_3), 22.69 (CH_2CH_3), 26.06 ($CH_2CH_2CH_2OAr$), 29.30–29.70 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.92 ($CH_3CH_2CH_2$), 52.07 (CO_2CH_3), 68.10 ($ArOCH_2CH_2$), 71.13, 71.50 ($ArOCH_2Ar$, 3′,4′ positions), 114.52 (ArCH, 2′ position), 114.79 (ArCH, G1: 3′,5′ positions), 115.22 (ArCH, 5′ position), 120.60 (ArCH, 6′ position), 126.57 (ArCH, 2,6 positions), 126.79 (ArCH, G1: 2,6 positions), 127.76, 127.95 (ArCH, G1: 3,5 positions), 128.04 (ArCH, G1: 2′,6′ positions), 128.40 (ArCCO$_2$CH$_3$), 130.07 (ArCH, 3,5 positions), 133.02 (ArC, G1: 1′ position), 133.44 (ArC, 1′ position), 135.36, 135.40 (ArC, G1: 1 positions), 140.50, 140.53 (ArC, G1: 4 positions), 145.19 (ArC, 1 position), 149.21 (ArC, 4′ position), 149.42 (ArC, 3′ position), 158.80 (ArC, G1: 4′ positions), 167.00 ppm (CO_2CH_3); MS (ESI-TOF): m/z: 968.2 $[M+Na]^+$; elemental analysis calcd (%) for $C_{64}H_{80}O_6$ (945.32): C 81.32, H 8.53; found: C 81.29, H 8.54.

Ethyl 3′,4′-bis(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-carboxylate [(4Bp-3,4Bp)12G1-CO$_2$C$_2$H$_5$] (25): A suspension of K_2CO_3 (3.45 G, 25 mmol) and **4b** (1.29 G, 50 mmol) in DMF (75 mL) was stirred for 1 h at 70 °C under Ar. Subsequently, **17** (3.86 G, 10 mmol) was added in small portions. The mixture was maintained at 70 °C for 15 h, then DMF (300 mL) was added and the mixture was poured into HCl (10 %, 400 mL) under vigorous stirring. The organic layer was collected, washed twice with H_2O, and dried over $MgSO_4$. After removal of the solvent under vacuum, the crude product was further purified by column chromatography (silica gel, $CHCl_3$). The eluent was evaporated and the residue was recrystallized from EtOAc to yield 3.73 G (77.9 %) of white crystals. $R_f=0.53$ ($CHCl_3$); m.p. 112.3 °C; purity (HPLC) 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=0.89$ (t, $J=7.1$ Hz, 6H; CH_2CH_3), 1.28 (m, 35H; $CO_2CH_2CH_3$, $CH_3(CH_2)_8$), 1.48 (qi, $J=7.3$ Hz, 4H; $ArOCH_2CH_2CH_2$), 1.81 (qi, $J=7.0$ Hz, 4H; $ArOCH_2CH_2$), 4.00 (t, $J=6.7$ Hz, 4H; $ArOCH_2$), 4.39 (t, $J=6.7$ Hz, 2H; $ArCO_2CH_2CH_3$), 5.25, 5.27 (2s, 4H; 3′,4′ $ArOCH_2$), 6.96 (d, $J=8.9$ Hz, 4H; G1: 3′,5′ ArH), 7.05 (d, $J=8.2$ Hz, 1H; 5′ ArH), 7.19 (dd, $J=2.3$, 8.3 Hz, 1H; 6′ ArH), 7.26

(overlapped with solvent peak, d, $J=2.0$ Hz, 1H; 2′ Ar*H*), 7.50 (m, 14H), 8.06 ppm (d, $J=8.3$ Hz, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta=14.08$ (CH_3), 14.35 ($CO_2CH_2CH_3$) 22.67 (CH_2CH_3), 26.07 ($CH_2CH_2CH_2OAr$), 29.31–29.66 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.91 ($CH_3CH_2CH_2$), 60.88 ($CO_2CH_2CH_3$), 68.13 ($ArOCH_2CH_2$), 71.21, 71.57 ($ArOCH_2Ar$, 3′,4′ positions), 114.67 (Ar*C*H, 2′ position), 114.82 (Ar*C*H, G1: 3′,5′ positions), 115.35 (Ar*C*H, 5′ position), 120.63 (Ar*C*H, 6′ position), 126.53 (ArCH, 2,6 positions), 126.79 (Ar*C*H, G1: 2,6 positions), 127.78, 127.96 (Ar*C*H, G1: 3,5 positions), 128.04 (Ar*C*H, G1: 2′,6′ positions), 128.40 ($ArCCO_2CH_3$), 130.03 (Ar*C*H, 3,5 positions), 133.06 (Ar*C*, G1: 1′ position), 133.57 (Ar*C*, 1′ position), 135.40, 135.44 (Ar*C*, G1: 1 positions), 140.52, 140.55 (Ar*C*, G1: 4 positions), 145.10 (Ar*C*, 1 position), 149.47 (overlapped, Ar*C*, 3′,4′ positions), 158.83 (Ar*C*, G1: 4′ positions), 166.51 ppm (CO_2CH_3); MS (ESI-TOF): m/z: 982.3 $[M+Na]^+$; elemental analysis calcd (%) for $C_{65}H_{82}O_6$ (959.34): C 81.38, H 8.62; found: C 80.98, H 8.80.

[3′,4′-Bis(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-yl]methanol [(4Bp-3,4Bp)12G1-CH_2OH] (26): Compound **24** (3.02 G, 3.2 mmol) was added portionwise under a stream of Ar to a suspension of $LiAlH_4$ (0.12 G, 3.2 mmol) in THF (200 mL) at 0°C. The mixture was heated to 50°C for 2 h under stirring. As TLC indicated a trace of the starting material, additional $LiAlH_4$ (50 mg) was added and stirring was continued for 1 h until complete reaction (TLC). The reaction mixture was filtered through Celite, washed with THF, and the solvent was evaporated. The product was recrystallized from THF to yield 2.92 G (94.5%) of fine white crystals. $R_f=0.12$ (hexanes/EtOAc 1:2); m.p. 124.5°C; purity (HPLC): 99+%; ^{1}H NMR (500 MHz, $CDCl_3$, 20°C): $\delta=0.88$ (t, $J=6.9$ Hz, 6H; CH_2CH_3), 1.27 (m, 32H; $CH_3(CH_2)_8$), 1.46 (qi, $J=7.3$ Hz, 4H; $ArOCH_2CH_2CH_2$), 1.63 (t, $J=5.9$ Hz, 1H), 1.80 (qi, $J=7.2$ Hz, 4H; $ArOCH_2CH_2$), 4.00 (t, $J=6.6$ Hz, 4H; $ArOCH_2$), 4.72 (d, $J=5.9$ Hz, 2H; CH_2OH), 5.24, 5.25 (2s, 4H; 3′,4′ $ArOCH_2Ar$), 6.95 (d, $J=8.5$ Hz, 4H; G1: 3′,5′ Ar*H*), 7.04 (d, $J=8.3$ Hz, 1H; 5′ Ar*H*), 7.13 (dd, $J=1.8$, 8.6 Hz, 1H; 6′ Ar*H*), 7.22 (d, $J=1.8$ Hz, 1H; 2′ Ar*H*), 7.40 (d, $J=8.0$ Hz, 2H; 2,6 Ar*H*), 7.52 ppm (m, 14H); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta=14.11$ (CH_3), 22.68 (CH_2CH_3), 26.06 ($CH_2CH_2CH_2OAr$), 29.30–29.70 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.91 ($CH_3CH_2CH_2$), 65.13 (CH_2OH), 68.10 ($ArOCH_2CH_2$), 71.24, 71.46 ($ArOCH_2Ar$, 3′,4′ positions), 114.47 (Ar*C*H, 2′ position), 114.78 (Ar*C*H, G1: 3′,5′ positions), 115.38 (Ar*C*H, 5′ position), 120.24 (Ar*C*H, 6′ position), 126.77 (Ar*C*H, G1: 2,6 positions), 126.97 (Ar*C*H, 2,6 positions), 127.45 (Ar*C*H, 3,5 positions), 127.78, 127.94 (Ar*C*H, G1: 3,5 positions), 128.04 (Ar*C*H, G1: 2′,6′ positions), 133.07 (Ar*C*, G1: 1′ position), 133.48 (Ar*C*, 1′ position), 135.54 (Ar*C*, G1: 1 position), 139.43 (Ar*C*, 1 position), 140.27, 140.46 (Ar*C*, G1: 4 positions), 140.43 (Ar*C*, 4 position), 148.76 (Ar*C*, 4′ position), 149.17 (Ar*C*, 3′ position), 158.78 ppm (Ar*C*, G1: 4′ positions); MS (ESI-TOF): m/z: 940.3 $[M+Na]^+$; elemental analysis calcd (%) for $C_{63}H_{80}O_5$ (917.31): C 82.49, H 8.79; found: C 82.59, H 8.65.

4-Chloromethyl-3′,4′-bis(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl [(4Bp-3,4Bp)12G1-CH_2Cl] (27): Compound **26** (1.50 G, 1.6 mmol), DTBMP (0.68 G, 3.3 mmol), and DMF (0.5 mL) were added to dry degassed CH_2Cl_2 (200 mL) under Ar. Compound **25** did not dissolve completely. Subsequently, $SOCl_2$ (0.18 mL, 2.64 mmol) was added dropwise under Ar and the reaction mixture was stirred for 1 h at 40°C. During this time, all solids had dissolved and TLC showed that **25** had been consumed. Additional CH_2Cl_2 (150 mL) was added and the organic layer was washed with H_2O (2×100 mL) and brine before drying over $MgSO_4$. Evaporation of the solvent gave a white powder, which was recrystallized from CH_2Cl_2. Yield 1.38 G (90%). $R_f=0.70$ (hexanes/CH_2Cl_2 1:1); m.p. 198–201°C; ^{1}H NMR (500 MHz, $CDCl_3$, 20°C): $\delta=0.89$ (t, $J=7.0$ Hz, 6H; CH_2CH_3), 1.28 (m, 32H; $CH_3(CH_2)_8$), 1.47 (qi, $J=7.3$ Hz, 4H; $ArOCH_2CH_2CH_2$), (1.80 qi, $J=7.2$ Hz, 4H; $ArOCH_2CH_2$), 4.00 (t, $J=6.6$ Hz, 4H; $ArOCH_2$), 4.62 (d, $J=5.9$ Hz, 2H; CH_2Cl), 5.24, 5.26 (2s, 4H; 3′,4′ $ArOCH_2$), 6.96 (d, $J=8.8$ Hz, 4H; G1: 3′,5′ Ar*H*), 7.04 (d, $J=8.4$ Hz, 1H; 5′ Ar*H*), 7.13 (dd, $J=2.0$, 8.4 Hz, 1H; 6′ Ar*H*), 7.22 (d, $J=2.0$ Hz, 1H; 2′ Ar*H*), 7.42 (d, $J=8.4$ Hz, 2H; 2,6 Ar*H*), 7.52 ppm (m, 14H); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta=14.11$ (CH_3), 22.68 (CH_2CH_3), 26.06 ($CH_2CH_2CH_2OAr$), 29.30–29.67 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.92 ($CH_3CH_2CH_2$), 46.08 (CH_2Cl), 68.09 ($ArOCH_2CH_2$), 71.20, 71.45 ($ArOCH_2Ar$, 3′,4′ positions), 114.47 (Ar*C*H, 2′ position), 114.78 (Ar*C*H, G1: 3′,5′ positions), 115.31 (Ar*C*H, 5′ position), 120.31 (Ar*C*H, 6′ position), 126.77 (Ar*C*H, G1: 2,6 positions), 127.11 (Ar*C*H, 2,6 positions), 127.77, 127.93 (Ar*C*H, G1: 3,5 positions), 128.04 (Ar*C*H, G1: 2′,6′ positions), 129.02 (Ar*C*H, 3,5 positions), 133.05 (Ar*C*, G1: 1′ position), 134.10 (Ar*C*, 1′ position), 135.49 (Ar*C*, G1: 1 position), 135.99 (Ar*C*, 4 position), 140.43, 140.73 (Ar*C*, G1: 4 positions), 140.99 (Ar*C*, 1 position), 148.93 (Ar*C*, 4′ position), 149.16 (Ar*C*, 3′ position), 158.78 ppm (Ar*C*, G1: 4′ positions); MS (ESI-TOF): m/z: 958.2 $[M+Na]^+$; elemental analysis calcd (%) for $C_{63}H_{79}O_4Cl$ (935.75): C 80.86, H, 8.51; found: C 80.65, H 8.29.

