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Designing Libraries of First Generation AB_3 and AB_2 Self-Assembling Dendrons via the Primary Structure Generated from Combinations of $(AB)_y$–AB_3 and $(AB)_y$–AB_2 Building Blocks

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Abstract: Structural analysis of three libraries of up to five generations of self-assembling dendrons based on AB_3, AB_2, and combinations of AB_3 with AB_2 building blocks (Percec et al. *J. Am. Chem. Soc.* **2001**, *123*, 1302) facilitated the discovery of several nanoscale lattices previously unknown for organic compounds (3-D $Pm\bar{3}n$ cubic, 3-D $P4_2/mnm$ tetragonal, and a crystallographically forbidden 12-fold symmetry liquid quasicrystal) and provided fundamental correlations between the molecular structure of the dendron and the shape and the diameter of the supramolecular dendrimers which, in these experiments, were limited to less than 75 Å. That study concluded that alternative design principles should be elaborated for the assembly of supramolecular dendrimers of larger dimensions. Here we report design principles, synthesis and analysis of first and higher generations AB_3 and AB_2 self-assembling dendrons, based on various primary structures, and combinations of $(AB)_y$–AB_3 and $(AB)_y$–AB_2 (i.e., from nondendritic AB where $y =$ 1 to 11 and dendritic AB_3 and AB_2) building blocks that produced the largest structural (including six new lattices) and dimensional (100 to 217 Å diameter) diversity of supramolecular dendrimers.

Introduction

Dendrimers and dendrons are architectural motifs that have provided powerful entries for the synthesis of complex functional nanostructures including biological mimics.[1] Biological macromolecules create an immense diversity of 3-D structures and functions from few monomers and their corresponding secondary structures that are determined by their primary structure.[2] Amphiphilic self-assembling dendrons provide a simple strategy to access the correlation between primary and 3-D structures with functions, in nonbiological macromolecules.[3–7] Both the divergent[8] and convergent[9] iterative methods employed in the synthesis of dendritic molecules provide access to monodisperse dendrimers and dendrons with predetermined primary structures generated from combinations of different building blocks. Nevertheless, most self-assembling dendrons reported to date are based on a single repeat unit.[3a,c,l] Very few examples have been constructed from combinations of different AB_2 and AB_3 building blocks.[3l,m,p] The results obtained with dendrons based on more than one repeat unit are rewarding, since they have provided access to supramolecular dendrimers that self-organize in lattices that were not previously encountered for organic compounds.[3e,p,q] However, the investigation of three libraries of self-assembling dendrons varying in generation

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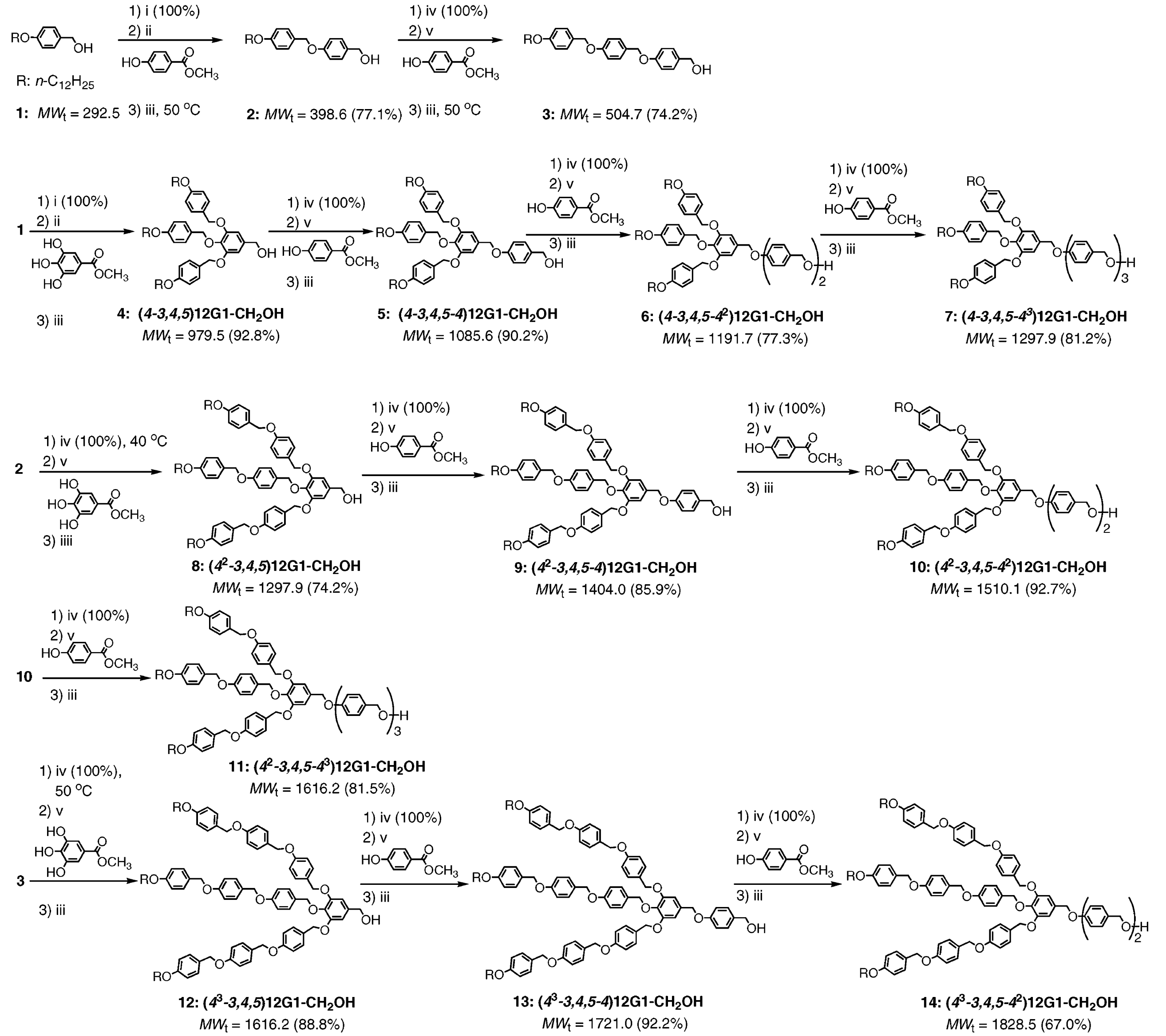
(1) (a) Fréchet, J. M. J., Tomalia, D. A., Eds. *Dendrimers and Other Dendritic Polymers*. Wiley: New York, 2001. (b) Newcome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons*. Wiley-VCH: Weinheim, 2001.
(2) Voet, D.; Voet, J. G.; Pratt, C. W. *Fundamentals of Biochemistry.* Wiley: New York, 1999.
(3) For selected examples from our laboratory of AB_3 and AB_2 dendrons that self-assemble in supramolecular dendrimers that self-organize in lattices, see: (a) Percec, V.; Chu, P.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1995**, *117*, 11441. (b) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855. (c) Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539. (d) Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. S. K. *Science* **1997**, *278*, 449. (e) Dukeson, D. R.; Ungar, G.; Balagurusamy, V. S. K.; Percec, V.; Johansson, G. A.; Glodde, M. *J. Am. Chem. Soc.* **2003**, *125*, 15974. (f) Percec, V.; Cho, W.-D.; Mosier, P. E.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 11061. (g) Percec, V.; Cho, W.-D.; Möller, M.; Prokhorova, S. A.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **2000**, *122*, 4249. (h) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1598. (i) Percec, V.; Cho, W.-D.; Ungar, G. *J. Am. Chem. Soc.* **2000**, *122*, 10273. (j) Yeardley, D. J. P.; Ungar, G.; Percec, V.; Holerca, M. N.; Johansson, G. *J. Am. Chem. Soc.* **2000**, *122*, 1684. (k) Duan, H.; Hudson, S. D.; Ungar, G.; Holerca, M. N.; Percec, V. *Chem.–Eur. J.* **2001**, *7*, 4134. (l) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **2001**, *123*, 1302. (m) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *Chem.–Eur. J.* **2002**, *8*, 2011. (n) Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyanovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H.-W.; Hudson, S. D.; Duan, H. *Nature* **2002**, *419*, 384. (o) Percec. V.; Glodde, M.; Johansson, G.; Balagurusamy, V. S. K.; Heiney, P. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 4338. (p) Ungar, G.; Liu, Y.; Zeng, X.; Percec, V.; Cho, W.-D. *Science* **2003**, *299*, 1208. (q) Zeng, X.; Liu, Y.; Ungar, G.; Percec, V.; Dulcey, A.; Hobbs, J. K. *Nature* **2004**, *428*, 157.

10.1021/ja049846j CCC: $27.50

Scheme 1. Synthesis of **(*4^n-3,4,5-4^m*)12G1-X** Dendrons (X = CO_2CH_3, CH_2OH, and CH_2Cl, n = 1−3 and m = 0−3)[a]



[a] Reagents and conditions: (i) $SOCl_2$, CH_2Cl_2, 20 °C; (ii) K_2CO_3, DMF, THF, 70 °C; (iii) $LiAlH_4$, THF; (iv) $SOCl_2$, DTBMP, CH_2Cl_2, 20 °C; (v) K_2CO_3, DMF, THF, 70 °C.

number from one to five[3g,h,l] demonstrated an unexpected size limitation for the supramolecular dendrimers designed by this strategy. The dimension of the supramolecular dendrimer was shown to be determined by the solid angle of the self-assembling dendron.[3l] These three libraries provided only two examples of first generation dendrons that self-assemble in columnar supramolecular dendrimers without the requirement of strong

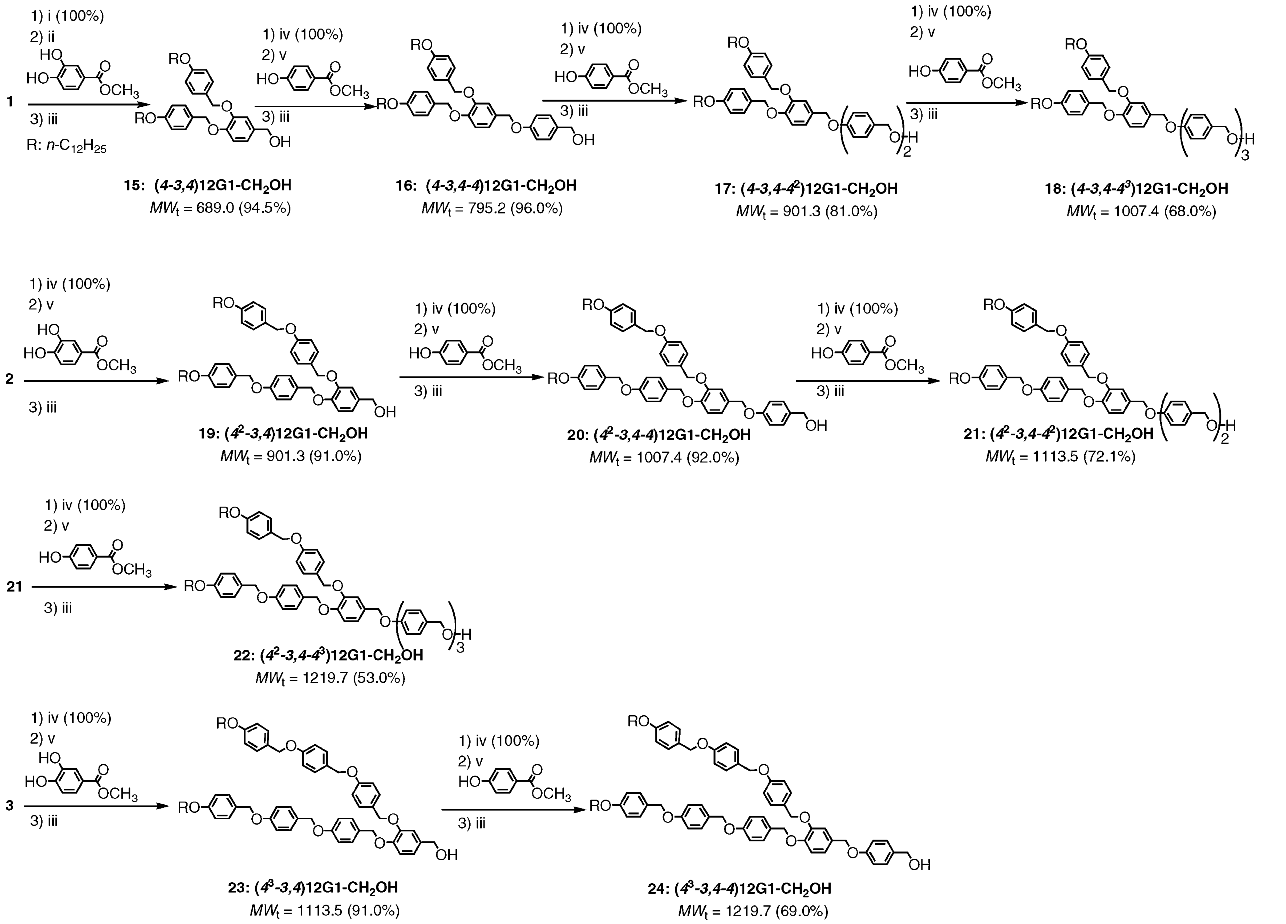
(4) For examples of self-assembling dendrons that self-assemble and coassemble in supramolecular superlattices, see: (a) Percec, V.; Ahn, C.-H.; Bera, T. K.; Ungar, G.; Yerardley, D. J. P. *Chem.*—*Eur. J.* **1999**, *5*, 1070. (b) Percec, V.; Bera, T. K.; Glodde, M.; Fu, Q.; Balagurusamy, V. S. K.; Heiney, P. A. *Chem.*—*Eur. J.* **2003**, *9*, 921.

(5) For selected examples from other laboratories on supramolecular dendrimers self-organizable in lattices, see: (a) Pesak, D. J.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1636. (b) Meier, H.; Lehmann, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 643. (c) Barbéra, J.; Marcos, M.; Serrano, J. L. *Chem.*—*Eur. J.* **1999**, *5*, 643. (d) Marcos, M.; Giménez, R.; Serrano, J. L.; Donnio, B.; Heinrich, B.; Guillon, D. *Chem.*—*Eur. J.* **2001**, *7*, 1006. (e) Suárez, M.; Lehn, J.-M.; Zimmerman, S. C.; Skoulios, A.; Heinrich, B. *J. Am. Chem. Soc.* **1998**, *120*, 9526. (f) Deschenaux, R.; Serrano, E.; Levelut, A.-H. *Chem. Commun.* **1997**, 1577. (g) Baars, M. W. P. L.; Söntjes, S. H. M.; Fischer, H. M.; Peerlings, H. W. I.; Meijer, E. W. *Chem.*—*Eur. J.* **1998**, *4*, 2456. (h) Cameron, J. H.; Facher, A.; Latterman, G.; Diele, S. *Adv. Mater.* **1997**, *9*, 398. (i) Kim, C.; Kim, K. T. I.; Chang, Y.; Song, H. H.; Cho, T.-Y.; Jeon, H.-J. *J. Am. Chem. Soc.* **2001**, *123*, 5586. (j) Saez, I. M.; Goodby, J. W. *Chem. Commun.* **2003**, 1726. (k) Lecommandoux, S.; Klok, H.-A.; Sayaz, M.; Stupp, S. I. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3501.

