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Self-Assembly of Hybrid Dendrons with Complex Primary Structure Into Functional Helical Pores

Virgil Percec,^{*,[a]} Jan Smidrkal,^[a] Mihai Peterca,^[a, b] Catherine M. Mitchell,^[a] Sami Nummelin,^[a] Andrés E. Dulcey,^[a] Monika J. Sienkowska,^[a] and Paul A. Heiney^[b]

Abstract: The synthesis of three libraries of self-assembling hybrid dendrons containing a primary structure based on the sequence **(4-3,4-3,5)12G2-CO₂CH₃** generated from benzyl ether, biphenyl-4-methyl ether, and AB₂ repeat units constructed from (AB)_y-AB₂ combinations of benzyl ethers, is reported. The structural and retrostructural analysis of their supramolecular dendrimers facilitated the discovery of new architectural principles that lead to the assembly of functional helical

pores. The self-assembly of an example of hybrid dendron containing -H, -CO₂CH₃, -CH₂OH, -COOH, -COOK, -CONH₂, -CONHCH₃, -CO₂-(CH₂)₂OCH₃, -(R) and -(S)-CONHCH-(CH₃)C₂H₅ as X-groups at the apex demonstrated that these self-assembling dendrons provide the simplest

strategy for the design and synthesis of porous columns containing a diversity of hydrophilic and hydrophobic functional groups in the inner part of the pore. The results reported here expand the scope and limitations of dendrons available for the self-assembly of functional pores that previously were generated mostly from dendritic dipeptides, to simpler architectures based on hybrid dendrons.

Keywords: functional pores • helical chirality • hybrid dendrons • liquid crystals • self-assembly

Introduction

Natural porous proteins function as viral helical coats,^[1a,b] transmembrane channels,^[1c,d] antibiotics,^[1e] pathogens,^[1f] and mediate protein folding.^[1g] Their remodeled structures are used for reversible encapsulation^[1h] and for stochastic sensing.^[1i] Various strategies to mimic the structure and functions of natural porous proteins have been elaborated.^[2] Our laboratory reported a general strategy for the design, synthesis, and self-assembly of helical pores from dendritic dipeptides.^[3] During investigations on the principles, the scope, and the limitations of self-assembly of helical pores from dendritic dipeptides, and on the development of new

classes of self-assembling dendrons, we have discovered several examples of dendrons without a dipeptide at their apex that self-assemble into helical pores.^[3a,e,4a,b] Of particular interest were nonfunctionalized hybrid dendrons with a primary structure based on combinations of (AB)_y-AB₃ and (AB)_y-AB₂ benzyl ether building blocks^[3a,4c] that resemble AB₃ and AB₂ biphenyl-4-methyl ether^[4b,8] dendritic repeat units. Both hybrid benzyl ether^[4c] and biphenyl-4-methyl ether^[4b,8] based dendrons provided several examples of porous assemblies.^[3a,5a] Therefore, we decided to search for potential helical-pore-forming dendrons with various architectures incorporated in the **(4-3,4-3,5)12G2-X** primary structure that was employed in the design of dendritic dipeptides.^[3] The supramolecular column self-assembled from the sequence **(4-3,4-3,5)12G2-X** generated from benzyl ether repeat units with X=CH₂OH and CO₂CH₃ does not exhibit a hollow center.^[3e] However, the same building blocks based on biphenylmethyl ether repeat units self-assemble both into porous columns and in spheres.^[4b] Consequently, we decided to investigate even more complex architectures generated from hybrid dendrons based on the same sequence of the primary structure and compositions that consist of repeat units generated from: (AB)_y-AB₂ combinations of 4- and 3,4-benzyl ethers as AB₂ units,^[4d] 4'-, 3',4'- and 3',5'-biphenyl-4-methyl ethers as AB and AB₂ units,^[4b]

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and 4-benzyl ether as AB and 3,4- and 3,5-benzyl ethers as AB₂ repeat units. The 3,4,5-benzyl and 3',4',5'-biphenyl-4-methyl ether structures were excluded from this study, since these architectural motifs provide mostly dendrons that self-assemble in spherical assemblies.^[5] The results of this study are reported here and are rewarding. These complex hybrid dendrons based on (4-3,4-3,5)12G2-X primary structure demonstrated a second general architectural motif, in addition to the dendritic dipeptides with the same primary sequence, that self-assemble into helical pores with pore diameter and functionality that are complementary to those accessible from the dendritic dipeptide^[3] building blocks.

Results and Discussion

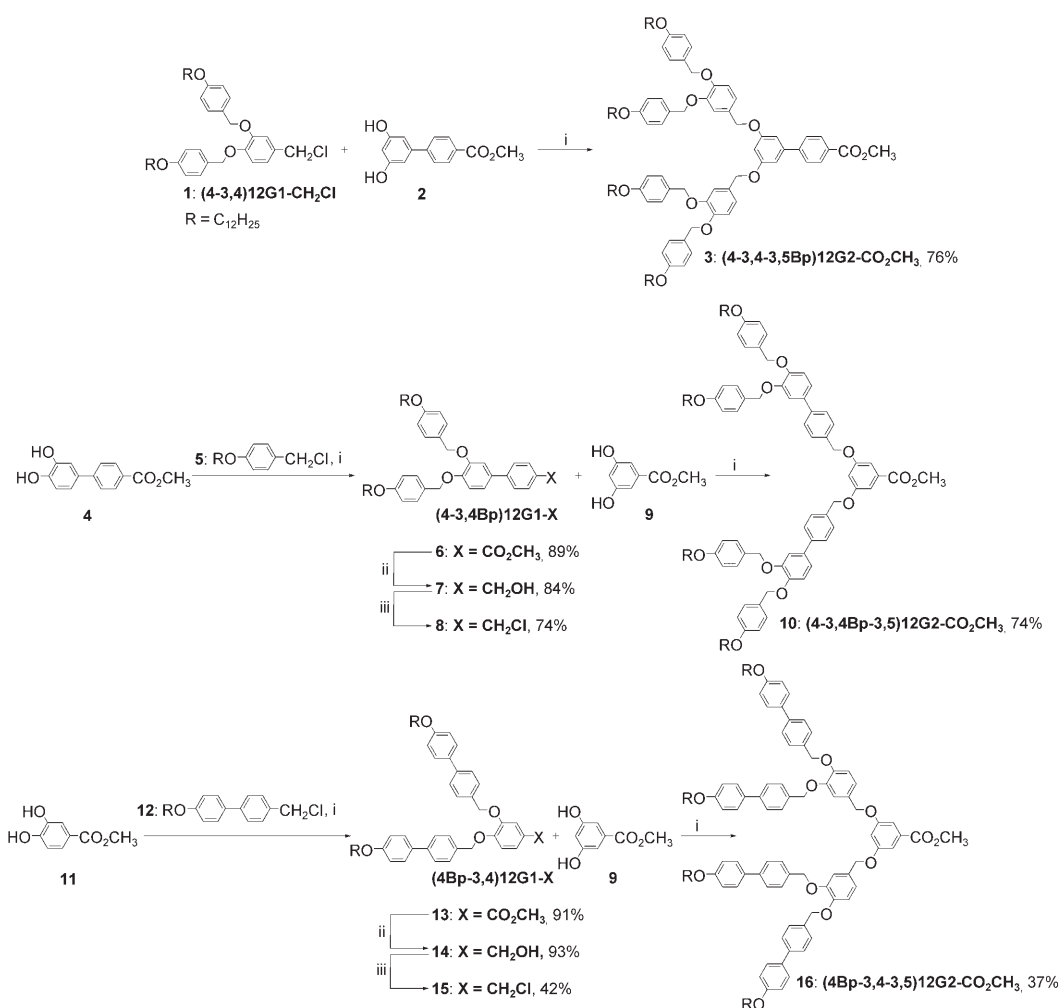
Synthesis of the self-assembling hybrid dendrons: The synthesis of the self-assembling dendrons, and the structural and the retrostructural analysis of their supramolecular assemblies were performed according to methods elaborated in our laboratory.^[3,4] The short nomenclature of the dendrons is similar to that used in previous publications.^[4b-d]

The synthesis of the first library of hybrid dendrons based on 4'-, 3',4'-, and 3',5'-biphenylmethyl ether and 4-, 3,4-, and 3,5-benzyl ether repeat units is outlined in Schemes 1 and 2.

Etherification of **2**^[4b] with **1**^[4d] in DMF at 90 °C (20 h), in the presence of K₂CO₃ produced **3** in 76 % yield. The first-generation hybrid dendron **6** was obtained in 89 % yield by the etherification of **4**^[4b] with **5**^[4d] in DMF at 90 °C (15 h) under Ar. Reduction of **6** with LiAlH₄ in THF produced **7** (84 % yield). Chlorination of **7** with SOCl₂ in CH₂Cl₂ at 25 °C (3 h) in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) proton trap^[10] afforded **8** (74 % yield).

The second-generation hybrid dendron **10** (74 % yield) was prepared by the etherification of **9**^[4d] with **8** in DMF at 90 °C (15 h) under Ar.

The second-generation dendron **16** was synthesized by following a similar sequence of reactions as the one described above. Thus, etherification of **11** with **12** in DMF at 90 °C for 15 h under Ar produced **13** in 91 % yield. Reduction of **13** with LiAlH₄ in THF yielded alcohol **14** (93 %), which was chlorinated with SOCl₂ in CH₂Cl₂ at 25 °C (2 h) in the presence DTBMP to produce **15** in 42 % yield. Etherification of **9** with **15** in DMF at 90 °C (20 h) afforded the second-gener-



Scheme 1. Synthesis of hybrid dendrons based on 4-, 3,4- and 3,5-benzyl ether and 4'-, 3',4'- and 3',5'-biphenyl-4-methyl ether repeat units. Conditions: i) K₂CO₃, DMF, 70–90 °C; ii) LiAlH₄, THF; iii) SOCl₂, DTBMP, CH₂Cl₂.

ation hybrid dendron **16** in 37% yield. The first-generation **13** and **14** and the second-generation **16** were isolated as pure products after recrystallization from acetone.

The synthesis of the second library of hybrid dendrons based on 4'-, 3',4'-, and 3',5'-biphenyl-4-methyl ether and 4-, 3,4-, and 3,5-benzyl ether repeat units is described in Scheme 2. Etherification of **2** with **8** and with **15** in DMF at 90°C under Ar in the presence of K₂CO₃ afforded **17** and **18** in 69 and 72% yields, respectively. Similarly, **20** (62% yield) was prepared by the etherification of **9** with **19**.

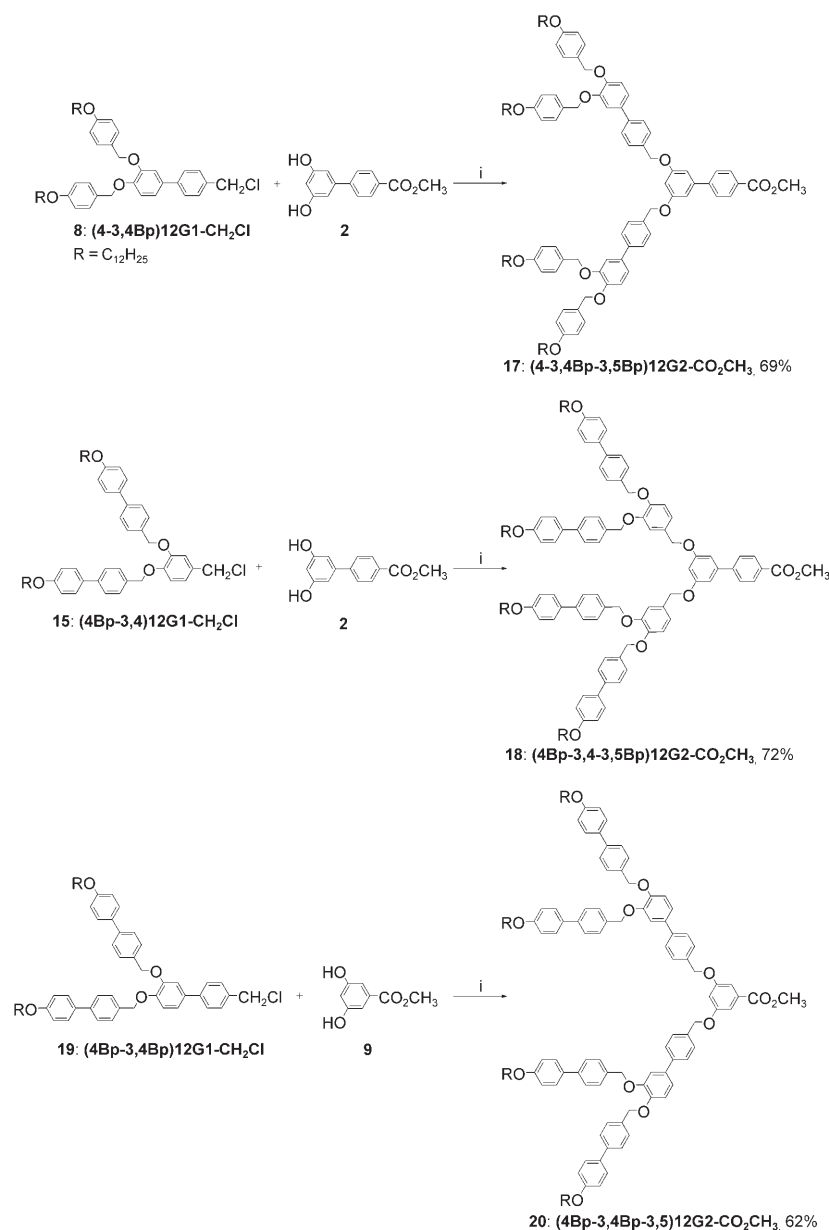
The synthesis of the library containing five (AB)_y-AB₂ hybrid dendrons based on 4-benzyl ether as AB and 3,4-benzyl ether as well as 3',4'- and 3',5'-biphenyl-4-methyl ether as AB₂ repeat units is outlined in Scheme 3. Etherification of **2** with **22**, **24**, **26**, **28** in DMF at 90°C under Ar in

the presence of K₂CO₃ afforded the second-generation dendrons **23**, **25**, **27**, **29** in 76, 68, 61, and 84% yields, respectively.

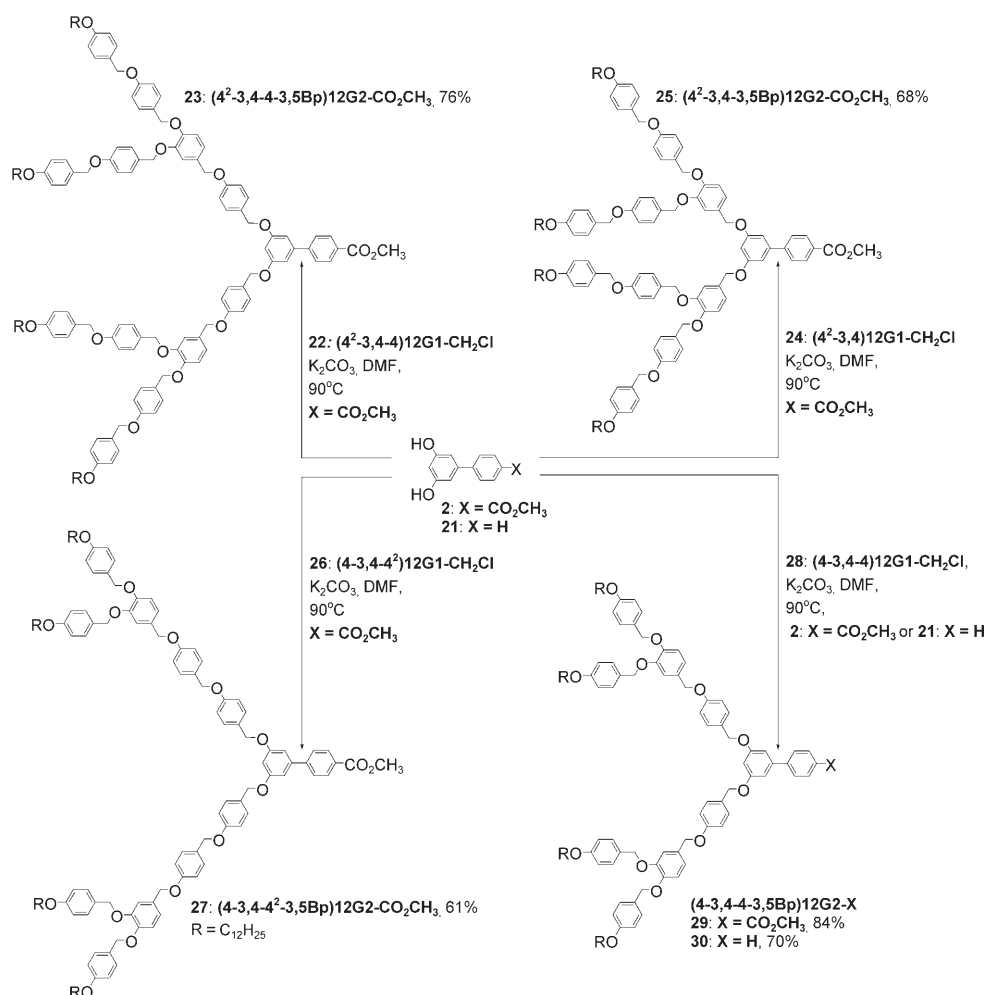
The last hybrid dendron of this series, which bears a hydrogen atom at the apex, was obtained by etherification of 3,5-dimethoxybiphenyl (**21**) with **28** under usual conditions to produce **30** (70% yield). All second-generation dendrons from Scheme 3 were purified by column chromatography.