Methyl 3′,4′-bis[3′,4′-bis(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-ylmethoxy]biphenyl-4-carboxylate [(4Bp-(3,4Bp)^2)12G2-CO_2CH_3] (28): Compound **4a** (0.123 G, 0.53 mmol) was added under Ar to a suspension of K_2CO_3 (0.37 G, 2.7 mmol) in DMF (200 mL) under stirring. Subsequently, **27** (1.53 G, 1.6 mmol) was added over 4 h under a stream of Ar and the reaction mixture was stirred for 48 h at 90°C. The reaction mixture was poured into H_2O, the solid was filtered and subsequently washed on the filter with H_2O, THF, and acetone to afford an off-white powder. The crude product was dissolved in refluxing $CHCl_3$, treated hot with solid Na_2CO_3, and filtered. The $CHCl_3$ solution was passed over a silica gel column. After removal of most of the solvent, the product crystallized on cooling. Yield: 1.00 G (83%). $R_f=0.55$ ($CHCl_3$); m.p. 90.7°C; purity (HPLC) 99+%; ^{1}H NMR (500 MHz, $CDCl_3$, 20°C): $\delta=0.88$ (t, $J=7.0$ Hz, 12H; CH_2CH_3), 1.27 (m, 64H; $CH_3(CH_2)_8$), 1.46 (m, 8H; $ArOCH_2CH_2CH_2$), 1.80 (m, 8H; $ArOCH_2CH_2$), 3.93 (s, 3H; CO_2CH_3), 3.98 (2t overlapped, $J=6.8$ Hz, 8H; $ArOCH_2$), 5.20, 5.21 (2s, 8H; G1: 3′,4′ $ArOCH_2Ar$), 5.24, 5.25 (2s, 4H; 3′,4′ $ArOCH_2Ar$), 6.92 (m, 8H; G2: 3′,5′ Ar*H*), 7.03 (d, $J=8.4$ Hz, 2H; G1: 5′ Ar*H*), 7.05 (d, $J=8.5$ Hz, 1H; 5′ Ar*H*), 7.12 (m, 2H; G1: 6′ Ar*H*), 7.19 (dd, $J=2.0$, 8.3, 1H; 6′ Ar*H*), 7.23 (m, 2H; G1: 2′ Ar*H*), 7.26 (overlapped with solvent peak, m, 1H; 2′ Ar*H*), 7.52 (m, 26H), 8.60 ppm (d, $J=8.4$ Hz, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta=14.11$ (CH_3), 22.69 (CH_2CH_3), 26.07 ($CH_2CH_2CH_2OAr$), 29.31–29.67 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.92 ($CH_3CH_2CH_2$), 52.08 (CO_2CH_3), 68.09 ($ArOCH_2CH_2$), 71.15, 71.23, 71.43, 71.52 ($ArOCH_2Ar$, 3′, 4′ and G1: 3′,4′ positions), 114.37 (Ar*C*H, G1: 2′ positions), 114.74 (Ar*C*H, G2: 3′ positions), 114.58 (Ar*C*H, 2′ position), 115.30 (Ar*C*H, 5′ position), 115.35 (Ar*C*H, G1: 5′ positions), 120.26 (Ar*C*H, G1: 6′ positions), 120.64 (Ar*C*H, 6′ position), 126.58 (ArCH, 2,6 positions), 126.74 (Ar*C*H, G2: 2,6 positions), 126.92 (Ar*C*H, G1: 2,6 positions), 127.80, 127.96, 128.03 (overlapped, ArCH, G1: 3,5 and G2: 3,5,2′ positions), 128.43 ($ArCCO_2CH_3$), 130.08 (Ar*C*H, 3,5 positions), 133.06 (Ar*C*, G2: 1′ positions), 133.50 (Ar*C*, 1′ position), 134.42 (Ar*C*, G1: 1′ positions), 135.50 (Ar*C*, G2: 1 positions), 135.64, 135.69 (Ar*C*, G1: 1 positions), 140.39, 140.42 (overlapped), 140.48 (Ar*C*, G1: 4 and G2: 4 positions), 145.16 (Ar*C*, 1 position), 148.84, 149.21, 149.41 (overlapped) (Ar*C*, 3′,4′ and G1: 3′,4′ positions), 158.77 (Ar*C*, G2: 4′ positions), 166.99 ppm (CO_2CH_3); MS (MALDI-TOF): m/z: 2065.7 $[M+Na]^+$; elemental analysis calcd (%) for $C_{140}H_{168}O_{12}$ (2042.82): C 82.31, H 8.29; found: C 81.93, H 8.48.

Methyl 3′,4′-bis(3′,4′-bisdodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-carboxylate [(3,4Bp)^{2}12G2-CO_2CH_3] (29): A mixture of **4a** (0.51 G, 2.2 mmol), K_2CO_3 (1.51 G, 11.0 mmol), and **20** (2.5 G, 4.38 mmol) in DMF (100 mL) was stirred at 70°C for 15 h, then poured into stirring H_2O. The organic phase was extracted with CH_2Cl_2 (3×200 mL), which was combined, treated with HCl (0.1 M, 100 mL) rapidly followed by Na_2CO_3 solution (0.4 M, 100 mL), then washed with brine and dried over Na_2SO_4. Evaporation and subsequent recrystallization from acetone yielded 2.44 G (86%) of the product. $R_f=0.52$ (hexanes/EtOAc 1:1); m.p. 79.1°C; purity (HPLC) 99+%; ^{1}H NMR (500 MHz, $CDCl_3$, 20°C): $\delta=0.88$ (m, 12H; CH_2CH_3), 1.27 (m, 64H; $CH_3(CH_2)_8$), 1.48 (m, 8H; $ArOCH_2CH_2CH_2$), 1.81 (qi, $J=6.3$ Hz, 8H; $ArOCH_2CH_2$), 3.93 (s, 3H; CO_2CH_3), 4.04 (2t overlapped, $J=6.8$ Hz, 8H; $ArOCH_2$), 5.26, 5.27 (2s, 4H; 3′,4′ $ArOCH_2Ar$), 6.94 (d, $J=8.1$ Hz, 2H; G1: 5′ Ar*H*), 7.05 (d, $J=8.4$ Hz, 1H; 5′ Ar*H*), 7.12 (m, 4H; G1: 2′,6′ Ar*H*), 7.18 (dd, $J=2.2$, 8.3 Hz, 1H; 6′ Ar*H*), 7.25 (d, $J=2.2$ Hz, 1H; 2′ Ar*H*), 7.53 (m, 10H), 8.06 ppm (d, $J=8.6$ Hz, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): $\delta=14.10$ (CH_3), 22.69 (CH_2CH_3), 26.67 ($CH_2CH_2CH_2OAr$), 29.34–29.69 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.91 ($CH_3CH_2CH_2$), 52.04 (CO_2CH_3), 69.33, 69.46 ($ArOCH_2CH_2$, G1: 3′,4′ positions), 71.05, 71.41 (ArOCH_2Ar, 3′,4′ positions), 113.07 (Ar*C*H, G1: 2′ positions), 114.04 (Ar*C*H, G1: 5′ positions), 114.43 (Ar*C*H, 2′ position), 115.18 (Ar*C*H, 5′ position), 119.56 (Ar*C*H, G1: 6′ positions), 120.55 (Ar*C*H, 6′ position), 126.54 (ArCH, 2,6 positions), 126.91 (Ar*C*H, G1: 2,6 positions), 127.68, 127.89 (Ar*C*H, G1: 3,5 positions), 128.39 (ArCCO_2CH_3), 130.05 (Ar*C*H, 3,5 positions), 133.40 (Ar*C*, G1: 1′ position), 133.73 (Ar*C*, 1′ position), 135.48, 135.51 (Ar*C*, G1: 1 positions), 140.72, 140.76 (Ar*C*, G1: 4 positions), 145.15 (Ar*C*, 1 position), 148.94, 149.16, 149.33, 149.35 (Ar*C*, 3′,4′, G1: 3′,4′ positions), 166.96 ppm (CO_2CH_3); MS (ESI-TOF): *m*/*z*: 1336.7 $[M+Na]^+$; elemental analysis calcd (%) for $C_{88}H_{128}O_8$ (1313.95): C 80.44, H 9.82; found: C 80.59, H 10.12.

Ethyl 3′,4′-bis(3′,4′-bisdodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-carboxylate [(3,4Bp)^{2}12G2-$CO_2C_2H_5$] (30): A mixture of **4b** (0.75 G, 2.9 mmol), K_2CO_3 (1.2 G, 8.7 mmol), and **20** (3.3 G, 5.8 mmol) in DMF (150 mL) was stirred at 70 °C for 15 h then poured into water and filtered. The solid was dissolved in $CHCl_3$, dried and purified by column chromatography (silica gel, $CHCl_3$). After the solvent was evaporated, the product was recrystallized from EtOAc to yield 2.53 G (65.7 %) of white crystals. $R_f=0.47$ ($CHCl_3$); m.p. 78.6; purity (HPLC) 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=0.88$ (m, 12 H; CH_2CH_3), 1.27 (m, 67 H; $CH_3(CH_2)_8$), 1.48 (m, 8 H; $ArOCH_2CH_2CH_2$), 1.81 (m, 8 H; $ArOCH_2CH_2$), 4.04 (2 t overlapped, $J=6.8$ Hz, 8 H $ArOCH_2$), 3.93 (q, $J=7.0$ Hz, 2 H; $CO_2CH_2CH_3$), 5.26, 5.28 (2 s, 4 H; 3′,4′ $ArOCH_2Ar$), 6.94 (m, 2 H; G1: 5′ ArH), 7.11 (m, 5 H; 5′ and G1: 2′,6′ ArH), 7.18 (dd, $J=2.2$, 8.3 Hz, 1 H; 6′ ArH), 7.26 (overlapped with solvent peak, m, 1 H; 2′ ArH), 7.53 (m, 10 H), 8.07 ppm (d, $J=8.6$ Hz, 2 H; 3,5 ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=14.08$ (CH_3), 14.34 ($CO_2CH_2CH_3$) 22.67 (CH_2CH_3), 26.07 ($CH_2CH_2CH_2OAr$), 29.36–29.70 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.92 ($CH_3CH_2CH_2$), 60.89 ($CO_2CH_2CH_3$), 69.42, 69.54 ($ArOCH_2CH_2$, G1: 3′,4′ positions), 71.16, 71.51 ($ArOCH_2Ar$, 3′,4′ positions), 113.25 (Ar*C*H, G1: 2′ positions), 114.23 (Ar*C*H, G1: 5′ positions), 114.62 (Ar*C*H, 2′ position), 115.35 (Ar*C*H, 5′ position), 119.63 (Ar*C*H, G1: 6′ positions), 120.60 (Ar*C*H, 6′ position), 126.53 (ArCH, 2,6 positions), 126.93 (Ar*C*H, G1: 2,6 positions), 127.72, 127.89 (Ar*C*H, G1: 3,5 positions), 128.82 ($ArCCO_2CH_3$), 130.03 (Ar*C*H, 3,5 positions), 133.57 (Ar*C*, G1: 1′ position), 133.82 (Ar*C*, 1′ position), 135.54, 135.58 (Ar*C*, G1: 1 positions), 140.76, 140.80 (Ar*C*, G1: 4 positions), 145.08 (Ar*C*, 1 position), 149.03, 149.25, 149.35, 149.43 (Ar*C*, 3′,4′, G1: 3′,4′ positions), 166.96 ppm (CO_2CH_3); MS (ESI-TOF): *m*/*z*: 1350.6 $[M+Na]^+$; elemental analysis calcd (%) for $C_{89}H_{130}O_8$ (1327.98): C 80.49, H 9.87; found: C 80.61, H 10.04.

[3′,4′-Bis(3′,4′-bisdodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-yl]methanol [(3,4Bp)^{2}12G2-CH_2OH] (31): Compound **29** (1.80 G, 1.38 mmol) was added portionwise under Ar to a suspension of $LiAlH_4$ (150 mg, 4.2 mmol) in THF (100 mL) at 0 °C, then stirred as it was warmed to 22 °C over 15 h. The reaction mixture was filtered through Celite, washed with THF, and the filtrate was evaporated. The residue was dissolved in hot $CHCl_3$ (300 mL), then filtered to remove residual inorganic solids. Evaporation and recrystallization from acetone yielded 1.47 G (83 %) of a fine white solid. $R_f=0.72$ (hexanes/CH_2Cl_2 1:2); m.p. 83.0 °C; purity (HPLC) 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=0.89$ (t, $J=6.9$ Hz, 12 H; CH_2CH_3), 1.28 (m, 64 H; $CH_3(CH_2)_8$), 1.46 (m, 8 H; $ArOCH_2CH_2CH_2$), 1.67 (t, $J=5.7$ Hz, 1 H; CH_2OH), 1.84 (m, 8 H; $ArOCH_2CH_2$), 4.04 (2 t overlapped, $J=6.9$ Hz, 8 H; $ArOCH_2$), 4.72 (d, $J=5.4$ Hz, 2 H; CH_2OH), 5.25, 5.27 (2 s, 4 H; 3′,4′$ArOCH_2Ar$), 6.94 (d, $J=8.5$ Hz, 2 H; G1, 5′ ArH), 7.04 (d, $J=8.3$ Hz, 1 H; 5′ ArH), 7.13 (m, 5 H; 6′ and G1: 2′,6′ ArH), 7.23 (d, $J=1.8$ Hz, 1 H; 2′ ArH), 7.40 (d, $J=8.0$ Hz, 2 H; 2,6 ArH), 7.54 ppm (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=14.10$ (CH_3), 22.68 (CH_2CH_3), 26.06 ($CH_2CH_2CH_2OAr$), 29.34–29.70 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.91 ($CH_3CH_2CH_2$), 65.08 (CH_2OH), 69.35, 69.45 ($ArOCH_2CH_2$, G1: 3′,4′ positions), 71.17, 71.37 ($ArOCH_2Ar$, 3′,4′ positions), 113.08 (Ar*C*H, G1: 2′ positions), 114.06 (Ar*C*H, G1: 5′ positions), 114.39 (Ar*C*H, 2′ position), 115.33 (Ar*C*H, 5′ position), 119.56 (Ar*C*H, G1: 6′ positions), 120.21 (Ar*C*H, 6′ position), 126.90 (Ar*C*H, G1: 2,6 positions), 126.93 (Ar*C*H, 2,6 positions), 127.42 (Ar*C*H, 3,5 positions), 127.70, 127.86 (Ar*C*H, G1: 3,5 positions), 133.78, 133.80 (Ar*C*, G1: 1′ positions), 134.45 (Ar*C*, 1′ position), 135.62 (Ar*C*, G1: 1 positions), 139.46 (Ar*C*, 4 position), 140.21 (Ar*C*, 1 position), 140.66, 140.69 (Ar*C*, G1: 4 positions), 148.64, 148.90, 149.12, 149.32 ppm (Ar*C*, 3′,4′, G1: 3′,4′ positions); MS (ESI-TOF): *m*/*z*: 1308.7 $[M+Na]^+$; elemental analysis calcd (%) for $C_{87}H_{128}O_7$ (1285.94): C 81.26, H 10.03; found: C 81.52, H 9.83.