(6) For selected examples of self-organizable dendronized polymers, see: (a) Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* **1998**, *391*, 161. (b) Percec, V.; Ahn, C.-H.; Cho, W.-D.; Jamieson, A. M.; Kim, J.; Leman, T.; Schmidt, M.; Gerle, M.; Möller, M.; Prokhorova, S. A.; Sheiko, S. S.; Cheng, S. Z. D.; Zhang, A.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 8619. (c) Rapp, A.; Schnell, I.; Sebastiani, D.; Brown, S. P.; Percec, V.; Spiess, H.-W. *J. Am. Chem. Soc.* **2003**, *125*, 13284.

(7) For selected brief recent reviews on supramolecular dendrimers self-organizable in lattices, see: (a) Matheus, O. A.; Shipway, A. N.; Stoddart, J. F. *Prog. Polym. Sci.* **1998**, *23*, 1. (b) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884. (c) Emrick, T.; Fréchet, J. M. J. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 15. (d) Moore, J. S. *Curr. Opin. Colloid Interface Sci*. **1999**, *4*, 108. (e) Schlenk, C.; Frey, H. *Monatsh. Chem.* **1999**, *130*, 3. (f) Smith, D. K.; Diederich, F. *Top. Curr. Chem*. **2000**, *210*, 183. (g) Ponomarenco, S. A.; Boiko, N. I.; Shibaev, V. P. *Polym. Sci. Ser. C.* **2001**, *43*, 1. (h) Guillon, D.; Deschenaux, R. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 515. (i) Tschierske, C. *Curr. Opin. Colloid Interface Sci*. **2002**, *7*, 69. (j) Tschierske, C. J. J. *Mater. Chem*. **2001**, *11*, 2647. (k) Diele, S. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 333. (l) Caminade, A.-M.; Turrin, C.-O.; Sutra, P.; Majoral, J.-P. *Curr. Opin. Colloid Interface Sci*. **2003**, *8*, 282.

Scheme 2. Synthesis of **(4^n-3,4-4^m)12G1-X** Dendrons (X = CO_2CH_3, CH_2OH, and CH_2Cl, n = 1−3 and m = 0−3)[a]



[a] Reagents and conditions: (i) $SOCl_2$, CH_2Cl_2, 20 °C; (ii) K_2CO_3, DMF, THF, 70 °C; (iii) $LiAlH_4$, THF; (iv) $SOCl_2$, DTBMP, CH_2Cl_2, 20 °C; (v) K_2CO_3, DMF, THF, 70 °C.

noncovalent interactions in their focal point.[3l] All other members of these libraries start to self-assemble only at their second generation. These two first generation self-assembling dendrons allowed us to demonstrate that the architecture of the first generation determines the dependence between the generation number and the incremental dimensional increase of the supramolecular dendrimer as a function of generation. Due to the shape change of the self-assembling dendron as a function of generation, in very few cases the increase in generation is accompanied by an increase in supramolecular dendrimer dimension.[3l] This is in spite of the fact that the molar mass of the dendron and of the supramolecular dendrimer increases exponentially. This study concluded that alternative design principles should be elaborated to overcome this architectural limitation.[3l] AB building blocks do not have the capability to create a branching point. Therefore, they have been previously used only to functionalize the periphery of first or higher generation self-assembling dendrons.[3f,i,l,m]

Here we report the use of combinations of $(AB)_y$−AB_3 and $(AB)_y$−AB_2 building blocks to design libraries of first generation AB_3 and AB_2 self-assembling dendrons. The design principles involve the incorporation of various compositions and sequences of $(AB)_y$−AB_3 and $(AB)_y$−AB_2 building blocks into novel architectural motifs that represent first generation AB_3 and AB_2 self-assembling dendrons. The self-assembling dendrons designed from combinations of different compositions and sequences of AB (nondendritic) and AB_n (dendritic) building blocks will be named, for the simplicity of this discussion, "hybrid" dendrons, to differentiate them from conventional dendrons that are generated from combinations of AB_n dendritic building blocks. The examples used to demonstrate this strategy have compositions produced from various ratios of one AB_3 or AB_2 building block and from one to eleven (y = 1 to 11) identical AB building blocks. These combinations were incorporated, with different sequences via a convergent iterative strategy, into a diversity of first generation AB_3 and AB_2 hybrid dendrons. Preliminary examples of their use in the synthesis of second generation dendrons will also be reported. The self-assembly of all hybrid dendrons was investigated by the retrostructural analysis[3l] of the lattices self-organized from their supramolecular dendrimers. The results of this retrostructural analysis demonstrated that the first generation hybrid AB_3 and AB_2 dendrons provided a larger diversity of supramolecular structures and dimensions than all previously investigated libraries based on up to five generations of self-assembling dendrons obtained from combinations of AB_3 and AB_2 building blocks.[3l] Therefore, the simplicity of the method employed in

(8) (a) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17*, 117. (b) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2003. (c) Tomalia, D. A.; Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2719.
(9) (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (b) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819.

the synthesis of these first generation AB$_3$ and AB$_2$ hybrid dendrons together with the variety of AB building blocks available provide novel and powerful architectural strategies to influence the mode of self-assembly, to increase the dimensions of the supramolecular dendrimers, and to discover new supramolecular structures.

Results and Discussion

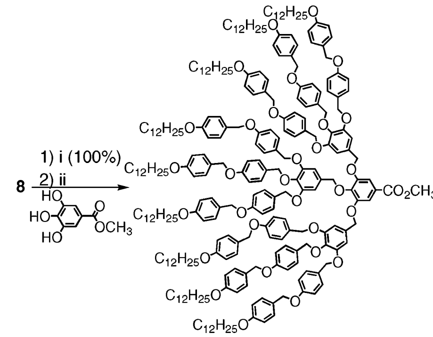
Synthesis of First Generation AB$_3$ Hybrid Dendrons from Combinations of (AB)$_y$ and AB$_3$ Building Blocks. Twelve AB$_3$ first generation self-assembling hybrid dendrons were synthesized from various molar ratios and sequences of the commercially available methyl 4-hydroxybenzoate AB and methyl 3,4,5-trihydroxybenzoate AB$_3$ building blocks. Scheme 1 outlines the divergent synthesis of this library. 4-(*n*-Dodecan-1-yloxy)benzyl alcohol **1** was prepared[10] by the etherification of methyl 4-hydroxybenzoate with dodecanyl bromide followed by reduction with LiAlH$_4$. 4-[*p*-(*n*-Dodecan-1-yloxy)benzyloxy]-benzyl alcohol [**(*4*^{2})-CH$_2$OH**], **2**, was obtained by the etherification of methyl 4-hydroxybenzoate with the freshly prepared benzyl chloride of **1** followed by reduction with LiAlH$_4$ (77.1%).

4-{4′-[*p*-(*n*-Dodecan-1-yloxy)benzyloxy]benzyloxy}benzyl alcohol [**(*4*^{3})-CH$_2$OH**], **3**, was synthesized by the etherification of methyl 4-hydroxybenzoate with the freshly prepared benzyl chloride of **2** followed by reduction (74.2% yield). Etherification of methyl 3,4,5-trihydroxybenzoate with the benzyl chlorides of **1**, **2**, and **3**, respectively, followed by reduction produced dendrons **4** (92.8%), **8** (74.2%), and **12** (88.8%). Dendrons **5** (90.2%), **9** (85.9%), and **13** (92.2%) were synthesized by the etherification of methyl 4-hydroxybenzoate with the benzyl chlorides of **4**, **8**, and **12**, followed by reduction. This iteration was repeated with the benzyl chlorides of **5**, **9**, and **13** and methyl 4-hydroxybenzoate to produce dendrons **6** (77.3% yield), **10** (92.7%), and **14** (67.0%). Reiteration of the same sequence with the benzyl chlorides of **6** and **10** generated **7** (81.2% yield) and **11** (81.5%). Due to low solubility, **14** was not used in this reaction step.

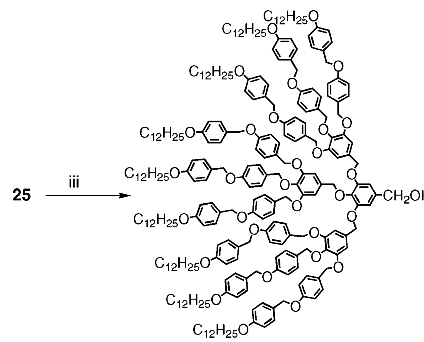
Synthesis of First Generation AB$_2$ Hybrid Dendrons from Combinations of (AB)$_y$ and AB$_2$ Building Blocks. Ten first generation AB$_2$ self-assembling hybrid dendrons were prepared by a similar strategy to the one outlined in Scheme 1, except that the AB$_3$ methyl 3,4,5-trihydroxibenzoate was replaced with a methyl 3,4-dihydroxybenzoate AB$_2$ building block (Scheme 2). Dendrons **15** (94.5% yield), **19** (91.0%), and **23** (91.0%) were synthesized by the etherification of methyl 3,4-dihydroxybenzoate with the benzyl chlorides derived from **1**, **2**, and **3** followed by reduction. Etherification of the benzyl chlorides of **15**, **18**, and **23** with methyl 4-hydroxybenzoate followed by reduction produced **16** (96.0% yield), **20** (92.0%), and **24** (69.0%). Reiteration of this sequence with the benzyl chlorides of **16** and **20** generated **17** (81.0% yield), **21** (72.1%), and **24** (69.0%). Finally, dendrons **18** (68.0% yield) and **22** (53.0%) were synthesized by the repetition of the previous iteration with the benzyl chlorides derived from **17** and **21**. Due to limited solubility, dendron **24** was not used in the last two iterations.

Synthesis of Second Generation Dendrons Based on AB$_3$ Hybrid Dendrons. All first generation hybrid dendrons synthesized as reported in Schemes 1 and 2 can be employed in the synthesis of higher generations dendrons and dendrimers by convergent or divergent methods. Scheme 3 outlines the synthesis of several examples of second generation dendrons

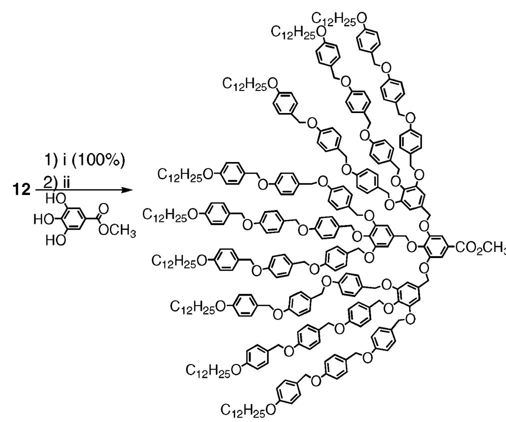
Scheme 3. Synthesis of Second Generation AB$_3$ Hybrid Dendrons



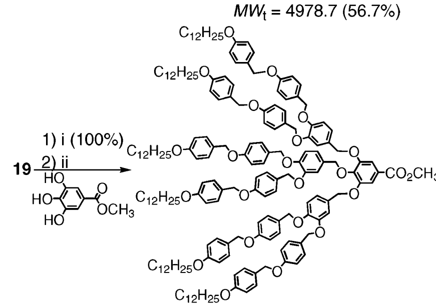
25: (*4*^{2}-(*3,4,5*)^2)12G2-CO$_2$CH$_3$
MW$_t$ = 4023.6 (50.3%)



26: (*4*^{2}-(*3,4,5*)^2)12G2-CH$_2$OH
MW$_t$ = 3995.5 (50.0%)



27: (*4*^{3}-(*3,4,5*)^2)12G2-CO$_2$CH$_3$
MW$_t$ = 4978.7 (56.7%)

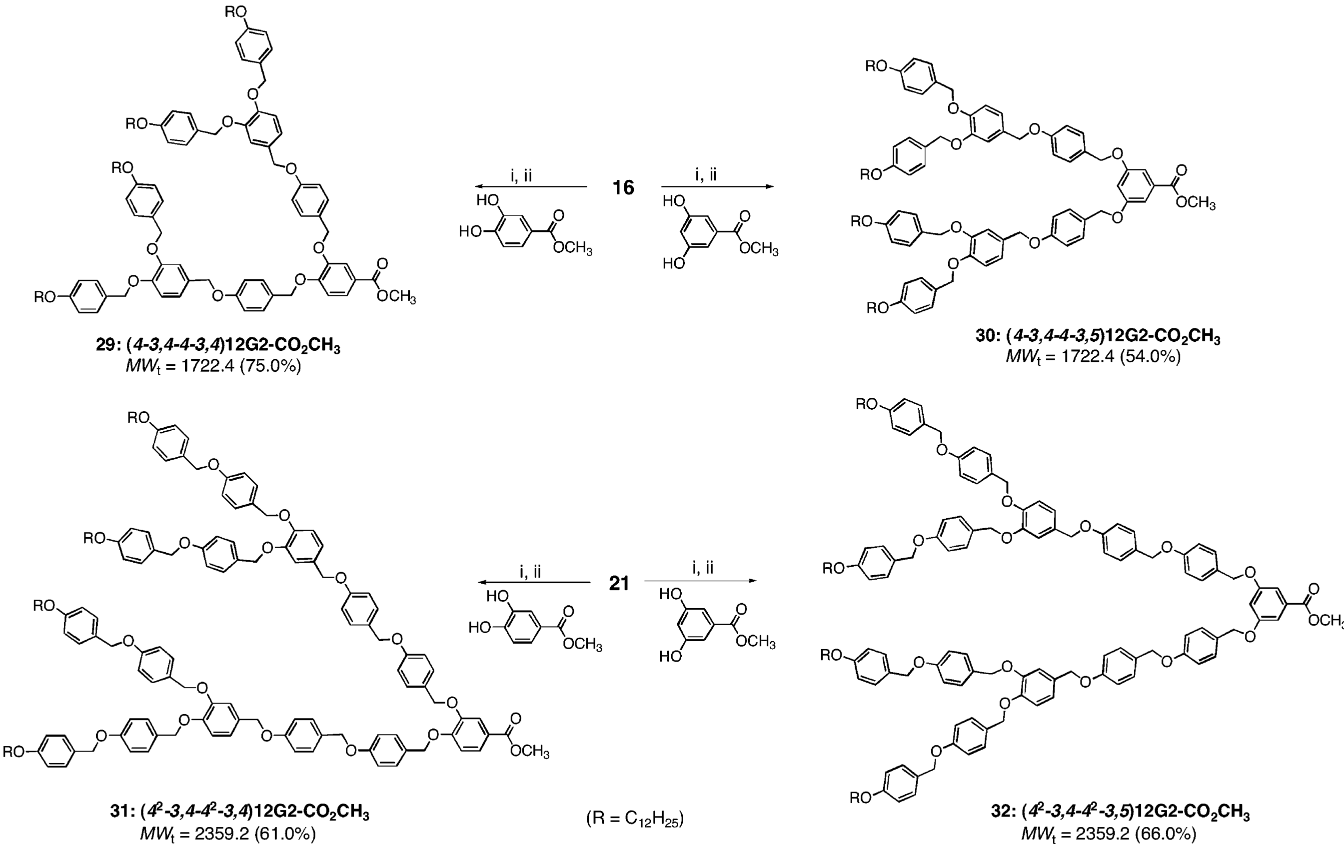


28: (*4*^{2}-*3,4*-*3,4,5*)12G2-CO$_2$CH$_3$
MW$_t$ = 2833.9 (59.8%)

[a] Reagents and conditions: (i) SOCl$_2$, DTBMP, CH$_2$Cl$_2$, 20 °C; (ii) K$_2$CO$_3$, DMF, THF, 70 °C; (iii) LiAlH$_4$, THF.