Synthesis of self-assembling hybrid dendrons with functional groups at the apex:

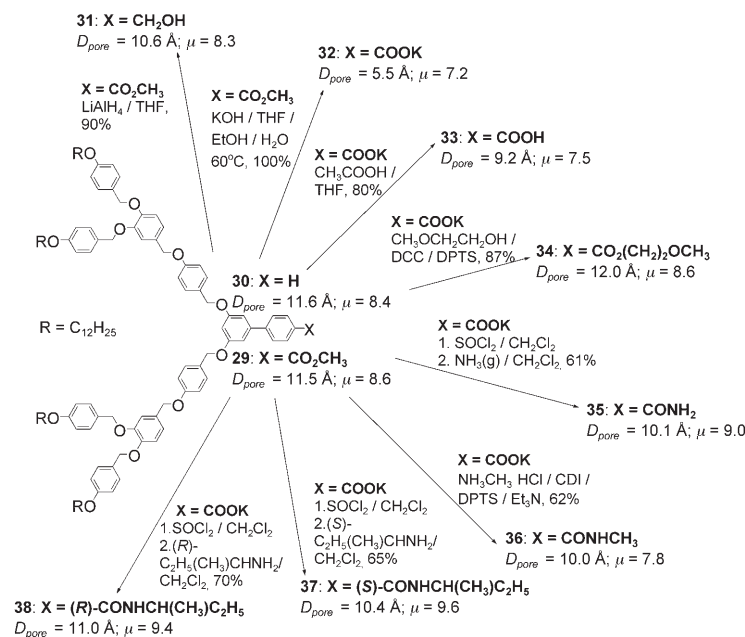
Scheme 4 shows the synthesis of eight additional dendrons based on (4-3,4-4-3,5Bp)12G2-X (**29**, **30**; Scheme 3). They contain a diversity of functional groups at their apex: X=H, CH₂OH, COOK, COOH, CO₂-(CH₂)₂OCH₃, CONH₂, CONHCH₃, (S)-CONHCH-(CH₃)C₂H₅, (R)-CONHCH-(CH₃)C₂H₅. Reduction of **29** with LiAlH₄ in THF (1 h) produced (4-3,4-4-3,5Bp)12G2-CH₂OH (**31**) in 90% yield. Saponification of the ester **29** in THF/H₂O mixture with KOH produced the potassium salt (4-3,4-4-3,5Bp)12G2-COOK (**32**) in quantitative yield. The salt **32** was acidified with acetic acid to generate the corresponding acid (4-3,4-4-3,5Bp)12G2-COOH (**33**) in 80% yield after recrystallization from acetone. Esterification of **32** with 2-methoxyethanol by using *N,N'*-dicyclohexylcarbodiimide (DCC) as an activating agent and 4-(dimethylamino)pyridinium-4-toluene-sulfonate (DPTS) as catalyst provided ester (4-3,4-4-3,5Bp)12G2-CO₂(CH₂)₂OCH₃ (**34**) in 87% yield. Chlorination of **32** with SOCl₂ in CH₂Cl₂ at 25°C (2 h) in the presence of a DTBMP proton trap, followed by the reaction with NH₃ produced the amide (4-3,4-4-3,5Bp)12G2-CONH₂ (**35**) in 61% yield. Both **34** and **35** were purified by column chromatography with CH₂Cl₂/MeOH (25:1 and 15:1 ratio, respectively) mixture as eluent followed by recrystallization from acetone. The amide (4-3,4-4-3,5Bp)12G2-CONHCH₃ (**36**) was synthesized in 62% yield by the reaction of **32** with methylammonium chlo-



Scheme 2. Synthesis of hybrid dendrons based on 4-, 3,4- and 3,5-benzyl ether and 4'-, 3',4'- and 3',5'-biphenyl-4-methyl ether repeat units. Conditions: i) K₂CO₃, DMF, 70–90°C.



Scheme 3. Synthesis of (AB)_y-AB₂ hybrid dendrons based on 4-benzyl ether as AB repeat unit and 3,4-benzyl ether and 3',5'-biphenyl-4-methyl ether as AB₂ repeat units.



Scheme 4. Functionalization of the apex of (4-3,4-4-3,5Bp)12G2-X dendron and the retrostructural analysis of the corresponding supramolecular dendrimers.

ride in the presence of carbonyl diimidazole (CDI), DPTS, and NEt₃. Pure **36** was obtained by recrystallization from acetone. Chlorination of **32** with SOCl₂ in CH₂Cl₂ at 25°C in the presence of DTBMP, followed by the amination with (*S*)-*sec*-butylamine or (*R*)-*sec*-butylamine afforded (*S*)-(4-3,4-4-3,5Bp)12G2-CONHCH(CH₃)C₂H₅ (**37**) and (*R*)-(4-3,4-4-3,5Bp)12G2-CONHCH(CH₃)C₂H₅ (**38**), respectively. Dendrons **37** and **38** were obtained in 65 and 70% yields, respectively, after chromatographic purification on basic alumina with CH₂Cl₂/acetone mixture (20:1 ratio) as eluent.

The structures of all dendrons from Schemes 1–4 were confirmed by a combination of analytical methods including 500 MHz ^1H NMR and 125 MHz ^{13}C NMR spectroscopy, matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry, high-pressure liquid chromatography (HPLC), and elemental analysis. In all cases their purity was >99%.

Helical structure by XRD and CD experiments: Wide-angle XRD obtained on aligned fibers of **(S)-(4-3,4-4-3,5Bp)12 G2-CONHCH(CH₃)C₂H₅ (37)** at 34°C and at 20°C after 9 h annealing at 90°C were used to indicate the helical structure of the porous columns in solid state (Figure 1). Figure 1a shows the appearance of X-shaped diffractions (*t*), which are correlated to the tilt angle of the dendritic molecules (40°). In addition, X-shaped diffractions (*i*) with very high intensity represent short-range intracolumnar helical correlation with a repeat distance of 4.5 Å.

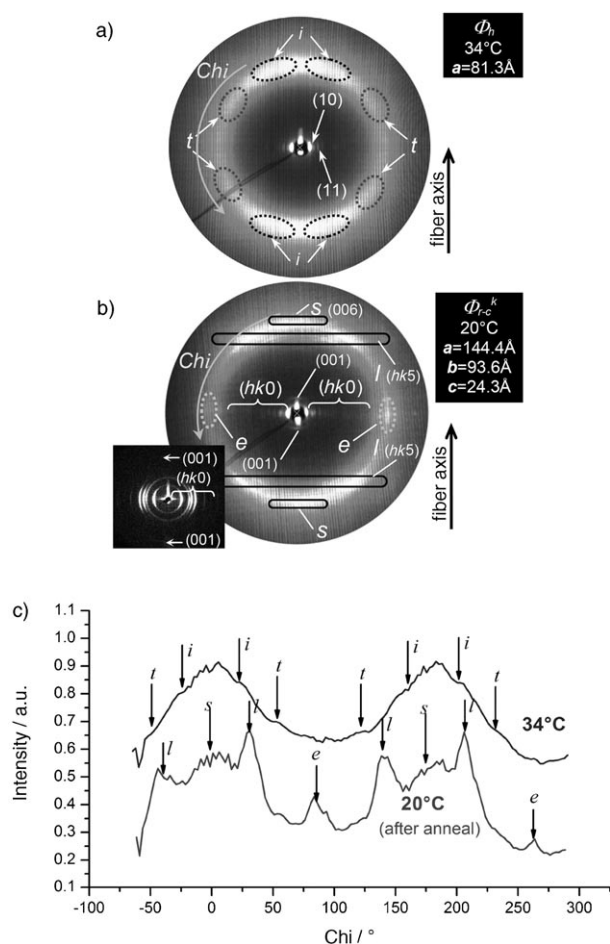


Figure 1. Wide-angle XRD patterns of aligned fibers of **(S)-(4-3,4-4-3,5Bp)12 G2-CONHCH(CH₃)C₂H₅ (37)** collected a) at 34°C and b) at 20°C after 9 h of annealing at 90°C (the inset depicts also the small angle fiber pattern), and the corresponding azimuthal angle Chi plots (c). $e=4.3\text{Å}$ diffuse equatorial feature; $s=4.3\text{Å}$ stacking along the column axis feature; l =helical layer line; (hkl) : high-order $(hk0)$ reflections; (10), (11): (hk) reflections of the hexagonal lattice; t =dendron tilt angle feature ($\approx 40^\circ$); i =short range helical feature ($\approx 4.5\text{Å}$).

The self-assembly in enantiomeric helical columns was demonstrated in cyclohexane by CD experiments performed with **(S)-** and **(R)-(4-3,4-4-3,5Bp)12 G2-CONHCH(CH₃)C₂H₅ (Figure 2)**. XRD analysis of oriented fibers shows that all the supramolecular columns self-assembled from achiral dendrons exhibit a helical structure in solid state. Therefore, these CD experiments demonstrate that the stereocenter attached to the apex of the **(4-3,4-4-3,5Bp)12 G2-CONHCH(CH₃)C₂H₅** dendron only selects the helix sense of an already helical structure.^[6]

The helical structure of the supramolecular columns is induced by the noninteger number of dendrons (μ) required to form the column stratum. The value of μ varies from 6.3 to 13.4 for the supramolecular columns (Table 4; see later). This result is similar to that observed for the case of helical pores self-assembled from dendritic dipeptides.^[3]

The self-assembly in cyclohexane of **(S)-** and **(R)-(4-3,4-4-3,5Bp)12 G2-CONHCH(CH₃)C₂H₅ (37 and 38, respectively)** enantiomeric pairs is demonstrated by the CD and UV/Vis spectra shown in Figure 2. The CD spectra of the supramolecular columns assembled from the two stereoisomers are concentration and temperature dependent and also are mirror images (Figure 2a, b). This is indicated by the values and the signs of the ellipticity of the Cotton effects at 223, 237, and 280 nm. The Cotton effects at 223 and 237 nm (Figure 2a, b) show the signature of an exciton coupling, as suggested by their zero crossover that corresponds to the maximum of the 227 nm from the UV/Vis absorption spectrum (Figure 2c, d). Both left- and right-handed supramolecular structures are stable in solution up to 36°C (lower right side insets in Figure 2a and b). The high-temperature stability of the supramolecular structures in solution is desirable for practical applications as membrane channels.^[3a] Such experiments will be reported elsewhere. These results demonstrate the helical arrangement of the **(4-3,4-4-3,5Bp)12 G2-CONHCH(CH₃)C₂H₅** dendrons in their supramolecular structure.

Electron-density maps of the porous hexagonal periodic array: A representative example for the calculation of the D_{pore} of the supramolecular columns self-organized in the hexagonal columnar phase is provided for **(S)-(4-3,4-4-3,5Bp)12 G2-CONHCH(CH₃)C₂H₅ (37)**. The details of this general method were published.^[3f] Electron-density distribution maps were reconstructed from the $F(hkl)$ peak amplitudes, which were extracted from the small-angle powder XRD (Figure 3). The enhanced amplitudes of the (11) and (20) diffractions indicate a porous column.^[3a] The XRD pattern from Figure 3c shows seven diffraction peaks in the Φ_h phase. All peaks were used in the calculation of the electron-density maps. Table 1 summarizes the experimental small-angle XRD data collected at 90°C along with the following parameters: $p6mm$ lattice peak indices (hk), peak multiplicity (m), experimental scattering vector (q_{meas}), calculated scattering vector (q_{calcd}), measured d -spacings (d), peak area (A), peak amplitude ($\sqrt{qA/m}$) and scaled amplitude (Amplitude).

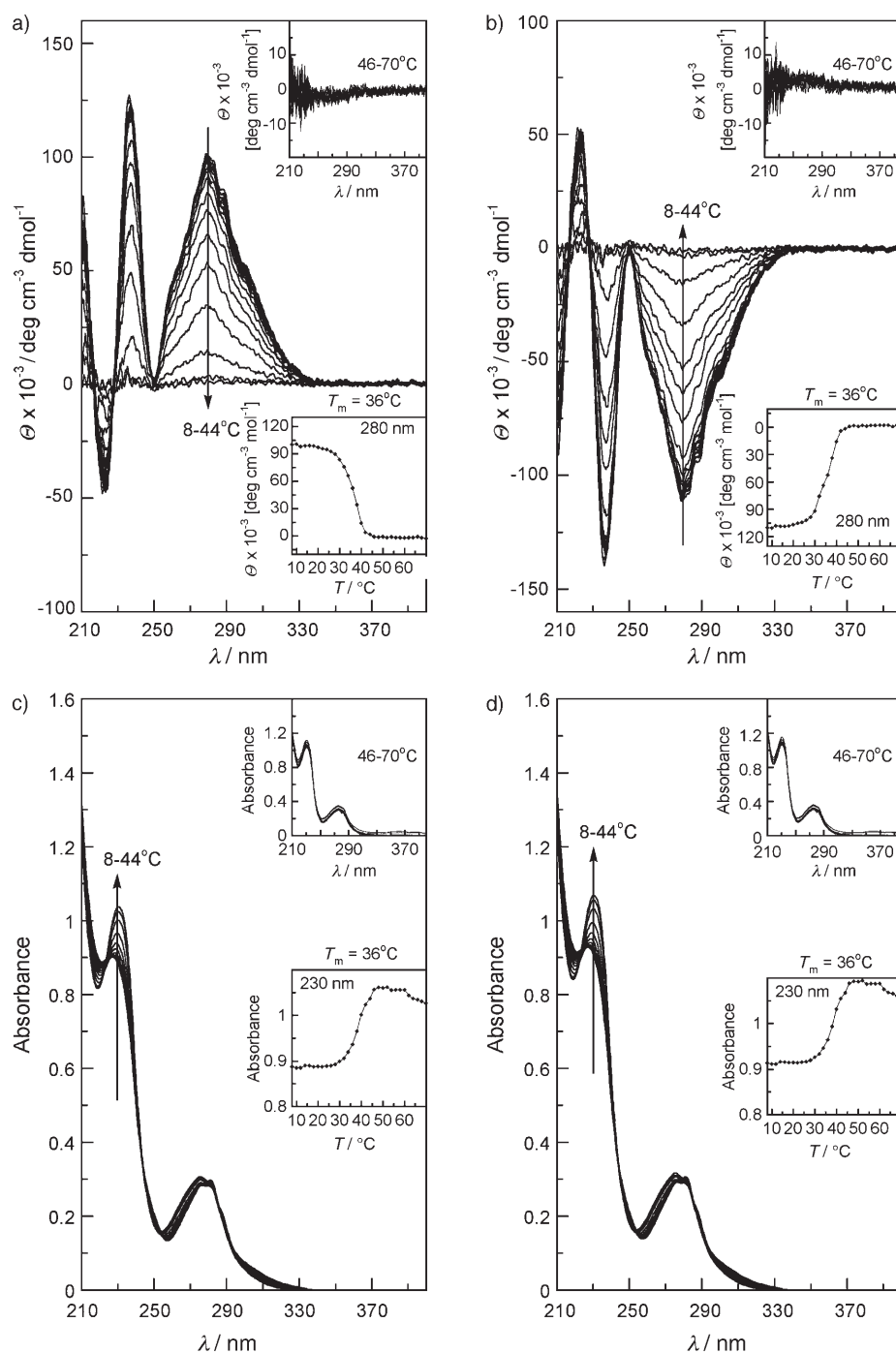


Figure 2. CD spectra of a) **(R)-(4-3,4-4-3,5 Bp)12 G2-CONHCH(CH₃)C₂H₅** and b) **(S)-(4-3,4-4-3,5 Bp)12 G2-CONHCH(CH₃)C₂H₅** in cyclohexane (1.6×10^{-4} M): a plot of θ at 280 nm is shown as a bottom inset in both a) and b); UV spectra of c) **(R)-(4-3,4-4-3,5 Bp)12 G2-CONHCH(CH₃)C₂H₅** and d) **(S)-(4-3,4-4-3,5 Bp)12 G2-CONHCH(CH₃)C₂H₅** in cyclohexane (1.6×10^{-4} M) exhibiting an isosbestic points at 222 and 244 nm; bottom insets shows the plots of A_{230} as a function of temperature.

Reconstructed electron-density maps were generated by using the equation $\rho(r) = \sum_{h,k,l} F_{hkl} e^{-2\pi i(hx+ky+lz)}$, in which $|F_{hkl}| \approx \sqrt{A}$ and A is the peak area.^[3a,f]

The gray-scale code on the electron-density distribution map with boundaries of electron-density values presented in

Figure 4a demonstrates three separated regions. The periphery of the column (marked in dark gray) indicates the low electron density that corresponds to the aliphatic part of the dendron. A lower electron density than that found for the aliphatic region is observed at the center of the columns (marked in darker gray). A high electron-density area generated by the aromatic part of the dendron surrounds this region. The electron-density maps from Figure 4 indicate that the self-assembly of **(S)-(4-3,4-4-3,5 Bp)12 G2-CONHCH(CH₃)C₂H₅** dendrons generates porous columns. However, the electron-density maps from Figure 4 do not allow the calculation of the pore diameter (D_{pore}).

Calculation of D_{pore} of the porous columns: The pore dimensions were determined by using a simplified three-level model of self-assembled supramolecular columns^[3a,f] represented by three concentric cylindrical shells. Each shell is approximated by a constant electron-density level. This model was used to reconstruct the peak amplitudes of the powder XRD pattern by means of a least-square fitting of calculated values to the experimental peak amplitudes. The three-level model is constructed from a hollow core that has the lowest electron-density level, a high electron-density region surrounding the pore that corresponds to the aromatic part of the **(S)-(4-3,4-4-3,5 Bp)12 G2-CONHCH(CH₃)C₂H₅** (37), and a low electron-density periphery that is due to the aliphatic region of the dendron.

The electron densities in each level of the model are calculated from the number of electrons present in the aromatic and aliphatic parts of the chemical structure of the **(S)-(4-3,4-4-3,5 Bp)12 G2-CONHCH(CH₃)C₂H₅** dendritic molecule, that is, $N_{\text{arom}} = 612$ and $N_{\text{aliph}} = 388$.^[3a,f] Figure 5a shows the

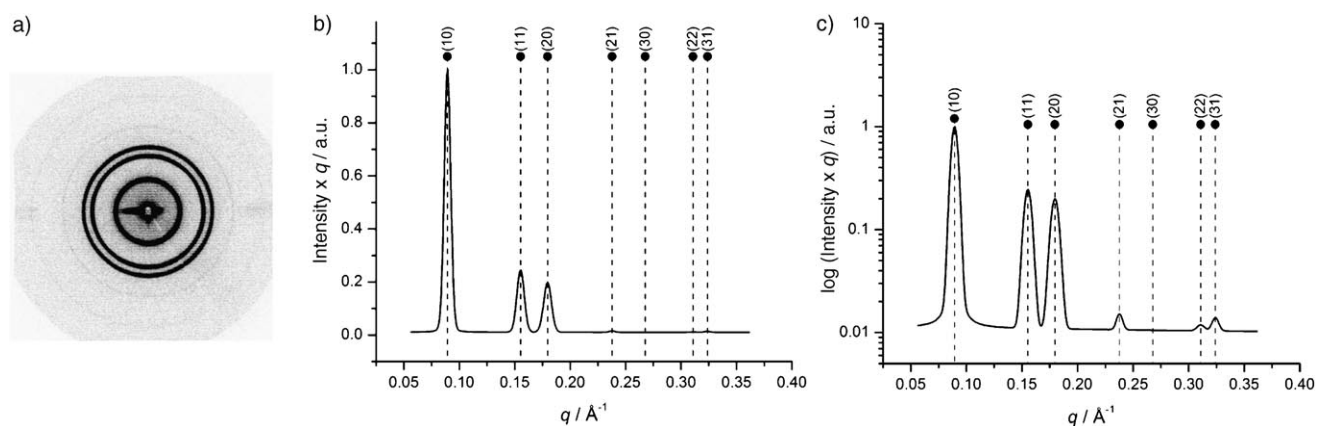


Figure 3. a) Small-angle XRD pattern and plots in b) linear scale and c) log scale for the **(S)-(4-3,4-4-3,5Bp)12G2-CONHCH(CH₃)C₂H₅** in the porous hexagonal columnar phase. In b) and c) the dotted lines indicate the expected (*hk*) peak positions based on the Φ_h with the lattice dimension $a = 80.97 \text{ \AA}$ (Table 1).