4-Chloromethyl-3′,4′-bis(3′,4′-bisdodecyloxybiphenyl-4-ylmethoxy)biphenyl [(3,4Bp)^{2}12G2-CH_2Cl] (32): Compound **31** (1.00 G, 0.78 mmol), $SOCl_2$ (0.09 mL, 1.20 mmol), and DTBMP (0.32 G, 1.57 mmol) in CH_2Cl_2 (150 mL) were stirred for 3 h at 22 °C. After workup as described for **27**, the product **32** was obtained as a white solid. Two recrystallizations from acetone gave fine white crystals (0.88 G, 87 %). A similar subsequent reaction yielded 92 % from a single recrystallization from EtOH. $R_f=0.36$ (hexanes/CH_2Cl_2 5:1); m.p. 128.0–129 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=0.89$ (t, $J=6.9$ Hz, 12 H; CH_2CH_3), 1.27 (m, $CH_3(CH_2)_8$), 64 H; 1.48 (m, 8 H; $ArOCH_2CH_2CH_2$), 1.84 (m, 8 H; $ArOCH_2CH_2$), 4.04 (2 t overlapped, $J=6.9$ Hz, 8 H; $ArOCH_2$), 4.62 (s, 2 H; CH_2Cl), 5.25, 5.27 (2 s, 4 H; 3′,4′ $ArOCH_2Ar$), 6.94 (d, $J=8.1$ Hz, 2 H; G1: 5′ ArH), 7.04 (d, $J=8.3$ Hz, 1 H; 5′ ArH), 7.12 (m, 5 H; 6′ and G1: 2′,6′ ArH), 7.21 (d, $J=1.8$ Hz, 1 H; 2′ ArH), 7.42 (d, $J=8.3$ Hz, 2 H; 2,6 ArH), 7.53 ppm (m, 10 H); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=14.10$ (CH_3), 22.68 (CH_2CH_3), 26.06 ($CH_2CH_2CH_2OAr$), 29.34–29.70 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.92 ($CH_3CH_2CH_2$), 46.06 (CH_2Cl), 69.35, 69.45 ($ArOCH_2CH_2$, G1: 3′,4′ positions), 71.14, 71.38 ($ArOCH_2Ar$, 3′,4′ positions), 113.08 (Ar*C*H, G1: 2′ positions), 114.06 (Ar*C*H, G1: 5′ positions), 114.42 (Ar*C*H, 2′ position), 115.28 (Ar*C*H, 5′ position), 119.57 (Ar*C*H, G1: 6′ positions), 120.28 (Ar*C*H, 6′ position), 126.92 (Ar*C*H, G1: 2,6 positions), 126.10 (Ar*C*H, 2,6 positions), 127.70, 127.85 (Ar*C*H, G1: 3,5 positions), 129.02 (Ar*C*H, 3,5 positions), 133.78, 133.80 (Ar*C*, G1: 1′ positions), 134.08 (Ar*C*, 1′ position), 135.63 (Ar*C*, G1: 1 positions), 136.02 (Ar*C*, 4 position), 140.70 (Ar*C*, G1: 4 positions), 140.99 (Ar*C*, 1 position), 148.67, 148.92, 149.11, 149.33 ppm (Ar*C*, 3′,4′, G1: 3′,4′ positions); MS (ESI-TOF): *m*/*z*: 1327.8 $[M+Na]^+$ elemental analysis calcd (%) for $C_{87}H_{127}ClO_6$ (1304.39): C 80.11, H 9.81; found: C 79.88, H 10.03.

Methyl 3′,4′-bis[3′,4′-bis(3′,4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-ylmethoxy]biphenyl-4-carboxylate [(3,4Bp)^{3}12G3-CO_2CH_3] (33): A mixture of **32** (65 mg, 0.49 mmol), K_2CO_3 (276 mg, 2.0 mmol), and **4a** (59 mg, 0.25 mmol) in DMF (200 mL) was maintained at 80 °C for 15 h, then poured into H_2O. The precipitate was filtered and washed with H_2O and acetone. The solid was subsequently recrystallized from CH_2Cl_2 to give 540 mg (80.0 %) of a fine white powder. $R_f=0.40$ (hexanes/CH_2Cl_2 1:2); m.p. 68.7 °C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=0.88$ (m, 24 H; CH_2CH_3), 1.27 (m, 128 H; $CH_3(CH_2)_8$), 1.48 (m, 16 H; $ArOCH_2CH_2CH_2$), 1.82 (m, 16 H; $ArOCH_2CH_2$), 3.93 (s, 3 H; CO_2CH_3), 4.02 (2 t overlapped, $J=6.8$ Hz, 16 H; $ArOCH_2$), 5.22, 5.23 (2 s, 8 H; G1: 3′,4′ $ArOCH_2Ar$), 5.25, 5.26 (2 s, 4 H; 3′,4′ $ArOCH_2Ar$), 6.92 (m, 4 H; G2: 5′ ArH), 7.03 (m, 3 H; 5′ and G1: 5′ ArH), 7.11 (m, 10 H; G1: 6′ and G2: 2′,6′ ArH), 7.18 (dd, $J=2.2$, 8.3 Hz, 1 H; 6′ ArH), 7.24 (m, 3 H; 2′ and G1: 2′ ArH), 7.52 (m, 26 H), 8.60 ppm (d, $J=8.6$ Hz, 2 H; 3,5 ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=14.10$ (CH_3), 22.68 (CH_2CH_3), 26.07 ($CH_2CH_2CH_2OAr$), 29.38–29.69 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.92 ($CH_3CH_2CH_2$), 52.07 (CO_2CH_3), 69.35, 69.45 ($ArOCH_2CH_2$, G1: 3′,4′ positions), 71.11. 71.19, 71.37, 71.47 ($ArOCH_2Ar$, 3′,4′ and G1: 3′,4′ positions), 113.12 (Ar*C*H, G2: 2′ positions), 114.10 (Ar*C*H, G2: 5′ positions), 114.37 (Ar*C*H, G1: 2′ positions), 114.58 (Ar*C*H, 2′ position), 115.31, 115.40 (Ar*C*H, 5′ and G1: 5′ positions), 119.58 (Ar*C*H, G2: 6′ positions), 120.26 (Ar*C*H, G1: 6′ positions), 120.62 (Ar*C*H, 6′ position), 126.54 (ArCH, 2,6 positions), 126.88 (Ar*C*H, G2: 2,6 positions), 126.92 (Ar*C*H, G1: 2,6 positions), 127.72 (overlapped), 127.89, 127.93 (Ar*C*H, G1: 3,5 and G2: 3,5 positions), 128.44 ($ArCCO_2CH_3$), 130.07 (Ar*C*H, 3,5 positions), 133.49 (Ar*C*, G1: 1′ positions), 133.80 (Ar*C*, G2: 1′ positions), 134.41 (Ar*C*, 1′ position), 135.68, 135.72 overlapped (Ar*C*, G1: 1 and G2: 1 positions), 140.31, 140.76 (Ar*C*, G1: 4 positions), 140.65, 140.69 (Ar*C*, G2: 4 positions), 145.14 (Ar*C*, 1 position), 148.81, 148.94, 149.20, 149.36, 149.39 overlapped (Ar*C*, 3′,4′, G1: 3′,4′, G2: 3′,4′ positions), 166.95 ppm (CO_2CH_3); MS (MALDI-TOF): *m*/*z*: 2800.6 $[M+Na]^+$; elemental analysis calcd (%) for $C_{188}H_{264}O_{16}$ (2780.10): C 81.22, H 9.57; found: C 81.40, H 9.68.

Methyl 3′,5′-bis[3′,4′-bis(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-ylmethoxy]biphenyl-4-carboxylate [(4Bp-3,4Bp-3,5Bp)12G2-CO_2CH_3] (34): A mixture of **10** (65 mg, 0.27 mmol), K_2CO_3 (150 mg, 1.08 mmol), and **27**

(500 mg, 0.54 mmol) in Ar-degassed DMF (50 mL) was stirred at 70 °C for 36 h, then poured into ice/water and stirred until a white precipitate developed. This was filtered off and washed with H_2O followed by acetone. The product was washed with THF. The solvent was evaporated and the product was purified by column chromatography (silica gel, $CHCl_3$/hexanes 5:1) to yield 120 mg (21.8 %) of **34**. R_f = 0.49 (hexanes/CH_2Cl_2 1:1); purity (HPLC): 99+ %; ^1H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 0.88 (m, 12 H; CH_2CH_3), 1.27 (t, J = 7.1 Hz, 64 H; $CH_3(CH_2)_8$), 1.47 (m, 8 H; $ArOCH_2CH_2CH_2$), 1.80 (qi, J = 6.8 Hz, 8 H; $ArOCH_2CH_2$), 3.94 (s, 3 H; CO_2CH_3), 3.99 (2 t overlapped, J = 6.8 Hz, 8 H; $ArOCH_2$), 5.12 (s, 4 H; 3′, 5′ $ArOCH_2Ar$), 5.23, 5.24 (2 s, 8 H; G1: 3′, 5′ $ArOCH_2Ar$), 6.68 (t, J = 2.0 Hz, 1 H; 4′ Ar*H*), 6.87 (d, J = 2.0 Hz, 2 H; 2′,6′ Ar*H*), 6.95 (m, 8 H; G2: 3′,5′ Ar*H*), 7.04 (d, J = 8.4 Hz, 2 H; G1: 5′ Ar*H*), 7.13 (dd, J = 2.2, 8.3 Hz, 2 H; G1: 6′ *H*), 7.23 (d, J = 2.0 Hz, 2 H; G1: 2′ Ar*H*), 7.50 (m, 32 H; Ar*H*), 7.63 (d, J = 8.3 Hz, 2 H; 2,6 Ar*H*), 8.09 ppm (d, J = 8.3 Hz, 2 H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ = 14.11 (CH_3), 22.69 (CH_2CH_3), 26.07 ($CH_2CH_2CH_2OAr$), 29.31–29.66 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.92 ($CH_3CH_2CH_2$), 52.14 (CO_2CH_3), 68.10 ($ArOCH_2CH_2$, G2: 4′ positions), 70.03 ($ArOCH_2Ar$, 3′,5′ positions), 71.24, 71.45 ($ArOCH_2CH_2$, G1: 3′,4′ positions), 101.62 (Ar*C*, 4′ position), 106.87 (Ar*C*H, 2′,6′ positions), 114.45 (Ar*C*H, G1: 2′ positions), 114.78 (Ar*C*H, G2: 3′,5′ positions), 115.36 (Ar*C*H, G1: 5′ positions), 120.30 (Ar*C*H, G1: 6′ positions), 126.77 (Ar*C*H, G1: 2,6 and G2: 2,6 positions), 127.05 (Ar*C*H, 2,6 positions), 127.79, 127.94 (Ar*C*H, G2: 3,5 positions), 128.04 (Ar*C*H, G1: 3,5 and G2: 2′,6′ positions), 129.19 ($ArCCO_2CH_3$), 130.06 (Ar*C*H, 3,5 positions), 133.08 (Ar*C*, G2: 1′ position), 134.37 (Ar*C*, G1: 1′ positions), 135.22 (Ar*C*, G1: 1 positions), 135.51 (Ar*C*, G2: 1 positions), 140.43, 140.47 (Ar*C*, G2: 4 positions), 140.70 (Ar*C*, G1: 4 positions), 142.22 (Ar*C*, 1′ position), 145.43 (Ar*C*, 1 position), 148.85, 149.20 (Ar*C*, G1: 3′,4′ positions), 158.78 (Ar*C*, G2: 4′ positions), 160.31 (Ar*C*, 3′,5′ positions), 166.92 ppm (CO_2CH_3); MS (MALDI-TOF): *m*/*z*: 2064.6 $[M+Na]^+$; elemental analysis calcd (%) for $C_{140}H_{168}O_{12}$ (2042.82): C 82.31, H 8.29; found: C 82.02, H 8.32.

{3′,5′-bis[3′,4′-bis(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-ylmethoxy]biphenyl-4-yl}methanol [(4Bp-3,4Bp-3,5Bp)12G2-CH_2OH] (35): Compound **34** (144 mg, 0.071 mmol) was dissolved in dry THF (60 mL) and added into a suspension of $LiAlH_4$ (29 mg, 0.705 mmol) in dry THF (20 mL) under Ar at 0 °C. The reaction mixture was stirred at 0 °C for 1.5 h until 100 % conversion by TLC (CH_2Cl_2/hexane 2:1), then quenched by addition of water (0.2 mL) and NaOH solution (15 %, 0.2 mL). Precipitation was removed by filtration through Celite. The filtrate was carefully precipitated with MeOH and purified by crystallization from THF. 110 mg (77 %) of **34** was obtained as white crystals. R_f = 0.25 (CH_2Cl_2); m.p. 94.0 °C; purity (HPLC): 99+ %; ^1H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 0.89 (m, 12 H; CH_2CH_3), 1.27 (t, J = 7.1 Hz, 64 H; $CH_3(CH_2)_8$), 1.65 (t, 1 H; CH_2OH), 1.47 (m, 8 H; $ArOCH_2CH_2CH_2$), 1.82 (m, 8 H; $ArOCH_2CH_2$), 3.99 (2 t overlapped, 8 H; $ArOCH_2$), 4.75 (d, J = 5.6 Hz, 2 H; CH_2OH), 5.13 (s, 4 H; 3′, 5′ $ArOCH_2Ar$), 5.24, 5.25 (2 s, 8 H; G1: 3′, 5′ $ArOCH_2Ar$), 6.66 (s, 1 H; 4′ Ar*H*), 6.86 (d, J = 2.1 Hz, 2 H; 2′,6′ Ar*H*), 6.97 (dd, J = 2.1, 8.6 Hz, 8 H; G2: 3′,5′ Ar*H*), 7.05 (d, J = 8.2 Hz, 2 H; G1: 5′ Ar*H*), 7.15 (dd, J = 1.8, 8.3 Hz, 2 H; G1: 6′ *H*), 7.25 (d, J = 2.0 Hz, 2 H; G1: 2′ Ar*H*), 7.40–7.60 ppm (overlapped m, 36 H; Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ = 14.31 (CH_3), 22.90 (CH_2CH_3), 26.31 ($CH_2CH_2CH_2OAr$), 29.56–28.89 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 32.14 ($CH_3CH_2CH_2$), 65.33 (CH_2OH), 68.39 ($ArOCH_2CH_2$, G2: 4′ positions), 70.27 ($ArOCH_2Ar$, 3′,5′ positions), 71.60, 71.80 ($ArOCH_2CH_2$, G1: 3′,4′ positions), 101.29 (Ar*C*, 4′ position), 107.01 (Ar*C*H, 2′,6′ positions), 114.89 (Ar*C*H, G1: 2′ positions), 115.08 (Ar*C*H, G2: 3′,5′ positions), 115.79 (Ar*C*H, G1: 5′ positions), 120.59 (Ar*C*H, G1: 6′ positions), 127.27 (Ar*C*H, G1: 2,6 and G2: 2,6 positions), 127.27 (Ar*C*H, 2,6 positions), 127.57 (Ar*C*H, G2: 3,5 positions), 128.05, 128.20 (Ar*C*H, G1: 3,5 and G2: 2′,6′ positions), 133.37 (Ar*C*H), 134.81 (Ar*C*), 135.67 (Ar*C*, G1: 1 positions), 135.82 (Ar*C*, G2: 1 positions), 140.50, 140.72 (Ar*C*, G2: 4 positions), 140.90 (Ar*C*, G1: 4 positions), 143.33 (Ar*C*), 149.18 (Ar*C*), 149.54 (Ar*C*, G1: 3′,4′ positions), 159.06 (Ar*C*, G2: 4′ positions), 160.52 ppm (Ar*C*, 3′,5′ positions); MS (MALDI-TOF): *m*/*z*: 2012.5 $[M-H^+]$; elemental analysis calcd (%) for $C_{139}H_{168}O_{11}$ (2014.81): C 82.86, H 8.40; found: C 82.73, H 8.32.