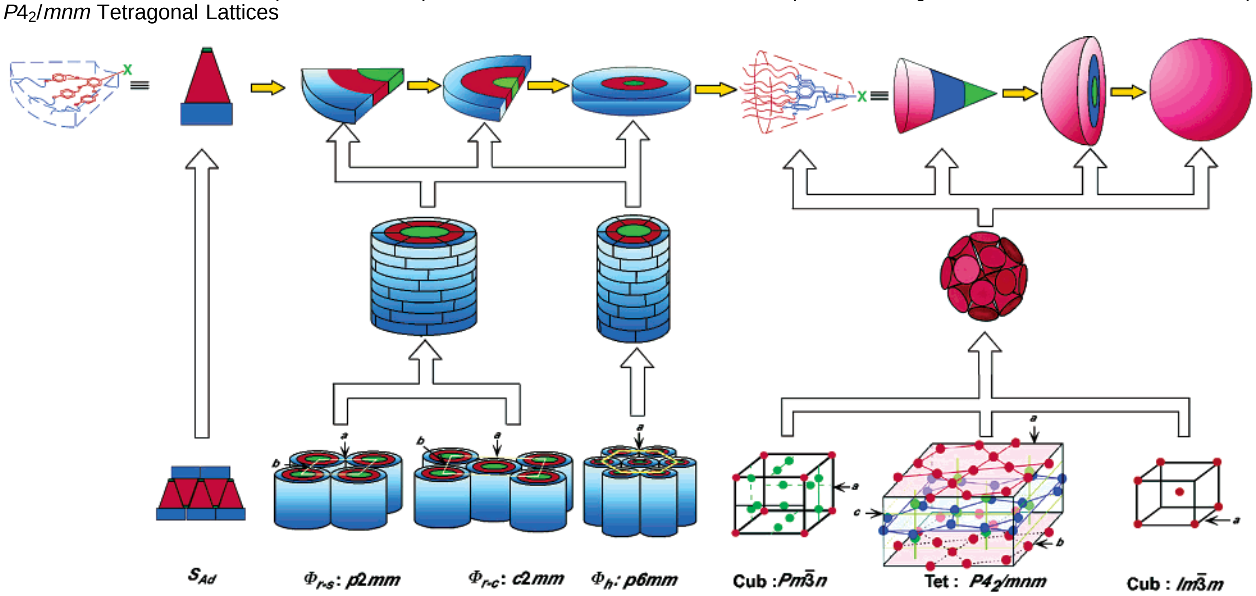
(10) Percec, V.; Johansson, G.; Heck, J.; Ungar, G.; Batty, S. V. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1411.

Scheme 4. Synthesis of Second Generation AB_2 Hybrid Dendrons[a]



[a] Reagents and conditions: (i) $SOCl_2$, DTBMP, CH_2Cl_2, 20 °C; (ii) K_2CO_3, DMF, THF, 65 °C.

Scheme 5. Schematic Representation of the Self-Assembly of Building Blocks Based on Flat Tapered Dendrons into Interdigitated Smectic A (S_{Ad}) Lattices, Supramolecular Cylindrical and Elliptical Columns, and Their Subsequent Self-Organization in a *p*6*mm* Hexagonal Columnar (Φ_h), *p*2*mm* Simple Rectangular Columnar (Φ_{r-s}), or *c*2*mm* Centered Rectangular Columnar (Φ_{r-c}) Lattices, and the Self-Assembly of the Conical Dendrons into Supramolecular Spherical Dendrimers and Their Subsequent Self-Organization in $Pm\bar{3}n$, $Im\bar{3}m$ Cubic (Cub), and $P4_2/mnm$ Tetragonal Lattices

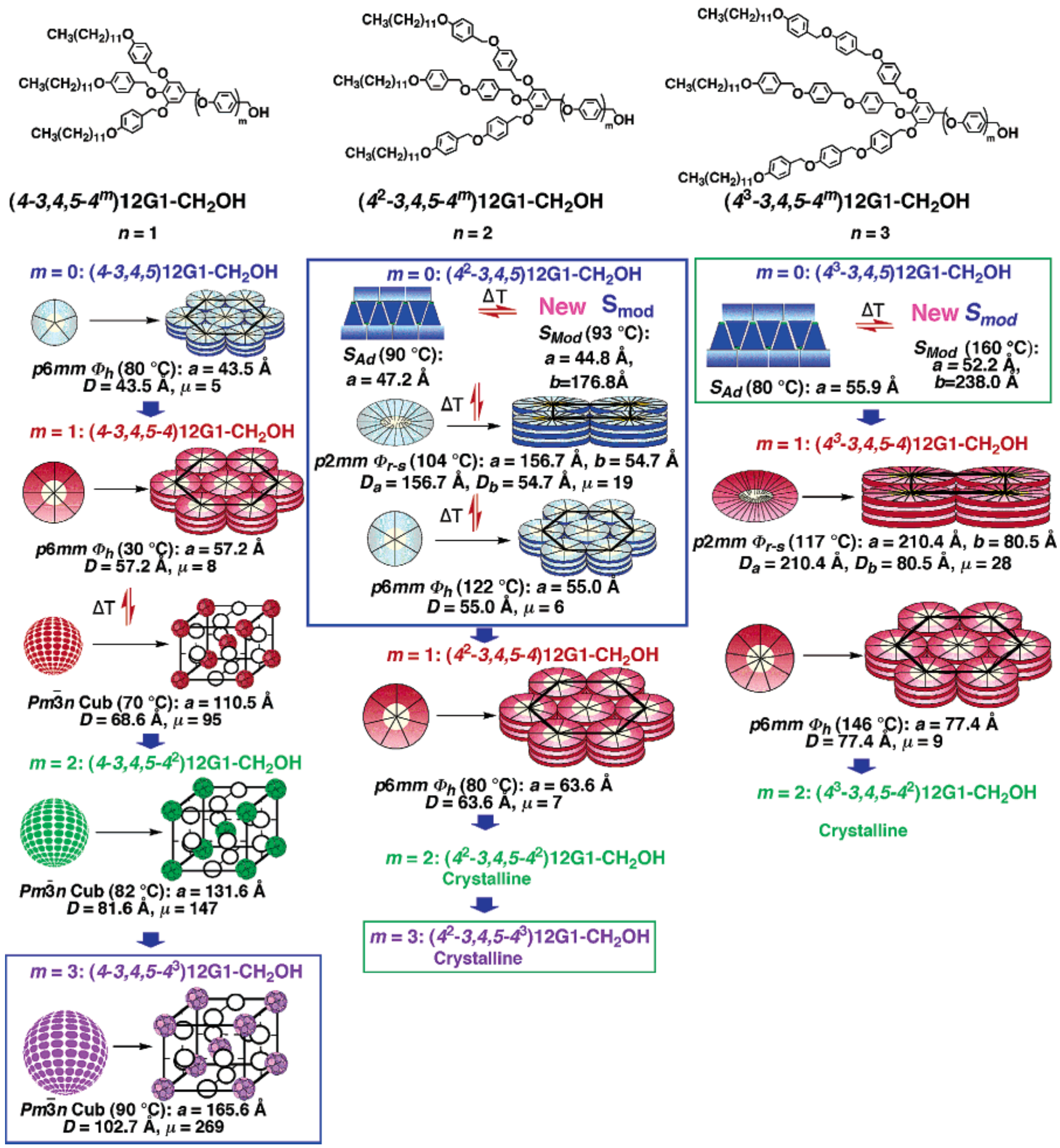


derived from **8**, **12**, and **19**. The freshly prepared benzyl chloride of **8** was etherified with methyl 3,4,5-trihydroxybenzoate to produce **25** (50.3% yield).

Reduction of **25** with $LiAlH_4$ generated **26** (50.0% yield). Etherification of methyl 3,4,5-trihydroxy benzoate with the benzyl chlorides of **12** and **19** produced **27** (56.7% yield) and **28** (59.8% yield), respectively.

Synthesis of Second Generation AB_2 Dendrons Based on AB_2 Hybrid Dendrons. Four examples of second generation dendrons containing 3,4- or 3,5-AB_2 building blocks at their apex were synthesized by using the first generation hybrid dendrons **16** and **21** (Scheme 4). The freshly prepared benzyl chloride of **16** was used in the etherification of methyl 3,4-dihydroxybenzoate and methyl 3,5-dihydroxybenzoate to pro-

Scheme 6. Retrostructural Analysis of Supramolecular Dendrimers Self-Assembled from **(4^n-3,4,5-4^m)12G1-CH$_2$OH** (n = 1−3 and m = 0−3)



duce the second generation dendrons **29** (75.0% yield) and **30** (54.0%). The benzyl chloride of **21** was etherified with methyl 3,4-dihydroxybenzoate and methyl 3,5-dihydroxybenzoate to produce **31** (61.0% yield) and **32** (66.0%). Compound **29** is a constitutional isomer of **30** while **31** is a constitutional isomer of **32**.

Structural and Retrostructural Analysis of AB_3 Hybrid Dendrons. Scheme 5 summarizes the methodology elaborated in our laboratory for the structural and retrostructural analysis of supramolecular dendrimers.[3b,c,j,p]

This method consists of a combination of techniques involving differential scanning calorimery (DSC, that determines transition temperatures and corresponding thermodynamic parameters), thermal optical polarized microscopy (TOPM, that estimates qualitatively the 1-D, 2-D, and 3-D nature of the lattice in which the supramolecular dendrimers are self-organized), small and wide-angle X-ray diffraction experiments (XRD, to quantitatively assign the lattice symmetry and calculate lattice dimensions when the structure of the lattice is known), and experimental densities (to calculate the number of supramolecular dendrimers forming a lattice, the number of dendrons forming a supramolecular spherical dendrimer or a cross-section of the columnar supramolecular dendrimers, and the shape of the dendron). The assignment of unknown lattices and their retrostructural analysis requires, in addition to the previously mentioned methods, a combination of absolute electron density calculations, electron density maps, and electron diffraction and transmission electron microscopy.[3b,c,d,e,k,o] Methods to perform the structural and retrostructural analysis of the lattices described in Scheme 5 were already elaborated.[3b,c,j,l,m,n,p,11]

Scheme 6 summarizes the analysis of the new AB_3 dendrons whose synthesis was described in Scheme 1. The discussion of Scheme 6 will be made by using a short nomenclature developed from the one used previously.[3l] Within each column in this

Table 1. Thermal Transitions of **(4^n-3,4,5-4^m)12G1-CH_2OH** (n = 1−3 and m = 0−3) Dendrons

dendron	thermal transitions (°C) and corresponding enthalpy changes (kcal/mol)[a] heating	cooling
(4-3,4,5)12G1-CH_2OH	k^b 79 (32.09) $\Phi_h{}^c$ 82 (0.88) i^d k 46 (4.31) −k 52 (26.13) k 75 (30.25) Φ_h 82 (1.12) i	i 78 (1.16) Φ_h 47 (1.08) k 30 (13.18) k 17 (0.19) k
(4-3,4,5-4)12G1-CH_2OH	k 5 (27.39) k 48 (20.01) Cub[e] 90 (0.42) i k 10 (0.12) Φ_h 50 (0.33) Cub 90 (0.48) i	i 84 (0.22) Cub 29 (0.64) Φ_h −24 (1.57) k
(4-3,4,5-4^2)12G1-CH_2OH	k 52 (28.11) Cub 92 (4.52) i Cub 93 (3.45) i	i 90 (2.74) Cub
(4-3,4,5-4^3)12G1-CH_2OH	k −14 (5.31) k 79 (26.16) Cub 106 (3.44) i k 18 (0.05) Cub 105 (3.15) i	i 102 (3.10) Cub 17 (0.14) k
(4^2-3,4,5)12G1-CH_2OH	k −18 (0.61) k 79 (10.56) $\Phi_{r-s}{}^f$ 97 (19.49) Φ_h 128 (2.33) i k 45 (0.71) S_{Ad} ∼95^h S_{mod} 99 (14.63) Φ_{r-s} 108 (1.36) Φ_h 128 (1.56) i	i 123 (1.04) Φ_h 101 (1.51) Φ_{r-s} 93 (3.92) $S_{mod}{}^g$ ∼90^h $S_{Ad}{}^i$ 78 (8.46) k
(4^2-3,4,5-4)12G1-CH_2OH	k 76 (30.20) -k 87 (11.89) k 106 (15.44) Φ_h 120 (6.26) i k 41 (7.26) Φ_h 119 (6.08) i	i 116 (6.79) Φ_h 23 (4.03) k
(4^2-3,4,5-4^2)12G1-CH_2OH	k 129 (3.32) k 137 (35.51) i k 59 (3.40) k 136 (24.28) i	i 125 (24.14) k 48 (1.45) k
(4^2-3,4,5-4^3)12G1-CH_2OH	k 133 (46.83) i k 133 (46.24) i	i 117 (46.02) k
(4^3-3,4,5)12G1-CH_2OH	k 130 (10.15) S_{Ad} 178 (15.17) i k 125 (8.80) S_{Ad} 177 (15.09) i	i 173 (14.81) S_{mod} ∼110^j S_{Ad} 102 (8.73) k
(4^3-3,4,5-4)12G1-CH_2OH	k 112 (11.92) -k 121 (9.53) Φ_{r-s} 141 (15.66) Φ_h 153 (10.44) i -k 68 (6.10) k 110 (13.14) Φ_{r-s} 144 (1.23) Φ_h 152 (9.67) i	i 148 (10.86) Φ_h 123 (0.80) Φ_{r-s} 73 (0.93) k
(4^3-3,4,5-4^2)12G1-CH_2OH	k 136 (0.96) k 157 (37.78) i k 134 (0.28) k 157 (37.78) i	i 148 (20.82) k 76 (0.91) k

[a] Data from the first heating and cooling DSC scans are on the first line, and data from the second heating are on the second line. [b] k, crystalline. [c] Φ_h, $p6mm$ hexagonal columnar lattice. [d] i, isotropic. [e] Cub, $Pm\bar{3}n$ cubic lattice. [f] Φ_{r-s}, $p2mm$ simple rectangular columnar lattice. [g] S_{mod}, smectic modulated lattice. [h] Shoulder in the DSC at 1 °C/min cooling rate. [i] S_{Ad}, interdigitated smectic A. [j] This phase was only observed on cooling by XRD.