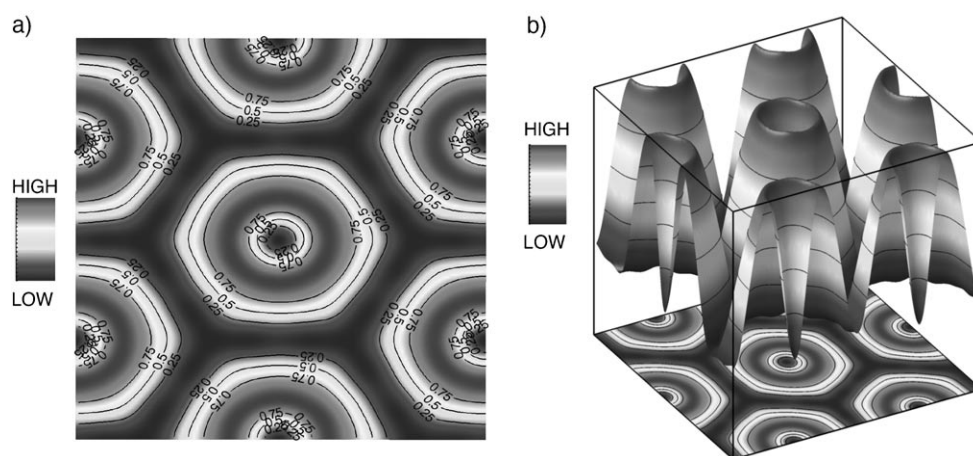


Figure 4. a) 2D view and b) 3D surface view of the reconstructed electron-density maps generated by the measured amplitudes from Table 1.

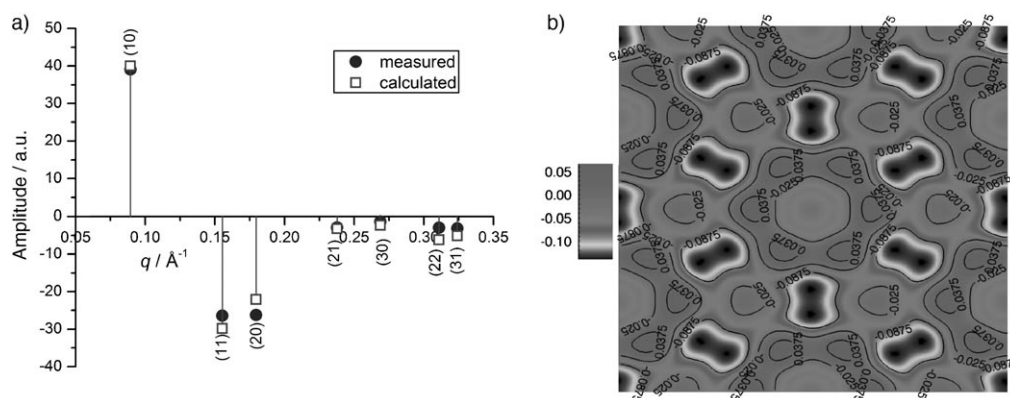


Figure 5. a) The agreement between the measured (filled circles) and three-level fitted (empty squares) amplitudes for the **(S)-(4-3,4-4-3,5Bp)12G2-CONHCH(CH₃)C₂H₅** in the hollow hexagonal columnar phase. b) The electron-density difference map $\rho(x,y) = \rho_{\text{measured}}(x,y) - \rho_{\text{fitted}}(x,y)$; the overall difference is less than 5%, with a maximum difference of about 15% localized in the aliphatic region along the direction of the column close-contact.

accuracy of the fit between the experimental and the model amplitudes. As observed from Figure 5b the overall difference between electron densities calculated from the experimental and fitted amplitudes is less than 5%. The maximum

difference of $\approx 15\%$ is located in the aliphatic region of the columns along the direction of their close-contact (Figure 5b).

Table 1. Powder XRD data for (S)-(4-3,4-4-3,5Bp)12G2-CONHCH(CH₃)C₂H₅ collected at 90 °C.

<i>h</i> ^[a]	<i>k</i> ^[a]	<i>m</i> ^[b]	<i>q</i> _{meas} ^[c] [Å ⁻¹]	<i>q</i> _{calc} ^[d] [Å ⁻¹]	<i>d</i> ^[e] [Å]	<i>A</i> ^[f]	$\sqrt{qA/m}$	Amplitude ^[g]
1	0	1	0.0893	0.0896	70.343	779.858	8.346	38.275
1	1	1	0.1553	0.1552	40.461	204.391	5.634	25.836
2	0	1	0.1796	0.1792	34.984	174.678	5.601	25.686
2	1	2	0.2378	0.2370	26.424	3.300	0.626	2.872
3	0	1	0.2688	0.2688	23.375	0.326	0.296	1.357
2	2	1	0.3108	0.3104	20.214	1.284	0.632	2.897
3	1	2	0.3240	0.3230	19.393	2.779	0.671	3.077

[a] *h**k**l* peak index. [b] Peak multiplicity. [c] Experimental scattering vector. [d] Calculated scattering vector using $q(hk) = \frac{4\pi\sqrt{h^2+k^2+lk}}{\sqrt{3}a}$, with the lattice parameter *a* given by $\bar{a} = \frac{4\pi l}{\sqrt{3}} \left(\frac{1}{q(10)} + \frac{\sqrt{3}}{q(11)} + \frac{2}{q(20)} \right) = 80.97 \text{ Å}$. [e] Measured (*h**k*) peak *d*-spacing computed using $d = \frac{2\pi}{q_{\text{meas}}}$. [f] (*h**k*) peak area. [g] Scaled amplitude calculated using the scaling factor given by $S = \sum_{(hk)} \sqrt{\frac{\text{Area}_{(hk)}}{q_{hk} m_{(hk)}}} = 21.806$.

Structural and retrostructural analysis: All hybrid dendrons self-assemble in columnar supramolecular dendrimers that self-organize in various periodic arrays. The phase behavior of all supramolecular dendrimers was analyzed by a combination of thermal optical polarized microscopy (TOPM), differential scanning calorimetry (DSC), and small- and wide-angle XRD performed as a function of temperature on powder and oriented fibers. The powder XRD experiments were carried out during first and second heating cycles up to the isotropic state and on cooling scans.

The fiber experiments were performed below the isotropic state. Structural and retrostructural analysis was performed by using methods elaborated previously.^[3] The transition temperatures (°C) and the corresponding enthalpy changes (kcal mol⁻¹) were determined by DSC with heating and cooling rates of 10 °C min⁻¹. DSC traces obtained from the first and second heating and from the first cooling scans for the hybrid dendrons from Schemes 1–3 are shown in Figure 6.

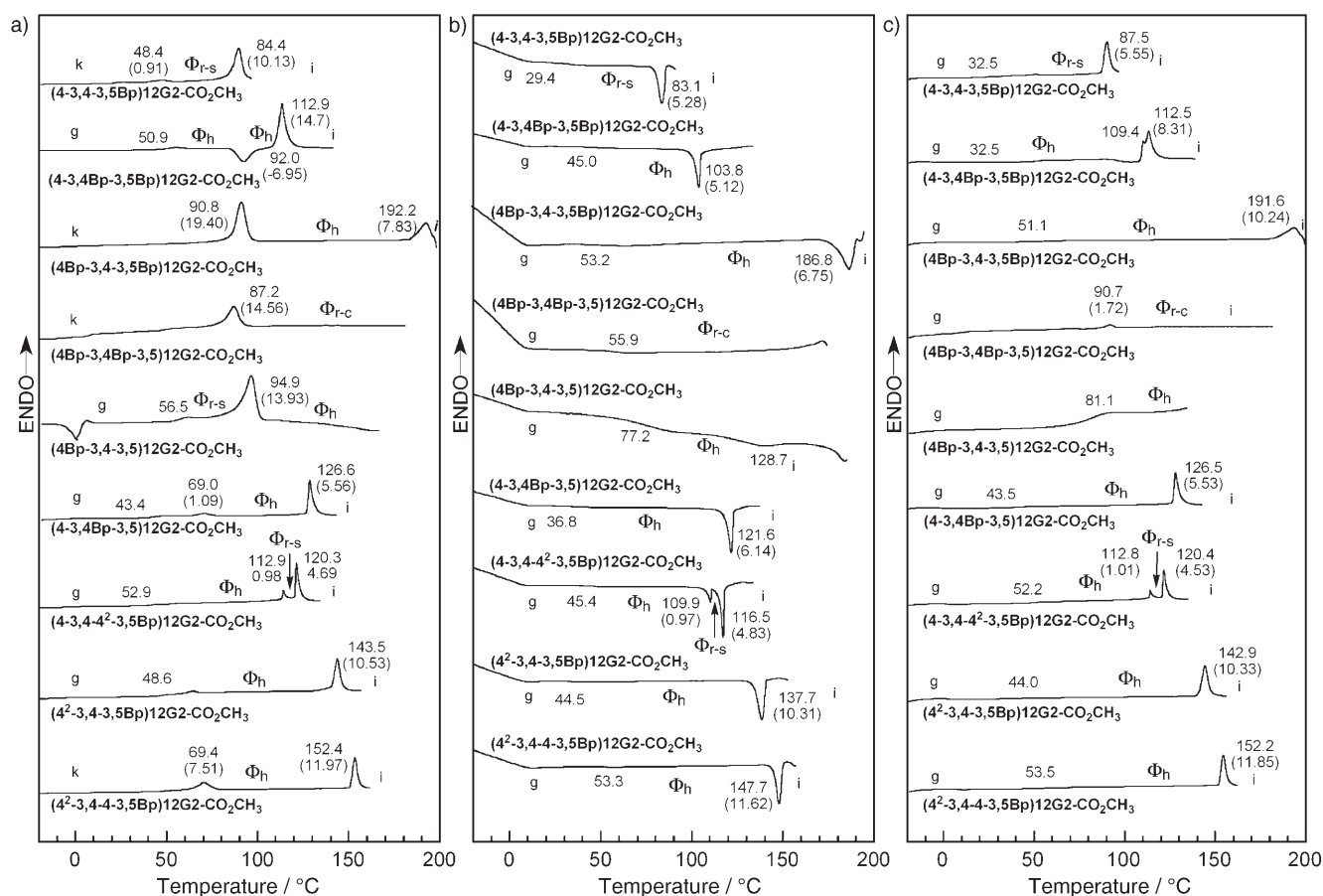


Figure 6. DSC traces (10 °C min⁻¹) of supramolecular dendrimers self-assembled from hybrid dendrons. Transition temperatures (°C) and enthalpy changes (in parentheses, kcal mol⁻¹) are marked in the figure: a) first heating scan; b) first cooling scan; c) second heating scan. Peak intensities are not scaled.

Figure 7 shows the DSC traces collected on the first and second heating and the first cooling scans for **(4-3,4-4-3,5Bp)12G2-X**, in which X represents the functional groups at the apex of the self-assembling dendrons (Scheme 4). The DSC traces marked "blend" at the bottom of Figure 7 show the thermal behavior of a mixture of seven hybrid dendrons **(4-3,4-4-3,5Bp)12G2-X** bearing -H, -CO₂CH₃, -CH₂OH, -CO₂(CH₂)₂OCH₃, -CONH₂, -CONHCH₃ or -(S)-CONHCH(CH₃)C₂H₅ at their apex. These dendrons were mixed in 1:1:1:1:1:1 weight ratio and their DSC provided a remarkable result. They are miscible, and their mixture provides a new mechanism to assemble supramolecular pores containing statistically distributed functional groups in the pore.

Table 2 summarizes the transition temperatures and corresponding enthalpy changes obtained from Figures 6 and 7 for all supramolecular structures self-assembled from hybrid

dendrons. They self-organize in a variety of liquid crystalline, crystalline, and ordered glassy phases.

All columnar phases were analyzed and assigned by XRD experiments. The *d*-spacing, their indices, and lattice symmetries are reported in Table 3.

Table 4 summarizes the lattice parameters (*a*) for the hexagonal columnar (Φ_h) or (*a*,*b*) for the columnar rectangular-centered (Φ_{r-c}) and columnar rectangular simple (Φ_{r-s}) lattices; the column diameters (D_{col} , D_a , D_b); the pore diameters (D_{pore}) for columnar hexagonal phases; the experimental densities (ρ_{20}); the number of dendrons per 4.7 Å supramolecular column stratum (μ); and the projection of the solid angle of the dendron (α').^[4a,c,d]

The most representative results of the structural and retrostructural analysis are summarized in Figures 8 and in Scheme 4.

Figure 8a summarizes the self-assembly of six second-generation dendrons that have various combinations of 4', 3', 4'-

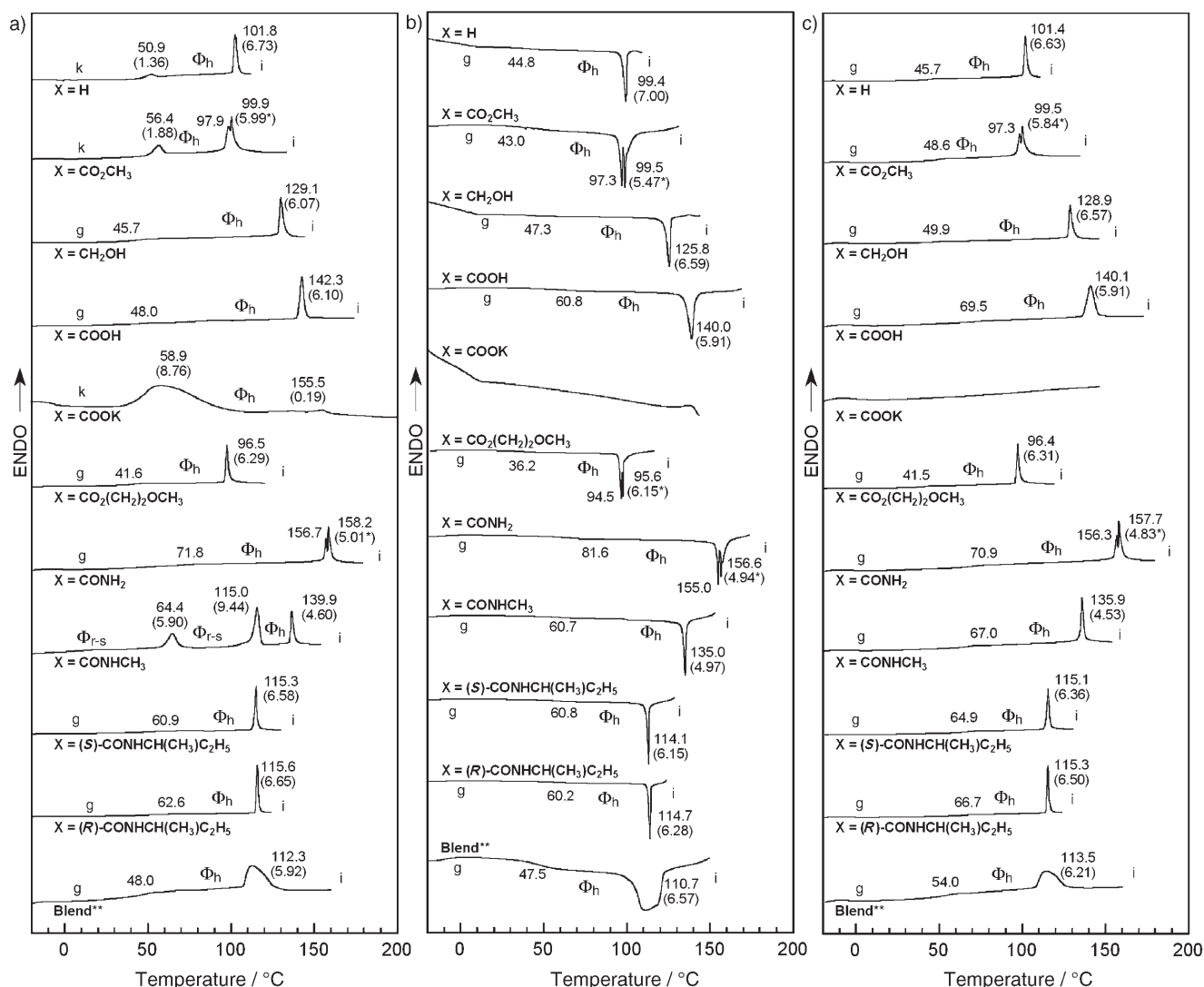


Figure 7. DSC traces (10°Cmin⁻¹) of **(4-3,4-4-3,5Bp)12G2-X**. Transition temperatures (°C) and enthalpy changes (in parentheses, kcal mol⁻¹) are marked in the figure: a) first heating scan; b) first cooling scan; c) second heating scan. Peak intensities are not scaled. * Enthalpy change was calculated based on overlapped peaks. ** Blend is a mixture of **(4-3,4-4-3,5Bp)12G2-X**, in which X = H, CO₂CH₃, CH₂OH, CO₂(CH₂)₂OCH₃, CONHCH₃, CONH₂, (S)-CONHCH(CH₃)C₂H₅ in 1:1:1:1:1:1:1 ratio.

and 3',5'-substituted biphenyl-4-methyl ether and 4-, 3,4-, and 3,5-benzyl ether repeat units incorporated in the **(4-3,4-3,5)12 G2-X** primary structure that was employed previously in the synthesis of dendritic dipeptides.^[3]

The primary structures containing the 3',5'-disubstituted biphenyl-4-carboxylate at the apex (**(4-3,4-3,5 Bp)12 G2-CO₂CH₃**, **3**), the 4'-substituted biphenyl-4-methyl ether at the periphery (**(4Bp-3,4-3,5)12 G2-CO₂CH₃**, **16**), and the 4'-substituted biphenyl-4-methyl ether at the periphery together with 3',4'-disubstituted biphenyl-4-carboxylate in the inner part of the dendron (**(4Bp-3,4Bp-3,5)12 G2-CO₂CH₃**, **20**) assemble into nonporous columns. However, the incorporation of the 3',4'-biphenyl-4-methyl ether in the inner part of a benzyl ether dendron that does not assemble into porous columns generated **(4-3,4Bp-3,5)12 G2-CO₂CH₃** (**10**), which does assemble into porous columns that self-organize into an enantiotropic Φ_h phase with $D_{col}=68.1$ Å and

$D_{pore}=8.2$ Å. Similarly, when the 3',5'-biphenyl-4-carboxylate was attached to the apex and the 3',4'-biphenyl-4-methyl ether in the inner part generated **(4-3,4Bp-3,5Bp)12 G2-CO₂CH₃** (**17**), which self-assembles into porous columns. Alternatively, when 4'-substituted biphenyl-4-methyl ether were incorporated on the periphery generated **(4Bp-3,4-3,5Bp)12 G2-CO₂CH₃** (**18**) that self-assemble into porous columns. The D_{col} of **(4-3,4Bp-3,5Bp)12 G2-CO₂CH₃** and **(4Bp-3,4-3,5Bp)12 G2-CO₂CH₃** are similar: $D_{col}=73.5$ Å and $D_{col}=72.5$ Å, respectively. However, surprisingly, D_{pore} is almost twice as small for **(4Bp-3,4-3,5Bp)12 G2-CO₂CH₃** dendron $D_{pore}=6.4$ Å relative to $D_{pore}=11.5$ Å for **(4-3,4Bp-3,5Bp)12 G2-CO₂CH₃**. In addition, DSC analysis of **(4-3,4-3,5Bp)12 G2-CO₂CH₃**, **(4-3,4Bp-3,5Bp)12 G2-CO₂CH₃**, and **(4Bp-3,4-3,5Bp)12 G2-CO₂CH₃** supramolecular dendrimers showed the following increasing trend of

Table 2. Thermal transitions of supramolecular dendrimers self-assembled from hybrid dendrons.