Methyl 3′,5′-bis[3′,4′-bis(3′,4′-bisdodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-ylmethoxy]biphenyl-4-carboxylate [$(3,4Bp)^2$-3,5Bp)12G3-CO_2CH_3] (36): A mixture of **10** (59 mg, 0.25 mmol), K_2CO_3 (138 mg, 1.0 mmol), and **32** (650 mg, 0.5 mmol) in DMF (50 mL) was stirred at 70 °C for 15 h then poured into H_2O. The precipitated solid was extracted with CH_2Cl_2 (2 × 150 mL). The solution was washed with H_2O and brine, dried over Na_2SO_4, and evaporated. The product was subsequently dissolved in warm hexanes. The hexanes solution was extracted with H_2O to remove residual DMF, then with brine, followed by concentrating to about 20 mL. The product was precipitated by the addition of acetone to yield 510 mg (74 %) of **36**. R_f = 0.49 (hexanes/CH_2Cl_2 1:2); m.p. 71.6 °C; purity (HPLC): 99+ %; ^1H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 0.88 (m, 24 H; CH_2CH_3), 1.27 (m, 128 H; $CH_3(CH_2)_8$), 1.48 (m, 16 H; $ArOCH_2CH_2CH_2$), 1.82 (m, 16 H; $ArOCH_2CH_2$), 3.94 (s, 3 H; CO_2CH_3), 4.03 (2 t overlapped, J = 6.8 Hz, 16 H; $ArOCH_2$), 5.13 (s, 4 H; 3′,5′ $ArOCH_2Ar$), 5.25, 5.26 (s, 8 H; G1: 3′,4′ $ArOCH_2Ar$), 6.70 (t, J = 2.0 Hz, 1 H; 4′ Ar*H*), 6.87 (d, J = 2.0 Hz, 2 H; G1: 2′,6′ Ar*H*), 6.93 (dd, J = 1.4, 8.8 Hz, 4 H; G2: 5′ Ar*H*), 7.03 (d, J = 8.4 Hz, 2 H; G1: 5′ Ar*H*), 7.11 (m, 10 H; G1: 6′ and G2: 2′,6′ Ar*H*), 7.30 (d, J = 2.2 Hz, 2 H; G1: 2′ Ar*H*), 7.52 (m, 24 H), 7.63 (d, J = 8.4 Hz, 2 H; 3,5 Ar*H*); 8.60 ppm (d, J = 8.4 Hz, 2 H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ = 14.10 (CH_3), 22.68 (CH_2CH_3), 26.06 ($CH_2CH_2CH_2OAr$), 29.34–29.70 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.92 ($CH_3CH_2CH_2$), 52.12 (CO_2CH_3), 69.36, 69.46 ($ArOCH_2CH_2$, G1: 3′,4′ positions), 70.03 ($ArOCH_2Ar$, 3′,5′ positions), 71.18, 71.38 ($ArOCH_2Ar$, G1: 3′,4′ positions), 101.60 (Ar*C*, 4′ position), 106.81 (Ar*C*H, 2′,6′ positions), 113.08 (Ar*C*H, G2: 2′ positions), 114.06 (Ar*C*H, G2: 5′ positions), 114.38 (Ar*C*H, G1: 2′ positions), 115.32 (Ar*C*H, G1: 5′ positions), 119.57 (Ar*C*H, G2: 6′ positions), 120.27 (Ar*C*H, G1: 6′ positions), 126.91 (Ar*C*H, G1: 2,6 and G2: 2,6 positions), 127.02 (Ar*C*H, 2,6 positions), 127.71, 127.87, 128.06 (Ar*C*H, G1: 3,5 and G2: 3,5 positions), 129.18 ($ArCCO_2CH_3$), 130.04 (Ar*C*H, 3,5 positions), 133.78, 133.80 (Ar*C*, G2: 1′ positions), 134.36 (Ar*C*, G1: 1′ positions), 135.21 (Ar*C*, 1′ position), 135.64, 135.66 overlapped (Ar*C*, G1: 1 and G2: 1 positions), 140.67, 140.71 (Ar*C*, G1: 4 and G2: 4 positions), 145.41 (Ar*C*, 1 position), 148.80, 148.91, 149.15, 149.32 (Ar*C*, G1: 3′ 4′ and G2: 3′4′ positions), 160.31 (Ar*C*, 3′,5′ positions), 166.90 ppm (CO_2CH_3); MS (MALDI-TOF): *m*/*z*: 2800.3 $[M+Na]^+$; elemental analysis calcd (%) for $C_{188}H_{264}O_{16}$ (2780.10): C 81.22, H 9.57; found: C 80.94, H 9.70.

Methyl 3′,5′-bis(3′,4′-bisdodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-carboxylate [(3,4Bp-3,5Bp)12G2-CO_2CH_3] (37): A mixture of **10** (367 mg, 1.6 mmol), K_2CO_3 (870 mg, 6.3 mmol), and **20** (1.85 G, 3.15 mmol) in DMF (70 mL) was stirred at 70 °C for 16 h under N_2. The reaction mixture was poured into H_2O and extracted with CH_2Cl_2 (3 × 200 mL). The CH_2Cl_2 solution was extracted once with HCl (100 mL, 0.1 M), followed by Na_2CO_3 (0.4 M, 100 mL), washed with brine, dried over Na_2SO_4, and evaporated to give a white solid that was further purified by column chromatography (silica gel, CH_2Cl_2) to give 1.42 G (69 %) of **37**. R_f = 0.78 (CH_2Cl_2); m.p. 61.3 °C; purity (HPLC) 99+ %; ^1H NMR (500 MHz, $CDCl_3$, 20 °C): δ = 0.88 (m, 12 H; CH_2CH_3), 1.27 (m, 64 H; $CH_3(CH_2)_8$), 1.48 (m, 8 H; $ArOCH_2CH_2CH_2$), 1.84 (qi, J = 6.8 Hz, 8 H; $ArOCH_2CH_2$), 3.94 (s, 3 H; CO_2CH_3), 4.05 (2 t overlapped, J = 6.8 Hz, 8 H; $ArOCH_2$), 5.14 (s, 4 H; 3′, 5′ $ArOCH_2Ar$), 6.70 (t, J = 2.2 Hz, 1 H; 4′ Ar*H*), 6.88 (d, J = 2.3 Hz, 2 H; 2′,6′ Ar*H*), 6.95 (d, J = 8.8 Hz, 2 H; G1: 5′ Ar*H*), 7.12 (m, 4 H; G1: 2′,6′ Ar*H*), 7.50 (d, J = 8.4 Hz, 4 H; G1: 2′,6′ Ar*H*), 7.48 (d, J = 8.4 Hz, 4 H; G1: 3′,5′ Ar*H*), 7.64 (d, J = 8.4 Hz, 2 H; 2,6 Ar*H*), 8.10 ppm (d, J = 8.6 Hz, 2 H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ = 14.11 (CH_3), 22.68 (CH_2CH_3), 26.57 ($CH_2CH_2CH_2OAr$), 29.32–29.70 ($ArOCH_2CH_2$, $CH_3CH_2CH_2(CH_2)_6$), 31.92 ($CH_3CH_2CH_2$), 52.12 (CO_2CH_3), 69.36, 69.48 ($ArOCH_2CH_2$, G1: 3′,4′ positions), 70.06 ($ArOCH_2Ar$, 3′,5′ positions), 101.66 (Ar*C*, 4′ position), 106.78 (Ar*C*H, 2′,6′ positions), 113.15 (Ar*C*H, G1: 2′ positions), 114.07 (Ar*C*H, G1: 5′ positions), 119.60 (Ar*C*H, G1: 6′ positions), 127.04 (Ar*C*H, G1: 2,6 positions), 127.08 (Ar*C*H, 2,6 positions), 128.04 (Ar*C*H, G1: 3,5 positions), 129.17 ($ArCCO_2CH_3$), 130.04 (Ar*C*H, 3,5 positions), 133.74 (Ar*C*, G1: 1′ position), 135.04 (Ar*C*, G1: 1 positions), 141.10 (Ar*C*, G1: 4 positions), 142.2 (Ar*C*, 1′ position), 145.43 (Ar*C*, 1 position), 148.93, 149.34 (Ar*C*, G1: 3′,4′ positions), 160.32 (Ar*C*, 3′,5′ positions), 166.91 ppm (CO_2CH_3); MS (ESI-TOF): *m*/*z*: 1336.7 $[M+Na]^+$; elemental analysis calcd (%) for $C_{88}H_{128}O_8$ (1313.95): C 80.44, H 9.82; found: C 80.31, H 10.08.

[3′,5′-Bis(3′,4′-bisdodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-yl]methanol [(3,4Bp-3,5Bp)12G2-$\mathrm{CH_2OH}$] (38): Compound **37** (1.22 G, 0.93 mmol) was added portionwise under Ar to a suspension of $\mathrm{LiAlH_4}$ (150 mg, 4.2 mmol) in THF (100 mL) at 0 °C and stirred as it was warmed to 22 °C for 1.5 h. After this time, TLC showed complete reaction. The reaction mixture was filtered through Celite, washed with more THF, followed by evaporation of the solvent. The residue was dissolved in hot $\mathrm{CHCl_3}$ (200 mL), the solution was filtered to remove the inorganic compounds and the solvent was evaporated. The product was subsequently recrystallized from acetone to yield 1.02 G (85 %) of a fine white solid. $R_f=0.17$ (hexanes/$\mathrm{CH_2Cl_2}$ 1:2); m.p. 42.2 °C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta=0.88$ (m, 12 H; $\mathrm{CH_2C}H_3$), 1.27 (m, 64 H; $\mathrm{CH_3(C}H_2)_8$), 1.48 (qi, $J=7.7$ Hz, 8 H; $\mathrm{ArOCH_2CH_2C}H_2$), 1.65 (t, $J=4.2$ Hz, 1 H; $\mathrm{CH_2O}H$), 1.84 (qi, $J=7.3$ Hz, 8 H; $\mathrm{ArOCH_2C}H_2$), 4.05 (2t overlapped, $J=6.6$ Hz, 8 H; $\mathrm{ArOC}H_2$), 4.75 (d, $J=4.2$ Hz, 2 H; $\mathrm{CH_2OH}$), 5.13 (s, 4 H; 3′,5′ $\mathrm{ArOC}H_2\mathrm{Ar}$), 6.67 (t, $J=2.2$ Hz, 1 H; 4′ ArH), 6.86 (d, $J=2.2$ Hz, 2 H; 2′,6′ ArH), 6.95 (d, $J=8.8$ Hz, 2 H; G1: 5′ ArH), 7.12 (m, 4 H; G1: 2′,6′ ArH), 7.43 (d, $J=8.1$ Hz, 2 H; 2,6 ArH), 7.49 (d, $J=8.1$ Hz, 4 H; G1: 3,5 ArH), 7.58 ppm (m, 6 H; 3,5 and G1: 2,6 ArH); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta=14.10$ ($C\mathrm{H_3}$), 22.68 ($C\mathrm{H_2CH_3}$), 26.05 ($C\mathrm{H_2CH_2CH_2OAr}$), 29.32–29.70 ($\mathrm{ArOCH_2}C\mathrm{H_2}$, $\mathrm{CH_3CH_2CH_2}$-$(C\mathrm{H_2})_6$), 31.92 ($\mathrm{CH_3CH_2}C\mathrm{H_2}$), 65.06 ($C\mathrm{H_2OH}$), 69.36, 69.48 ($\mathrm{ArO}C\mathrm{H_2CH_2}$, G1: 3′,4′ positions), 70.00 ($\mathrm{ArO}C\mathrm{H_2Ar}$, 3′,5′ positions), 100.96 (ArC, 4′ position), 106.61 (ArCH, 2′,6′ positions), 113.16 (ArCH, G1: 2′ positions), 114.08 (ArCH, G1: 5′ positions), 119.60 (ArCH, G1: 6′ positions), 127.02 (ArCH, G1: 2,6 positions), 127.32, 127.37 (ArCH, 3,5 and 2,6 positions), 128.03 (ArCH, G1: 3,5 positions), 133.76 (ArC, G1: 1′ position), 135.19 (ArC, G1: 1 positions), 140.23 (ArC, 4 position), 140.43 (ArC, 1 position), 140.94 (ArC, G1: 4 positions), 143.05 (ArC, 1′ position), 148.97, 149.34 (ArC, G1: 3′,4′ positions), 160.26 ppm (ArC, 3′,5′ positions); MS (ESI-TOF): m/z: 1308.8 $[M+\mathrm{Na}]^+$; elemental analysis calcd (%) for $\mathrm{C_{87}H_{128}O_7}$ (1285.0): C 81.26, H 10.03; found: C 81.56, H 10.28.