Table 2. Measured d-Spacings (in Å) of the $Pm\bar{3}n$ Cubic, Interdigitated Smectic (S_{Ad}), Modulated Smectic (S_{mod}), $p2mm$ Simple Rectangular Columnar (Φ_{r-s}), and $p6mm$ Hexagonal Columnar (Φ_h) Lattices Generated by **(4^n-3,4,5-4^m)12G1-CH_2OH** Dendrons (n = 1−3 and m = 0−3)

dendron	T (°C)	lattice	$d_{100}{}^a$ $d_{200}{}^b$ $d_{001}{}^c$ $d_{001}{}^d$ $d_{010}{}^f$	$d_{110}{}^a$ $d_{210}{}^b$ $d_{002}{}^c$ $d_{002}{}^d$ $d_{300}{}^f$	$d_{200}{}^a$ $d_{211}{}^b$ $d_{010}{}^e$ $d_{210}{}^f$	$d_{220}{}^b$ $d_{020}{}^e$ $d_{310}{}^f$	$d_{310}{}^b$ $d_{030}{}^e$ $d_{400}{}^f$	$d_{222}{}^b$ $d_{040}{}^e$ $d_{020}{}^f$	$d_{320}{}^b$ $d_{050}{}^e$ $d_{500}{}^f$	$d_{321}{}^b$ $d_{510}{}^f$	$d_{400}{}^b$ $d_{220}{}^f$	$d_{420}{}^b$ $d_{320}{}^f$	$d_{421}{}^b$	$d_{422}{}^b$	$d_{520}{}^b$
(4-3,4,5)12G1-CH_2OH	80	$p6mm$	38.3^a	21.7^a	18.6^a										
(4-3,4,5-4)12G1-CH_2OH	30	$p6mm$	49.1^a	28.7^a	24.8^a										
	70	$Pm\bar{3}n$	54.9^b	49.2^b	45.0^b	39.0^b	35.1^b		30.7^b	29.7^b	27.7^b	24.8^b			
(4-3,4,5-4^2)12G1-CH_2OH	82	$Pm\bar{3}n$	65.0^b	58.3^b	53.4^b	46.4^b	41.6^b	38.0^b	36.6^b	35.3^b	33.0^b	29.6^b	28.8^b	27.0^b	24.5^b
(4-3,4,5-4^3)12G1-CH_2OH	90	$Pm\bar{3}n$	81.6^b	73.9^b	68.3^b	59.3^b	52.4^b			43.9^b	41.3^b		36.3^b		
(4^2-3,4,5)12G1-CH_2OH	90	S_{Ad}	47.6^c	23.4^c											
	93	S_{mod}	44.9^d	22.3^d	179.5^e	89.8^e	60.4^e	40.8^e	36.1^e						
	104	$p2mm$	55.6^f		45.5^f		39.3^f		31.3^f	27.1^f	25.5^f	24.4^f			
	122	$p6mm$	48.3^a	27.3^a	23.6^a										
(4^2-3,4,5-4)12G1-CH_2OH	80	$p6mm$	55.1^a	31.7^a	27.7^a										
(4^2-3,4,5-4^2)12G1-CH_2OH	110	k													
(4^2-3,4,5-4^3)12G1-CH_2OH	120	k													
(4^3-3,4,5)12G1-CH_2OH	80	S_{Ad}	55.6^c	28.1^c											
	160	S_{mod}	51.7^d	26.3^d	251.3^e	117.4^e	78.1^e	62.2^e	44.2^e						
(4^3-3,4,5-4)12G1-CH_2OH	117	$p2mm$	81.2^f	71.3^f	63.7^f	53.0^f		40.1^f		37.3^f					
	146	$p6mm$	67.6^a	38.6^a	33.2^a										
(4^3-3,4,5-4^2)12G1-CH_2OH	150	k													

[a] d-Spacings of hexagonal columnar lattice. [b] d-Spacings of cubic $Pm\bar{3}n$ lattice. [c] d-Spacings of smectic S_{Ad} lattice. [d] These d-spacings arise from the usual S_{Ad}-like arrangement of modulated layer. [e] The peaks with very large d-spacings correspond to the large period modulation within the smectic layer. [f] d-Spacings of simple rectangular lattice.

scheme the compounds have identical dendron architectures but differ in the number of AB benzyl ether units (m = 0, 1, 2, 3) at the apex. Within a horizontal row the structures differ by the number of AB benzyl ether units (n = 1, 2, 3) in their branches. In all structures, $m + n = y$. Since the numbers in the short names of the dendrons refer to the substitution pattern of their repeat unit (i.e., 4- stands for AB; 3,4,5-, for AB_3; and 3,4-, for AB_2 derived repeat units), the composition and sequence of the hybrid dendrons are written in the short name (Schemes 1 and 6). The most relevant structural information of this library is summarized in Scheme 6, i.e., lattice symmetry, lattice parameters (a,b) and temperature at which they were measured, diameter D of the supramolecular cylindrical column or sphere for 2-D $p6mm$ columnar hexagonal (Φ_h) and 3-D $Pm\bar{3}n$ cubic

Table 3. Structural Characterization of Supramolecular Dendrimers Self-Assembled from **(4^{n}-3,4,5-4^{m})12G1-CH_2OH** (n = 1−3 and m = 0−3) Dendrons

dendron	T (°C)	lattice	$\langle d_{100}\rangle^{a}$ (Å)	a (a,b) (Å)	ρ_{20}^{b} (g/cm^3)	D(D_a, D_b) (Å)	μ'^{c}	μ
(4-3,4,5)12G1-CH_2OH	80	*p*6*mm*	37.7	43.5^{d}	1.02	43.5^{e}		5^{f}
(4-3,4,5-4)12G1-CH_2OH	30	*p*6*mm*	49.5	57.2^{d}	1.02	57.2^{e}		8^{f}
	70	$Pm\bar{3}n$		110.5^{g}	1.02	68.6^{h}	763	95^{i}
(4-3,4,5-4^2)12G1-CH_2OH	82	$Pm\bar{3}n$		131.6^{g}	1.02	81.6^{h}	1175	147^{i}
(4-3,4,5-4^3)12G1-CH_2OH	90	$Pm\bar{3}n$		165.6^{g}	1.02	102.7^{h}	2149	269^{i}
(4^2-3,4,5)12G1-CH_2OH	90	S_{Ad}		47.2^{j}		47.2^{j}		
	93	$S_{mod}{}^{k}$		44.8, 176.8^{k}				
	104	*p*2*mm*		156.7, 54.7^{l}	1.02	156.7, 54.7^{m}		19^{n}
	122	*p*6*mm*	47.6	55.0^{d}	1.02	55.0^{e}		6^{f}
(4^2-3,4,5-4)12G1-CH_2OH	80	*p*6*mm*	55.1	63.6^{d}	1.02	63.6^{e}		7^{f}
(4^2-3,4,5-4^2)12G1-CH_2OH	110	*k*						
(4^2-3,4,5-4^3)12G1-CH_2OH	120	*k*						
(4^3-3,4,5)12G1-CH_2OH	80	S_{Ad}		55.9^{j}		55.9^{j}		
	160	$S_{mod}{}^{k}$		52.2, 238.0^{k}				
(4^3-3,4,5-4)12G1-CH_2OH	117	*p*2*mm*		210.4 80.5^{l}	1.02	210.4 80.5^{m}		28^{n}
	146	*p*6*mm*	67.1	77.4^{d}	1.02	77.4^{e}		9^{f}
(4^3-3,4,5-4^2)12G1-CH_2OH	150	*k*						

^{a} averaged from all *p*6*mm* reflections: $\langle d_{100}\rangle = (d_{100} + \sqrt{3}d_{110} + \sqrt{4}d_{200})/3$. ^{b} ρ_{20} = experimental density at 20 °C. ^{c} Number of dendrons per unit cell $\mu' = (a^3N_A\rho)/M$. ^{d} *p*6*mm* hexagonal columnar lattice parameter $a = 2\langle d_{100}\rangle\times 98/\sqrt{3}$. ^{e} Experimental column diameter $D = 22\langle d_{100}\rangle\times 98/\sqrt{3}$. ^{f} Number of dendrons per 4.7 Å column stratum $\mu = (\sqrt{3}N_AD^2t\rho)/2M$ (Avogadro's number N_A = 6.022 045 5 × 10^{23} mol^{-1}, the average height of the column stratum t = 4.7 Å, M = molecular weight of dendron). ^{g} $Pm\bar{3}n$ cubic lattice parameter $a = (\sqrt{2}\, d_{110} + \sqrt{4}\, d_{200} + \sqrt{5}\, d_{210} + \sqrt{6}\, d_{211} + \sqrt{8}\, d_{220} + \sqrt{10}\, d_{310} + \sqrt{12}\, d_{222} + \sqrt{13}\, d_{320} + \sqrt{14}\, d_{321} + \sqrt{16}\, d_{400} + \sqrt{20}\, d_{420} + \sqrt{21}\, d_{421} + \sqrt{24}\, d_{422} + \sqrt{29}\, d_{520})/14$. ^{h} Experimental sphere diameter $D = 2\sqrt[3]{3a^3/32\pi}$. ^{i} Number of dendrons per $Pm\bar{3}n$ spherical dendrimer $\mu = \mu'/8$. ^{j} Smectic A lattice parameter (= layer separation) $a = (d_{001} + 2d_{002} + 3d_{003} + 4d_{004} + 5d_{005} + 6d_{006})/6$. ^{k} Modulated smectic; the layer separation and the periodicity of the modulation along the layers, respectively. ^{l} *p*2*mm* = simple rectangular columnar lattice parameters a and b; $a = hd$, $b = kd$; (h0) and (k0) from diffractions. ^{m} Experimental elliptical column diameters of *p*2*mm* simple rectangular columnar lattice $D_a = a$ and $D_b = b$. ^{n} Number of dendrons per elliptical *p*2*mm* simple rectangular column of single stratum thickness (t = 4.7 Å) $\mu = (N_Aabt\rho)/M$.

lattices, the smectic layer spacing (a) of the 1-D interdigitated smectic A lattice (S_{Ad}), the lattice dimensions (a,b) of the 2-D *p*2*mm* columnar simple rectangular (Φ_{r-s}) and *c*2*mm* centered rectangular (Φ_{r-c}) lattices self-assembled from supramolecular elliptical columns, and the long and short diameters (D_a, D_b) of the ellipse.

Column diameters were calculated under the approximation of close packed hard cylinders. D_a and D_b were obtained as $D_b = b$ and $D_a = (a/\sqrt{3})$. Note that, while columns are treated as impenetrable hard cylinders, the calculation of the reported sphere diameters for the $Pm\bar{3}n$ cubic phase is based on penetrating spheres whose volume is $a^3/8$. If the hard sphere approximation was employed, the sphere diameter would be $D = a/2$. The number of dendrons μ forming a 4.7 Å thick cross-section of a column[3l] is also reported. Table 1 provides detailed information about the transition temperatures determined by DSC of the supramolecular dendrimers self-assembled from the AB_3 dendrons from Scheme 6. The DSC traces of the compounds reported in Table 1 are available in the Supporting Information (Figure S1). Tables 2 and 3 summarize the *d*-spacings and structural parameters calculated from XRD and density measurements. Representative powder X-ray diffractograms of selected lattices are shown in Figure 1, while thermal optical polarized micrographs of various phases are presented in Figure 2.

All first generation hybrid dendrons from Scheme 6 self-assemble in supramolecular dendrimers. Let us first inspect the left column that depicts the series **(4-3,4,5-4^{m})12G1-CH_2OH** in which m varies from 0 to 3. The dendrons with m = 0 and m = 1 self-assemble in columns that self-organize in a Φ_h lattice. In the closed packed rigid bodies approximation, the diameter of the cylindrical column increases from 43.5 to 57.2 Å when m changes from 0 to 1. This is an expected trend since the addition of an extra benzyl ether provides a maximum increase in dendron length of 6 Å and, therefore, in dendron diameter of 12 Å. At higher temperatures the columnar dendrimer from m = 1 undergoes a reversible transition to spherical supramolecular dendrimers that form the cubic $Pm\bar{3}n$ phase (Figure 3). The direct visualization of this transition by X-ray experiments is illustrated in Figure 3. The diffractograms from the *p*6*mm* lattice to the $Pm\bar{3}n$ lattice of Figure 3 were taken at every 4 °C with a heating rate of 5 °C/min.

If one takes as the sphere diameter D the spacing between spheres along face bisectors (white spheres Scheme 6; these are the directions of closest approach[3e,3p]), then $D = a/2 = 55.3$ Å for m = 1 dendron, i.e., slightly smaller than D of the cylindrical column. When m increases from 1 to 2 and to 3, the dendrons self-assemble only in spherical supramolecular dendrimers. The sphere diameters for m = 1 (D = 68.6 Å) and m = 2 (D = 81.6 Å) are in agreement with the expected increase based on the addition of an extra benzyl ether (6 Å) in the apex of the dendron and two benzyl ethers (12 Å) in the focal point of the supramolecular dendrimer.