Dendron	Thermal transitions [°C] and corresponding enthalpy changes [kcal mol ⁻¹] ^[a]	
	Heating	Cooling
(4-3,4-3,5Bp)12G2-CO₂CH₃	k 48.4 (0.91) Φ_{rs} 84.4 (10.13) i g 32.5 Φ_{rs} 87.5 (5.55) i	i 83.1 (5.28) Φ_{rs} 29.4 g
(4-3,4Bp-3,5)12G2-CO₂CH₃	g 43.4 69.0 (1.09) Φ_h 126.6 (5.56) i g 43.5 Φ_h 126.5 (5.53) i	i 121.6 (6.14) Φ_h 36.8 g
(4Bp-3,4-3,5)12G2-CO₂CH₃	Φ_{rs} 56.5 Φ_{rs} 94.9 (13.93) Φ_h g 81.1 Φ_h	128.7 Φ_h 72.2 g
(4-3,4Bp-3,5Bp)12G2-CO₂CH₃	g 50.9 Φ_h 92.0 (-6.95) Φ_h 112.9 (14.7) i g 32.5 Φ_h 109.4 112.5 (8.31) i	i 103.8 (5.12) Φ_h 45.0 g
(4Bp-3,4-3,5Bp)12G2-CO₂CH₃	k 90.8 (19.40) Φ_h 192.2 (7.83) i g 51.5 Φ_h 191.6 (10.24) i	i 186.8 (6.75) Φ_h 53.2 g
(4Bp-3,4Bp-3,5)12G2-CO₂CH₃	k 87.2 (14.56) Φ_{rc} g 90.7 (1.72) Φ_{rc}	Φ_{rc} 55.9 g
(4-3,4-4²-3,5Bp)12G2-CO₂CH₃	g 52.9 Φ_h 112.9 (0.98) Φ_{rs} 120.3 (4.69) i g 52.2 Φ_h 112.8 (1.01) Φ_{rs} 120.4 (4.53) i	i 116.5 (4.83) Φ_{rs} 109.9 (0.97) Φ_h 45.4 g
(4²-3,4-3,5Bp)12G2-CO₂CH₃	g 48.6 Φ_h 143.5 (10.53) i g 44.0 Φ_h 142.9 (10.33) i	i 137.7 (10.31) Φ_h 44.5 g
(4²-3,4-4-3,5Bp)12G2-CO₂CH₃	k 69.4 (7.51) Φ_h 152.4 (11.97) i g 53.5 Φ_h 152.2 (11.85) i	i 147.7 (11.62) Φ_h 53.3 g
(4-3,4-4-3,5Bp)12G2-H^[c]	k 50.9 (1.36) Φ_h 101.5 (6.73) i g 45.7 Φ_h 101.4 (6.63) i	i 99.4 (7.00) Φ_h 44.8 g
(4-3,4-4-3,5Bp)12G2-CO₂CH₃^[c]	k 56.4 (1.88) Φ_h 97.9 99.9 (5.99) ^[b] i g 48.6 Φ_h 97.3 99.5 (5.64) ^[b] i	i 99.5 (5.47) ^[b] 97.3 Φ_h 43.9 g
(4-3,4-4-3,5Bp)12G2-CH₂OH^[c]	g 45.7 Φ_h 129.1 (6.07) i g 49.9 Φ_h 128.9 (6.57) i	i 125.8 (6.59) Φ_h 47.3 g
(4-3,4-4-3,5Bp)12G2-COOH	g 48.0 Φ_h 142.3 (6.10) i g 69.5 Φ_h 140.1 (5.91) i	i 140.0 (5.91) Φ_h 60.8 g
(4-3,4-4-3,5Bp)12G2-COOK	k 58.9 (8.76) Φ_h 155.5 (0.19)	
(4-3,4-4-3,5Bp)12G2-CO₂(CH₂)₂OCH₃^[c]	g 41.6 Φ_h 96.5 (6.29) i g 41.5 Φ_h 96.4 (6.31) i	i 96.4 (6.31) ^[b] 94.5 Φ_h 36.2 g
(4-3,4-4-3,5Bp)12G2-CONH₂^[c]	g 71.8 Φ_h 156.7 158.2 (5.01) ^[b] i g 70.9 Φ_h 156.3 157.7 (4.83) ^[b] i	i 156.6 (4.94) ^[b] 155.0 Φ_h 81.6 g
(4-3,4-4-3,5Bp)12G2-CONHCH₃^[c]	Φ_{rs} 64.4 (5.90) Φ_{rs} 115.0 (9.44) Φ_h 139.9 (4.60) i g 67.0 Φ_h 135.9 (4.53) i	i 135.0 (4.97) Φ_h 60.7 g
(S)-(4-3,4-4-3,5Bp)12G2-CONHCH(CH₃)C₂H₅^[c]	g 60.9 Φ_h 115.3 (6.38) i g 66.7 Φ_h 115.1 (6.36) i	i 114.1 (6.15) Φ_h 60.8 g
(R)-(4-3,4-4-3,5Bp)12G2-CONHCH(CH₃)C₂H₅	g 62.6 Φ_h 115.6 (6.65) i g 66.7 Φ_h 115.3 (6.50) i	i 114.1 (6.28) Φ_h 60.2 g
blend ^[c]	g 48.0 Φ_h 112.3 (5.92) i g 54.0 Φ_h 113.5 (6.21) i	i 110.7 (6.37) Φ_h 47.5 g

[a] Thermal transitions and enthalpy changes (in parentheses) were determined by DSC (10°Cmin⁻¹), data from the first heating and the first cooling is on the first line, and the data from the second heating is on the second line. [b] Enthalpy changes based on overlapped peaks. [c] Dendrons included in Blend in the 1:1:1:1:1:1 ratio; $\Phi_{rc}=c2mm$ centered rectangular columnar lattice; $\Phi_{rs}=p2mm$ simple rectangular columnar lattice; $\Phi_h=p6mm$ hexagonal columnar lattice; k = crystalline; g = glassy; i = isotropic.

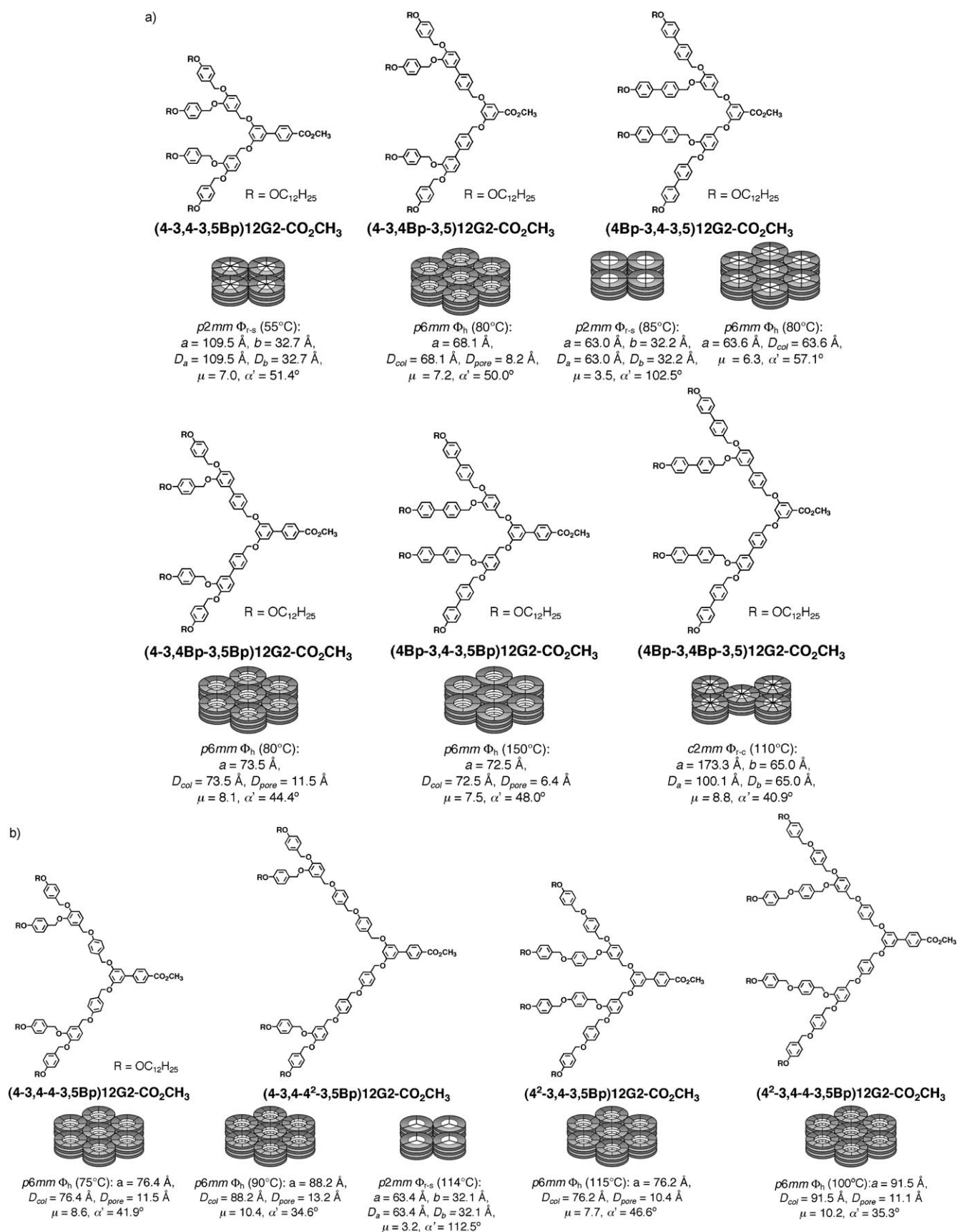


Figure 8. Retrostructural analysis of supramolecular dendrimers self-assembled from a) **(4-3,4Bp)12G1-X**, in which $X = \text{CO}_2\text{CH}_3$, CH_2OH , and **(4-3,4-3,5)12G2-CO₂CH₃** hybrid dendrons containing benzyl ether and biphenyl-4-methyl ether repeat units and b) **(4-3,4-3,5)12G2-X** hybrid dendrons containing 4-, 3,4-benzyl, 3',5'-biphenyl-4-methyl, and combinations of (AB)₁-AB₂ 4-benzyl ether hybrid dendrons.

Table 3. Measured d -spacing [in Å] of $p2mm$ simple rectangular columnar (Φ_{rs}), $c2mm$ centered rectangular columnar (Φ_{rc}), and $p6mm$ hexagonal columnar (Φ_h) lattices generated by biphenyl-benzyl ether combined dendrons.

Dendron	T [°C]	Lattice	LC phase	d -spacings [Å] and their indices							
				$d_{10}^{[a]}$	d_{11}	d_{20}	d_{21}	d_{30}	d_{22}	d_{31}	
				$d_{20}^{[b]}$	d_{11}	d_{31}	d_{40}	d_{02}	d_{22}		
				$d_{10}^{[c]}$	d_{11}	d_{03}	d_{20}	d_{30}	d_{01}	d_{21}	
(4-3,4-3,5Bp)12G2-CO ₂ CH ₃	55	$p2mm$	Φ_{rs}				53.7 ^[c]	36.5	32.6	28.2	
(4-3,4Bp-3,5)12G2-CO ₂ CH ₃	80	$p6mm$	Φ_h	59.0 ^[a]	34.0	29.5	22.3				
(4Bp-3,4-3,5)12G2-CO ₂ CH ₃	85	$p2mm$	Φ_{rs}	63.0 ^[c]							
	100	$p6mm$	Φ_h	65.6 ^[a]	31.5	27.5				32.2	
(4-3,4Bp-3,5Bp)12G2-CO ₂ CH ₃	80	$p6mm$	Φ_h	63.4 ^[a]	36.8	31.8	24.1				
(4Bp-3,4-3,5Bp)12G2-CO ₂ CH ₃	150	$p6mm$	Φ_h	62.8 ^[a]	36.3	31.4					
(4Bp-3,4Bp-3,5)12G2-CO ₂ CH ₃	65	$c2mm$	Φ_{rc}	87.4 ^[b]	59.8	32.6	30.5				
(4-3,4-4 ² -3,5Bp)12G2-CO ₂ CH ₃	90	$p6mm$	Φ_h	76.8 ^[a]	44.0	38.2	28.8				21.1
	114	$p2mm$	Φ_{rs}	64.3 ^[c]						32.1	
(4 ² -3,4-3,5Bp)12G2-CO ₂ CH ₃	115	$p6mm$	Φ_h	65.8 ^[a]	38.1	33.0	25.0				
(4 ² -3,4-4-3,5Bp)12G2-CO ₂ CH ₃	100	$p6mm$	Φ_h	79.7 ^[a]	45.8	39.6	29.8	22.9	21.9		
(4-3,4-4-3,5Bp)12G2-H ^[d]	80	$p6mm$	Φ_h	64.1 ^[a]	36.9	32.0	24.2				
(4-3,4-4-3,5Bp)12G2-CO ₂ CH ₃ ^[d]	75	$p6mm$	Φ_h	66.1 ^[a]	38.3	33.1	25.0				
(4-3,4-4-3,5Bp)12G2-CH ₂ OH ^[d]	100	$p6mm$	Φ_h	64.0 ^[a]	36.9	32.0	24.2				
(4-3,4-4-3,5Bp)12G2-COOH	132	$p6mm$	Φ_h	61.5 ^[a]	35.4	30.6	23.2				
(4-3,4-4-3,5Bp)12G2-COOK	170	$p6mm$	Φ_h	60.7 ^[a]	34.9	30.3	22.9	20.2			
(4-3,4-4-3,5Bp)12G2-CO ₂ (CH ₂) ₂ OCH ₃ ^[d]	90	$p6mm$	Φ_h	67.5 ^[a]	38.8	33.6	24.4				
(4-3,4-4-3,5Bp)12G2-CONH ₂ ^[d]	76	$p6mm$	Φ_h	67.3 ^[a]	38.6	33.6	25.3				
(4-3,4-4-3,5Bp)12G2-CONHCH ₃ ^[d]	100	$p2mm$	Φ_{rs}	66.4 ^[a]	56.6	38.2	33.1				
	125	$p6mm$	Φ_h	62.9 ^[a]	36.2	31.3	23.7				
(S)-(4-3,4-4-3,5Bp)12G2-CONHCH(CH ₃)C ₂ H ₅ ^[d]	90	$p6mm$	Φ_h	70.6 ^[a]	40.6	35.1	26.6				
(R)-(4-3,4-4-3,5Bp)12G2-CONHCH(CH ₃)C ₂ H ₅	100	$p6mm$	Φ_h	70.0 ^[a]	40.2	34.9	26.4				
blend ^[d]	100	$p6mm$	Φ_h	64.2 ^[a]	37.6	32.5	24.6				

[a] Hexagonal lattice $p6mm$ (Φ_h). [b] Rectangular center lattice (Φ_{rc}). [c] Rectangular simple lattice (Φ_{rs}). [d] Dendrons included in Blend in the 1:1:1:1:1:1 ratio.

Table 4. Structural and retrostructural analysis of supramolecular dendrimers self-assembled from hybrid dendrons.