4-Chloromethyl-3′,5′-bis(3′,4′-bisdodecyloxybiphenyl-4-ylmethoxy)biphenyl [(3,4Bp-3,5Bp)12G2-$\mathrm{CH_2Cl}$] (39): A mixture of compound **38** (820 mg, 0.65 mmol), $\mathrm{SOCl_2}$ (0.09 mL, 1.20 mmol), and DTBMP (0.32 G, 1.57 mmol) was stirred in degassed $\mathrm{CH_2Cl_2}$ (50 mL) under Ar for 3 h. At this time, TLC showed complete reaction and the mixture was poured into $\mathrm{H_2O}$. The product was extracted with $\mathrm{CH_2Cl_2}$, the organic phase was dried over $\mathrm{Na_2SO_4}$, and evaporated to yield a white solid. Subsequent recrystallization from acetone gave 0.73 G (87.0 %) of **39**. $R_f=0.40$ (hexanes/$\mathrm{CH_2Cl_2}$ 1:1); purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta=0.88$ (m, 12 H; $\mathrm{CH_2C}H_3$), 1.27 (m, 64 H; $\mathrm{CH_3(C}H_2)_8$), 1.47 (qi, $J=7.7$ Hz, 8 H; $\mathrm{ArOCH_2CH_2C}H_2$), 1.84 (qi, $J=7.3$ Hz 8 H; $\mathrm{ArOCH_2C}H_2$), 4.05 (2t overlapped, $J=6.8$ Hz, 8 H; $\mathrm{ArOC}H_2$), 4.63 (s, 2 H; $\mathrm{CH_2Cl}$), 5.13 (s, 4 H; 3′, 5′ $\mathrm{ArOC}H_2\mathrm{Ar}$), 6.67 (t, $J=2.2$ Hz, 1 H; 4′ ArH), 6.85 (d, $J=2.2$ Hz, 2 H; 2′,6′ ArH), 6.95 (d, $J=9.0$ Hz, 2 H; G1: 5′ ArH), 7.12 (m, 4 H; G1: 2′,6′ ArH), 7.45 (d, $J=8.4$ Hz, 2 H; 2,6 ArH), 7.49 (d, $J=8.3$ Hz, 4 H; G1: 3,5 ArH), 7.58 ppm (m, 6 H; 3,5 and G1: 2,6 ArH); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta=14.10$ ($C\mathrm{H_3}$), 22.68 ($C\mathrm{H_2CH_3}$), 26.05 ($C\mathrm{H_2CH_2CH_2OAr}$), 29.32–29.70 ($\mathrm{ArOCH_2}C\mathrm{H_2}$, $\mathrm{CH_3CH_2CH_2}$-$(C\mathrm{H_2})_6$), 31.92 ($\mathrm{CH_3CH_2}C\mathrm{H_2}$), 45.96 ($C\mathrm{H_2Cl}$), 69.35, 69.47 ($\mathrm{ArO}C\mathrm{H_2CH_2}$, G1: 3′,4′ positions), 70.00 ($\mathrm{ArO}C\mathrm{H_2Ar}$, 3′,5′ positions), 101.16 (ArC, 4′ position), 106.64 (ArCH, 2′,6′ positions), 113.15 (ArCH, G1: 2′ positions), 114.07 (ArCH, G1: 5′ positions), 119.60 (ArCH, G1: 6′ positions), 127.02 (ArCH, G1: 2,6 positions), 127.49 (ArCH, 2,6 positions), 128.02 (ArCH, G1: 3,5 positions), 128.99 (ArCH, 3,5 positions), 133.74 (ArC, G1: 1′ position), 135.14 (ArC, G1: 1 positions), 136.76 (ArC, 4 position), 140.96 (ArC, G1: 4 positions), 141.20 (ArC, 1 position), 142.70 (ArC, 1′ position), 148.98, 149.34 (ArC, G1: 3′,4′ positions), 160.26 ppm (ArC, 3′,5′ positions); MS (ESI-TOF): m/z: 1327.8 $[M+\mathrm{Na}]^+$; elemental analysis calcd (%) for $\mathrm{C_{87}H_{127}ClO_6}$ (1304.39): C 80.11, H 9.81; found: C 80.39, H 10.07.

Methyl 3′,5′-bis[3′,5′-bis(3′,4′-bisdodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-ylmethoxy]biphenyl-4-carboxylate [(3,4Bp-(3,5Bp)^2)12G3-$\mathrm{CO_2CH_3}$] (40): A mixture of **10** (47 mg, 0.2 mmol), $\mathrm{K_2CO_3}$ (110 mg, 0.8 mmol), and **39** (520 mg, 0.4 mmol) in Ar degassed DMF (50 mL) was heated to 70 °C under stirring for 16 h and then poured into $\mathrm{H_2O}$. The organic precipitate was extracted with hexanes (2 × 100 mL), then with a similar volume of $\mathrm{CH_2Cl_2}$. The combined organic layer was washed with brine, dried over $\mathrm{Na_2SO_4}$, and evaporated. The residues were redissolved in $\mathrm{CH_2Cl_2}$ and extracted with hexanes to remove some residual DMF. The solution was concentrated to about 30 mL, and the product was precipitated by the addition of acetone and then recrystallized from $\mathrm{CH_2Cl_2}$/acetone to yield 0.46 G (85.0 %) of **40** as a white solid. $R_f=0.56$ (hexanes/$\mathrm{CH_2Cl_2}$ 1:2); m.p. 61.4 °C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta=0.89$ (m, 24 H; $\mathrm{CH_2C}H_3$), 1.28 (m, 128 H; $\mathrm{CH_3(C}H_2)_8$), 1.48 (m, 16 H; $\mathrm{ArOCH_2CH_2C}H_2$), 1.84 (qi, $J=6.8$ Hz, 16 H; $\mathrm{ArOCH_2C}H_2$), 3.94 (s, 3 H; $\mathrm{CO_2C}H_3$), 4.05 (2t overlapped, $J=6.8$ Hz, 16 H; $\mathrm{ArOC}H_2$), 5.13 (s, 8 H; G1: 3′, 5′ $\mathrm{ArOC}H_2\mathrm{Ar}$), 5.15 (s, 4 H; 3′, 5′ $\mathrm{ArOC}H_2\mathrm{Ar}$), 6.68 (t, $J=1.8$ Hz, 2 H; G1: 4′ ArH), 6.70 (t, $J=1.7$ Hz, 1 H; 4′ ArH), 6.87 (d, $J=2.0$ Hz, 4 H; G1: 2′,6′ ArH), 6.89 (d, $J=2.0$ Hz, 2 H; 2′,6′ ArH), 6.95 (d, $J=8.8$ Hz, 4 H; G2: 5′ ArH), 7.12 (m, 8 H; G2: 2′,6′ ArH), 7.56 (m, 26 H; ArH), 8.11 ppm (d, $J=8.1$ Hz, 2 H; 3,5 ArH); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta=14.11$ ($C\mathrm{H_3}$), 22.68 ($C\mathrm{H_2CH_3}$), 26.06 ($C\mathrm{H_2CH_2CH_2OAr}$), 29.33–29.70 ($\mathrm{ArOCH_2}C\mathrm{H_2}$, $\mathrm{CH_3CH_2CH_2(}C\mathrm{H_2)_6}$), 31.92 ($\mathrm{CH_3CH_2}C\mathrm{H_2}$), 52.12 ($\mathrm{CO_2}C\mathrm{H_3}$), 69.36, 69.48 ($\mathrm{ArO}C\mathrm{H_2CH_2}$, G2: 3′,4′ positions), 70.01 ($\mathrm{ArO}C\mathrm{H_2Ar}$, 3′,5′ and G1: 3′,5′ positions), 101.03 (ArC, G1: 4′ position), 101.66 (ArC, 4′ position), 106.62 (ArCH, G1: 2′,6′ positions), 106.84 (ArCH, 2′,6′ positions), 113.14 (ArCH, G2: 2′ positions), 114.06 (ArCH, G2: 5′ positions), 119.60 (ArCH, G2: 6′ positions), 127.02 (ArCH, G1: 2,6 and G2: 2,6 positions), 127.07 (ArCH, 2,6 positions), 127.42 (ArCH, G1: 3,5 positions), 128.04 (ArCH, G2: 3,5 positions), 129.19 (Ar$C\mathrm{CO_2CH_3}$), 130.05 (ArCH, 3,5 positions), 133.74 (ArC, G2: 1′ position), 135.16 (ArC, G2: 1 positions), 135.99 (ArC, G1: 1 positions), 140.92, 140.95 (overlapped ArC, G1: 4 and G2: 4 positions), 142.24 (ArC, 1′ position), 142.95 (ArC, G1: 1′ position), 145.40 (ArC, 1 position), 148.97, 149.33 (ArC, G2: 3′,4′ positions), 160.28, 160.31 (ArC, 3′,5′ and G1: 3′,5′ positions), 166.93 ppm ($C\mathrm{O_2CH_3}$); MS (MALDI-TOF): m/z: 2800.0 $[M+\mathrm{Na}]^+$; elemental analysis calcd (%) for $\mathrm{C_{188}H_{264}O_{16}}$ (2780.10): C 81.22, H 9.57; found: C 80.57, H 9.66.

Methyl 3′,4′,5′-tris(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-carboxylate [(4Bp-3,4,5Bp)12G1-$\mathrm{CO_2CH_3}$] (41): Trihydroxy compound **15** (135 mg, 0.52 mmol) was added to a thoroughly degassed suspension of $\mathrm{K_2CO_3}$ (645 mg, 4.67 mmol) in DMF (100 mL). The reaction mixture was heated to 70 °C. A degassed solution of **17** (608 mg, 1.57 mmol) in DMF/THF mixture (1:1, 20 mL) was added and heating was continued for another 25 h until the complete absence of **17** in the reaction mixture was confirmed by ^{1}H NMR analysis. The reaction mixture was allowed to cool to 22 °C and then poured into water (250 mL). The precipitate was filtered, dissolved in THF (100 mL), carefully precipitated with MeOH, and filtered. 563 mg (83 %) of **41** was obtained after drying. $R_f=0.9$ ($\mathrm{CH_2Cl_2}$); m.p. 133.0 °C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta=0.89$ (t, 9 H; $\mathrm{CH_2C}H_3$), 1.29 (m, 48 H; $(\mathrm{C}H_2)_8\mathrm{CH_3}$), 1.48 (m, 6 H; $\mathrm{ArOCH_2CH_2C}H_2$), 1.82 (m, 6 H; $\mathrm{ArOCH_2C}H_2$), 3.95 (s, 3 H; $\mathrm{CO_2C}H3$), 4.00 (m, 6 H; 4′ $\mathrm{ArOC}H_2$), 5.18 (s, 2 H; 4′ $\mathrm{ArOC}H_2\mathrm{Ar}$), 5.23 (s, 4 H; 3′,5′ $\mathrm{ArOC}H_2\mathrm{Ar}$), 6.92 (s, 2 H; G1: 3′,5′ ArH), 6.95 (s, 2 H; 2′,6′ ArH), 6.96 (s, 2 H; G1: 3′,5′ ArH), 6.98 (s, 2 H; G1: 3′,5′ ArH), 7.45–7.60 (overlapped m, 20 H; 2,6 ArH, G1: 2,2′,3,5,6,6′ H), 8.08 ppm (d, $J=8.7$ Hz, 2 H; 3,5 ArH); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta=14.32$ ($C\mathrm{H_3}$), 22.92 ($C\mathrm{H_2CH_3}$), 26.32 ($C\mathrm{H_2}$), 29.58 ($C\mathrm{H_2}$), 29.68–29.91 ($C\mathrm{H_2}$), 32.15 ($\mathrm{ArOCH_2}C\mathrm{H_2}$), 52.31 ($\mathrm{CO_2}C\mathrm{H_3}$), 68.41 ($\mathrm{ArO}C\mathrm{H_2}$), 71.68 (3′,5′ $\mathrm{ArO}C\mathrm{H_2Ar}$), 75.50 (4′ $\mathrm{ArO}C\mathrm{H_2Ar}$), 107.86 (2′,6′ Ar$C$H), 115.06 (3′,5′ Ar$C$H), 127.02 (Ar$C$H), 127.11 (Ar$C$H), 128.26 (Ar$C$H), 129.12 (Ar$C$H), 129.30 (Ar$C$H), 130.32 (3,5 Ar$C$H), 133.29 (Ar$C$), 133.48 (Ar$C$), 135.52 (Ar$C$), 135.96 (Ar$C$), 136.40 (4-4 Ar$C$), 139.44 (Ar$C$), 140.63 (Ar$C$), 140.85 (Ar$C$), 145.72 (4 Ar$C$), 153.51 (Ar$C$), 159.01 (Ar$C$), 159.12 (Ar$C$), 167.16 ppm ($C\mathrm{O_2CH_3}$); MS (ESI-TOF): m/z: 1310.53 $[M^+]$; elemental analysis calcd (%) for $\mathrm{C_{89}H_{114}O_8}$ (1311.85): C 81.48, H 8.76; found: C 81.43, H 9.58.

[3′,4′,5′-Tris(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-yl]methanol [(4Bp-3,4,5Bp)12G1-$\mathrm{CH_2OH}$] (42): Methyl ester **41** (300 mg, 0.23 mmol) was dissolved in dry THF (20 mL) and added into a suspension of $\mathrm{LiAlH_4}$ (46 mg, 1.14 mmol) in dry THF (20 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and quenched by addition of 0.3 mL of water, NaOH solution (0.3 mL, 15 %), and water (0.3 mL). The precipitate was removed by filtration through Celite. The filtrate was carefully precipitated with MeOH. 257 mg (87 %) of **42** was obtained as white crystals. $R_f=0.3$ ($\mathrm{CH_2Cl_2}$); m.p. 71.5 °C purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta=0.89$ (t, 9 H; $\mathrm{CH_2C}H_3$), 1.29 (m, 48 H;

$(CH_2)_8CH_3$), 1.48 (m, 6H; $ArOCH_2CH_2CH_2$), 1.65 (t, 1H; CH_2OH), 1.83 (m, 6H; $ArOCH_2CH_2$), 4.01 (m, 6H; 4′ $ArOCH_2$), 4.75 (d, $J=5.1$ Hz, 2H; CH_2OH), 5.17 (s, 2H; 4′ $ArOCH_2Ar$), 5.22 (s, 4H; 3′,5′ $ArOCH_2Ar$), 6.90–7.00 (m, 8H; overlapped 2′,6′ and G1: 2′,3′,5′,6′ Ar*H*), 7.40–7.58 ppm (overlapped m, 22H; 2,3,5,6 Ar*H*, G1: 2,2′,3,5,6,6′ H; ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=14.32$ (CH_3), 22.91 (CH_2CH_3), 26.32 (CH_2), 29.58 (CH_2), 29.66–29.90 (CH_2), 32.15 ($ArOCH_2CH_2$), 65.33 (CH_2OH), 68.38 ($ArOCH_2$), 71.61 (3′,5′ $ArOCH_2Ar$), 75.51 (4′ $ArOCH_2Ar$), 107.65 (2′,6′ Ar*C*H), 115.04 (3′,5′ Ar*C*H), 126.65 (Ar*C*H), 127.00 (Ar*C*H), 127.42 (Ar*C*H), 127.65 (Ar*C*H), 128.25 (Ar*C*H), 128.27 (3,5 Ar*C*H), 129.29 (Ar*C*H), 133.33 (Ar*C*), 133.52 (Ar*C*), 135.67 (Ar*C*), 136.53 (4-4 Ar*C*), 136.88 (Ar*C*), 138.80 (Ar*C*), 140.56 (Ar*C*), 140.77 (Ar*C*), 153.40 (4-3,5 Ar*C*), 158.99 ppm (G1, 4′ Ar*C*); MS (ESI-TOF): *m*/*z*: 1285.2 $[M+H^+]$; elemental analysis calcd (%) for $C_{88}H_{114}O_7$ (1283.84): C 82.33, H 8.95; found: C 82.00, H 8.48.

