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Synthesis and Structural Analysis of Two Constitutional Isomeric Libraries of AB$_2$-Based Monodendrons and Supramolecular Dendrimers

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Abstract: The synthesis and structural analysis of two constitutional isomeric libraries of self-assembling AB$_2$ monodendrons based on 3,4- and 3,5-disubstituted benzyl ether internal repeat units containing four different first generation monodendrons, i.e., 3,4,5-tris(*n*-dodecan-1-yloxy)benzyl ether, 3,4-bis(*n*-dodecan-1-yloxy)-benzyl ether, 3,4,5-tris[*p*-(*n*-dodecan-1-yloxy)benzyloxy]benzyl ether, and 3,4-bis[*p*-(*n*-dodecan-1-yloxy)-benzyloxy]benzyl ether, on their periphery are described. Regardless of the repeat unit on their periphery, the first three or four generations of the 3,4-disubstituted series of monodendrons self-assemble into spherical supramolecular dendrimers that self-organize into a $Pm\bar{3}n$ 3-D cubic lattice while the same generations of the 3,5-disubstituted series of monodendrons self-assemble into cylindrical supramolecular dendrimers that self-organize into a $p6mm$ hexagonal columnar 2-D lattice. The internal repeat unit of the monodendrons determines the shape of the supramolecular dendrimers. However, for a particular internal repeat unit, the architecture from its periphery determines the size of the monodendron, the number of monodendrons that self-assemble into a supramolecular dendrimer, the solid angle of the monodendron, and the dependence of the size of the supramolecular dendrimer on generation number. Since ultimately all monodendrons must reach the shape of a single sphere, the diameter of cylindrical and spherical supramolecular dendrimers constructed from these building blocks is limited to less than 100 Å. The library of 3,5-disubstituted monodendrons also provided the first five examples of supramolecular dendrimers that undergo reversible shape changes induced by temperature and functionality at their focal point. In addition, a spherical supramolecular dendrimer based on a 3,5-disubstituted repeat unit that self-assembles in an $Im\bar{3}m$ 3-D cubic lattice was discovered in the same library. The structural information generated by these two AB$_2$ and the previously reported AB$_3$ libraries of *quasi-equivalent* monodendrons provides building blocks that enable the construction of externally regulated functional supramolecular, macromolecular, and single-molecule-based nanosystems self-organizable in predictable lattices.

Introduction

In the past decade, dendrimers[1a,c] and monodendrons[1b,c] provided some of the most powerful entries to building blocks employed in the synthesis of complex functional nanostructures.[1] New methodologies to access strategies for the design of controlled microenvironment,[2a−c,h] site isolation,[2a−f] antenna effect,[2d,g−i] carriers for drugs, genes,[1j] and contrast agents in medicine and diagnostics,[1r] etc., have been developed with the aid of dendritic building blocks.

We are involved in the elaboration of strategies for the synthesis of monodendritic building blocks that self-assemble in bulk into supramolecular dendrimers with well-defined shapes that subsequently self-organize and co-organize in lattices and superlattices. Three-dimensional (3-D) $Pm\bar{3}n$ and $Im\bar{3}m$ cubic lattices[3,4] self-organized from spherical supramolecular dendrimers, two-dimensional (2-D) $p6mm$ hexagonal columnar lattices[5] self-organized from cylindrical supramolecular dendrimers, and hexagonal columnar superlattices[6] co-organized from mixtures of three-cylindrical bundle supramolecular mini-

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(1) For selected recent reviews on dendrimers and monodendrons, see: (a) Tomalia, D. A. *Adv. Mater.* **1994**, *6*, 529. (b) Fréchet, J. M. J. *Science* **1994**, *263*, 1710. (c) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules. Concepts, Synthesis, Perspectives*; VCH: Weinheim, 1996. (d) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402. (e) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681. (f) Smith, D. K.; Diederich, F. *Chem. Eur. J.* **1998**, *4*, 1353. (g) Frey, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2193. (h) Vögtle, F., Ed.; *Dendrimers*; Topics in Current Chemistry 197; Springer: Berlin, 1998. (i) Mathews, O. A.; Shipway, A. N.; Stoddart, J. F. *Prog. Polym. Sci.* **1998**, *23*, 1. (j) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884. (k) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665. (l) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747. (m) Moore, J. S. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 108. (n) Roovers, J.; Comanita, B. *Adv. Polym. Sci.* **1999**, *142,* 179. (o) Schlüter, A. D.; Rabe, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 864. (p) Hawker, C. J. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 117. (q) Emrick, T.; Fréchet, J. M. J. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 15. (r) Krause, W.; Hackmann-Schlichter, N.; Maier, F. K.; Müller, R. *Top. Curr. Chem.* **2000**, *210*, 261. (s) Smith, D. K.; Diederich, F. *Top. Curr. Chem.* **2000**, *210*, 183.