Dendron	T [°C]	Lattice	LC Phase	$\langle d_{100} \rangle^{[a]}$ [Å]	a (a, b) [Å]	D_{col} (D_a, D_b) [Å]	D_{pore} [Å]	$\rho_{20}^{[g]}$ [g cm ⁻³]	μ	$\alpha'^{[k]}$
(4-3,4-3,5Bp)12G2-CO ₂ CH ₃	55	$p2mm$	Φ_{rs}		109.5, 32.7 ^[b]	109.5, 32.7 ^[f]		1.09*	7.0 ^[j]	51.4
(4-3,4Bp-3,5)12G2-CO ₂ CH ₃	80	$p6mm$	Φ_h	59.0	68.1 ^[a]	68.1 ^[d]	8.2	1.05	7.2 ^[h]	50.0
(4Bp-3,4-3,5)12G2-CO ₂ CH ₃	85	$p2mm$	Φ_{rs}		63.0, 32.2 ^[b]	63.0, 32.2 ^[f]		1.11	3.5 ^[j]	102.5
	105	$p6mm$	Φ_h	55.1	63.6 ^[a]	63.6 ^[d]			6.3 ^[h]	57.1
(4-3,4Bp-3,5Bp)12G2-CO ₂ CH ₃	80	$p6mm$	Φ_h	63.6	73.5 ^[a]	73.5 ^[d]	11.5	1.07	8.1 ^[h]	44.4
(4Bp-3,4-3,5Bp)12G2-CO ₂ CH ₃	150	$p6mm$	Φ_h	62.8	72.5 ^[a]	72.5 ^[d]	6.4	1.07	7.5 ^[h]	48.0
(4Bp-3,4Bp-3,5)12G2-CO ₂ CH ₃	65	$c2mm$	Φ_{rc}		173.3, 65.0 ^[c]	100.1, 65.0 ^[e]		1.09	8.8 ^[j]	40.9
(4-3,4-4 ² -3,5Bp)12G2-CO ₂ CH ₃	90	$p6mm$	Φ_h	76.4	88.2 ^[a]	88.2 ^[d]	13.2	1.10	10.4 ^[h]	34.6
	114	$p2mm$	Φ_{rs}		64.3, 32.1 ^[b]	64.3, 32.1 ^[f]			3.2 ^[j]	112.5
(4 ² -3,4-3,5Bp)12G2-CO ₂ CH ₃	115	$p6mm$	Φ_h	66.0	76.2 ^[a]	76.2 ^[d]	10.4	1.09	7.7 ^[h]	46.6
(4 ² -3,4-4-3,5Bp)12G2-CO ₂ CH ₃	100	$p6mm$	Φ_h	79.3	91.5 ^[a]	91.5 ^[d]	11.1	1.10	10.2 ^[h]	35.3
(4-3,4-4-3,5Bp)12G2-H ^[m]	80	$p6mm$	Φ_h	64.1	73.3 ^[a]	73.3 ^[d]	11.6	1.09	8.4 ^[h]	42.9
(4-3,4-4-3,5Bp)12G2-CO ₂ CH ₃ ^[m]	75	$p6mm$	Φ_h	66.2	76.4 ^[a]	76.4 ^[d]	11.5	1.08	8.6 ^[h]	41.9
(4-3,4-4-3,5Bp)12G2-CH ₂ OH ^[m]	100	$p6mm$	Φ_h	64.0	73.9 ^[a]	73.9 ^[d]	10.6	1.09*	8.2 ^[h]	43.4
(4-3,4-4-3,5Bp)12G2-COOH	132	$p6mm$	Φ_h	61.3	70.8 ^[a]	70.8 ^[d]	9.2	1.09*	7.5 ^[h]	48.0
(4-3,4-4-3,5Bp)12G2-COOK	170	$p6mm$	Φ_h	60.6	70.0 ^[a]	70.0 ^[d]	5.5	1.09*	7.2 ^[h]	50.0
(4-3,4-4-3,5Bp)12G2-CO ₂ (CH ₂) ₂ OCH ₃ ^[m]	90	$p6mm$	Φ_h	66.6	76.9 ^[a]	76.9 ^[d]	12.0	1.09*	8.6 ^[h]	41.9
(4-3,4-4-3,5Bp)12G2-CONH ₂ ^[m]	76	$p6mm$	Φ_h	67.1	77.4 ^[a]	77.4 ^[d]	10.1	1.09*	9.0 ^[h]	40.0
(4-3,4-4-3,5Bp)12G2-CONHCH ₃ ^[m]	100	$p2mm$	Φ_{rs}		66.1, 111.5 ^[b]	66.1, 111.5 ^[f]	10.0	1.09*	12.6 ^[j]	28.64
	125	$p6mm$	Φ_h	62.7	72.4 ^[a]	72.4 ^[d]			7.8 ^[h]	6.2
(S)-(4-3,4-4-3,5Bp)12G2-CONHCH(CH ₃)C ₂ H ₅ ^[m]	90	$p6mm$	Φ_h	70.4	81.3 ^[a]	81.3 ^[d]	10.4	1.09*	9.6 ^[h]	37.5
(R)-(4-3,4-4-3,5Bp)12G2-CONHCH(CH ₃)C ₂ H ₅	100	$p6mm$	Φ_h	69.8	80.6 ^[a]	80.6 ^[d]	11.0	1.09*	9.4 ^[h]	38.3
blend	100	$p6mm$	Φ_h	64.9	74.9 ^[a]	74.9 ^[d]	11.0	1.09*	8.3 ^[h]	13.4

[a] For $p6mm$ hexagonal columnar lattice parameter $a = 2\langle d_{100} \rangle\sqrt{3}$; $\langle d_{100} \rangle = (d_{100} + \sqrt{3}d_{110} + \sqrt{4}d_{200} + \sqrt{7}d_{210})/4$. [b] $p2mm$ =simple rectangular columnar lattice parameters a and b ; $a=hd$, $b=kd$; ($h0$) and ($k0$) from diffractions. [c] $c2mm$ =centered rectangular columnar lattice parameters a and b ; $a=hd$, $b=kd$; ($h0$) and ($k0$) from diffractions. [d] Experimental column diameter of $p6mm$ hexagonal columnar lattice $D = 2\langle d_{100} \rangle/\sqrt{3}$. [e] Experimental elliptical column diameters of $c2mm$ centered rectangular columnar lattice $D_a = a/\sqrt{3}$ and $D_b = b$. [f] Experimental elliptical column diameters of $p2mm$ simple rectangular columnar lattice. [g] ρ_{20} =Experimental density at 20°C. * In cases in which ρ was not measured, it is assumed to be 1.09 [g mL⁻¹]. [h] Number of dendrons per $p6mm$ hexagonal column stratum $\mu = (\sqrt{3}N_A D^2 \rho)/2M$. [i] Number of dendrons per elliptical $c2mm$ centered rectangular column stratum $\mu = (N_A ab \rho)/2M$. [j] Number of dendrons per elliptical $p2mm$ simple rectangular column stratum $\mu = (N_A ab \rho)/M$. [k] Projection of the solid angle for tapered dendron $\alpha' = 360/\mu$ [°]. Avogadro's number $N_A = 6.0220455 \times 10^{23}$ mol⁻¹, the average height of the column stratum $t = 4.7$ Å, and M =molecular weight of dendron. [m] Dendrons included in Blend in the 1:1:1:1:1:1 ratio.

their isotropisation temperatures, 87.5, 112.5, and 191.6 °C, respectively.

Second-generation hybrid dendrons obtained from combinations of biphenyl-4-methyl ether and benzyl ether repeat units tend to self-assemble exclusively into columns rather than spheres. Supramolecular spheres were commonly observed in the case of biphenyl-4-methyl ether dendrons.^[4b]

Figure 8b summarizes the self-assembly of the last group of hybrid dendrons. They contain 3',5'-disubstituted biphenyl-4-methyl ester at the apex and various combinations of (AB)_y-AB₂ benzyl ether repeat units in the inner part of the dendron such as in the case of **(4-3,4-4-3,5Bp)12G2-CO₂CH₃** (**29**) and **(4-3,4-4²-3,5Bp)12G2-CO₂CH₃** (**27**), on the periphery of the dendron as in **(4²-3,4-3,5Bp)12G2-CO₂CH₃** (**25**), and both in the inner part and on the periphery of the dendron as in **(4²-3,4-4-3,5Bp)12G2-CO₂CH₃** (**23**). In this library of hybrid dendrons, the 4-biphenyl-4-methyl ether-like repeat units were constructed from (AB)₂ dimers generated from 4-benzyl ether as AB repeat units. This is the most rewarding group of dendrons, since all of them self-assemble into porous columns.

It is interesting to recall at this point that **(4-3,4-3,5)12G2-X**^[3a,c] self-assembles into nonporous columns. At the same time, **(4Bp-3,4Bp-3,5Bp)12G2-X** self-assembles into porous columns and supramolecular spheres.^[4b] However, the incorporation of hybrid repeat units from each of them into the same **(4-3,4-3,5)12G2-X** primary structure induces the assembly of porous columns and eliminates the formation of supramolecular spheres. This is a remarkable example of the influence of the nature of the repeat units of an identical sequence of the primary structure of the dendron on the tertiary structure of its supramolecular assembly. The molecular mechanism that generates this change is not yet known.

The **(4-3,4-4-3,5Bp)12G2-CO₂CH₃** (**29**) dendron from Figure 4 was selected to investigate the role of the nature of the functional group from its apex on self-assembly. The synthesis of dendrons **(4-3,4-4-3,5Bp)12G2-X** containing ten different functional groups at the apex together with the structural and the retrostructural analysis of their supramolecular dendrimers are summarized in Scheme 4.

Table 5 gives reaction conditions and lattice parameters generated from the structural and retrostructural analysis of the library of supramolecular dendrimers self-assembled from the **(4-3,4-4-3,5Bp)12G2-X** dendrons. A large diversity of functional groups that are able to promote hydrogen bonding (-CH₂OH, -COOH, -CONH₂, -CONHCH₃); ionic interactions (-COOK); and achiral nonpolar (-H, -CO₂CH₃), achiral polar (-CO₂(CH₂)₂OCH₃), and chiral polar (-(*R*)-CONHCH(CH₃)C₂H₅, -(*S*)-CONHCH(CH₃)C₂H₅) interactions are tolerated by this self-assembly process. This indicates pathways to assemble a large diversity of functional pores through very simple architectural principles.

The dependence of *d*-spacings and their amplitudes on the structure of the functional group X from the apex of the dendron is illustrated by the XRD plots in Figure 9. The increased intensities of the higher order 11, 20, and 12 diffraction peaks indicate that the Φ_h phase is generated from porous columns.^[3,4a,b] These XRD data also demonstrate that a mixture of seven dendritic dipeptides with the general primary structure **(4-3,4-4-3,5Bp)12G2-X** containing a diversity of different X groups at the apex, X = H, CO₂CH₃, CH₂OH, CO₂(CH₂)₂OCH₃, CONH₂, CONHCH₃, (*S*)-CONHCH(CH₃)C₂H₅ in a 1:1:1:1:1:1:1 (mass ratio) co-assemble in a porous structure with *D*_{col} = 74.9 Å and *D*_{pore} = 11.0 Å. This simple strategy opens new pathways to functionalize the internal structure of the pore.

Table 5. Synthesis of the **(4-3,4-4-3,5Bp)12G2-X** library. The error of the *D*_{pore} is ± 1.2 Å.

Starting material	Reaction conditions	X	Yield [%]	<i>T</i> ^[b] [°C]	Lattice parameters
(4-3,4-4)12G2-CH₂Cl	21 , K ₂ CO ₃ , DMF, 90 °C	H	70	80	<i>D</i> _{col} = 73.3 Å, <i>D</i> _{pore} = 11.6 Å, <i>μ</i> = 8.4 °' = 42.9°
(4-3,4-4)12G2-CH₂Cl	2 , K ₂ CO ₃ , DMF, 90 °C	CO ₂ CH ₃	84	75	<i>D</i> _{col} = 76.4 Å, <i>D</i> _{pore} = 11.5 Å, <i>μ</i> = 8.6 °' = 41.9°
(4-3,4-4-3,5Bp)12G2-CO₂CH₃	LiAlH ₄ , THF ^[a]	CH ₂ OH	90	100	<i>D</i> _{col} = 73.9 Å, <i>D</i> _{pore} = 10.6 Å, <i>μ</i> = 8.2 °' = 43.4°
(4-3,4-4-3,5Bp)12G2-CO₂CH₃	KOH, THF, EtOH, H ₂ O, 60 °C	COOK	100	170	<i>D</i> _{col} = 70.0 Å, <i>D</i> _{pore} = 5.5 Å, <i>μ</i> = 7.2 °' = 50.0°
(4-3,4-4-3,5Bp)12G2-COOK	CH ₃ CO ₂ H, THF ^[a]	COOH	80	132	<i>D</i> _{col} = 70.8 Å, <i>D</i> _{pore} = 9.2 Å, <i>μ</i> = 7.5 °' = 48.0°
(4-3,4-4-3,5Bp)12G2-COOK	2-methoxyethanol, DCC, DPTS ^[a]	CO ₂ (CH ₂) ₂ OCH ₃	87	90	<i>D</i> _{col} = 76.9 Å, <i>D</i> _{pore} = 12.0 Å, <i>μ</i> = 8.6 °' = 41.9°
(4-3,4-4-3,5Bp)12G2-COOK	1. SOCl ₂ , CH ₂ Cl ₂ 2. NH ₃ (g), CH ₂ Cl ₂ ^[c]	CONH ₂	61	76	<i>D</i> _{col} = 77.4 Å, <i>D</i> _{pore} = 10.1 Å, <i>μ</i> = 9.0 °' = 40.0°
(4-3,4-4-3,5Bp)12G2-COOK	NH ₂ CH ₃ , HCl, CDI, DPTS, Et ₃ N ^[a]	CONHCH ₃	62	125	<i>D</i> _{col} = 72.4 Å, <i>D</i> _{pore} = 10.0 Å, <i>μ</i> = 7.8 °' = 46.2°
(4-3,4-4-3,5Bp)12G2-COOK	1. SOCl ₂ , CH ₂ Cl ₂ ^[a] 2. (<i>S</i>)-C ₂ H ₅ (CH ₃)CHNH ₂ , CH ₂ Cl ₂ ^[a]	(<i>S</i>)-CONHCH(CH ₃)C ₂ H ₅	65	90	<i>D</i> _{col} = 81.3 Å, <i>D</i> _{pore} = 10.4 Å, <i>μ</i> = 9.6 °' = 37.5°
(4-3,4-4-3,5Bp)12G2-COOK	1. SOCl ₂ , CH ₂ Cl ₂ ^[a] 2. (<i>R</i>)-C ₂ H ₅ (CH ₃)CHNH ₂ , CH ₂ Cl ₂ ^[a]	(<i>R</i>)-CONHCH(CH ₃)C ₂ H ₅	70	100	<i>D</i> _{col} = 80.6 Å, <i>D</i> _{pore} = 11.0 Å, <i>μ</i> = 9.4 °' = 38.3°

[a] The reaction was performed at 25 °C. [b] Temperature of XRD measurement. The error of *μ* is 10 %.

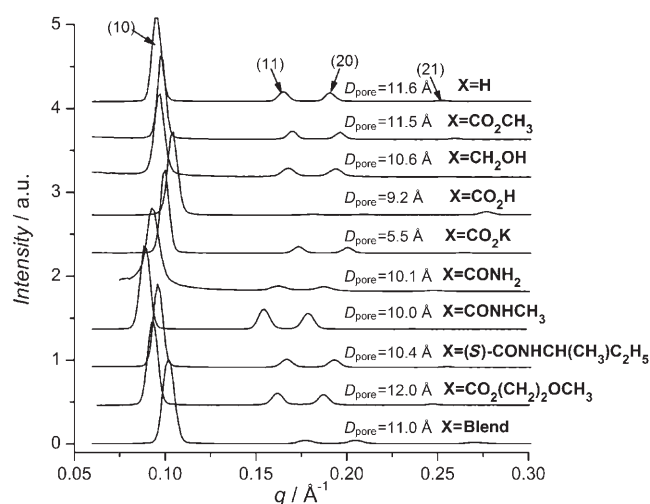


Figure 9. Small-angle XRD plots of **(4-3,4-4-3,5 Bp)12 G2-X** dendrons with the X-groups shown in the figure and of a blend of **(4-3,4-4-3,5 Bp)12 G2-X**, with X=H, CO₂CH₃, CH₂OH, CO₂(CH₂)₂OCH₃, CONH₂, CONHCH₃, (S)-CONHCH(CH₃)C₂H₅ in the 1:1:1:1:1:1:1 mass ratio.

Model of supramolecular porous column: Molecular models of a single porous column layer, the top view of the column, the hydrogen-bonding network, and the cross-section of the porous column for supramolecular porous dendrimer self-assembled from **(S)-(4-3,4-4-3,5 Bp)12 G2-CONHCH-(CH₃)C₂H₅ (37)** simulated by using the small-angle powder and wide-angle fiber XRD experimental results are shown in Figure 10.

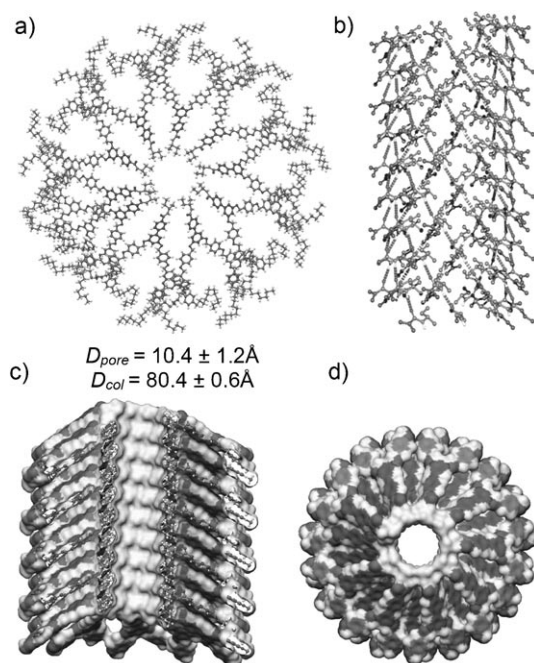


Figure 10. **(S)-(4-3,4-4-3,5 Bp)12 G2-CONHCH(CH₃)C₂H₅** molecular model: a) one column stratum top view, b) detail of the pore region hydrogen-bonding network, c) pore cross-section, and d) top view.

Assembling hybrid dendrons into phospholipid bilayers: Figure 11 shows the UV spectra recorded during the self-assembly in cyclohexane. Cyclohexane resembles the structure

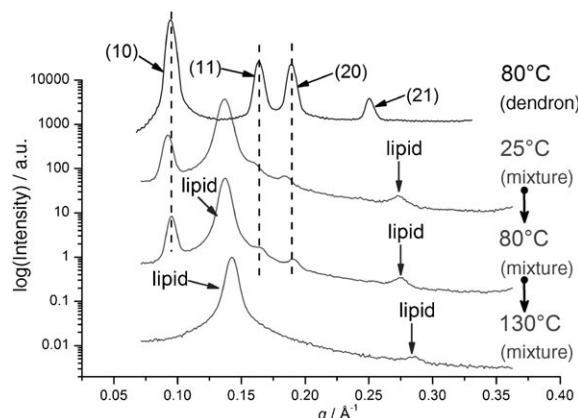


Figure 11. Small-angle XRD stack plots of the **(4-3,4-4-3,5 Bp)12 G2-CO₂CH₃/L-phosphatidylcholine** mixture (1:7 mass ratio) at the indicated temperatures. The peaks of the Φ_h phase generated from supramolecular columns and the lipid peaks are indicated.

of the aliphatic part of the phospholipid bilayers. Therefore, by analogy to the case of dendritic dipeptides,^[3a] it is expected that these dendrons self-assemble into porous columns in the presence of phospholipids. This was indeed demonstrated by the XRD analysis of a mixture of 1/7 (mass ratio) of **(4-3,4-4-3,5 Bp)12 G2-CO₂CH₃ (29)** with L-phosphatidylcholine (Figure 11).

X-ray diffraction patterns for the mixture at 25 and 80°C show the presence of the diffraction peaks resembling the pattern defining the Φ_h lattice exhibited by the pure dendron at 80°C, along with diffraction peaks characteristic for the lipid. This demonstrates the microphase segregation of hexagonal domains of supramolecular porous columns consisting of 8 ± 2 columns in a continuous phospholipid bilayer containing 14 ± 2 layers, as determined from the powder XRD half-maxima peak widths. The domain size of the pure columnar hexagonal phase generated from the same porous columns is approximately two times larger.