4-Chloromethyl-3′,4′,5′-tris(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl [(4Bp-3,4,5Bp)12G1-CH_2Cl] (43): Compound **42** (300 mg, 0.23 mmol) and DTBMP (144 mg, 0.70 mmol) were dissolved in dry CH_2Cl_2 (15 mL) under Ar at 25 °C. $SOCl_2$ (1.7 mL of 0.27 M solution in CH_2Cl_2, 0.46 mmol) was added. The reaction mixture was stirred for 6 h. DTBMP (144 mg, 0.70 mmol) and $SOCl_2$ (1.7 mL of 0.27 M solution in CH_2Cl_2, 0.46 mmol) were added and stirring was continued for another 12 h until 100% conversion was detected by TLC. The reaction mixture was carefully precipitated with MeOH. The solid product was filtered, washed with MeOH, and dried. 285 mg (94%) of white **43** was obtained. $R_f=0.95$ (CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=0.89$ (t, 9H; CH_2CH_3), 1.29 (m, 48H; $(CH_2)_8CH_3$), 1.47 (m, 6H; $ArOCH_2CH_2CH_2$), 1.82 (m, 6H; $ArOCH_2CH_2$), 4.00 (m, 6H; 4′ $ArOCH_2$), 4.63 (s, 2H; CH_2Cl), 5.17 (s, 2H; 4′ $ArOCH_2Ar$), 5.21 (s, 4H; 3′,5′ $ArOCH_2Ar$), 6.90–6.98 (m, 8H; overlapped 2′,6′ and G1: 2′,3′,5′,6′ Ar*H*), 7.45–7.58 ppm (overlapped m, 22H; 2,3,5,6 Ar*H*, G1: 2,2′,3,5,6,6′ Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=14.31$ (CH_3), 22.91 (CH_2CH_3), 26.33 (CH_2), 29.57 (CH_2), 29.00–30.11 (CH_2), 32.05 ($ArOCH_2CH_2$), 46.91 (CH_2Cl), 69.02 ($ArOCH_2$), 71.12 (3′,5′ $ArOCH_2Ar$), 76.01 (4′ $ArOCH_2Ar$), 106.77 (2′,6′ Ar*C*H), 116.04 (3′,5′ Ar*C*H), 126.20 (Ar*C*H), 128.01 (Ar*C*H), 128.04 (Ar*C*H), 128.08 (Ar*C*H), 128.91 (3,5 Ar*C*H), 133.32 (Ar*C*), 133.39 (Ar*C*H), 133.51 (Ar*C*), 135.68 (Ar*C*), 136.91 (4-4 Ar*C*), 137.61 (Ar*C*), 139.92 (Ar*C*), 140.89 (Ar*C*), 153.09 (4-3,5 Ar*C*), 160.21 ppm (G1, 4′ Ar*C*); elemental analysis calcd (%) for $C_{88}H_{113}ClO_6$ (1302.29): C 81.16, H 8.75; found: C 80.57, H 8.67.

Methyl 3′5′-bis[3′,4′,5′-tris(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-ylmethoxy]biphenyl-4-carboxylate [(4Bp-3,4,5Bp-3,5Bp)12G2-CO_2CH_3] (44): Dihydroxy compound **10** (24.2 mg, 0.099 mmol) in THF (10 mL) was added into a thoroughly degassed suspension of K_2CO_3 (83 mg, 0.600 mmol) in DMF (50 mL) and heated to 80 °C. Benzyl chloride **43** (260 mg, 0.200 mmol) dissolved in degassed THF (10 mL) was added and heating was continued for another 16 h until 100% conversion was confirmed by ^1H NMR analysis of the reaction mixture. The reaction mixture was allowed to cool to ~22 °C, poured into water (300 mL), and stirred overnight. The white precipitate was filtered off, dissolved in CH_2Cl_2, precipitated with MeOH, filtered off, and washed with MeOH. Slow addition of MeOH into stirred CH_2Cl_2 solution at 22 °C appeared to be the most feasible procedure for gaining an isolable precipitation. The product was purified by column chromatography (CH_2Cl_2/hexane 2:1). 229 mg (83%) of **44** was obtained. $R_f=0.3$ (CH_2Cl_2/hexane 2:1); m.p. 109.9 °C; purity (HPLC): 99+ %; ^1H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=0.90$ (t, 18H; CH_2CH_3), 1.29 (m, 96H; $(CH_2)_8CH_3$), 1.49 (m, 12H; $ArOCH_2CH_2CH_2$), 1.81 (m, 12H; $ArOCH_2CH_2$), 3.95 (s, 3H; CO_2CH_3), 4.00 (m, 12H; $ArOCH_2$), 5.16 (s, 8H; 3′,5′ $ArOCH_2Ar$, G1: 4′ $ArOCH_2Ar$), 5.21 (s, 8H; G1: 3′,5′ $ArOCH_2Ar$), 6.70 (s, 1H; 4′ Ar*H*), 6.89 (d, $J=2.2$ Hz, 2H; 2′,6′ Ar*H*), 6.90–6.98 (m, 16H; G1: 2′,6′ Ar*H*, G2: 3′,5′ Ar*H*), 7.42–7.58 (overlapped m, 44H; G1: 2,3,5,6 Ar*H*, G2: 2,2′,3,5,6,6′ H), 7.64 (d, $J=8.0$ Hz, 2H; 2,6 Ar*H*), 8.11 ppm (d, $J=7.9$ Hz, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=14.31$ (CH_3), 22.91 (CH_2CH_3), 26.32 (CH_2), 29.58 (CH_2), 29.68–29.91 (CH_2), 32.15 ($ArOCH_2CH_2$), 52.30 (CO_2CH_3), 68.40 ($ArOCH_2$), 71.61 (3′,5′ $ArOCH_2Ar$), 75.48 (4′ $ArOCH_2Ar$), 107.20 (2′,6′ Ar*C*H), 107.66 (G1: 2′,6′ Ar*C*H), 115.05, 115.09 (2′,6′ Ar*C*H, G1: 2′,6′ Ar*C*H, G2: 3′,5′ Ar*C*H), 126.65 (Ar*C*H), 126.99 (Ar*C*H), 127.33 (Ar*C*H), 127.52 (Ar*C*H), 127.70 (Ar*C*H), 128.26 (Ar*C*H), 129.27 (Ar*C*H), 129.50 (G1: 3,5 Ar*C*H), 133.31 (Ar*C*), 133.50 (Ar*C*), 135.63 (Ar*C*), 136.00 (Ar*C*), 136.51 (4-4 Ar*C*), 140.50 (Ar*C*), 140.78 (Ar*C*), 141.20 (Ar*C*), 142.53 (4 Ar*C*), 153.44 (Ar*C*), 159.09 (Ar*C*), 160.63 (Ar*C*), 167.01 ppm (CO_2CH_3); MS (MALDI-TOF): *m*/*z*: 2797.2 $[M+Na^+]$; elemental analysis calcd (%) for $C_{190}H_{236}O_{16}$ (2775.90): C 82.21, H 8.57; found: C 81.60, H 8.22.

{3′,5′-bis[3′,4′,5′-tris(4′-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-ylmethoxy]biphenyl-4-yl}methanol [(4Bp-3,4,5Bp-3,5Bp)12G2-CH_2OH] (45): Compound **44** (90 mg, 0.032 mmol) was dissolved in dry THF (6 mL) and added into suspension of $LiAlH_4$ (9 mg, 0.24 mmol) in dry THF (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. $LiAlH_4$ (9 mg, 0.24 mmol) was added and the reaction mixture was stirred for another hour until 100% conversion by TLC (CH_2Cl_2/hexane, 8:1), then quenched by addition of water (0.1 mL), NaOH solution (0.1 mL, 15%), and water (0.1 mL). Precipitation was removed by filtration through Celite. The filtrate was carefully precipitated with MeOH and purified by column chromatography (CH_2Cl_2/hexane, 8:1) and another precipitation (CH_2Cl_2/MeOH). 25 mg (28%) of compound **45** was obtained as white crystals. $R_f=0.4$ (CH_2Cl_2/hexane 2:1); m.p. 73.2 °C; purity (HPLC): 99+ %; ^1H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=0.90$ (t, 18H; CH_2CH_3), 1.29 (m, 96H; $(CH_2)_8CH_3$), 1.48 (m, 12H; $ArOCH_2CH_2CH_2$), 1.64 (m, 1H; $ArCH_2OH$), 1.81 (m, 12H; $ArOCH_2CH_2$), 4.00 (m, 12H; $ArOCH_2$), 4.75 (d, $J=5.6$ Hz, $ArCH_2OH$), 5.15 (m, 8H; 3′,5′ $ArOCH_2Ar$, G1: 4′ $ArOCH_2Ar$), 5.21 (m, 8H; G1: 3′,5′ $ArOCH_2Ar$), 6.68 (s, 1H; 4′ Ar*H*), 6.87 (d, $J=2.2$ Hz, 2H; 2′,6′ Ar*H*), 6.90–6.98 (m, 16H; G1: 2′,6′ Ar*H*, G2: 3′,5′ Ar*H*), 7.40–7.60 ppm (overlapped m, 48H; 2,3,5,6 Ar*H*, G1: 2,3,5,6 Ar*H*, G2: 2,2′,3,5,6,6′ H); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=14.33$ (CH_3), 22.92 (CH_2CH_3), 26.32 (CH_2), 29.58 (CH_2), 29.68–29.90 (CH_2), 32.15 ($ArOCH_2CH_2$), 65.33 ($ArCH_2OH$), 68.36 ($ArOCH_2$), 70.23 (3′,5′ $ArOCH_2Ar$), 71.57 (G1: 3′,5′ $ArOCH_2Ar$), 75.52 (4′ $ArOCH_2Ar$), 101.30 (Ar*C*H), 107.02 (2′,6′ Ar*C*H), 107.60 (G1: 2′,6′ Ar*C*H), 115.02, 115.08 (2′,6′ Ar*C*H, G1: 2′,6′ Ar*C*H, G2: 3′,5′ Ar*C*H), 126.66 (Ar*C*H), 127.00 (Ar*C*H), 127.30 (Ar*C*H), 127.52 (Ar*C*H), 127.59 (Ar*C*H), 128.26 (Ar*C*H), 129.28 (Ar*C*H), 133.31 (Ar*C*), 133.50 (Ar*C*), 135.63 (Ar*C*), 136.11 (Ar*C*), 136.54 (4-4 Ar*C*), 136.83 (Ar*C*), 140.54 (Ar*C*), 140.76 (Ar*C*), 141.20 (Ar*C*), 142.51 (4 Ar*C*), 153.42 (Ar*C*), 158.97 (Ar*C*), 160.50 ppm (Ar*C*); MS (MALDI-TOF): *m*/*z*: 2768.5 $[M+Na^+]$; elemental analysis calcd (%) for $C_{189}H_{236}O_{15}$ (2747.89): C 82.61, H 8.66; found: C 82.38, H 8.54.

Methyl 3′,4′,5′-tris(3′,4′,5′-trisdodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-carboxylate [(3,4,5Bp)^{2}12G2-CO_2CH_3] (46): Compound **15** (128 mg, 0.49 mmol) was added into a thoroughly degassed suspension of K_2CO_3 (612 mg, 4.43 mmol) in DMF (100 mL). The reaction mixture was heated to 70 °C. A degassed solution of **17** (1.16 G, 1.48 mmol) in a DMF/THF mixture (1:1, 50 mL) was added and heating was continued for another 18 h. The reaction mixture was allowed to cool to 22 °C and then poured into water (600 mL). The resultant precipitate was filtered, dissolved in CH_2Cl_2, precipitated into MeOH, and collected to give 970 mg (82%) of **46** after drying; $R_f=0.5$ (hexane/EtOAc 6:1); purity (HPLC): 99+ %; ^1H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta=0.89$ (t, 27H; CH_2CH_3), 1.27 (m, 144H; $(CH_2)_8CH_3$), 1.49 (m, 18H; $ArOCH_2CH_2CH_2$), 1.80 (m, 18H; $ArOCH_2CH_2$), 3.95 (s, 3H; $COOCH_3$), 3.98 (t, $J=8.1$ Hz, 6H; 4′ $ArOCH_2$), 4.05 (t, $J=6.4$ Hz, 12H; 3′,5′ $ArOCH_2$), 5.20 (s, 2H; 4′ $ArOCH_2Ar$), 5.24 (t, 4H; 3′,5′ $ArOCH_2Ar$), 6.73 (s, 2H; G1: 2′,6′ Ar*H*), 6.76 (s, 4H; G1: 2′,6′ Ar*H*), 6.93 (s, 2H; 2′,6′ Ar*H*), 7.47–7.59 (overlapped m, 14H, 2,6 Ar*H*, G1: 2,3,5,6H), 8.08 ppm (d, $J=8.5$ Hz, 2H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): $\delta=14.33$ (CH_3), 22.91 (CH_2CH_3), 26.38 (CH_2), 29.59 (CH_2), 29.71–30.00 (CH_2), 32.15 ($ArOCH_2CH_2$), 52.36 (CO_2CH_3), 69.48 (3′,5′ $ArOCH_2$), 71.53 (3′,5′ $ArOCH_2Ar$), 73.78 (4′ $ArOCH_2$), 75.20 (4′ $ArOCH_2Ar$), 106.16 (G1, 2′,6′ Ar*C*H), 107.86 (2′,6′ Ar*C*H), 127.07 (Ar*C*H), 127.41 (Ar*C*H), 128.00 (Ar*C*H), 129.10 (Ar*C*H), 129.19 (Ar*C*H), 130.30 (Ar*C*H), 136.03 (Ar*C*), 136.22 (Ar*C*), 138.35 (Ar*C*), 141.36 (Ar*C*), 141.50 (Ar*C*), 145.59 (Ar*C*), 153.41 (Ar*C*), 153.59 (Ar*C*), 153.64 (Ar*C*), 167.10 ppm (CO_2CH_3); MS (MALDI-TOF): *m*/*z*: 2413.9 $[M-H^+]$; elemental analysis calcd (%) for $C_{161}H_{258}O_{14}$ (2417.76): C 79.98, H 10.76; found: C 79.78, H 10.92.