However, the transition from the dendron with m = 2 to m = 3 is accompanied by an increase of 21.1 Å in the supramolecular sphere diameter rather than the maximum expected value of 12 Å. Consequently, the diameter of the sphere self-assembled from **(4-3,4,5-4^3)12G1-CH_2OH** is 102.7 Å. Regardless of generation number, this is the largest diameter obtained so far for a spherical supramolecular dendrimer. Previously the largest one was obtained from a third generation dendron (D = 75 Å).[3l] One possible explanation for this dramatic increase in diameter is a supramolecular sphere with a hollow center. Research to confirm this hypothesis is in progress. The increase in sphere

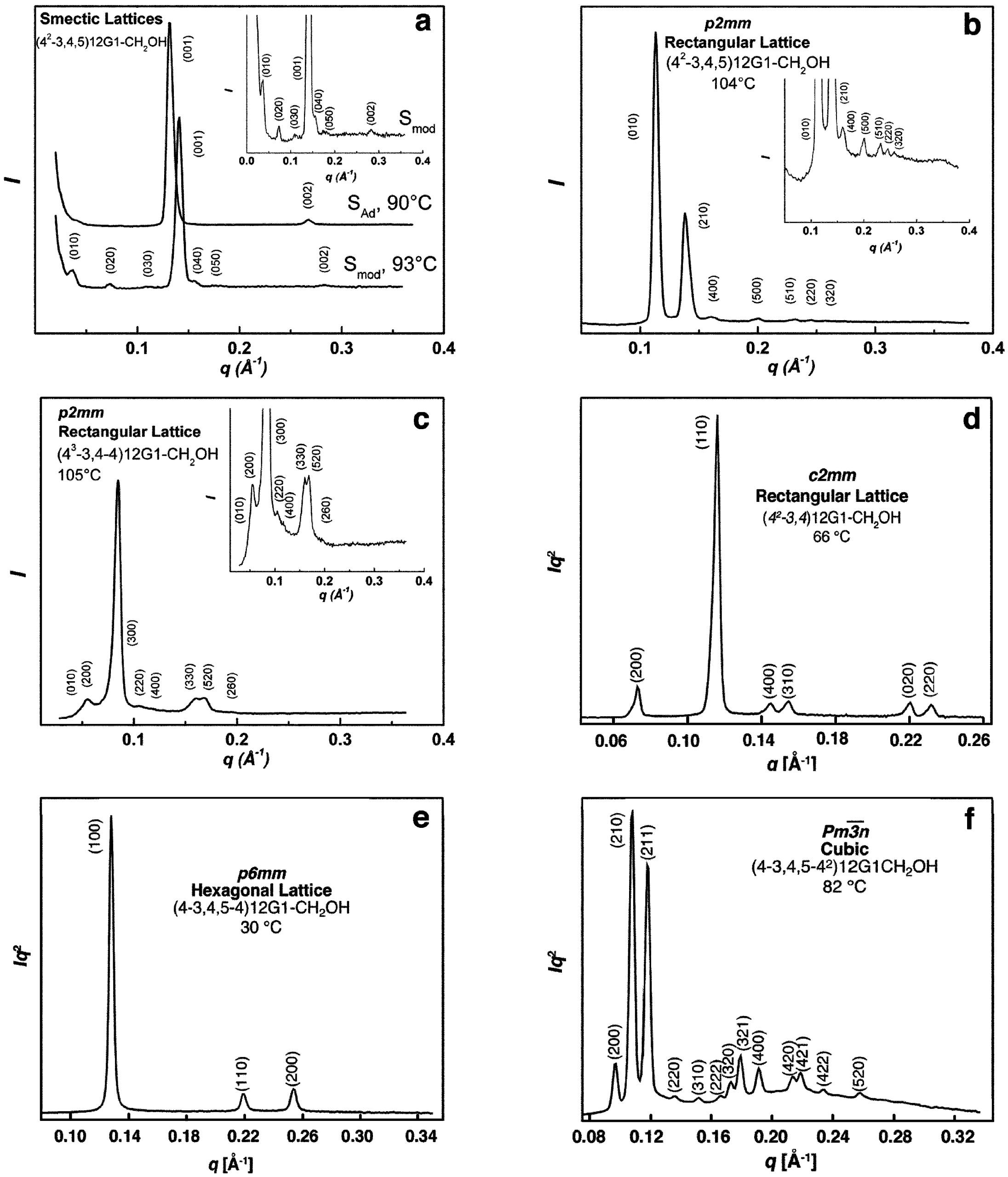


Figure 1. X-ray diffractograms of the various LC phases at different temperatures. (a) smectic phases (S_{Ad} and S_{mod}); (b) and (c) *p2mm* simple rectangular columnar phases; (d) *c2mm* centered rectangular columnar phase; (e) *p6mm* hexagonal columnar phase; and (f) $Pm\bar{3}n$ cubic phase.

diameter produced by the increase from $m = 1$ to $m = 3$ is accompanied by a decrease in the solid angle[12] of the conical dendrimer and by an accompanying increase in μ from 95 for $m = 1$ to 147 for $m = 2$ and to 269 for $m = 3$. In view of the previous results on the dependence of supramolecular dimensions on solid angle and generation number, this decrease in solid angle seems unexpected.[12] However, previous trends were obtained for a dendron with identical primary structure and different generations. The current results demonstrate that the solid angle is only one of the structural parameters that determines this complex mechanism of self-assembly, at least in the case of dendrons with different primary structures. The calculated molar mass of the supramolecular dendrimer generated from the dendron with $m = 3$ is $M_{sphere} = 434\,757.8$. Regardless of generation, this is the largest molar mass supramolecular dendritic sphere synthesized to date.[3l,p] The previous largest molar mass supramolecular sphere ($M_{sphere} = 139\,342.5$) was self-assembled from the third generation dendron **(*4*-(*3,4*)^3)12G3-CO$_2$CH$_3$**[3l] and had $D = 75.0$ Å. The AB_3 dendrons with $m = 1$, 2, and 3 from Scheme 6 are the first examples of first generation dendrons that self-assemble in spherical dendrimers.[3l]

Increasing the number of AB benzyl ether repeat units in the branched part of the dendron to two per arm ($n = 2$) produces the series of dendrons shown in the middle column of Scheme 6. The mechanism of self-assembly of the dendrons reported in this column is strikingly different from that of those from

(11) Percec, V.; Holerca, M. N.; Uchida, S.; Cho, W.-D.; Ungar, G.; Lee, Y.; Yeardley, D. J. P. *Chem.—Eur. J.* **2002**, *8*, 1106.

(12) For the elaboration of the solid-angle concept to explain the correlation between molecular dendron structure and its supramolecular dendrimer dimensions, see: Ungar, G.; Percec, V.; Holerca, M. N.; Johansson, G.; Heck, J. A. *Chem.—Eur. J.* **2000**, *6*, 1258.

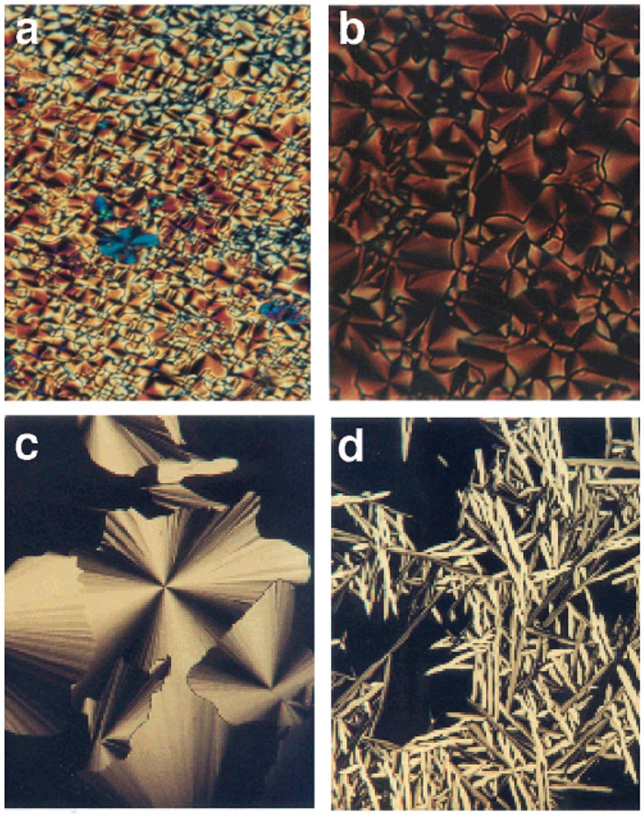


Figure 2. Representative optical polarized textures exhibited by the following: (a) **(4³-3,4,5)12G1-CH₂OH** obtained upon cooling from 143 to 125 °C with 1 °C/min (modulated smectic, S_{mod}); (b) **(4³-3,4)12G1-CH₂OH** obtained upon cooling from 183 to 176 °C with 1 °C/min (*c*2*mm* centered rectangular columnar lattice, Φ_{r-c}); (c) **(4²-3,4,5)12G1-CH₂OH** obtained upon cooling from 132 to 121 °C with 1 °C/min (*p*6*mm* hexagonal columnar lattice, Φ_h); (d) **(4²-3,4,5-4)12G1-CH₂OH** obtained upon cooling from 124 to 114 °C with 1 °C/min (*p*6*mm* hexagonal columnar lattice, Φ_h).

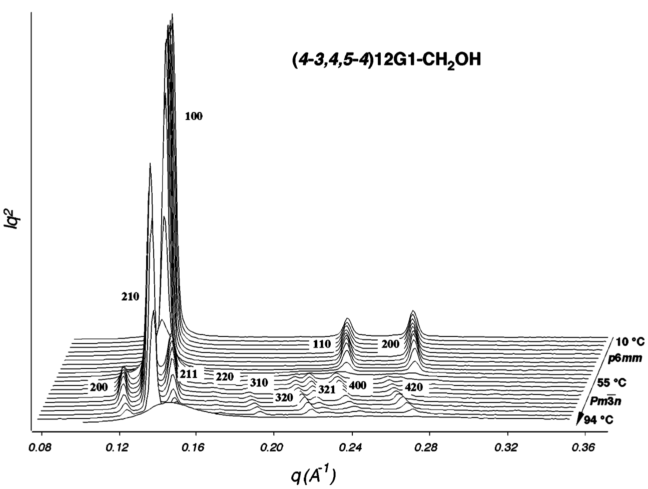


Figure 3. Series of X-ray diffractograms and corresponding phase assignments for **(4-3,4,5-4)12G1-CH₂OH**. The diffractograms from the *p*6*mm* lattice to the $Pm\bar{3}n$ lattice were taken at every 4 °C with a rate of heating of 5 °C/min.

the left column. Thus, $n = 2$ and $m = 0$ produces a dendron that self-organizes in smectic S_{Ad} and in the novel 2-D modulated smectic S_{mod} lattices. Non interdigitated S_A lattices were previously obtained from dendritic crown ethers.[3m] The detailed structural analysis of the novel S_{mod} lattice by electron density calculations is in progress. However, a schematic representation

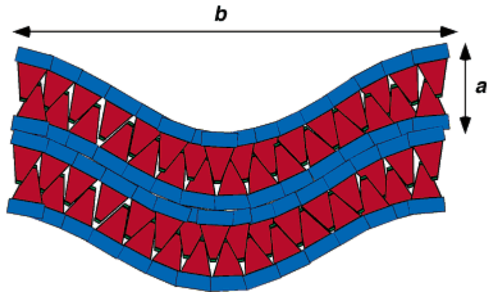


Figure 4. Schematic representation of the smectic modulated (S_{mod}) 2-D lattice (*a* and *b* lattice dimensions are reported in Scheme 6).

of the S_{mod} lattice with its lattice dimensions is outlined in Figure 4. At higher temperature, the smectic phase becomes 2-D *p*2*mm* (Φ_{r-s}), and at even higher temperature, it transforms into a *p*6*mm* hexagonal (Φ_h) phase. Most interestingly, the two diameters of the elliptical columns of Φ_{r-s} are very large, i.e., $D_a = 156.7$ Å and $D_b = 54.7$ Å. The diameter of the cylindrical column forming the Φ_h phase is within the expected range observed for **(4-3,4,5-4)12G1-CH₂OH** from the left column. The dendron **(4²-3,4,5-4²)12G1-CH₂OH** forms supramolecular columns with an expected diameter while the dendrons with $n = 2$ and $m = 3$ form 3-D crystals. Their structures were not yet determined. No spherical dendrimers are self-assembled from the dendrons reported in this middle column. Other examples of elliptical columns were self-assembled from first generation minidendrons equipped with functional groups that provide strong noncovalent interactions in their focal point.[3n,13]

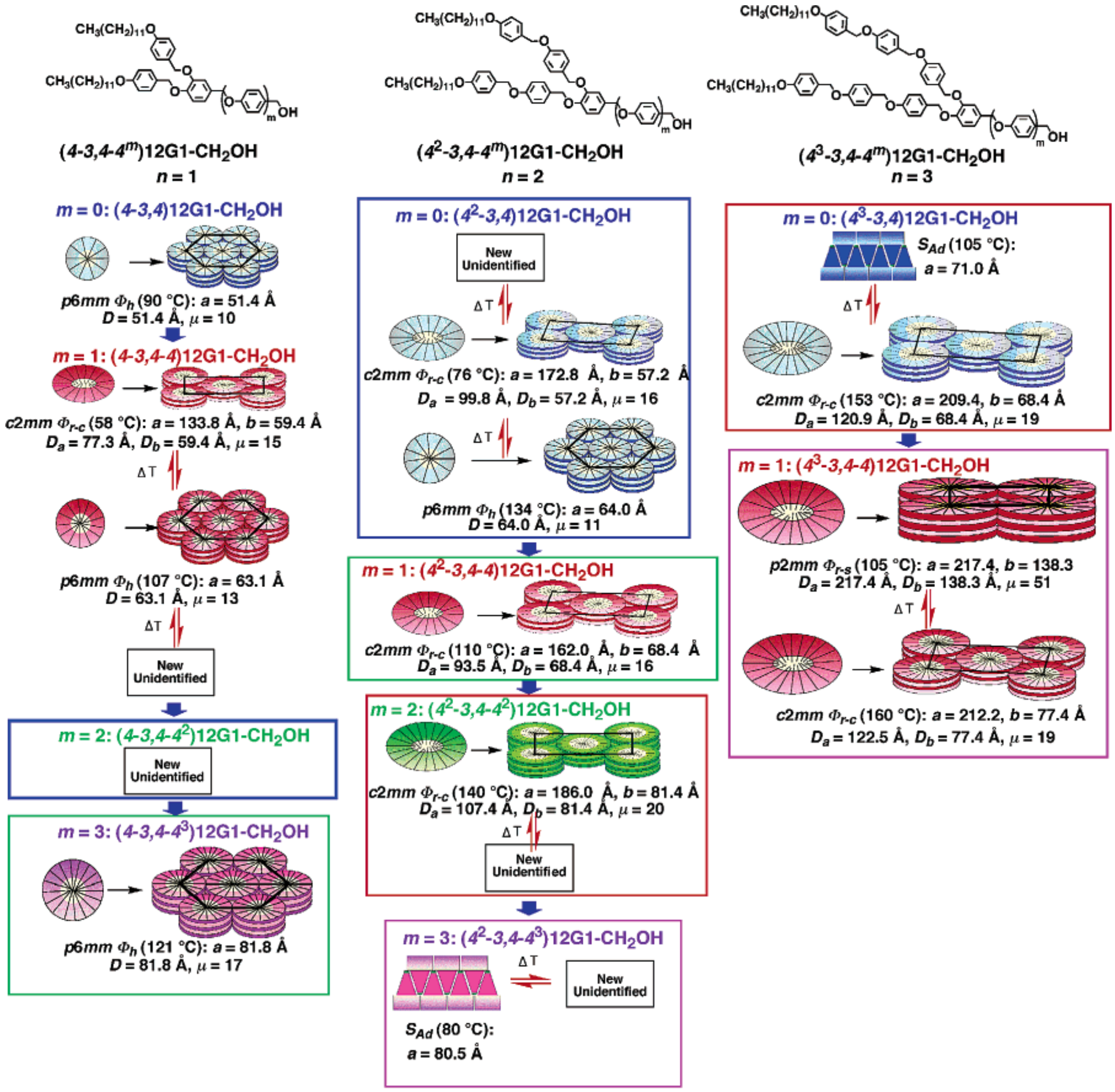
The right column of Scheme 6 lists AB_3 dendrons containing three oligo benzyl ethers in each branch ($n = 3$). The self-assembly of these dendrons as a function of *m* follows the same pattern as the dendrons from the middle column except that all lattice dimensions are larger. The dendron with $m = 0$ self-assemble in S_{Ad} and the new S_{mod} phases. The dendron with $m = 1$ self-assembles into a *p2mm* (Φ_{r-s}) lattice with extremely large elliptical column diameters, $D_a = 210.4$ Å and $D_b = 80.5$ Å. At higher temperature this lattice changes reversibly into a Φ_h lattice that is generated from cylindrical columns of expected diameter ($D = 77.4$ Å). As in the previous column, the dendron with $m = 2$ forms 3-D crystals that were not yet analyzed. The cylindrical columns obtained from **(4²-3,4,5-4)12G1-CH₂OH** and **(4³-3,4,5-4)12G1-CH₂OH** have diameters that are up to 20 Å larger than any of the similar structures self-assembled previously from larger generation dendrons.[3l]