Conclusion

In conclusion, the results reported here demonstrate that for the same dendron primary structure, the sequence and structure of its repeat units provide a simple, powerful, and general approach to the design and synthesis of hybrid dendrons that self-assemble into helical pores. The range of D_{pore} accomplished with the experiments reported here vary between 6.4 and 12.0 Å. Therefore, this concept is complementary to that of dendritic dipeptides that produced $D_{\text{pore}} = 8.7$ to 15.8 Å.^[3] These building blocks tolerate a large diversity of functional groups at their apex and therefore, provide the simplest method to assemble functional helical

pores. The principles by which the complex primary structure of hybrid dendrons determines the supramolecular structure are not yet elucidated. However, the self-assembly of hybrid dendrons with complex primary structure reported here expands the scope and the limitations of the self-assembling dendritic architectural motifs.^[7]

Experimental Section

Materials: Al₂O₃ (activated, basic, Brokmann I, standard grade, ≈150 mesh, 58 Å) and silica gel (ICN EcoChrom SiliTech 23-63D 60 Å) were used as received. THF, dioxane and Et₂O (Fisher, A.C.S. reagents) were refluxed over sodium ketyl and freshly distilled before use. CH₂Cl₂ (Fisher, A.C.S. reagent) was refluxed over CaH₂ and freshly distilled before use. MeOH, EtOH, DMSO, CHCl₃, DMF, toluene, Na₂S₂O₃, KOH, MgSO₄, K₂CO₃, acetic acid (Fisher, A.C.S. reagents) were used as received. Pyridine and 2,6-di-*tert*-butyl-4-methyl pyridine (DTBMP) (from Lancaster) were used as received. Neutral chromatographic Al₂O₃, SOCl₂ (97%), LiAlH₄ (95+%), (from Aldrich) were used as received. 2-Methoxy-ethanol, *N,N'*-dicyclohexylcarbodiimide (DCC), carbonyl diimidazole (CDI), and methylammonium chloride were purchased from Acros, and (*R*)-(-)-*sec*-butylamine, (*S*)-(+)-*sec*-butylamine and DPTS were purchased from Aldrich.

Techniques: ¹H NMR (200, 250 and 500 MHz) spectra were recorded on a Bruker DRX500 instrument. ¹³C NMR (90 MHz, 125 MHz) spectra were recorded on a Bruker DRX 500 spectrometer. Melting points were measured by using a uni-melt capillary melting point apparatus (Arthur H. Thomas Company, Philadelphia, USA) and are uncorrected. Thin-layer chromatography (TLC) was performed on precoated TLC plates (silica gel with F₂₅₄ indicator; layer thickness, 200 μm; particle size, 5–25 μm; pore size, 60 Å, SIGMA-Aldrich). HPLC analyses were performed on a Shimadzu LC-10 AT high-pressure liquid chromatograph equipped with CTO-10 A column oven (40°C), PE Nelson Analytical 900 Series integrator data station, Shimadzu RID-10 A RI detector, SPD-10 A 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 on a Hewlett-Packard HP68 gas chromatograph. Thermal transitions were measured on 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 (100× magnification) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to verify thermal transitions. Small- and wide-angle X-ray diffraction measurements were carried out with CuK_α radiation from a Bruker-Nonius FR-591 rotating anode X-ray source with a 0.2×2.0 mm² filament operated at 3.4 kW. The beam was collimated and focused by a single bent mirror and sagittally focusing Ge(111) monochromator, resulting in a 0.2×0.2 mm² spot on a multiwire detector 125 cm from the sample. To minimize attenuation and background scattering, an integral vacuum was maintained along the length of the flight tube and within the sample chamber. The samples were held in a temperature-controlled (± 0.1°C) oven. Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectra were recorded on a PerSpective Biosystems Voyager DE spectrometer by 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 THF (1 mL). The sample (ca. 10 mg) was also dissolved in THF (1 mL). The matrix solution (50 μL) and the sample solution (10 μL) were mixed. To the mixture, a solution of AgTFA in THF (10 μL; 1 mg mL⁻¹) was added, and the mixture was mixed well. The mixture (5 μL) was loaded on a MALDI plate, and air-dried before inserting into the vacuum chamber of the MALDI instrument. Mass spectra were run by direct sample introduction on 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 value within ± 0.4%.

Synthesis: The synthesis of (4-3,4)12 G1-CH₂Cl (**1**),^[4d] 3',5'-dihydroxybiphenyl-4-carboxylic acid methyl ester (**2**),^[4b] 3',4'-dihydroxybiphenyl-4-carboxylic acid methyl ester (**4**),^[4b] 1-chloromethyl-4-(dodecyloxy)benzene (**5**),^[4d] 3,5-dihydroxybenzoic acid methyl ester (**9**),^[4d] 3,4-dihydroxybenzoic acid methyl ester (**11**),^[4d] 4-chloromethyl-4'-(dodecyloxy)biphenyl (**12**),^[4b] (4Bp-3,4Bp)12 G1-CH₂Cl (**19**),^[4b] 3,5-dimethoxybiphenyl (**21**),^[8] (4²-3,4-4²)12 G1-CH₂Cl (**22**),^[4c] (4²-3,4)12 G1-CH₂Cl (**24**),^[4c] (4-3,4-4²)12 G1-CH₂Cl (**26**),^[4c] and (4-3,4-4²)12 G1-CH₂Cl (**28**),^[4c] was achieved according to literature procedures. All new dendrons were synthesized using the previously reported convergent iterative strategy.^[3a, 4b-d, 5a, 8, 9]

Methyl 3,5-bis[3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]biphenyl-4-carboxylate [(4-3,4-3,5Bp)12 G2-CO₂CH₃] (3**):** A suspension of K₂CO₃ (0.42 g, 3.00 mmol) in DMF (10 mL) was thoroughly degassed. Compounds **2** (122 mg, 0.5 mmol) and **1** (714 mg, 1.01 mmol) were added. The reaction mixture was heated to 90°C under Ar for 20 h, then allowed to cool to 25°C and poured into water (100 mL). The formed precipitate was filtered, dissolved in CH₂Cl₂ and precipitated with MeOH. A colorless solid (0.60 g, 76%) was obtained by recrystallization from acetone. Purity (HPLC): 99+%; *R*_f=0.75 (hexane/EtOAc 4:1); ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=0.89 (t, *J*=6.3 Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.94 (overlapped m, 11H), 4.98 (s, 4H), 5.07 (s, 8H), 6.62 (t, *J*=2.2 Hz, 1H), 6.83 (d, *J*=2.1 Hz, 2H), 6.86 (m, 8H), 6.95 (s, 4H), 7.07 (s, 2H), 7.32 (d, *J*=4.6 Hz, 8H), 7.61 (d, *J*=8.2 Hz, 2H), 8.09 ppm (d, *J*=8.2 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃, 25°C, TMS): δ=14.3, 22.9, 26.3, 29.6, 29.7, 29.8, 29.9, 32.2, 52.3, 68.3, 70.5, 71.6, 102.0, 107.1, 114.7, 115.3, 115.8, 121.2, 127.3, 129.2, 129.3, 129.4, 130.2, 130.3, 142.4, 145.7, 149.4, 149.7, 159.2, 160.6 ppm; MS (MALDI-TOF): *m/z* calcd for C₁₀₄H₁₄₄O₁₂: 1585.1; found: 1608.3 [M+Na]⁺; elemental analysis calcd (%) for C₁₀₄H₁₄₄O₁₂: C 78.68, H 9.15; found: C 78.68, H 9.27.

Methyl 3,4-bis(4-dodecyloxybenzyloxy)biphenyl-4-carboxylate [(4-3,4Bp)12 G1-CO₂CH₃] (6**):** A suspension of K₂CO₃ (2.14 g, 15.45 mmol) in DMF (150 mL) was thoroughly degassed. Compounds **4** (1.26 g, 5.15 mmol) and **5** (3.20 g, 10.29 mmol) were added. The reaction mixture was heated to 90°C under Ar for 15 h, then allowed to cool to 25°C and poured into water (300 mL). The formed precipitate was filtered, dissolved in CH₂Cl₂ and precipitated with MeOH. A colorless solid (3.64 g, 89%) was obtained by recrystallization from acetone. Purity (HPLC): 99+%; *R*_f=0.40 (CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=0.89 (t, *J*=6.3 Hz, 6H), 1.28 (m, 32H), 1.47 (m, 4H), 1.80 (m, 4H), 3.94 (s, 3H), 3.97 (t, *J*=6.6 Hz, 4H), 5.12 (s, 2H), 5.14 (s, 2H), 6.89 (d, *J*=8.7 Hz, 4H), 7.01 (d, *J*=8.3 Hz, 1H), 7.16 (d, *J*=8.3 Hz, 1H), 7.22 (s, 1H), 7.36 (m, 4H), 7.56 (d, *J*=8.3 Hz, 2H), 8.06 ppm (d, *J*=8.3 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃, 25°C, TMS): δ=14.3, 22.9, 26.3, 29.6, 29.7, 29.9, 32.2, 52.3, 68.3, 71.5, 71.9, 114.8, 115.1, 115.8, 120.8, 126.8, 129.2, 129.3, 129.4, 130.3, 145.5, 149.8, 159.3, 167.3 ppm; elemental analysis calcd (%) for C₅₂H₇₂O₆: C 78.75, H 9.15; found: C 78.60, H 9.25.

[3',4'-Bis(4'-dodecyloxybenzyloxy)biphenyl-4-yl]methanol [(4-3,4Bp)12 G1-CH₂OH] (7**):** Dendron **6** (2.80 g, 3.22 mmol) was added to a suspension of LiAlH₄ (0.30 g, 7.82 mmol) in THF (100 mL). Reaction mixture was stirred at 25°C for 2 h, quenched by addition of water and 15% (w/v) NaOH, filtered through Celite, concentrated, and precipitated with MeOH. The precipitate was filtered. The product (2.52 g, 84%) was obtained by recrystallization from acetone. Purity (HPLC): 99+%; *R*_f=0.40 (CHCl₃); ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=0.89 (t, *J*=6.3 Hz, 6H), 1.29 (m, 32H), 1.47 (m, 4H), 1.80 (m, 4H), 3.96 (t, *J*=6.6 Hz, 4H), 4.73 (d, *J*=6.0 Hz, 2H), 5.11 (s, 2H), 5.14 (s, 2H), 6.89 (d, *J*=8.7 Hz, 4H), 7.01 (d, *J*=8.3 Hz, 1H), 7.12 (d, *J*=8.3 Hz, 1H), 7.20 (s, 1H), 7.36 (m, 4H), 7.41 (d, *J*=8.3 Hz, 2H), 7.50 ppm (d, *J*=8.3 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃, 25°C, TMS): δ=14.4, 22.9, 26.3, 29.6, 29.7, 29.8, 29.9, 32.2, 65.4, 68.3, 71.6, 71.8, 114.8, 115.1, 116.0, 120.4, 127.2, 127.7, 129.3, 129.4, 134.7, 139.7, 140.6, 149.2, 149.6, 159.2 ppm; elemental analysis calcd (%) for C₅₁H₇₂O₅: C 80.06, H 9.49; found: C 80.22, H 9.45.

4-Chloromethyl-3',4'-bis(4'-dodecyloxybenzyloxy)biphenyl [(4-3,4Bp)12 G1-CH₂Cl] (8**):** Dendron **7** (2.25 g, 2.94 mmol) and DTBMP (1.21 g, 5.88 mmol) were dissolved in CH₂Cl₂ (120 mL). SOCl₂ (0.32 mL,

4.41 mmol) was added. The reaction mixture was stirred at 25°C for 3 h, concentrated on rotary evaporator at 25°C to 20 mL and precipitated by MeOH at 0°C. The precipitate was filtered and quickly purified by column chromatography (SiO₂, CH₂Cl₂/hexane 2:1) to give a colorless solid (1.67 g, 74%). Purity (HPLC): 99+%; *R*_f=0.95 (CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=0.89 (t, *J*=6.3 Hz, 6H), 1.29 (m, 32H), 1.47 (m, 4H), 1.80 (m, 4H), 3.96 (t, *J*=6.6 Hz, 4H), 4.63 (s, 2H), 5.11 (s, 2H), 5.14 (s, 2H), 6.89 (d, *J*=8.7 Hz, 4H), 7.00 (d, *J*=8.3 Hz, 1H), 7.11 (d, *J*=8.3 Hz, 1H), 7.18 (s, 1H), 7.36 (m, 4H), 7.42 (d, *J*=8.3 Hz, 2H), 7.49 ppm (d, *J*=8.3 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃, 25°C, TMS): δ=14.4, 22.9, 26.3, 29.6, 29.7, 29.9, 32.2, 68.3, 71.6, 71.8, 114.8, 115.1, 115.3, 116.0, 120.4, 127.2, 127.7, 129.3, 134.7, 139.7, 140.6, 149.2, 149.6, 159.2 ppm; elemental analysis calcd (%) for C₅₁H₇₁ClO₄: C 78.17, H 9.13; found: C 78.65, H 9.31.

3',5'-Bis[3',4'-bis(4'-dodecyloxybenzyloxy)biphenyl-4-ylmethoxy] benzoic acid methyl ester [(4-3,4Bp-3,5)12G2-CO₂CH₃] (10): A suspension of K₂CO₃ (0.60 g, 4.36 mmol) in DMF (50 mL) was thoroughly degassed. Compound **9** (92 mg, 0.54 mmol) and dendron **8** (810 mg, 1.09 mmol) were added. The reaction mixture was heated to 90°C under Ar for 15 h, then allowed to cool to 25°C and poured into water (150 mL) and extracted with CH₂Cl₂ (2×100 mL) and with CHCl₃ (2×100 mL). The organic extracts were washed with water (100 mL), concentrated, and precipitated by MeOH. The precipitate was filtered, dried, and purified by column chromatography (SiO₂, CH₂Cl₂) to yield a colorless solid (0.67 g, 74%). Purity (HPLC): 99+%; *R*_f=0.40 (CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=0.89 (t, *J*=6.3 Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.92 (s, 3H), 3.97 (t, *J*=6.7 Hz, 8H), 5.11 (s, 8H), 5.13 (s, 4H), 6.84 (t, *J*=2.2 Hz, 1H), 6.89 (d, *J*=8.7 Hz, 8H), 7.00 (d, *J*=8.5 Hz, 2H), 7.12 (d, *J*=2.2 Hz, 2H), 7.20 (s, 2H), 7.33 (d, *J*=2.9 Hz, 2H), 7.37 (overlapped m, 8H), 7.46 (d, *J*=8.3 Hz, 4H), 7.52 ppm (d, *J*=8.3 Hz, 4H); ¹³C NMR (500 MHz, CDCl₃, 25°C, TMS): δ=14.4, 23.0, 26.4, 29.6, 29.7, 29.9, 30.0, 32.2, 52.6, 68.4, 70.5, 71.7, 71.9, 107.7, 108.8, 114.8, 114.9, 115.1, 116.0, 120.6, 127.3, 128.3, 129.3, 129.5, 132.4, 134.6, 135.3, 141.1, 149.3, 149.7, 159.3, 160.2, 167.1 ppm; MS (MALDI-TOF): *m/z* calcd for C₁₁₀H₁₄₈O₁₂: 1661.1; found: 1684.8 [M+Na]⁺; elemental analysis calcd (%) for C₁₁₀H₁₄₈O₁₂: C 79.48, H 8.97; found: C 79.29, H 8.78.

3,4-Bis(4'-dodecyloxy-biphenyl-4-yl-methoxy)benzoic acid methyl ester [(4Bp-3,4)12G1-CO₂CH₃] (13): A suspension of K₂CO₃ (1.61 g, 11.63 mmol) in DMF (120 mL) was thoroughly degassed. Compounds **11** (0.65 g, 3.88 mmol) and **12** (3.00 g, 7.75 mmol) were added. The reaction mixture was heated to 90°C under Ar for 15 h, then allowed to cool to 25°C and poured into water (300 mL). The precipitate formed was filtered, dissolved in CH₂Cl₂, and precipitated with MeOH. A colorless solid (3.08 g, 91%) was obtained by recrystallization from acetone. Purity (HPLC): 99+%; *R*_f=0.80 (CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=0.89 (t, *J*=6.3 Hz, 6H), 1.29 (m, 32H), 1.47 (m, 4H), 1.82 (m, 4H), 3.89 (s, 3H), 4.01 (m, 4H), 5.22 (s, 2H), 5.26 (s, 2H), 6.95–7.00 (overlapped m, 5H), 7.45–7.57 (overlapped m, 12H), 7.66 (d, *J*=8.5 Hz, 1H), 7.70 ppm (s, 1H); ¹³C NMR (500 MHz, CDCl₃, 25°C, TMS): δ=14.3, 22.9, 26.3, 29.5, 29.6, 29.8, 29.9, 32.1, 51.1, 52.1, 68.3, 71.0, 71.4, 113.7, 115.0, 116.0, 123.4, 124.3, 127.0, 127.0, 127.8, 128.1, 128.2, 133.2, 133.3, 135.0, 135.3, 140.8, 140.8, 148.7, 153.2, 159.1, 165.4, 166.7, 167.0 ppm; elemental analysis calcd (%) for C₅₈H₇₆O₆: C 80.14, H 8.81; found: C 79.86, H 8.66.

[3,4-Bis(4'-dodecyloxy-biphenyl-4-yl-methoxy)phenyl]methanol [(4Bp-3,4)12G1-CH₂OH] (14): Dendron **13** (2.80 g, 3.22 mmol) was added into a suspension of LiAlH₄ (0.25 g, 6.44 mmol) in THF (100 mL). The reaction mixture was stirred at 25°C for 3 h, quenched by addition of water and 15% (w/v) NaOH, filtered through Celite, concentrated, and precipitated with MeOH. The precipitate was filtered. The product (2.54 g, 93%) was obtained by recrystallization from acetone. Purity (HPLC): 99+%; *R*_f=0.50 (CHCl₃); ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=0.89 (t, *J*=6.3 Hz, 6H), 1.29 (m, 32H), 1.47 (m, 4H), 1.82 (m, 4H), 4.01 (t, *J*=6.5 Hz, 4H), 4.60 (d, *J*=6.6 Hz, 2H), 5.20 (s, 2H), 5.21 (s, 2H), 6.89 (d, *J*=7.1 Hz, 1H), 6.97 (m, 5H), 7.05 (d, *J*=1.8 Hz, 1H), 7.46–7.56 ppm (overlapped m, 12H); ¹³C NMR (500 MHz, CDCl₃, 25°C, TMS): δ=0.89 14.5, 23.1, 26.5, 29.8, 29.8, 30.0, 30.1, 32.3, 65.7, 68.6, 71.6, 71.8, 114.7, 115.2, 115.9, 120.7, 127.2, 128.2, 128.3, 128.5, 133.5, 134.9,

136.0, 136.0, 140.8, 149.1, 149.7, 159.2 ppm; elemental analysis calcd (%) for C₅₇H₇₆O₅: C 81.38, H 9.11; found: C 81.18, H 9.00.