[3′,4′,5′-Tris(3′,4′,5′-trisdodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-yl]methanol [(3,4,5Bp)^{2}12G2-CH_2OH] (47): Methyl ester **46** (630 mg, 0.26 mmol) was dissolved in dry THF (20 mL) and added into a suspension of LiAlH$_4$ (156 mg, 3.91 mmol) in dry THF (20 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and quenched by addition of water (0.5 mL), NaOH solution (0.5 mL, 15 %), and water (1 mL). The precipitate was removed by filtration through Celite. The filtrate was evaporated to dryness, dissolved in CH$_2$Cl$_2$, and precipitated with MeOH. 590 mg (95 %) of **47** was obtained as white crystals. $R_f=0.2$ (hexane/EtoAc 6:1); m.p. 43.5 °C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, CDCl$_3$, 20 °C): $\delta=0.89$ (t, 27 H; CH$_2$C*H*$_3$), 1.27 (m, 144 H; (C*H*$_2$)$_8$CH$_3$), 1.48 (m, 18 H; ArOCH$_2$CH$_2$C*H*$_2$), 1.63 (t, 1 H; CH$_2$O*H*), 1.81 (m, 18 H; ArOCH$_2$C*H*$_2$), 4.01 (m, 18 H; ArOC*H*$_2$), 4.74 (d, $J=6.00$ Hz, 2 H; C*H*$_2$OH), 5.19 (s, 2 H; 4′ ArOC*H*$_2$Ar), 5.23 (t, 4 H; 3′,5′ ArOC*H*$_2$Ar), 6.73 (s, 2 H; G1: 2′,6′ Ar*H*), 6.76 (s, 4 H; G1: 2′,6′ Ar*H*), 6.89 (s, 2 H; 2′,6′ Ar*H*), 7.42 (d, $J=8.2$ Hz, 2 H; 2,6 Ar*H*), 7.50–7.57 ppm (overlapped m, 14 H; 3,5 Ar*H*, G1: 2,3,5,6 H); ^{13}C NMR (125 MHz, CDCl$_3$, 20 °C): $\delta=14.32$ (*C*H$_3$), 22.91 (*C*H$_2$CH$_3$), 26.38 (*C*H$_2$), 29.58–30.12 (*C*H$_2$), 30.68 (*C*H$_2$), 32.21 (ArOCH$_2$*C*H$_2$), 65.29 (*C*H$_2$OH), 69.58 (3′,5′ ArO*C*H$_2$), 71.61 (3′,5′ ArO*C*H$_2$Ar), 73.77 (4′ ArO*C*H$_2$), 75.18 (4′ ArO*C*H$_2$Ar), 106.31 (G1, 2′,6′ Ar*C*H), 127.12 (Ar*C*H), 127.37 (Ar*C*H), 127.63 (Ar*C*H), 128.00 (Ar*C*H), 129.21 (Ar*C*H), 129.24 (Ar*C*H), 136.23 (Ar*C*), 141.39 (Ar*C*), 144.28 (Ar*C*), 153.41 (Ar*C*), 153.61 (Ar*C*), 153.69 ppm (Ar*C*); MS (MALDI-TOF): *m*/*z*: 2391.3 [$M+\mathrm{H}^+$]; elemental analysis calcd (%) for $C_{160}H_{258}O_{13}$ (2389.75): C 80.41, H; 10.88; found: C 80.12, H 10.90.

4-Chloromethyl-3′,4′,5′-tris(3′,4′,5′-trisdodecyloxybiphenyl-4-ylmethoxy)-biphenyl [(3,4,5Bp)^{2}12G2-CH$_2$Cl] (48): Compound **47** (532 mg, 0.22 mmol) and DTBMP (125 mg, 0.60 mmol) were dissolved in dry CH$_2$Cl$_2$ (25 mL) under Ar at 0 °C. SOCl$_2$ (1.5 mL of 0.27 M solution in CH$_2$Cl$_2$, 0.41 mmol) was added. The reaction mixture was stirred at 0 °C for 1.5 h, concentrated to 3 mL, and precipitated with MeOH. The solid product was filtered off, washed with MeOH, and dried to give 510 mg (95 %) of yellow-white **48**. $R_f=0.7$ (hexane/EtOAc 6:1); purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, CDCl$_3$, 20 °C): $\delta=0.89$ (t, 27 H; CH$_2$C*H*$_3$), 1.27 (m, 144 H; (C*H*$_2$)$_8$CH$_3$), 1.50 (m, 18 H; ArOCH$_2$CH$_2$C*H*$_2$), 1.80 (m, 18 H; ArOCH$_2$C*H*$_2$), 4.01 (m, 18 H; ArOC*H*$_2$), 4.63 (d, $J=6.00$ Hz, 2 H; C*H*$_2$Cl), 5.20 (s, 2 H; 4′ ArOC*H*$_2$Ar), 5.23 (t, 4 H; 3′,5′ ArOC*H*$_2$Ar), 6.73 (s, 2 H; G1: 2′,6′ Ar*H*),), 6.76 (s, 4 H; G1: 2′,6′ Ar*H*), 6.89 (s, 2 H; 2′,6′ Ar*H*), 7.39–7.57 ppm (overlapped m, 16 H; 2,3,5,6 Ar*H*, G1: 2,3,5,6 H); ^{13}C NMR (125 MHz, CDCl$_3$, 20 °C): $\delta=14.31$ (*C*H$_3$), 22.91 (*C*H$_2$CH$_3$), 26.42 (*C*H$_2$), 29.10–31.24 (*C*H$_2$), 30.19 (*C*H$_2$), 31.88 (ArOCH$_2$*C*H$_2$), 46.12 (*C*H$_2$Cl), 68.89 (3′,5′ ArO*C*H$_2$), 71.18 (3′,5′ ArO*C*H$_2$Ar), 73.22 (4′ ArO*C*H$_2$), 75.54 (4′ ArO*C*H$_2$Ar), 104.28 (G1, 2′,6′ Ar*C*H), 122.12 (Ar*C*H), 127.14 (Ar*C*H), 128.00 (Ar*C*H), 129.31 (Ar*C*H) 136.18 (Ar*C*), 140.19 (Ar*C*), 153.43 (Ar*C*), 153.02 (Ar*C*), 153.72 (Ar*C*), 154.66 ppm.

Methyl 3′,4′,5′-tris[3′,4′,5′-tris(3′,4′,5′-trisdodecyloxybiphenyl-4-ylmethoxy)-biphenyl-4-ylmethoxy]biphenyl-4-carboxylate [(3,4,5Bp)^{3}12G3-CO$_2$CH$_3$] (49): Trihydroxy compound **15** (17.3 mg, 0.066 mmol) was added into a thoroughly degassed suspension of K$_2$CO$_3$ (83 mg, 0.600 mmol) in DMF (50 mL). The reaction mixture was heated to 70 °C. A degassed solution of **48** (480 mg, 0.199 mmol) in THF (10 mL) was added and heating was continued for another 20 h. Then, THF (20 mL) was added and the temperature was raised to 90 °C in an unsuccessful attempt to dissolve all reaction components. Heating to 90 °C was continued for another 4 h after which 100 % conversion was confirmed by ^{1}H NMR analysis of the reaction mixture. The reaction mixture was allowed to cool to 22 °C. The dark precipitate was isolated by decantation, dissolved in CH$_2$Cl$_2$, precipitated with MeOH, and filtered. Dissolving and precipitation was repeated twice. Slow addition of CH$_2$Cl$_2$ solution into a stirred excess of MeOH at 22 °C appeared to be the most feasible procedure for gaining isolable precipitate. 285 mg (59 %) of **49** was obtained. $R_f=0.5$ (hexane/EtOAc 6:1); m.p. 94.0 °C; purity (HPLC): 99+ %; ^{1}H NMR (500 MHz, CDCl$_3$, 20 °C): $\delta=0.89$ (m, 81 H; CH$_2$C*H*$_3$, 20 °C), 1.28 (m, 432 H; (C*H*$_2$)$_8$CH$_3$), 1.48 (m, 54 H; ArOCH$_2$CH$_2$C*H*$_2$), 1.81 (m, 18 H; ArOCH$_2$C*H*$_2$), 3.93 (s, 3 H; CO$_2$C*H*$_3$), 3.93–4.05 (m, 54 H; ArOC*H*$_2$), 5.13 (s, 2 H; G1, 4′,4′ ArOC*H*$_2$Ar), 5.15 (s, 8 H; G1: 4′,3′,5′ and 3′,5′,4′ ArOC*H*$_2$Ar), 5.20 (s, 10 H; G1: 3′,5′,3′,5′ and 4′ ArOC*H*$_2$Ar), 5.25 (s, 4 H; 3′,5′ ArOC*H*$_2$Ar), 6.70 (s, 2 H; G2: 2′,6′ Ar*H* (4′,4′)), 6.71 (s, 4 H; G2: 2′,6′ Ar*H* (4′,3′,5′)), 6.73 (s, 4 H; G2: 2′,6′ Ar*H* (3′,5″,4′)), 6.75 (s, 8 H; G2: 2′,6′ Ar*H* (3′,5′,3′,5′)), 6.91 (s, 2 H; G1: 2′,6′ Ar*H* (4′)), 6.93 (s, 2 H; 2′,6′ Ar*H*), 6.95 (s, 4 H; G1: 2′,6′ Ar*H* (3′,5′)), 7.43–7.60 (overlapped m, 50 H; 2,6, G1: 2,3,5,6 H, G2: 2,3,5,6 H Ar*H*), 8.07 ppm (d, $J=8.3$ Hz, 2 H; 3,5 Ar*H*); ^{13}C NMR (125 MHz, CDCl$_3$, 20 °C): $\delta=14.31$ (*C*H$_3$), 22.91 (*C*H$_2$CH$_3$), 26.42 (*C*H$_2$), 29.60 (*C*H$_2$), 29.71–30.01 (*C*H$_2$), 32.16 (ArOCH$_2$*C*H$_2$), 52.30 (CO$_2$*C*H$_3$), 69.54, 69.58 (3′,5′ ArO*C*H$_2$), 71.57, 71.57 (3′,5′ ArO*C*H$_2$Ar), 73.78 (4′ ArO*C*H$_2$), 75.28 (4′ ArO*C*H$_2$Ar), 106.28 (G2, 2′,6′ Ar*C*H), 107.71 (G1, 2′,6′ Ar*C*H), 108.20 (2′,6′ Ar*C*H), 127.08 (Ar*C*H), 127.36 (Ar*C*H), 127.45 (Ar*C*), 127.48 (Ar*C*H), 128.06 (Ar*C*H), 129.05 (Ar*C*H), 129.08 (Ar*C*H), 129.31 (Ar*C*H), 130.33 (Ar*C*), 136.12 (Ar*C*), 136.26 (Ar*C*), 136.45 (Ar*C*), 137.00 (Ar*C*), 138.51 (Ar*C*), 141.43 (Ar*C*), 141.43 (Ar*C*), 145.60 (Ar*C*), 153.45 (Ar*C*), 153.48 (Ar*C*), 153.63 (Ar*C*), 153.68 (Ar*C*), 167.00 ppm (*C*O$_2$CH$_3$); MS (MALDI-TOF): *m*/*z*: 7397.5 [$M+\mathrm{Na}^+$]; elemental analysis calcd (%) for $C_{494}H_{78O}O_{41}$ (7375.45): C 80.45, H 10.66; found: C 80.67, H 10.81.

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[1] a) E. Buhleier, W. Wehner, F. Vögtle, *Synthesis* **1978**, 155–158; b) D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Polym. J.* **1985**, *17*, 117–132; c) G. R. Newkome, Z. Yao, G. R. Baker, V. K. Gupta, *J. Org. Chem.* **1985**, *50*, 2003–2004.

[2] a) C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7638–7647; b) T. M. Miller, T. X. Neenan, *Chem. Mater.* **1990**, *2*, 346–349.

[3] a) J. M. J. Fréchet, D. A. Tomalia, *Dendrimers and Other Dendritic Polymers,* Wiley, New York, **2001**; b) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons*, Wiley-VCH, Weinheim, **2001**.

[4] a) J. S. Moore, *Acc. Chem. Res.* **1997**, *30*, 402–413; b) Y. Kim, S. C. Zimmerman, *Curr. Opin. Chem. Biol.* **1998**, *2*, 733–742; c) D. Seebach, P. B. Rheiner, G. Greiveldinger, T. Butz, H. Sellner, *Top. Curr. Chem.* **1998**, *197*, 125–164; d) J.-P. Majoral, A.-M. Caminade, *Top. Curr. Chem.* **1998**, *197*, 79–124; e) D. K. Smith, F. Diederich, *Chem. Eur. J.* **1998**, *4*, 1353–1361; f) M. Fischer, F. Vögtle, *Angew. Chem.* **1999**, *111*, 2415–2417; *Angew. Chem. Int. Ed.* **1999**, *38*, 885–905; g) A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chem. Rev.* **1999**, *99*, 1665–1688; h) D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991–3024; i) R. Haag, *Chem. Eur. J.* **2001**, *7*, 327–335; j) S. Hecht, J. M. J. Fréchet, *Angew. Chem.* **2001**, *113*, 76–94; *Angew. Chem. Int. Ed.* **2001**, *40*, 74–91; k) D. C. Tully, J. M. J. Fréchet, *Chem. Commun.* **2001**, 1229–1239; l) S.-E. Stiriba, H. Frey, R. Haag, *Angew. Chem.* **2002**, *114*, 1385–1390; *Angew. Chem. Int. Ed.* **2002**, *41*, 1329–1334; m) R. Esfand, D. A. Tomalia, *Drug Discovery Today* **2001**, *6*, 427–436; n) E. R. Gillies, J. M. J. Fréchet, *Drug Discovery Today* **2005**, *10*, 35–43; o) D.-L. Jiang, T. Aida, *Prog. Polym. Sci.* **2005**, *30*, 403–422; p) R. Van de Coevering, R. J. M. K. Gebbink, G. Van Koten, *Prog. Polym. Sci.* **2005**, *30*, 474–490; q) A.-M. Caminade, J.-P. Majoral, *Prog. Polym. Sci.* **2005**, *30*, 491–505; r) U. Boas, P. M. H. Heegaard, *Chem. Soc. Rev.* **2004**, *33*, 43–63; s) M. W. Grinstaff, *Chem. Eur. J.* **2002**, *8*, 2838–2846; t) S. M. Grayson, J. M. J. Fréchet, *Chem. Rev.* **2001**, *101*, 3819–3867.