The first generation hybrid AB_3 dendrons reported in Scheme 6 provide new mechanisms to construct cylindrical and elliptical columns, and spheres with substantially larger diameters than any of the supramolecular dendrimers reported previously from higher generation dendrons.[3l,p] Last but not least, the blue and green marked boxes contain self-assembling dendrons that are constitutional isomers. An interesting message comes from the analysis of these two constitutional isomeric pairs of dendrons: they self-assemble into different supramolecular structures that exhibit different properties.

Structural and Retrostructural Analysis of Supramolecular Dendrimers Self-Assembled from AB_2 Hybrid Dendrons. Scheme 7 summarizes the analysis of the AB_2 hybrid dendrons

(13) Percec, v.; Holerca, M. N.; Uchida, S.; Cho, W.-D.; Ungar, G.; Lee, Y.; Yeardley, D. J. P. *Chem.—Eur. J.* **2002**, *8*, 1106.

Scheme 7. Retrostructural Analysis of Supramolecular Dendrimers Self-Assembled from **(4^n-3,4-4^m)12G1-CH_2OH** (n = 1−3 and m = 0−3)



whose synthesis was described in Scheme 2. The data summarized in Scheme 7 will be discussed in the same manner as those from Scheme 6. Table 4 provides detailed information about the transition temperatures of the AB_2 dendrons from Scheme 7 as determined by DSC. Tables 5 and 6 summarize the *d*-spacings and structural parameters from XRD and density measurements.

A brief comparison of the left column in Scheme 6 with the left column in Scheme 7 demonstrates that no spherical supramolecular dendrimers self-assemble from the AB_2 library. The dendrons with $m = 0$ from the left column of Scheme 7 self-assemble into columns and in a new unidentified supramolecular structure.

The supramolecular dendron with $m = 1$ self-organizes in a *c2mm* columnar centered rectangular lattice (Φ_{r-c}) that undergoes a temperature-induced reversible change to a Φ_h lattice. The dendron with $m = 2$ self-assembles into a new supramolecular dendrimer that generates a novel unidentified lattice. The dendron with $m = 3$ self-assembles in cylindrical columns of an even larger diameter (D = 81.8 Å) than the one obtained from **(4^3-3,4,5-4)12G1-CH_2OH** (D = 77.4 Å, Scheme 6).

The middle column in Scheme 7 follows a trend that is almost the reverse of that in the middle column of Scheme 6. The dendron with $m = 0$ self-assembles into elliptical columns self-organized into a Φ_{r-c} lattice that becomes Φ_h at higher temperature. Both $m = 1$ and $m = 2$ derived dendrons self-assemble into elliptical columns forming the Φ_{r-c} lattice. A new unidentified lattice was observed at higher temperatures when $m = 2$. The dendron with $m = 3$ from this column behaves in a similar way as the dendron with $m = 0$ from the same column in Scheme 6. At low temperatures, it exhibits S_{Ad}, and at higher temperatures, it displays a new unidentified lattice that is different from the other new lattices mentioned in this manuscript.

The right-hand column of Scheme 7 shows dendrons that self-assemble in elliptical columns forming Φ_{r-c} (for $m = 0$) and Φ_{r-s} together with Φ_{r-c} (for $m = 1$). The Φ_{r-s} lattice generated from **(4^3-3,4-4)12G1-CH_2OH** contains columns with the largest lateral dimensions observed to date in supramolecular dendrimers (D_a = 217.4 Å and D_b = 138.3 Å).

In summary, the new library of first generation AB_2 hybrid dendrons from Scheme 7 provides mechanisms to self-

Table 4. Thermal Transitions of **(*4^n-3,4-4^m*)12G1-CH_2OH** (n = 1−3 and m = 0−3) Dendrons

dendron	thermal transitions (°C) and corresponding enthalpy changes (kcal/mol)[a]: heating	cooling
(*4-3,4*)12G1-CH_2OH	k[b] 0 (3.05) k 64 (6.17) k 71 (8.30) k 82 (8.50) Φ_h[c] 96 (1.28) i[d] k 13 (7.43) k 82 (12.13) Φ_h 96 (1.23) i	i 92 (1.17) Φ_h 57 (10.93) k 5 (6.30) k
(*4-3,4*-4)12G1-CH_2OH	k 67 (23.85) Φ_{r-c}[e] 106 (0.28) Φ_h 112 (0.01) LC[f] 116 (5.45) i k −2 (2.00) −k 50 (21.70) k 66 (21.42) Φ_{r-c} 105 (0.32) Φ_h 112 (0.01) LC[f] 116 (5.03) i	i 111 (5.52) LC[f] 105 (0.01) Φ_h 99 (0.35) Φ_{r-c} 4 (0.38) k −10 (0.90) k
(*4-3,4*-4^2)12G1-CH_2OH	k 86 (2.54) k 103 (18.86) LC[f] 128 (6.85) i −k 30 (10.05) k 68 (10.01) −k 78 (11.17) k 102 (11.15) LC 127 (6.71) i	i 124 (7.07) LC[f]
(*4-3,4*-4^3)12G1-CH_2OH	k 99 (1.14) k 119 (0.42) k 127 (15.27) Φ_h 147 (7.11) i -k 64 (4.32) k 127 (16.18) Φ_h 147 (7.09) i	i 144 (7.28) Φ_h 51 (4.84) k
(*4^2-3,4*)12G1-CH_2OH	k 64 (6.67) −k 68 (3.01) k 94 (13.67) 125 Φ_{r-c} (0.02) Φ_h 142 (1.87) i k 60 (4.55) k 91 (3.91) Φ_{r-c} 125 (0.02) Φ_h 141 (1.18) i	i 137 (1.24) Φ_{r-c} 75 (0.28) *LC*[f] 22 (4.47) k
(*4^2-3,4*-4)12G1-CH_2OH	k 94 (39.59) −k 97 (9.20) k 102 (4.90) Φ_{r-c}[e] 153 (12.48) i -k 28 (13.27) k 94 (20.20) Φ_{r-c} 152 (12.31) i	i 148 (12.77) Φ_{r-c}
(*4^2-3,4*-4^2)12G1-CH_2OH	k 106 (10.78) k 118 (2.06) k 137 (28.37) Φ_{r-c}[e] 155[g] LC[f]162 (11.93) i −k 71 (39.59) k 100 (2.22)[h] −k 108 (2.60) k 136 (26.12) Φ_{r-c} 155[g] LC[f] 161 (12.24) i	i 156 (13.26) LC[f] ∼140[g] Φ_{r-c} 51 (13.13) k
(*4^2-3,4*-4^3)12G1-CH_2OH	k 146 (0.50) k 159 (22.02) S_{Ad}[i] 176 (11.85) i −k 86 (5.11) k 159 (20.95) S_{Ad} 176 (11.53) i	i 172 (12.02) *LC*[f] 63 (9.58) S_{Ad}[i]
(*4^3-3,4*)12G1-CH_2OH	k 90 (16.51) k 114 (19.02)) Φ_{r-c} 177 (14.25) i −k 74 (10.83) k 86 (21.66) Φ_{r-c} 176 (14.05) i	i 172 (13.99) Φ_{r-c} 125 (0.58) S_{Ad} 61 (0.86) k
(*4^3-3,4*-4)12G1-CH_2OH	k 84 (15.54) k 121 (22.96) Φ_{r-c} 181 (16.14) i k 120 (16.30) Φ_{r-c}180 (14.84) i	i 176 (15.86) Φ_{r-c} 133 (0.62) Φ_{r-s}[j] 79 (12.26) k

[a] Data from the first heating and cooling DSC scans are on the first line, and data from the second heating are on the second line. [b] k, crystalline. [c] Φ_h, *p*6*mm* hexagonal columnar lattice. [d] i, isotropic. [e] Φ_{r-c}, *c*2*mm* centered rectangular columnar lattice. [f] LC, unknown liquid crystalline lattice. [g] Phase transition detected by XRD. [h] Sum of enthalpies from overlapped peaks. [i] S_{Ad}, interdigitated smectic A. [j] Φ_{r-s}, *p*2*mm* simple rectangular columnar lattice.

Table 5. Measured *d*-Spacings (in Å) of the Interdigitated Smectic (S_{Ad}), Modulated Smectic (S_{Mod}), *c*2*mm* Centered Rectangular (Φ_{r-c}), *p*2*mm* Simple Rectangular (Φ_{r-s}), and *p*6*mm* Hexagonal Columnar (Φ_h) Lattice Generated by **(*4^n-3,4-4^m*)12G1-CH_2OH** (n = 1−3 and m = 0−3) Dendrons

dendron	T (°C)	lattice	d_{100}[a] d_{200}[b] d_{110}[c] d_{001}[d] d_{010}[e]	d_{110}[a] d_{110}[b] d_{200}[c] d_{002}[d] d_{200}[e]	d_{200}[a] d_{310}[b] d_{010}[c] d_{003}[d] d_{300}[e]	d_{400}[b] d_{210}[c] d_{220}[e]	d_{020}[b] d_{020}[c] d_{400}[e]	d_{220}[b] d_{310}[c] d_{330}[e]	d_{510}[b] d_{510}[c] d_{520}[e]	d_{420}[b] d_{420}[c] d_{260}[e]	d_{600}[b]	d_{130}[b]
(*4-3,4*)12G1-CH_2OH	90	*p*6*mm*	44.9[a]	25.7[a]	22.1[a]							
(*4-3,4*-4)12G1-CH_2OH	58	*c*2*mm*	66.9[b]	53.9[b]	35.9[b]	33.8[b]	29.7[b]	27.2[b]	24.6[b]	22.3[b]		
	107	*p*6*mm*	54.3[a]	31.6[a]	27.4[a]							
	116	LC[e]										
(*4-3,4*-4^2)12G1-CH_2OH	117	LC[e]										
(*4-3,4*-4^3)12G1-CH_2OH	121	*p*6*mm*	71.2[a]	40.8[a]	35.2[a]							
(*4^2-3,4*)12G1-CH_2OH	76	*c*2*mm*	86.4[b]	54.2[b]	41.0[b]	43.7[b]	28.6[b]	27.0[b]				
	134	*p*6*mm*	55.3[a]	32.0[a]	27.7[a]							
(*4^2-3,4*-4)12G1-CH_2OH	110	*c*2*mm*	81.0[b]	62.6[b]	42.7[b]	41.2[b]	34.2[b]	31.7[b]	29.8[b]	26.4[b]		
(*4^2-3,4*-4^2)12G1-CH_2OH	140	*c*2*mm*	93.0[c]	74.2[c]	49.6[c]	47.0[c]	40.7[c]	37.3[c]	34.4[c]		31.2[c]	27.0[c]
	160	LC[e]										
(*4^2-3,4*-4^3)12G1-CH_2OH	80	S_{Ad}	80.3[d]	40.3[d]								
	172	*LC*[e]										
(*4^3-3,4*)12G1-CH_2OH	105	S_{Ad}	71.7[d]	35.3[d]	23.6[d]							
	153	*c*2*mm*	105.8[b]	65.1[b]	49.1[b]	52.9[b]	34.2[b]	32.5[b]				
(*4^3-3,4*-4)12G1-CH_2OH	105	*p*2 mm	136.6[e]	110.2[e]	73.1[e]	58.7[e]	53.2[e]	38.8[e]	36.7[e]	32.2[e]		
	160	*c*2*mm*	106.1[b]	72.5[b]	53.0[b]	54.2[b]	38.7[b]	36.5[b]		31.6[b]		

[a] *d*-Spacings of the hexagonal columnar lattice. [b] *d*-Spacings of the centered rectangular lattice. [c] *d*-Spacings of the simple rectangular lattice. [d] *d*-Spacings of interdigitated smectic (S_{Ad}) lattices. [e] Unknown LC lattice.

assemble supramolecular columns with large dimensions that self-organize in previously known Φ_h, Φ_{r-s}, and Φ_{r-c} lattices[3b,n] and in three new supramolecular dendrimers that self-organize into unidentified lattices. The dimensions of these first generation supramolecular dendrimers are much larger than of those obtained previously from higher generation dendrons.[3l,p] Four pairs of constitutional isomeric dendrons from Scheme 7 are indicated by frames of the same color (pink, blue, green, and