3,4-Bis(4'-dodecyloxybiphenyl-4-ylmethoxy)benzyl chloride [(4Bp-3,4)12G1-CH₂Cl] (15): Dendron **14** (0.95 g, 1.13 mmol) and DTBMP (0.37 g, 1.81 mmol) were dissolved in CHCl₃ (200 mL). SOCl₂ (2.6 mL of 0.57 M solution, 1.47 mmol) dissolved in dry CH₂Cl₂ was added. The reaction mixture was stirred at 25°C for 2 h, concentrated on rotary evaporator at 25°C to 20 mL, and precipitated with MeOH at 0°C. The precipitate was filtered and quickly purified by column chromatography (SiO₂, CH₂Cl₂) to give a colorless solid (0.40 g, 42%). Purity (HPLC): 99+%; *R*_f=0.95 (CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=0.89 (t, *J*=6.3 Hz, 6H), 1.29 (m, 32H), 1.47 (m, 4H), 1.82 (m, 4H), 4.01 (t, *J*=6.5 Hz, 4H), 4.64 (s, 2H), 5.20 (s, 4H), 6.90–7.00 (overlapped m, 6H), 7.03 (s, 1H), 7.46–7.56 ppm (overlapped m, 12H); ¹³C NMR (500 MHz, CDCl₃, 25°C, TMS): δ=14.5, 23.1, 26.5, 29.8, 30.0, 30.1, 32.3, 65.7, 68.6, 71.6, 71.8, 114.7, 115.2, 115.9, 120.7, 127.2, 128.2, 128.5, 133.5, 134.9, 136.0, 136.0, 140.8, 149.1, 149.7 ppm.

3',5'-Bis[3',4'-bis(4'-dodecyloxybiphenyl-4-ylmethoxy)benzyloxy] benzoic acid methyl ester [(4Bp-3,4,3,5)12G2-CO₂CH₃] (16): A suspension of K₂CO₃ (48 mg, 0.348 mmol) in DMF (30 mL) was thoroughly degassed. Compound **9** (19 mg, 0.116 mmol) and dendron **15** (200 mg, 0.233 mmol) were added. The reaction mixture was heated to 90°C under Ar for 20 h, then allowed to cool to 25°C and poured into water (100 mL) and extracted with CH₂Cl₂ (4×150 mL). The organic extracts were washed with water (100 mL), concentrated, and precipitated with MeOH. The precipitate was filtered, dried, and purified by column chromatography (SiO₂, CHCl₃) to yield a colorless solid (77 mg, 37%). Purity (HPLC): 99+%; *R*_f=0.20 (CHCl₃); ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=0.89 (t, *J*=6.3 Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.90 (s, 3H), 4.00 (m, 8H), 4.96 (s, 4H), 5.19 (s, 8H), 6.75 (t, *J*=2.3 Hz, 1H), 6.96 (overlapped m, 12H), 7.08 (m, 2H), 7.45–7.55 ppm (overlapped m, 26H); ¹³C NMR (500 MHz, CDCl₃, 25°C, TMS): δ=14.4, 23.0, 26.4, 29.6, 29.7, 29.9, 30.0, 32.2, 52.6, 68.4, 70.5, 71.7, 71.9, 107.7, 108.8, 114.8, 114.9, 115.1, 116.0, 120.6, 127.3, 128.3, 129.3, 129.5, 132.4, 134.6, 135.3, 141.1, 149.3, 149.7, 159.3, 160.2, 167.1 ppm; MS (MALDI-TOF): *m/z* calcd for C₁₂₂H₁₅₆O₁₂: 1813.2; found: 1837.0 [M+Na]⁺; elemental analysis calcd (%) for C₁₂₂H₁₅₆O₁₂: C 81.35, H 8.80; found: C 81.16, H 8.62.

Methyl 3',5'-bis[3',4'-bis(4'-dodecyloxybenzyloxy)biphenyl-4-yl-methoxy]-biphenyl-4-carboxylate [(4-3,4Bp-3,5Bp)12G2-CO₂CH₃] (17): A suspension of K₂CO₃ (0.60 g, 4.36 mmol) in DMF (50 mL) was thoroughly degassed. Compound **2** (133 mg, 0.54 mmol) and dendron **8** (810 mg, 1.09 mmol) were added. The reaction mixture was heated to 90°C under Ar for 15 h; it was then allowed to cool to 25°C, was poured into water (150 mL), and was extracted with CH₂Cl₂ (2×100 mL) and CHCl₃ (2×100 mL). The organic extracts were washed with water (100 mL), concentrated, and precipitated with MeOH. The precipitate was filtered, dried, and purified by column chromatography (SiO₂, CH₂Cl₂) to yield a colorless solid (0.65 g, 69%). Purity (HPLC): 99+%; *R*_f=0.50 (CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ=0.89 (t, *J*=6.3 Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.96 (overlapped m, 11H), 5.11 (s, 4H), 5.13 (s, 4H), 5.14 (s, 4H), 6.70 (t, *J*=2.2 Hz, 1H), 6.89 (m, 10H), 7.01 (d, *J*=8.4 Hz, 2H), 7.12 (d, *J*=8.4 Hz, 2H), 7.20 (s, 2H), 7.36 (m, 8H), 7.48 (d, *J*=8.2 Hz, 2H), 7.53 (d, *J*=8.2 Hz, 2H), 7.64 (d, *J*=8.3 Hz, 2H), 8.10 ppm (d, *J*=8.3 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃, 25°C, TMS): δ=14.5, 23.1, 26.5, 29.7, 29.8, 30.0, 30.1, 32.3, 68.5, 71.8, 72.0, 94.7, 97.6, 107.3, 114.9, 127.5, 128.4, 129.4, 129.6, 130.5, 135.6, 137.3, 141.2, 149.4, 149.8, 159.4, 160.8, 164.8 ppm; MS (MALDI-TOF): *m/z* calcd for C₁₁₆H₁₅₂O₁₂: 1737.1; found: 1777.6 [M+K]⁺; elemental analysis calcd (%) for C₁₂₈H₁₆₀O₁₂: C 81.32, H 8.53; found: C 81.11, H 8.39.

3',5'-Bis[3',4'-bis(4'-dodecyloxybiphenyl-4-ylmethoxy)benzyloxy]biphenyl-4-carboxylate [(4Bp-3,4,3,5Bp)12G2-CO₂CH₃] (18): A suspension of K₂CO₃ (48 mg, 0.348 mmol) in DMF (30 mL) was thoroughly degassed. Compound **2** (28 mg, 0.116 mmol) and dendron **15** (200 mg, 0.233 mmol) were added. The reaction mixture was heated to 90°C under Ar for 20 h; it was then allowed to cool to 25°C, was poured into water (100 mL), and was extracted with CH₂Cl₂ (4×150 mL). The organic extracts were washed with water (100 mL), concentrated, and precipitated with MeOH. The precipitate was filtered, dried, and purified by column chromatogra-

phy (SiO_2 , CHCl_3) to yield a colorless solid (156 mg, 72%). Purity (HPLC): 99+%; $R_f=0.15$ (CHCl_3); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.94 (s, 3H), 4.00 (m, 8H), 4.99 (s, 4H), 5.20 (s, 8H), 6.62 (t, $J=2.2$ Hz, 1H), 6.83 (m, 2H), 6.90–7.00 (overlapped m, 12H), 7.10 (m, 2H), 7.45–7.55 (overlapped m, 24H), 7.60 (d, $J=8.2$ Hz, 2H), 8.08 ppm (d, $J=8.2$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.4$, 22.9, 26.3, 29.6, 29.7, 29.8, 29.9, 32.2, 52.3, 68.4, 70.4, 71.5, 101.9, 107.1, 115.1, 115.5, 121.3, 127.0, 127.3, 128.0, 128.1, 128.3, 129.4, 130.3, 133.3, 135.7, 135.8, 140.7, 145.7, 149.3, 149.5, 159.0, 160.5 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{128}\text{H}_{160}\text{O}_{12}$: 1889.2; found: 1912.1 $[M+\text{Na}]^+$; elemental analysis calcd (%) for $\text{C}_{134}\text{H}_{164}\text{O}_{12}$: C 81.83, H 8.40; found: C 81.60, H 8.22.

Methyl 3',5'-bis[3',4'-bis(4'-dodecyloxybiphenyl-4-ylmethoxy)biphenyl-4-ylmethoxy]biphenyl-4-carboxylate [(4Bp-3,4Bp-3,5)12 G2-CO₂CH₃] (20): A suspension of K_2CO_3 (134 mg, 0.972 mmol) in DMF (50 mL) was thoroughly degassed. Compound **9** (27 mg, 0.162 mmol) and dendron **19** (330 mg, 0.328 mmol) were added. The reaction mixture was heated to 80°C under Ar for 24 h; it was then allowed to cool to 25°C and was poured into water (300 mL). The precipitate was filtered, dried, and purified by column chromatography (SiO_2 , CHCl_3) to yield a colorless solid (200 mg, 62%). Purity (HPLC): 99+%; $R_f=0.90$ (CHCl_3); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.92 (s, 3H), 4.00 (m, 8H), 5.11 (s, 4H), 5.24 (s, 4H), 5.26 (s, 4H), 6.84 (t, $J=2.2$ Hz, 1H), 6.96 (m, 8H), 7.05 (d, $J=8.4$ Hz, 2H), 7.14 (d, $J=8.4$, 2H), 7.25 (d, $J=2.1$ Hz, 2H), 7.33 (d, $J=2.3$ Hz, 2H), 7.44–7.60 ppm (overlapped m, 32H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.3$, 22.9, 26.3, 29.6, 29.7, 29.9, 32.2, 52.5, 68.4, 70.4, 71.6, 71.8, 107.6, 108.8, 114.9, 115.1, 115.8, 120.6, 127.0, 127.3, 128.1, 128.2, 128.3, 132.4, 133.4, 134.7, 135.3, 135.8, 140.7, 140.8, 141.0, 149.2, 149.6, 159.1, 160.1, 167.0 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{134}\text{H}_{164}\text{O}_{12}$: 1965.2; found: 1988.4 $[M+\text{Na}]^+$; elemental analysis calcd (%) for $\text{C}_{134}\text{H}_{164}\text{O}_{12}$: C 81.83, H 8.40; found: C 81.60, H 8.22.

Methyl 3,5-bis[4-[3,4-bis(4-(4-dodecyloxybenzyloxy)benzyloxy]benzyloxy]biphenyl-4'-carboxylate [(4²-3,4-4-3,5 Bp)12 G2-CO₂CH₃] (23): A suspension of K_2CO_3 (96 mg, 0.696 mmol) in DMF (20 mL) was thoroughly degassed. Compound **2** (28 mg, 0.116 mmol) and dendron **22** (240 mg, 0.236 mmol) were added. The reaction mixture was heated to 90°C under Ar for 20 h; it was then allowed to cool to 25°C, was poured into water (60 mL), and was extracted with CH_2Cl_2 (3×70 mL). The organic extracts were washed with water (50 mL), concentrated, and precipitated with MeOH. The precipitate was filtered, dried, and purified by column chromatography (SiO_2 , CH_2Cl_2) to yield a colorless solid (195 mg, 76%). Purity (HPLC): 99+%; $R_f=0.60$ (CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.94 (overlapped m, 11H), 4.96 (s, 4H), 4.98 (s, 8H), 5.02 (s, 4H), 5.07 (s, 8H), 6.65 (t, $J=2.0$ Hz, 1H), 6.85 (d, $J=2.2$ Hz, 2H), 6.88–7.00 (overlapped m, 24H), 7.05 (s, 2H), 7.31–7.37 (overlapped m, 20H), 7.62 (d, $J=8.6$ Hz, 2H), 8.08 ppm (d, $J=8.6$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.4$, 22.9, 26.3, 29.5, 29.6, 29.7, 29.8, 29.9, 32.2, 68.3, 70.2, 70.3, 71.5, 71.6, 114.9, 115.1, 115.3, 121.1, 127.3, 129.0, 129.2, 129.4, 129.5, 129.8, 130.3, 149.3, 149.6, 158.9, 159.3, 167.0 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{146}\text{H}_{180}\text{O}_{18}$: 2221.3; found: 2245.3 $[M+\text{Na}]^+$; elemental analysis calcd (%) for $\text{C}_{146}\text{H}_{180}\text{O}_{18}$: C 78.88, H 8.16; found: C 78.63, H 8.09.

Methyl 3,5-bis[3,4-bis[4-(4-dodecyloxy-benzyloxy)benzyloxy]benzyloxy]biphenyl-4'-carboxylate [(4²-3,4-3,5 Bp)12 G2-CO₂CH₃] (25): A suspension of K_2CO_3 (124 mg, 0.897 mmol) in DMF (25 mL) was thoroughly degassed. Compound **2** (73 mg, 0.299 mmol) and dendron **24** (550 mg, 0.598 mmol) were added. The reaction mixture was heated to 90°C under Ar for 12 h; it was then allowed to cool to 25°C, was poured into of water (100 mL), and was extracted with CH_2Cl_2 (5×150 mL) and with CHCl_3 (150 mL). The organic extracts were washed with water (100 mL), concentrated, and precipitated with MeOH. The precipitate was filtered, dried, and purified by column chromatography (SiO_2 , CH_2Cl_2) to yield a colorless solid (410 mg, 68%). Purity (HPLC): 99+%; $R_f=0.50$ (CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.95 (overlapped m, 11H), 4.95 (s, 4H), 4.98 (s, 4H), 4.99 (s, 4H), 5.07 (s, 8H), 6.62 (t,

$J=2.2$ Hz, 1H), 6.84 (d, $J=2.2$ Hz, 2H), 6.88–6.97 (overlapped m, 20H), 7.07 (s, 2H), 7.30–7.36 (overlapped m, 16H), 7.62 (d, $J=8.3$ Hz, 2H), 8.09 ppm (d, $J=8.3$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.3$, 22.9, 26.3, 29.5, 29.6, 29.7, 29.8, 29.9, 32.2, 52.3, 68.3, 70.2, 70.4, 71.5, 102.0, 107.1, 114.8, 115.1, 115.3, 115.7, 121.2, 127.3, 129.0, 129.2, 129.3, 129.4, 129.7, 129.8, 130.2, 130.3, 142.4, 145.7, 149.3, 149.6, 158.9, 159.3, 160.6, 167.1 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{132}\text{H}_{168}\text{O}_{16}$: 2009.2; found: 2032.1 $[M+\text{Na}]^+$; elemental analysis calcd (%) for $\text{C}_{132}\text{H}_{168}\text{O}_{16}$: C 78.85, H 8.42; found: C 78.58, H 8.19.

Methyl 3,5-bis[4-[4-[3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]benzyloxy]biphenyl-4'-carboxylate [(4-3,4-4²-3,5 Bp)12 G2-CO₂CH₃] (27): A suspension of K_2CO_3 (34 mg, 0.243 mmol) in DMF (10 mL) was thoroughly degassed. Compound **2** (20 mg, 0.081 mmol) and dendron **26** (150 mg, 0.163 mmol) were added. The reaction mixture was heated to 90°C under Ar for 15 h; it was then allowed to cool to 25°C, was poured into water (50 mL), and was extracted with CH_2Cl_2 (5×50 mL). The organic extracts were washed with water (100 mL), concentrated, and precipitated by MeOH. The precipitate was filtered, dried, and purified by column chromatography (SiO_2 , CH_2Cl_2 /hexane 10:1) to yield a colorless solid (100 mg, 61%). Purity (HPLC): 99+%; $R_f=0.60$ (CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.95 (overlapped m, 11H), 4.95 (s, 4H), 5.01 (s, 4H), 5.03 (s, 4H), 5.07 (s, 8H), 6.65 (t, $J=2.2$ Hz, 1H), 6.85 (d, $J=2.2$ Hz, 2H), 6.88 (d, $J=8.5$ Hz, 8H), 6.93 (s, 4H), 6.96 (d, $J=8.7$ Hz, 4H), 7.00 (d, $J=8.7$ Hz, 2H), 7.05 (s, 2H), 7.31–7.39 (overlapped m, 16H), 7.62 (d, $J=8.3$ Hz, 2H), 8.09 ppm (d, $J=8.3$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.5$, 23.1, 26.5, 29.7, 29.8, 29.9, 30.0, 30.1, 32.4, 52.5, 68.5, 70.3, 70.4, 70.5, 71.7, 96.2, 107.2, 114.9, 115.4, 115.8, 121.3, 127.5, 129.4, 129.5, 129.6, 129.7, 130.5, 137.0, 149.4, 149.7, 159.1, 159.3, 160.8 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{132}\text{H}_{168}\text{O}_{16}$: 2009.2; found: 2048.1 $[M+\text{K}]^+$.

Methyl 3,5-bis[4-[3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]biphenyl-4'-carboxylate [(4-3,4-4-3,5 Bp)12 G2-CO₂CH₃] (29): A suspension of K_2CO_3 (0.50 g, 3.64 mmol) in DMF (50 mL) was thoroughly degassed and heated to 50°C. Compound **2** (0.30 g, 1.21 mmol) and dendron **28** (1.98 mg, 2.43 mmol) were added. The reaction mixture was heated to 90°C under Ar for 15 h; it was then allowed to cool to 25°C, was poured into water (300 mL), and was extracted with CH_2Cl_2 (3×250 mL) and with CHCl_3 (2×200 mL). The organic extracts were washed with water (100 mL), concentrated, and precipitated by MeOH. The precipitate was filtered, dried, and purified by column chromatography (SiO_2 , CH_2Cl_2 /hexane 5:1) to yield a colorless solid (1.83 g, 84%). Purity (HPLC): 99+%; $R_f=0.65$ (CH_2Cl_2 /hexane 5:1); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.95 (overlapped m, 11H), 4.96 (s, 4H), 5.03 (s, 4H), 5.07 (s, 8H), 6.65 (t, $J=2.2$ Hz, 1H), 6.85 (d, $J=2.2$ Hz, 2H), 6.87 (d, $J=8.1$ Hz, 8H), 6.94 (s, 2H), 6.98 (d, $J=8.6$ Hz, 4H), 7.05 (s, 2H), 7.31–7.38 (overlapped m, 14H), 7.63 (d, $J=8.4$ Hz, 2H), 8.09 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.3$, 22.9, 26.3, 29.6, 29.7, 29.8, 29.9, 32.2, 52.3, 68.3, 70.3, 71.6, 101.9, 107.0, 114.7, 115.3, 115.7, 121.1, 127.3, 129.2, 129.3, 129.4, 129.5, 130.3, 142.4, 145.8, 149.3, 149.6, 159.0, 159.2, 160.6, 167.2 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{118}\text{H}_{156}\text{O}_{14}$: 1797.1; found: 1820.7 $[M+\text{Na}]^+$; elemental analysis calcd (%) $\text{C}_{132}\text{H}_{168}\text{O}_{16}$: C 78.80, H 8.74; found: C 78.60, H 8.16.