[5] For selected recent reviews on supramolecular dendrimers self-organized in lattices, see: a) S. C. Zimmerman, *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 89–99; b) O. A. Matthews, A. N. Shipway, J. F. Stoddart, *Prog. Polym. Sci.* **1998**, *23*, 1–56; c) M. Fischer, F. Vögtle, *Angew. Chem.* **1999**, *111*, 2415–2417; *Angew. Chem. Int. Ed.* **1999**, *38*, 885–905; d) T. Emrick, J. M. J. Fréchet, *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 15–23; e) C. Schlenk, H. Frey, *Monatsh. Chem.* **1999**, *130*, 3–14; f) D. K. Smith, F. Diederich, *Top. Curr. Chem.* **2000**, *210*, 183–227; g) S. A. Ponomarenko, N. I. Boiko, V. P. Shi-

baev, *Polym. Sci. Ser. C* **2001**, *43*, 1–45; h) D. Guillon, R. Deschenaux, *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 515–525; i) C. Tschierske, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 69–80; j) C. Diele, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 333–342; k) A.-M. Caminade, C.-O. Turrin, P. Sutra, J.-P. Majoral, *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 282–295; l) D. K. Smith, A. R. Hirst, C. S. Love, J. G. Hardy, S. V. Brignell, B. Huang, *Prog. Polym. Sci.* **2005**, *30*, 220–293.

[6] For examples of functions mediated by the three-dimensional structures generated by self-assembling dendrons, see: a) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurysamy, P. A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S. D. Hudson, H. Duan, *Nature* **2002**, *419*, 384–387; b) V. Percec, A. E. Dulcey, V. S. K. Balagurusamy, Y. Miura, J. Smidrkal, M. Peterca, S. Nummelin, U. Edlund, S. D. Hudson, P. A. Heiney, H. Duan, S. N. Magonov, S. A. Vinogradov, *Nature* **2004**, *430*, 764–768; c) Y. K. Kwon, S. Chvalun, A.-I. Schneider, J. Blackwell, V. Percec, J. A. Heck, *Macromolecules* **1994**, *27*, 6129–6132; d) Y. K. Kwon, C. Danko, S. Chvalun, J. Blackwell, J. A. Heck, V. Percec, *Macromol. Symp.* **1994**, *87*, 103–114; e) Y. K. Kwon, S. N. Chvalun, J. Blackwell, V. Percec, J. A. Heck, *Macromolecules* **1995**, *28*, 1552–1558.

[7] For selected examples of supramolecular dendrimers self-organizable in lattices based on mesogenic repeat units, mesogenic dendrons and dendrimers, and conventional dendrimers functionalized with mesogens on their periphery, see: a) V. Percec, M. Kawasumi, *Macromolecules*, **1992**, *25*, 3843–3850; b) V. Percec, P. Chu, M. Kawasumi, *Macromolecules* **1994**, *27*, 4441–4453; c) V. Percec, P. Chu, G. Ungar, J. Zhou, *J. Am. Chem. Soc.* **1995**, *117*, 11441–11454; d) V. Percec, C. G. Cho, C. Pugh, D. Tamazos, *Macromolecules* **1992**, *25*, 1164–1176; e) V. Percec, *Pure Appl. Chem.* **1995**, *67*, 2031–2038; f) S. Bauer, H. Fisher, H. Ringsdorf, *Angew. Chem.* **1993**, *105*, 1658–1660; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1589–1592; g) D. J. Pesak, J. S. Moore, *Angew. Chem.* **1997**, *109*, 1709–1712; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1636–1639; h) R. Deschenaux, E. Serrano, A.-M. Levelut, *Chem. Commun.* **1997**, 1577–1578; i) J. H. Cameron, A. Facher, G. Lattermann, S. Diele, *Adv. Mater.* **1997**, *9*, 398–403; j) M. W. P. L. Baars, S. H. M. Sontjens, H. M. Fischer, H. W. I. Peerlings, E. W. Meijer, *Chem. Eur. J.* **1998**, *4*, 2456–2466; k) H. Meier, M. Lehmann, *Angew. Chem.* **1998**, *110*, 666–669; *Angew. Chem. Int. Ed.* **1998**, *37*, 643–645; l) I. M. Saez, J. W. Goodby, *Chem. Commun.* **2003**, 1726–1727; m) S. Lecommandoux, H.-A. Klok, M. Sayar, S. I. Stupp, *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 3501–3518; n) L. Gehringer, C. Bourgogne, D. Guillon, B. Donnio, *J. Am. Chem. Soc.* **2004**, *126*, 3856–3867.

[8] For selected examples of amphiphilic self-assembling dendrons and self-organizing dendrimers based on AB$_3$ benzyl ether repeat units, see: a) V. Percec, G. Johansson, J. Heck, G. Ungar, S. V. Batty, *J. Chem. Soc. Perkin Trans. 1* **1993**, 1411–1420; b) G. Johansson, V. Percec, G. Ungar, D. Abramic, *J. Chem. Soc. Perkin Trans. 1* **1994**, 447–459; c) V. Percec, G. Johansson, G. Ungar, J. Zhou, *J. Am. Chem. Soc.* **1996**, *118*, 9855–9866; d) V. S. K. Balagurusamy, G. Ungar, V. Percec, G. Johansson, *J. Am. Chem. Soc.* **1997**, *119*, 1539–1555; e) S. D. Hudson, H.-T. Jung, V. Percec, W.-D. Cho, G. Johansson, G. Ungar, V. S. K. Balagurusamy, *Science* **1997**, *278*, 449–452; f) V. Percec, W.-D. Cho, P. E. Mosier, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **1998**, *120*, 11061–11070; g) G. Ungar, V. Percec, M. N. Holerca, G. Johannson, J. A. Heck, *Chem. Eur. J.* **2000**, *6*, 1258–1266; h) V. Percec, W.-D. Cho, M. Möller, S. A. Prokhorova, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **2000**, *122*, 4249–4250; i) V. Percec, W.-D. Cho, G. Ungar, *J. Am. Chem. Soc.* **2000**, *122*, 10273–10281; j) D. R. Dukeson, G. Ungar, V. S. K. Balagurusamy, V. Percec, G. A. Johansson, M. Glodde, *J. Am. Chem. Soc.* **2003**, *125*, 15974–15980; k) V. Percec, M. Glodde, G. Johansson, V. S. K. Balagurusamy, P. A. Heiney, *Angew. Chem.* **2003**, *115*, 4474–4478; *Angew. Chem. Int. Ed.* **2003**, *42*, 4338–4342; l) J. Malthête, *New J. Chem.* **1996**, *20*, 925–928.

[9] For selected examples of amphiphilic self-assembling dendrons based on 3,4- and 3,5- benzyl ethers, see: a) V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *Angew. Chem.* **2000**, *112*, 1661–1666; *Angew. Chem. Int. Ed.* **2000**, *39*, 1598–1602; b) V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **2001**, *123*, 1302–1315; c) M. Suárez, J.-M. Lehn, S. C. Zimmerman, A. Skoulios, B. Heinrich, *J. Am. Chem. Soc.* **1998**, *120*, 9526–9532.

[10] For examples of amphiphilic self-assembling dendrons based on combinations of (AB)$_y$, AB$_2$, and AB$_3$ benzyl ether dendrons, see: V. Percec, C. M. Mitchell, W.-D. Cho, S. Uchida, M. Glodde, G. Ungar, X. Zeng, Y. Liu, V. S. K. Balagurusamy, P. A. Heiney, *J. Am. Chem. Soc.* **2004**, *126*, 6078–6094.

[11] For examples of dendrons that self-assemble and co-assemble into supramolecular lattices and/or complex supramolecules, see: a) V. Percec, C.-H. Ahn, T. K. Bera, G. Ungar, D. J. P. Yeardley, *Chem. Eur. J.* **1999**, *5*, 1070–1083; b) V. Percec, T. K. Bera, M. Glodde, Q. Fu, V. S. K. Balagurusamy, P. A. Heiney, *Chem. Eur. J.* **2003**, *9*, 921–935; c) V. Percec, M. R. Imam, T. K. Bera, V. S. K. Balagurusamy, M. Peterca, P. A. Heiney, *Angew. Chem.* **2005**, *117*, 4817–4823; *Angew. Chem. Int. Ed.* **2005**, *44*, 4739–4745.

[12] For new periodic and quasiperiodic lattices self-organized from supramolecular dendrimers, see: a) G. Ungar, Y. Liu, X. Zeng, V. Percec, W.-D. Cho, *Science* **2003**, *299*, 1208–1211; b) X. Zeng, G. Ungar, Y. Liu, V. Percec, A. E. Dulcey, J. K. Hobbs, *Nature* **2004**, *428*, 157–160.

[13] V. Percec, M. Peterca, M. J. Sienkowska, M. A. Ilies, E. Aqad, J. Smidrkal, P. A. Heiney, *J. Am. Chem. Soc.* **2006**, *128*, 3324–3334.

[14] For architectural examples of self-assembling non-mesogenic amphiphilic dendrons, see: a) C. Kim, K. T. Kim, Y. Chang, H. H. Song, T.-Y. Cho, H.-J. Jeon, *J. Am. Chem. Soc.* **2001**, *123*, 5586–5587; b) B.-K. Cho, A. Jain, S. M. Gruner, U. Wiesner, *Science* **2004**, *305*, 1598–1601; c) B.-K. Cho, A. Jain, S. Mahajan, H. Ow, S. M. Gruner, U. Wiesner, *J. Am. Chem. Soc.* **2004**, *126*, 4070–4071.

[15] For selected examples of self-organizable polymers dendronized with self-assembling dendrons, see: a) V. Percec, J. Heck, D. Tomazos, F. Falkenberg, H. Blackwell, G. Ungar, *J. Chem. Soc. Perkin Trans. 1* **1993**, 2799–2811; b) V. Percec, D. Tomazos, J. Heck, H. Blackwell, G. Ungar, *J. Chem. Soc. Perkin Trans. 2* **1994**, 31–44; c) V. Percec, C.-H. Ahn, G. Ungar, D. J. P. Yeardley, M. Möller, S. S. Sheiko, *Nature* **1998**, *391*, 161–164; d) V. Percec, C.-H. Ahn, W.-D. Cho, A. M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M. Möller, S. A. Prokhorova, S. S. Sheiko, S. Z. D. Cheng, A. Zhang, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **1998**, *120*, 8619–8631; e) D. J. P. Yeardley, G. Ungar, V. Percec, M. N. Holerca, G. Johannson, *J. Am. Chem. Soc.* **2000**, *122*, 1684–1689; f) A. Rapp, I. Schnell, D. Sebastiani, S. P. Brown, V. Percec, H. W. Spiess, *J. Am. Chem. Soc.* **2003**, *125*, 13284–13297; g) V. Percec, J. G. Rudick, M. Peterca, M. Wagner, M. Obata, C. M. Mitchell, W.-D. Cho, V. S. K. Balagurusamy, P. A. Heiney, *J. Am. Chem. Soc.* **2005**, *127*, 15257–15264; h) Y. Q. Tian, K. Kamata, H. Yoshita, T. Iyoda, *Chem. Eur. J.* **2006**, *12*, 584–591.

[16] For a recent review on dendronized polymers, see: H. Frauenrath, *Prog. Polym. Sci.* **2005**, *30*, 325–384.

[17] M.-L. Huber, J. T. Pinhey, *J. Chem. Soc. Perkin Trans. 1* **1990**, 715–720.

[18] a) B. Andersh, D. C. Murphy, R. V. Olson, *Synth. Commun.* **2000**, *30*, 2091–2098; b) D. R. Coulsen, *Inorg. Synth.* **1972**, *13*, 121–123; c) N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, *11*, 513–519; d) J. M. Andreu, B. Perez-Ramirez, M. J. Gorbunoff, D. Ayala, S. N. Timasheff, *Biochemistry* **1998**, *37*, 8356–8368.

[19] V. Percec, G. M. Golding, J. Smidrkal, O. Weichold, *J. Org. Chem.* **2004**, *69*, 3447–3452.

[20] F. L. Benton, T. E. Dillon, *J. Am. Chem. Soc.* **1942**, *64*, 1128–1129.

[21] a) V. Prey, *Ber. Dtsch. Chem. Ges.* **1941**, *74*, 1216–1225; b) M. Gates, G. Tschudi, *J. Am. Chem. Soc.* **1956**, *78*, 1380–1393.

[22] J. C. Norrild, H. Eggert, *J. Am. Chem. Soc.* **1995**, *117*, 1479–1484.

[23] J. P. Wolfe, R. A. Singer, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 9550–9561.

[24] G. C. Dol, P. C. J. Kramer, P. W. N. M. van Leeuwen, *Eur. J. Org. Chem.* **1998**, 359–364.

[25] J. W. Foley, Synthesis (Polaroid Corp.), US-4182912; [*Chem. Abstr.* **1980**, *92*, 163705x].

[26] V. Percec, D. Schlueter, G. Ungar, S. Z. D. Cheng, A. Zhang, *Macromolecules* **1998**, *31*, 1745–1762.

[27] A. G. Anderson, P. J. Stang, *J. Org. Chem.* **1976**, *41*, 3034–3036.

[28] G. W. Gray, J. W. Goodby, *Smectic Liquid Crystals*, Leonard Hill, London, **1984**.

[29] a) V. Percec, A. E. Dulcey, M. Peterca, M. Ilies, J. Ladislaw, B. M. Rosen, U. Edlund, P. A. Heiney, *Angew. Chem.* **2005**, *117*, 6674–6679; *Angew. Chem. Int. Ed.* **2005**, *44*, 6516–6521; b) V. Percec, A. Dulcey, M. Peterca, M. Ilies, Y. Miura, U. Edlund, P. A. Heiney, *Aust. J. Chem.* **2005**, *58*, 472–482; c) V. Percec, A. E. Dulcey, M. Peterca, M. Ilies, M. J. Sienkowska, P. A. Heiney, *J. Am. Chem. Soc.* **2005**, *127*, 17902–17909; d) V. Percec, A. E. Dulcey, M. Peterca, M. Ilies, S. Nummelin, M. J. Sienkowska, P. A. Heiney, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 2518–2523; e) M. Peterca, V. Percec, A. E. Dulcey, S. Nummelin, S. Korey, M. Ilies, P. A. Heiney, *J. Am. Chem. Soc.* **2006**, *128*, 6713–6720.

[30] a) R. Adams, M. H. Gold, *J. Am. Chem. Soc.* **1940**, *62*, 56–61; b) N. J. Leonard, S. N. Boyd, Jr., *J. Org. Chem.* **1946**, *11*, 405–418; c) A. Kreuchunas, *J. Org. Chem.* **1956**, *21*, 368–369.

[31] Z. Che, P. V. Mocharia, M. J. Farmer, G. R. Pettit, E. Hamel, K. G. Pinney, *J. Org. Chem.* **2000**, *65*, 8811–8815.

[32] V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *Chem. Eur. J.* **2002**, *8*, 2011–2025.

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