Table 6. Structural Characterization of Supramolecular Dendrimers Self-Assembled from **(4^n-3,4-4^m)12G1-CH$_2$OH** (n = 1−3 and m = 0−3) Dendrons

dendron	T (°C)	lattice	$\langle d_{100}\rangle^a$ (Å)	a (a,b) (Å)	ρ_{20}^b (g/cm^3)	D (D_a, D_b) (Å)	μ
(4-3,4)12G1-CH$_2$OH	90	*p6mm*	44.5	51.4[c]	1.03	51.4[d]	10[e]
(4-3,4-4)12G1-CH$_2$OH	58	*c2mm*		133.8, 59.4[f]	1.03	77.3, 59.4[g]	15[h]
	107	*p6mm*	54.6	63.1[c]	1.03	63.1[d]	13[e]
	116	LC[i]					
(4-3,4-4^2)12G1-CH$_2$OH	117	LC[i]					
(4-3,4-4^3)12G1-CH$_2$OH	121	*p6mm*	70.8	81.8[c]	1.02	81.8[d]	17[e]
(4^2-3,4)12G1-CH$_2$OH	76	*c2mm*		172.8, 57.2[f]	1.02	99.8, 57.2[g]	16[h]
	134	*p6mm*	55.4	64.0[c]	1.02	64.0[d]	11[e]
(4^2-3,4-4)12G1-CH$_2$OH	110	*c2mm*		162.0, 68.4[f]	1.03	93.5, 68.4[g]	16[h]
(4^2-3,4-4^2)12G1-CH$_2$OH	140	*c2mm*		186.0, 81.4[f]	1.03	107.4, 81.4[g]	20[h]
	160	LC[i]					
(4^2-3,4-4^3)12G1-CH$_2$OH	80	S_{Ad}		80.5[j]	1.03	80.5[k]	
	172	LC[i]					
(4^3-3,4)12G1-CH$_2$OH	105	S_{Ad}		71.0[j]		71.0[k]	
	153	*c2mm*		209.4, 68.4[f]	1.02	120.9, 68.4[g]	19[h]
(4^3-3,4-4)12G1-CH$_2$OH	105	*p2mm*		217.4, 138.3[l]	1.02	217.4, 138.3[m]	71[n]
	160	*c2mm*		212.2, 77.4[f]	1.02	122.5, 77.4[g]	19[h]

[a] $\langle d_{100}\rangle = (d_{100} + \sqrt{3}d_{110} + \sqrt{4}d_{200})/3$. [b] ρ_{20} = experimental density at 20 °C. [c] *p6mm* hexagonal columnar lattice parameter $a = 2\langle d_{100}\rangle/\sqrt{3}$. [d] Experimental column diameter $D = 2\langle d_{100}\rangle/\sqrt{3}$. [e] Number of dendrons per 4.7 Å column stratum $\mu = (\sqrt{3}\ N_A D^2 t\rho)/2M$ (Avogadro's number $N_A = 6.022\ 045\ 5 \times 10^{23}$ mol^{-1}, the average height of the column stratum t = 4.7 Å, M = molecular weight of dendron). [f] *c2mm* = centered rectangular columnar lattice parameters a and b; $a = hd$, $b = kd$; (h0) and (k0) from diffractions. [g] Experimental elliptical column diameters of *c2mm* centered rectangular columnar lattice $D_a = a/\sqrt{3}$ and $D_b = b$. [h] Number of dendrons per elliptical *c2mm* centered rectangular column layer $\mu = (N_A abt\rho)/2M$. [i] Unknown LC lattice. [j] Smectic A lattice parameter $a = (d_{001} + 2d_{002} + 3d_{003})/3$. [k] Layer spacing. [l] *p2mm* = simple rectangular columnar lattice parameters a and b; $a = hd$, $b = kd$; d is the d-spacing corresponding to either (h0) or (k0) reflections. [m] Experimental elliptical column diameters of *p2mm* simple rectangular columnar lattice $D_a = a$ and $D_b = b$. [n] Number of dendrons per elliptical *p2mm* simple rectangular column layer $\mu = (N_A abt\rho)/M$.

Table 7. Thermal Transitions of Second Generation AB_3 and AB_2 Hybrid Dendrons

dendron	thermal transitions (°C) and corresponding enthalpy changes (kcal/mol)[a] heating	cooling
(4^2-(3,4,5)^2)12G2-CO$_2$Me	k 70.5 (7.95) Φ_h 158.4 (5.72) i k 69.8 (7.95) Φ_h 158.3 (7.78) i	i 153.6 (5.10) Φ_h −8.1 (13.5) k
(4^2-(3,4,5)^2)12G2-CH$_2$OH	k 42.5 (4.42) Φ_h 147.9 (2.95) i k 49.9 (3.71) Φ_h 147.3 (2.66) i	i 142.0 (3.00) Φ_h 105.7 (0.20) k
(4^3-(3,4,5)^2)12G2-CO$_2$Me	k 82.6 (38.3) k 133.4 (8.0) k 161.4 (119.2) i k 48.2 (38.1) k 55.9 (8.3) k 135.3 (9.5) k 161.3 (116.5) i	i 154.0 (104.2) k 126.6 (8.2) k 51.0 (7.3) k 19.0 (19.9) k
(4^2-3,4-3,4,5)12G2-CO$_2$Me	k −2.1 (16.5) Φ_h 181.4 (3.8) Cub 202.4 (3.3) i k −9.0 (10.1) Φ_h 173.4 (3.9) Cub 201.7 (3.4) i	i 198.3 (3.2) Cub 167.3 (1.6) Φ_h
(4-(3,4)^2)12G2-CO$_2$CH$_3$	k[b] 55 (14.39) Cub[c] 162 (7.46) i[d] k −17 (2.25) Cub 158 (6.04) i	i 153 (6.89) Cub −18 (3.12) k
(4-3,4-4-3,4)12G2-CO$_2$CH$_3$	k 77 (22.98) Φ_h[e] ∼100[f] Cub 165 (13.52) i k 83 Φ_h ∼100[f] Cub 165 (15.52) i	i 160 (14.15) Cub ∼100[f] Φ_h 51 (5.44) k
(4^2-3,4-4^2-3,4)12G2-CO$_2$CH$_3$	k 154 (38.28) Cub[g] 206 (20.17) i k 48 (2.02) Cub 205 (19.06) i	i 202 (20.65) Cub
(4-3,4-3,5)12G1-CO$_2$CH$_3$	k −15 (4.89) k 52 (1.31) k 77 (6.27)[h] Φ_h 103 (8.24) i k 14 (4.60) Φ_h 104 (8.05) i	i 91 (6.90) Φ_h 9 (4.43) k
(4-3,4-4-3,5)12G2-CO$_2$CH$_3$	k 67 (12.80) Φ_h 111 (8.18) i Φ_{r-c} 70 (0.40) Φ_h 110 (7.47) i	i 105 (6.84) Φ_h 59 (0.39) Φ_{r-c}[i]
(4^2-3,4-4^2-3,5)12G2-CO$_2$CH$_3$	k 121 (46.74) Φ_{r-c} 168 (25.61)[h] i k 97 (0.90) Φ_{r-c} 167 (26.01)[h] i	i 163 (27.04) Φ_{r-c} 92 (1.00) k

[a] Data from the first heating and cooling DSC scans are on the first line, and data from the second heating are on the second line. [b] k, crystalline. [c] Cub, $Pm\bar{3}n$ cubic lattice. [d] i, isotropic. [e] Φ_h, *p6mm* hexagonal columnar lattice. [f] Transition detected by thermal optical polarized microscopy and by XRD. [g] Cub, new unidentified cubic lattice. [h] Sum of enthalpies from overlapped peaks. [i] Φ_{r-c}, *c2mm* centered rectangular columnar lattice.

violet). As in the case of the AB_3 library, they self-assemble in different supramolecular dendrimers. The pink colored pair self-assembles in elliptical columns that have different lattice dimensions.

Structural and Retrostructural Analysis of Supramolecular Dendrimers Self-Assembled from Second Generation AB_3 Hybrid Dendrons. Only several examples of second generation AB_3 dendrons were prepared (Scheme 3). Their transition temperatures, structural and retrostructural analysis are summarized in Tables 7−9 and in the second column of Scheme 8. **(4^2-(3,4,5)^2)12G2-X** with X=CO$_2$CH$_3$ and CH$_2$OH self-assemble into cylindrical columns that self-organize in a

Table 8. Measured *d*-Spacings (in Å) of the $Pm\bar{3}n$ Cubic, *p*6*mm* Hexagonal Columnar (Φ_h), and *c*2*mm* Centered Rectangular Columnar (Φ_{r-c}) Lattices Generated by Second Generation AB$_3$ and AB$_2$ Hybrid Dendrons

dendron	*T* (°C)	lattice	$d_{100}{}^a$ $d_{200}{}^b$ $d_{110}{}^c$	$d_{110}{}^a$ $d_{210}{}^b$ $d_{200}{}^c$	$d_{200}{}^a$ $d_{211}{}^b$ $d_{220}{}^c$	$d_{210}{}^a$ $d_{220}{}^b$ $d_{310}{}^c$	$d_{222}{}^b$ $d_{400}{}^c$	$d_{310}{}^b$ $d_{020}{}^c$	$d_{320}{}^b$	$d_{321}{}^b$	$d_{400}{}^b$	$d_{420}{}^b$	$d_{421}{}^b$	$d_{520}{}^b$	$d_{422}{}^b$
(4^2-(3,4,5)^2)12G2-CO$_2$Me	130	*p6mm*	48.4^a	27.9^a	24.1^a										
(4^2-(3,4,5)^2)12G2-CH$_2$OH	120	*p6mm*	47.6^a	27.4^a	23.8^a										
(4^3-(3,4,5)^2)12G2-CO$_2$Me	120	*k*													
(4^2-3,4-3,4,5)12G2-CO$_2$Me	118	*p6mm*	57.5^a	33.3^a	28.9^a										
	182	$Pm\bar{3}n$	65.0^b	58.2^b	53.4^b				36.1^b	34.9^b	32.7^b				
(4-(3,4)^2)12G2-CO$_2$CH$_3$	89	$Pm\bar{3}n$	58.5^b	52.5^b	47.9^b	41.6^b	33.9^b	37.1^b	32.5^b	31.3^b	29.3^b				
(4-3,4-4-3,4)12G2-CO$_2$CH$_3$	85	*p6mm*	59.7^a	34.7^a	30.0^a										
	154	$Pm\bar{3}n$	78.9^b	70.9^b	64.4^b	56.7^b		50.5^b	44.4^b	42.7^b	40.2^b	35.9^b	35.1^b	30.0^b	32.7^b
(4^2-3,4-4^2-3,4)12G2-CO$_2$CH$_3$	153	Cub^d													
(4-3,4-3,5)12G2-CO$_2$CH$_3$	100	*p6mm*	49.0^a	28.4^a	24.6^a	18.5^a									
(4-3,4-4-3,5)12G2-CO$_2$CH$_3$	60	*c2mm*	56.3^c	87.3^c	28.4^c	44.4^c	42.2^c	30.1^c							
	100	*p6mm*	58.8^a	34.2^a	29.8^a										
(4^2-3,4-4^2-3,5)12G2-CO$_2$CH$_3$	160	*c2mm*	74.2^c	111.2^c	36.7^c		55.6^c	39.0^c							

^{a} *p6mm*, hexagonal columnar lattice. ^{b} $Pm\bar{3}n$, cubic lattice. ^{c} *c2mm*, centered rectangular lattice. ^{d} New unidentified cubic lattice.

Table 9. Structural Characterization of Supramolecular Dendrimers Self-Assembled from Second Generation AB$_3$ and AB$_2$ Hybrid Dendrons

dendron	*T* (°C)	lattice	$\langle d_{100}\rangle^a$ (Å)	*a* (*a*,*b*) (Å)	$\rho_{20}{}^b$ (g/cm^3)	*D* (D_a, D_b) (Å)	$\mu'^{\,c}$	μ
(4^2-(3,4,5)^2)12G2-CO$_2$Me	130	*p6mm*	48.3	55.9^d	(1.02)^e	55.9^f		2^g
(4^2-(3,4,5)^2)12G2-CH$_2$OH	120	*p6mm*	47.6	55.0^d	(1.02)^e	55.0^f		2^g
(4^3-(3,4,5)^2)12G2-CO$_2$Me	120	*K*						
(4^2-3,4-3,4,5)12G2-CO$_2$Me	118	*p6mm*	57.8	65.9^d	(1.02)^e	65.9^f		4^g
	182	$Pm\bar{3}n$		130.5^h	(1.02)^e	80.9^i		60^j
(4-(3,4)^2)12G2-CO$_2$CH$_3$	89	$Pm\bar{3}n$		117.3^h	0.99	72.8^i	637	80^j
(4-3,4-4-3,4)12G2-CO$_2$CH$_3$	85	*p6mm*	59.9	69.2^d	1.03	69.2^f		7^g
	154	$Pm\bar{3}n$		159.8^h	1.03	99.1^i	1469	184^j
(4^2-3,4-4^2-3,4)12G2-CO$_2$CH$_3$	153	Cub^k						
(4-3,4-3,5)12G2-CO$_2$CH$_3$	100	*p6mm*	49.1	56.7^d	1.00	56.7^f		5^g
(4-3,4-4-3,5)12G2-CO$_2$CH$_3$	60	*c2mm*		174.6, 60.2^l	1.01	100.5, 60.2^m		9^n
	100	*p6mm*	59.2	68.4^d	1.01	68.4^f		7^g
(4^2-3,4-4^2-3,5)12G2-CO$_2$CH$_3$	160	*c2mm*		222.4, 78.0^l	1.02	128.4, 78.0^m		11^n

^{a} For *p6mm*, $\langle d_{100}\rangle = (d_{100} + \sqrt{3}d_{110} + \sqrt{4}d_{200} + \sqrt{7}d_{210})/4$. ^{b} ρ_{20} = experimental density at 20 °C. ^{c} Number of dendrons per unit cell $\mu' = (a^3N_A\rho)/M$. ^{d} *p*6*mm* hexagonal columnar lattice parameter $a = 2\langle d_{100}\rangle/\sqrt{3}$. ^{e} Estimated value. ^{f} Experimental column diameter $D = 2\langle d_{100}\rangle/\sqrt{3}$. ^{g} Number of dendrons per 4.7 Å column stratum $\mu = (\sqrt{3}\ N_AD^2t\rho)/2M$ (Avogadro's number $N_A = 6.022\ 045\ 5 \times 10^{23}$ mol^{-1}, the average height of the column stratum $t = 4.7$ Å, M = molecular weight of dendron). ^{h} $Pm\bar{3}n$ cubic lattice parameter $a = (\sqrt{3}d_{110} + \sqrt{4}d_{200} + \sqrt{5}d_{210} + \sqrt{6}d_{211} + \sqrt{8}d_{220} + \sqrt{10}d_{310} + \sqrt{12}d_{222} + \sqrt{13}d_{320} + \sqrt{14}d_{321} + \sqrt{16}d_{400} + \sqrt{20}d_{420} + \sqrt{21}d_{421} + \sqrt{24}d_{422} + \sqrt{29}d_{520})/14$. ^{i} Experimental sphere diameter $D = 2\sqrt[3]{3a^3/32\pi}$. ^{j} Number of dendrons per spherical dendrimer $\mu = \mu'/8$. ^{k} New unidentified cubic lattice. ^{l} *c2mm* centered rectangular columnar lattice parameters *a* and *b*; $a = 2d_{200}$, $b = 2d_{020}$. ^{m} Experimental elliptical column diameters of *c2mm* rectangular columnar lattice $D_a = a/\sqrt{3}$ and $D_b = b$. ^{n} Number of dendrons per elliptical column layer $\mu = (N_Aabt\rho)/2M$.