3,5-Bis[4-[3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]biphenyl [(4-3,4-4-3,5 Bp)12 G2-H] (30): A suspension of K_2CO_3 (78 mg, 0.551 mmol) in DMF (20 mL) was thoroughly degassed. Compound **21** (35 mg, 0.188 mmol) and dendron **28** (306 mg, 0.376 mmol) were added. The reaction mixture was heated to 80°C under Ar for 15 h; it was then allowed to cool to 25°C, was poured into water (300 mL), and was extracted with CH_2Cl_2 (3×50 mL). The organic extracts were washed with water (100 mL), concentrated, and precipitated by MeOH. The precipitate was filtered, dried, and purified by column chromatography (SiO_2 , CH_2Cl_2) to yield a colorless solid (230 mg, 70%). Purity (HPLC): 99+%; $R_f=0.20$ (CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.96 (t, $J=6.6$ Hz, 8H), 4.96 (s, 4H), 5.03 (s, 4H), 5.07 (s, 8H), 6.62 (t, $J=2.4$ Hz, 1H), 6.83 (d, $J=2.3$ Hz, 2H), 6.88 (d, $J=8.1$ Hz, 8H), 6.94 (s, 4H), 6.98

(d, $J=8.6$ Hz, 4H), 7.05 (s, 2H), 7.31–7.38 (overlapped m, 15H), 7.57 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.4$, 22.9, 26.3, 29.5, 29.6, 29.7, 29.9, 32.2, 32.5, 68.3, 70.2, 70.3, 71.5, 71.6, 101.2, 106.8, 114.7, 115.2, 115.3, 115.7, 121.1, 127.4, 128.9, 129.2, 129.3, 129.5, 130.3, 149.2, 149.5, 159.1, 160.5 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{116}\text{H}_{154}\text{O}_{12}$: 1739.1; found: 1763.2 $[M+\text{Na}]^+$.

[3,5-Bis[4-(3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]biphenyl-4'-yl] methanol [(4-3,4-4-3,5 Bp)12 G2-CH₂OH] (31): Dendron 29 (200 g, 0.111 mmol) was added into suspension of LiAlH_4 (13 mg, 0.333 mmol) in THF (5 mL). The reaction mixture was stirred at 25°C for 1 h, quenched by addition of water and 15% (w/v) NaOH, filtered through Celite, concentrated, and precipitated with MeOH. The precipitate was filtered and a colorless solid was obtained (180 g, 90%). Purity (HPLC): 99+%; $R_f=0.50$ (CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.95 (m, 8H), 4.74 (d, $J=5.8$ Hz, 2H), 4.96 (s, 4H), 5.02 (s, 4H), 5.07 (s, 8H), 6.62 (t, $J=2.2$ Hz, 1H), 6.82 (d, $J=2.2$ Hz, 2H), 6.88 (d, $J=8.1$ Hz, 8H), 6.94 (s, 4H), 6.98 (d, $J=8.6$ Hz, 4H), 7.05 (s, 2H), 7.31–7.38 (overlapped m, 12H), 7.43 (d, $J=7.9$ Hz, 2H), 7.55 ppm (d, $J=7.9$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.6$, 23.1, 26.5, 29.2, 29.5, 29.6, 29.7, 29.8, 29.9, 30.0, 30.1, 30.2, 31.9, 32.4, 65.5, 68.5, 70.4, 71.7, 71.8, 101.4, 107.0, 114.9, 115.4, 115.5, 115.9, 121.3, 127.7, 127.8, 129.4, 129.5, 129.5, 129.7, 130.5, 140.6, 140.9, 143.4, 149.4, 149.7, 159.2, 159.3, 160.7 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{117}\text{H}_{156}\text{O}_{13}$: 1765.1; found: 1792.8 $[M+\text{Na}]^+$; elemental analysis calcd (%) for $\text{C}_{132}\text{H}_{168}\text{O}_{16}$: C 78.80, H 8.74; found: C 78.60, H 8.16.

Potassium 3,5-bis[4-[3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]biphenyl-4'-carboxylate [(4-3,4-4-3,5 Bp)12 G2-CO₂K] (32): Dendron 29 (2.10 g, 1.17 mmol) was dissolved in of THF/ H_2O mixture (20:1, 21 mL). KOH (0.33 g, 5.84 mmol) was added. The reaction mixture was heated to 65°C for 15 h, concentrated, and precipitated with MeOH. Filtration and drying yielded a colorless solid (2.10 g, 100%). Purity (HPLC): 99+%; $R_f=0.65$ ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 15:1); ^1H NMR (500 MHz, CDCl_3 , 50°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.96 (t, $J=6.6$ Hz, 8H), 4.83 (s, 4H), 4.87 (s, 4H), 4.96 (s, 4H), 4.98 (s, 4H), 6.50 (s, 1H), 6.69 (s, 2H), 6.83 (m, 8H), 6.90 (m, 8H), 7.04 (s, 2H), 7.25 (m, 8H), 7.35 (d, $J=7.2$ Hz, 2H), 7.92 ppm (d, $J=7.0$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.4$, 22.8, 26.4, 29.7, 29.8, 29.9, 32.2, 52.4, 68.1, 70.5, 71.7, 101.3, 106.9, 113.8, 115.0, 121.2, 127.3, 129.2, 129.3, 129.4, 129.5, 130.1, 142.1, 145.8, 149.3, 149.4, 159.0, 159.1 ppm.

3,5-Bis[4-[3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]biphenyl-4'-carboxylic acid [(4-3,4-4-3,5 Bp)12 G2-COOH] (33): Dendron 32 (150 mg, 0.082 mmol) was dissolved in THF (4 mL). Acetic acid (1 mL) was added. The reaction mixture was stirred at 25°C for 5 min and was then precipitated with MeOH. The precipitate was filtered and recrystallized from acetone to yield a colorless solid (120 mg, 80%). Purity (HPLC): 99+%; $R_f=0.95$ ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 15:1); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.95 (overlapped m, 11H), 4.96 (s, 4H), 5.03 (s, 4H), 5.07 (s, 8H), 6.67 (s, 1H), 6.87 (d, $J=2.2$ Hz, 2H), 6.88 (d, $J=8.1$ Hz, 8H), 6.94 (s, 2H), 7.05 (d, $J=8.6$ Hz, 4H), 7.05 (s, 2H), 7.33–7.38 (overlapped m, 12H), 7.66 (d, $J=8.4$ Hz, 2H), 8.16 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.3$, 22.8, 26.3, 29.6, 29.7, 29.9, 32.1, 52.2, 68.2, 70.4, 71.6, 101.7, 107.0, 114.0, 115.3, 121.2, 127.3, 129.3, 129.3, 129.5, 129.6, 130.3, 142.3, 145.9, 149.3, 149.6, 159.0, 159.2, 160.6 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{117}\text{H}_{154}\text{O}_{14}$: 1783.1; found: 1822.9 $[M+K]^+$.

2-Methoxy-ethyl 3,5-bis[4-[3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]biphenyl-4'-carboxylate [(4-3,4-4-3,5 Bp)12 G2-CO₂-(CH₂)₂OCH₃] (34): Dendron 32 (200 mg, 0.110 mmol), 2-methoxy-ethanol (17 mg, 0.220 mmol), DCC (34 mg, 0.165 mmol), and DPTS (32 mg, 0.110 mmol) were dissolved in dry CH_2Cl_2 (5 mL) under Ar. The reaction mixture was stirred at 25°C for 5 h, concentrated, and purified by column chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{methanol}$ 25:1). Recrystallization from acetone yielded a colorless solid (175 mg, 87%). Purity (HPLC): 99+%; $R_f=0.90$ ($\text{CH}_2\text{Cl}_2/\text{methanol}$ 25:1); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m,

8H), 3.45 (s, 3H), 3.76 (t, $J=4.2$ Hz, 2H), 3.95 (t, $J=4.3$ Hz, 8H), 4.51 (t, $J=4.2$ Hz, 2H), 4.96 (s, 4H), 5.03 (s, 4H), 5.07 (s, 8H), 6.65 (m, 1H), 6.85 (d, $J=8.2$ Hz, 2H), 6.87 (d, $J=8.1$ Hz, 8H), 6.94 (s, 4H), 6.98 (d, $J=8.6$ Hz, 4H), 7.05 (s, 2H), 7.32–7.37 (overlapped m, 12H), 7.62 (d, $J=8.4$ Hz, 2H), 8.12 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.3$, 22.9, 26.3, 29.6, 29.7, 29.8, 29.9, 32.2, 52.3, 58.8, 63.8, 68.3, 70.4, 71.6, 101.9, 107.0, 115.3, 115.7, 121.1, 127.3, 129.3, 129.4, 130.3, 142.4, 145.8, 149.3, 149.6, 159.0, 159.2, 160.6, 167.2 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{120}\text{H}_{160}\text{O}_{15}$: 1841.2; found: 1864.9 $[M+\text{Na}]^+$.

3,5-Bis[4-[3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]biphenyl-4-carboxylic acid amide [(4-3,4-4-3,5 Bp)12 G2-CONH₂] (35): Dendron 32 (200 mg, 0.110 mmol) and DTBMP (22 mg, 0.110 mmol) were dissolved in dry CH_2Cl_2 (5 mL). SOCl_2 (12 μL , 0.165) dissolved in dry CH_2Cl_2 (0.5 mL). The reaction mixture was stirred for 2 h. $\text{NH}_3(\text{g})$ was bubbled through the reaction mixture for 5 min. The reaction mixture was then stirred at 25°C for another hour, concentrated, and precipitated with MeOH. The precipitate was purified by column chromatography (basic alumina, $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 15:1). Recrystallization from acetone yielded a colorless solid (123 mg, 61%). Purity (HPLC): 99+%; $R_f=0.80$ ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 15:1); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.95 (t, $J=6.5$ Hz, 8H), 4.98 (s, 4H), 5.04 (s, 4H), 5.05 (s, 4H), 5.06 (s, 4H), 5.79 (brs, 2H), 6.66 (t, $J=2.1$ Hz, 1H), 6.82 (d, $J=2.1$ Hz, 2H), 6.87 (d, $J=8.1$ Hz, 8H), 6.94 (s, 4H), 6.98 (d, $J=8.4$ Hz, 2H), 7.06 (s, 2H), 7.31–7.38 (overlapped m, 12H), 7.59 (d, $J=8.4$ Hz, 2H), 7.85 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.4$, 22.9, 26.3, 27.0, 29.5, 29.6, 29.7, 29.9, 32.3, 70.2, 70.3, 71.5, 101.8, 106.9, 108.3, 114.7, 115.1, 115.3, 115.6, 121.1, 124.6, 127.4, 127.5, 129.2, 129.3, 130.3, 146.6, 149.3, 149.5, 159.0, 159.2, 160.6, 164.6 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{117}\text{H}_{155}\text{NO}_{12}$: 1782.1; found: 1806.8 $[M+\text{Na}]^+$; elemental analysis calcd (%) for $\text{C}_{132}\text{H}_{168}\text{O}_{16}$: C 78.80, H 8.74; found: C 78.60, H 8.16).

3,5-Bis[4-[3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]biphenyl-4-carboxylic acid methylamide [(4-3,4-4-3,5 Bp)12 G2-CONHCH₃] (36): Dendron 32 (200 mg, 0.110 mmol), CDI (36 mg, 0.220 mmol), and DPTS (7 mg, 0.022 mmol) were dissolved in dry CH_2Cl_2 (5 mL). The reaction mixture was stirred at 25°C for 2 h. Triethylamine (29 mg, 0.275 mmol) and methylammonium chloride (19 mg, 0.275 mmol) were dissolved in dry CH_2Cl_2 (1 mL) and added to reaction mixture. The reaction mixture was stirred at 25°C for 20 h to achieve 30% conversion by TLC. CDI (71 mg, 0.440 mmol) and methylammonium chloride (30 mg, 0.440 mmol) were added to reaction mixture. The reaction mixture was stirred at 25°C for another 24 h, concentrated, and precipitated with MeOH. A colorless solid (125 mg, 62%) was obtained after recrystallization from acetone. Purity (HPLC): 99+%; $R_f=0.90$ ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 15:1); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.3$ Hz, 12H), 1.27 (m, 64H), 1.43 (m, 8H), 1.79 (m, 8H), 3.95 (t, $J=6.6$ Hz, 8H), 4.97 (s, 4H), 5.03 (s, 4H), 5.05 (s, 4H), 5.07 (s, 4H), 6.20 (2s, 2H), 6.65 (m, 1H), 6.81 (d, $J=2.1$ Hz, 2H), 6.87 (d, $J=8.1$ Hz, 8H), 6.93 (s, 4H), 6.97 (d, $J=8.4$ Hz, 4H), 7.05 (s, 2H), 7.31–7.38 (overlapped m, 12H), 7.56 (d, $J=8.4$ Hz, 2H), 7.80 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=14.4$, 22.9, 26.3, 27.0, 29.5, 29.6, 29.7, 29.9, 32.2, 68.3, 70.2, 70.3, 71.5, 101.8, 106.9, 108.3, 110.7, 114.7, 115.1, 115.3, 115.6, 121.1, 124.6, 127.4, 127.5, 129.2, 129.3, 129.4, 130.3, 142.8, 146.6, 149.2, 149.5, 158.9, 159.2, 160.6, 164.6, 175.4 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{118}\text{H}_{157}\text{NO}_{13}$: 1796.2; found: 1818.9 $[M+\text{Na}]^+$.

(S)-3,5-Bis[4-[3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]biphenyl-4-carboxylic acid sec-butylamide [(S)-(4-3,4-4-3,5 Bp)12 G2-CONHCH(CH₃)C₂H₅] (37): Dendron 32 (400 mg, 0.219 mmol) and DTBMP (67 mg, 0.329 mmol) were dissolved in dry CH_2Cl_2 (5 mL). DMF (1 drop) and SOCl_2 (52 mg, 0.437 mmol) were added to reaction mixture, which was then stirred at 25°C under Ar for 2 h; (S)-sec-butylamine (192 mg, 2.625 mmol) was then added. The reaction mixture was stirred at 25°C under Ar for a further 15 h, was concentrated by heating to 50°C, and was precipitated with MeOH. Column chromatography (Al_2O_3 , $\text{CH}_2\text{Cl}_2/\text{acetone}$ 20:1) yielded a colorless solid (260 mg, 65%). Purity (HPLC): 99+%; $R_f=0.80$ ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 15:1); ^1H NMR (500 MHz, CDCl_3 , 25°C, TMS): $\delta=0.89$ (t, $J=6.2$ Hz, 12H), 0.99 (t, $J=$

7.2 Hz, 3H), 1.27 (m, 66H), 1.43 (m, 8H), 1.52 (m, 2H), 1.79 (m, 8H), 3.95 (t, $J=4.3$ Hz, 8H), 4.17 (m, 1H), 4.96 (s, 4H), 5.02 (s, 4H), 5.07 (s, 8H), 5.88 (d, $J=5.3$ Hz, 2H), 6.64 (t, $J=2.2$ Hz, 1H), 6.85 (s, 2H), 6.87 (d, $J=8.1$ Hz, 8H), 6.94 (s, 4H), 6.98 (d, $J=8.6$ Hz, 4H), 7.05 (s, 2H), 7.32–7.37 (overlapped m, 12H), 7.62 (d, 2H, $J=8.4$ Hz), 7.81 ppm (d, $J=8.4$ Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3 , 25 °C, TMS): $\delta=14.3$, 20.8, 22.8, 26.3, 29.4, 29.9, 30.0, 30.1, 32.1, 47.2, 68.2, 70.3, 71.5, 114.8, 115.1, 115.2, 115.4, 115.6, 121.2, 127.5, 127.6, 129.3, 129.6, 130.1, 158.9, 159.1, 159.2 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{121}\text{H}_{163}\text{NO}_{13}$: 1838.2; found: 1861.4 $[M+\text{Na}]^+$.

(R)-3,5-Bis[4-[3,4-bis(4-dodecyloxybenzyloxy)benzyloxy]benzyloxy]bi-phenyl-4-carboxylic acid sec-butylamide [(R)-(4-3,4-4-3,5 Bp)12 G2-CONHCH(CH₃)C₂H₅] (38): Dendron **32** (400 mg, 0.219 mmol) and DTBMP (67 mg, 0.329 mmol) were dissolved in dry CH_2Cl_2 (5 mL). DMF (1 drop) and SOCl_2 (52 mg, 0.437 mmol) were added to reaction mixture, which was then stirred at 25 °C under Ar for 3 h; then (R)-sec-butylamine (192 mg, 2.625 mmol) was added. The reaction mixture was stirred at 25 °C under Ar for a further 20 h, was concentrated by heating to 50 °C, and was precipitated with MeOH. Column chromatography (Al_2O_3 , CH_2Cl_2 /acetone 20:1) yielded a colorless solid (280 mg, 70 %). Purity (HPLC): 99+ %; $R_f=0.80$ (CH_2Cl_2 /MeOH 15:1); ^1H NMR (500 MHz, CDCl_3 , 25 °C, TMS): $\delta=0.89$ (t, $J=6.2$ Hz, 12H), 1.00 (t, $J=7.1$ Hz, 3H), 1.27 (m, 66H), 1.43 (m, 8H), 1.52 (m, 2H), 1.79 (m, 8H), 3.95 (t, $J=4.3$ Hz, 8H), 4.18 (m, 1H), 4.96 (s, 4H), 5.02 (s, 4H), 5.06 (s, 8H), 5.80 (d, $J=5.2$ Hz, 2H), 6.64 (t, $J=2.2$ Hz, 1H), 6.85 (s, 2H), 6.87 (d, $J=8.1$ Hz, 8H), 6.95 (s, 4H), 7.00 (d, $J=8.6$ Hz, 4H), 7.05 (s, 2H), 7.31–7.36 (overlapped m, 12H), 7.63 (d, $J=8.4$ Hz, 2H), 7.82 ppm (d, $J=8.4$ Hz, 2H). ^{13}C NMR (500 MHz, CDCl_3 , 25 °C, TMS): $\delta=14.3$, 20.8, 22.9, 26.3, 29.5, 29.6, 29.8, 29.9, 30.0, 32.1, 47.3, 68.3, 70.2, 71.5, 114.7, 115.2, 115.3, 115.6, 115.7, 121.1, 127.4, 127.5, 129.3, 129.5, 130.2, 159.0, 159.1 ppm; MS (MALDI-TOF): m/z calcd for $\text{C}_{121}\text{H}_{163}\text{NO}_{13}$: 1838.2; found: 1862.1 $[M+\text{Na}]^+$.

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