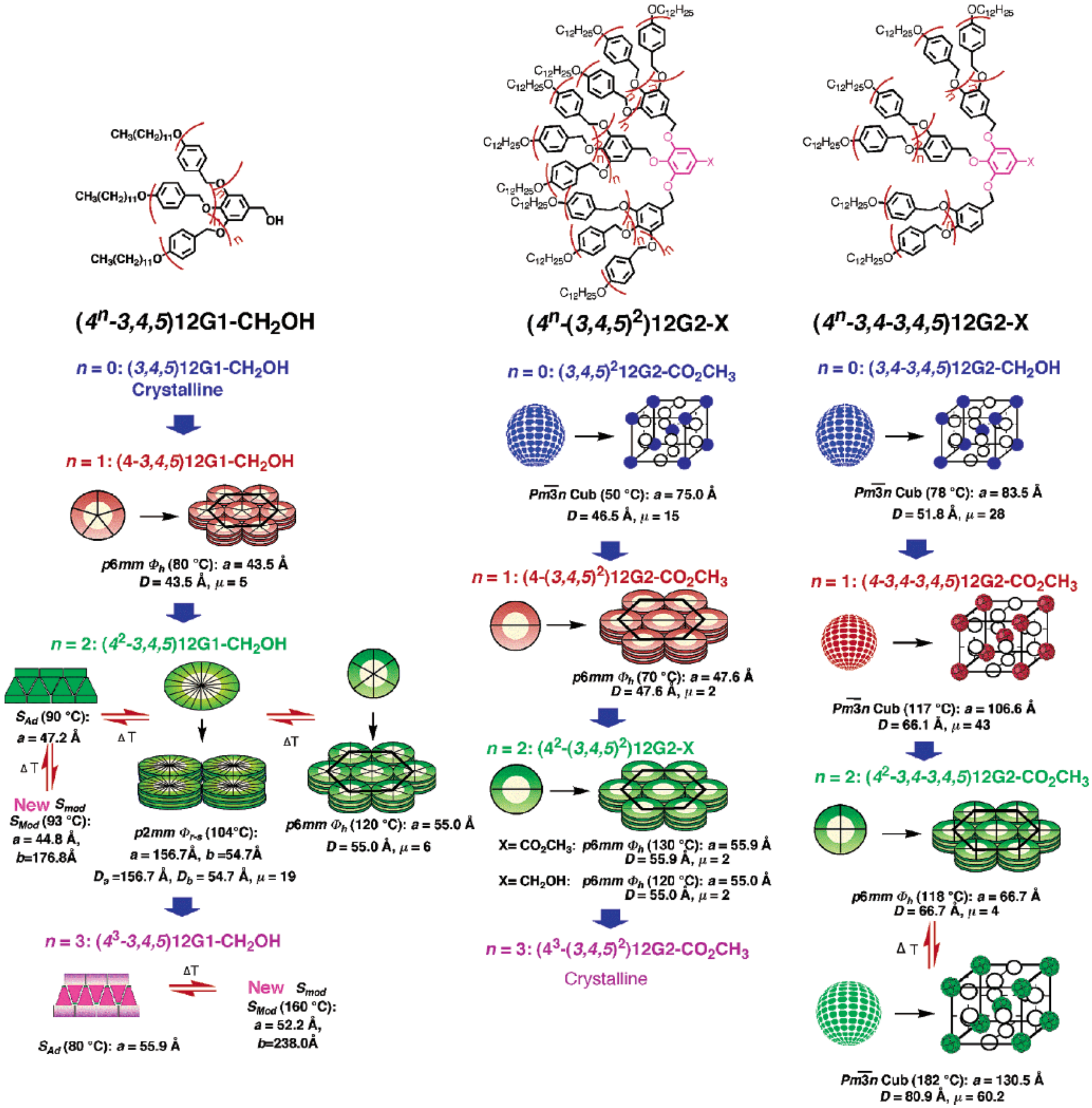
Φ_h lattice. **(4^3-(3,4,5)^2)12G2-CO$_2$CH$_3$** forms a 3-D crystal. **(4^2-3,4-3,4,5)12G2-CO$_2$CH$_3$** self-assembles in a cylindrical column that generates a Φ_h lattice (third column of Scheme 8). Although the maximum diameter of **(4^2-3,4-3,4,5)12G2-CO$_2$CH$_3$** should be smaller than that of **(4^2-(3,4,5)^2)12G2-X**, its experimental value is in fact more than 10 Å larger. This value can be explained by the difference between the solid angle of these two dendrons (Scheme 8).[3l,12] The second generation of the column-forming dendrons reported in Schemes 3 and 8 are the highest molar mass second generation dendrons synthesized so far.[3l] They are of particular interest for the design of self-organizable cylindrical macromolecules derived from dendronized polymer backbones.[6]

Influence of the Number of AB Repeat Units (*n*) on the Self-Assembly of AB$_3$ Hybrid Dendrons. For a simpler analysis, Scheme 8 provides the horizontal structural information of all AB$_3$ hybrid dendrons from Scheme 6 arranged in columns. This scheme allows one to understand the role of the number of AB repeat units from each branch of the dendron, *n*, on its mode of self-assembly. The left column summarizes the series **(4^n-3,4,5)12G1-CH$_2$OH**. When $n = 0$, the dendron forms a 3-D crystal. Increasing *n* to 1 produces a dendron that self-organizes in a cylindrical column. The dendron with $n = 2$ forms, depending on temperature, smectic, Φ_{r-s}, and Φ_h phases. The dendron with $n = 3$ produces only smectic phases. Therefore, in this series the increase of *n* decreases the tendency to self-assemble in 2-D supramolecular columns and increases the tendency to form 1-D and 2-D smectic phases.

The second column in Scheme 8 summarizes the self-assembly data for **(4^n-(3,4,5)^2)12G2-X**. The first two members of this series, **(3,4,5)^{2}12G2-CO$_2$CH$_3$**[3f,o] and **(4-(3,4,5)^2)12G2-CH$_2$OH**[3f] were reported previously and are shown here for comparison. The increase in *n* from 0 to 2 changes the self-assembly mode from spheres to cylindrical columns. The dendron with $n = 3$ forms only a 3-D crystal.

The trend in the last column of Scheme 8 resembles that in the middle column except that even at $n = 2$ a combination of self-assembly in cylindrical columns and spheres persists.

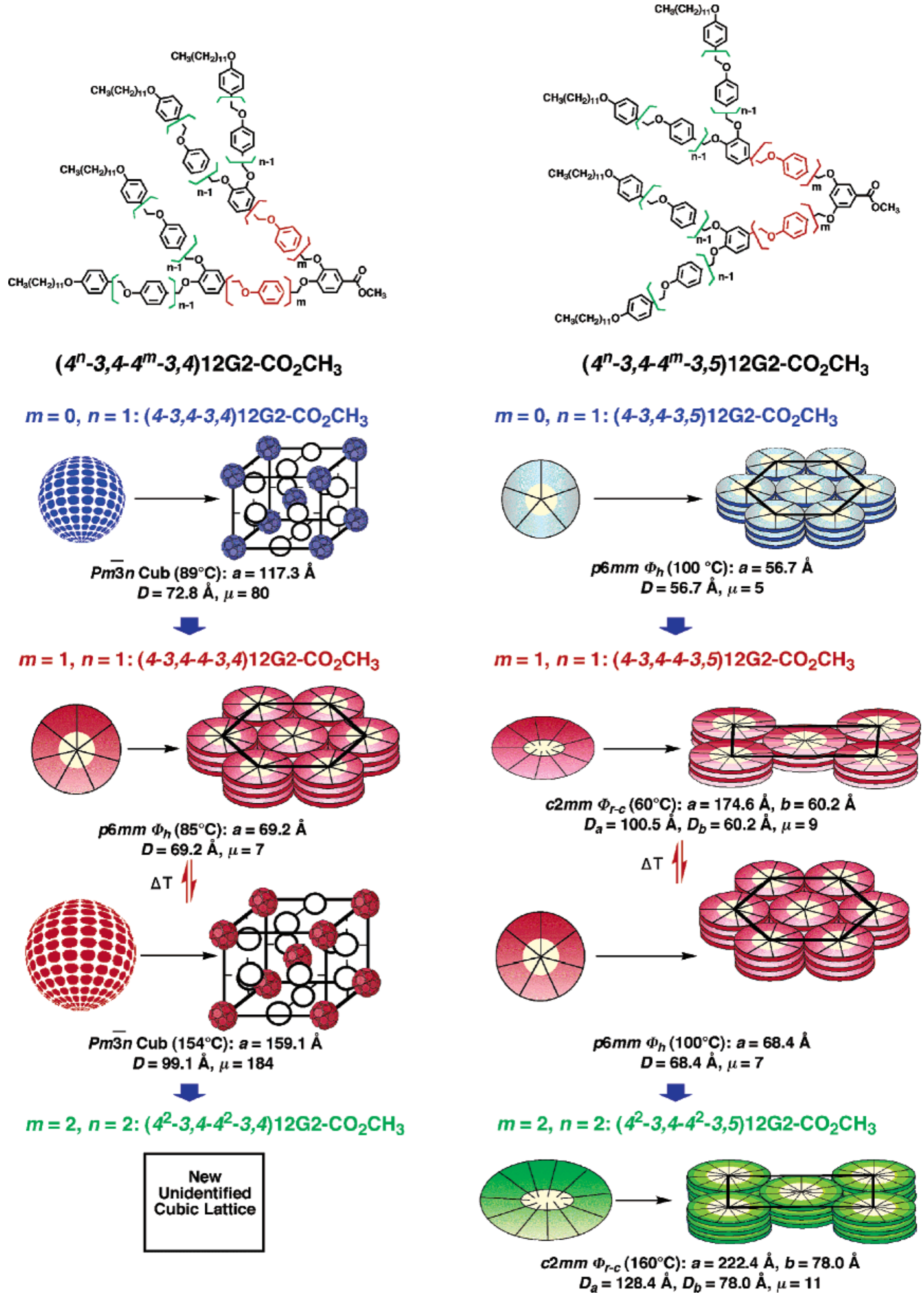
Scheme 8. Retrostructural Analysis of Supramolecular Dendrimers Self-Assembled from Second Generation AB_3 Hybrid Dendrons



Structural and Retrostructural Analysis of Supramolecular Dendrimers Self-Assembled from Second Generation AB_2 Hybrid Dendrons. The data of the structural and retrostructural analysis of the second generation AB_2 hybrid dendrons from Scheme 4 are reported in Tables 7−9. Scheme 9 summarizes their structural and retrostructural analysis. All hybrid dendrons in the left column of Scheme 9 are constitutional isomers of those from the right column of the same scheme. The only structural difference between these two columns is the isomerism of the AB_2 repeat unit at the focal point. The molecules in the left-hand column have a 3,4-disubstituted methyl benzoate repeat unit, while those in the right-hand column have one that is 3,5-disubstituted at their apex. All pairs of constitutional isomers self-assemble in different supramolecular structures. The 3,5-disubstituted apex favors self-assembly in cylindrical and elliptical columns, while the 3,4-apex mediates self-assembly in supramolecular spheres and cylindrical columns.

In the left column of Scheme 9, the increase in n and m maintains the ability of the dendrons to self-assemble into supramolecular spheres. The dendron with $n = 1$, $m = 1$ forms also a cylindrical column. An increase in n and m in the right column causes elliptical columns (Φ_{r-c}) to be favored over circular columns (Φ_h). The dendron with $m = 2$ and $n = 2$ self-organizes in a new unidentified cubic lattice. In both columns from Scheme 9, the diameter of the supramolecular dendrimer increases with the increase in n and m. A much larger increase in diameter is obtained by the strategy outlined in Scheme 9 than

Scheme 9. Retrostructural Analysis of Supramolecular Dendrimers Self-Assembled from Second Generation AB_2 Hybrid Dendrons



by the one reported in Scheme 8. The analysis of the mode and mechanism of self-assembly of the supramolecular dendrimers reported here is in progress.

Conclusions

Design principles for the synthesis of libraries of first generation AB_3 and AB_2 self-assembling dendrons starting from combinations of nondendritic AB and dendritic AB_3 and AB_2 building blocks, i.e., $(AB)_y{-}AB_3$ and $(AB)_y{-}AB_2$ (where $y =$ 1 to 11), incorporated via various primary structures in the dendron architecture were elaborated. The first generation supramolecular dendrimers synthesized via these principles self-organize in most of the lattices exhibited previously by larger generations of supramolecular dendrimers and exhibit up to three times larger dimensions than the previously designed higher generations of supramolecular dendrimers. These experiments have also demonstrated the capability of the primary structure in the design of an unexpectedly rich supramolecular structural diversity from an extremely small number of building blocks. The analysis of four libraries of first and second generation dendrimers based on these new architectures allowed the discovery of six new lattices, one elucidated (the 2-D smectic modulated) and five unelucidated. One of these five new lattices is an unknown cubic phase. The simplicity of the architectural design reported here, together with the large diversity of AB building blocks commercially available or synthetically accessible, open numerous pathways for the design of self-organizable supramolecular nanostructures that are of interest for the design of complex soft-matter.[14] Given the previously reduced number of column-forming self-assembling dendrons[3l] and their potential in self-processed supramolecular electronic and optoelectronic materials,[3n] surface nanopatterning,[3d] and other complex organic nanostrutures,[14−17] the architectural design principles reported here will most probably expand the synthetic capabilities of this field.

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Experimental Section

The synthesis of all dendrons, their structural analysis, and techniques used are based on methods elaborated in our laboratory.[3l,n,p] They are presented in the Supporting Information.

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Supporting Information Available: Experimental section containing techniques, materials, the synthesis, and analytical data for all dendrons (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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