(2) (a) Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1993**, *115*, 4375. (b) Devadoss, C.; Bharathi, P.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1633. (c) Piotti, M. E.; Rivera, F., Jr.; Bond, R.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1999**, *121*, 9471. (d) Jiang, D.-L.; Aida, T. *Nature* **1997**, *388*, 454. (e) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226. (f) Sato, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658. (g) Andronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701. (h) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635. (i) Adronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 1175.

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dendrimers (i.e., first-generation dendrimers) with cylindrical supramolecular minidendrimers were reported. The structural analysis required for the design of these building blocks involves the identification of the bulk phase in which the supramolecular dendrimers are self-organized by a combination of differential scanning calorimetry (DSC) and thermal optical polarized microscopy (TOPM) followed by the selection of the lattice symmetry by X-ray diffraction experiments (XRD) performed on single crystal or single crystal liquid crystal specimens.[3−5] The decision on the shape of the supramolecular dendrimer that generates the lattice is made by a combination of electron density calculations, transmission electron microscopy (TEM), and electron diffraction experiments.[3] Various modes of self-assembly of the monodendritic building blocks into supramolecular objects of different shapes are screened and eliminated during this process. Finally, the retrostructural analysis of the lattices generated from supramolecular dendrimers of known shapes by using the lattice dimensions and density data provides access to the shape, size, and number of monodendritic building blocks that create the supramolecular dendrimer.

To date we have investigated a library containing from three to five generations of self-assembling 3,4,5-trisubstituted benzyl ether monodendrons containing four different minidendritic architectural motifs on their periphery[3a,7] and five generations of a 3,5-disubstituted benzyl ether monodendron.[8] Structural analysis of these monodendrons allowed the discovery of building blocks displaying the following shapes: tapered, twin-tapered, half-disk, disklike, conical, half-sphere, and spherical. These experiments have confirmed and quantified[7a,8] the prediction that the shape of a monodendron or dendrimer should change by increasing the generation number[9] both in solution and in bulk. In addition, they demonstrated that the shape of the monodendrons and dendrimers is determined both by the structure of the repeat unit attached to their periphery[7,10] and by the core multiplicity.[11,12] Most recently we have discovered that the solid angle of a monodendron determines the dependence between the size and shape of a supramolecular dendrimer and its generation number.[7c,13] Simultaneously we have learned that the first-generation AB_3 minimonodendron functionalized with a suitable group in its core self-assembles in cylindrical objects that at high temperatures[13] undergo a reversible shape change to spherical objects. However, both the $Im\bar{3}m$ lattice[4] and the hexagonal columnar superlattice[6] were obtained so far only with the first-generation supramolecular dendrimers (i.e., minidendrimers).

This diversity of tertiary and quaternary structural control accomplished by the modification of the primary structure of monodendrons is extremely rewarding since it produced libraries of *quasi-equivalent*[11] building blocks that have been used to generate new concepts in organic and polymerization reactions in restricted geometries[14] and also opened strategies for the synthesis of single-molecule functional nanosystems.[15] Nevertheless, the transplant of the discoveries made with minimonodendrons[4,6,13] to larger generations of monodendrons is most efficiently pursued at this time by investigating libraries of self-assembling monodendrons.

Toward this goal we are reporting here the synthesis and the structural analysis of three to four generations from the two constitutional isomeric libraries of AB_2 3,4- and, respectively, 3,5-disubstituted benzyl ether self-assembling monodendrons containing four minimonodendrons with different architectural motifs on their periphery. This series of experiments will provide access to the discovery of novel architectural and structural concepts and will clarify some of the structural limitations of these classes of self-assembling monodendrons.

Results and Discussion

Synthesis of Constitutional Isomeric Libraries of AB_2 Monodendrons. Two constitutional isomeric libraries of AB_2 monodendrons based on 3,4- and 3,5-disubstituted benzyl ether repeat units functionalized on their periphery with 3,4,5-tris(*n*-dodecan-1-yloxy)benzyl ether, 3,4-bis(*n*-dodecan-1-yloxy)benzyl ether, 3,4,5-tris[*p*-(*n*-dodecan-1-yloxy)benzyloxy]benzyl ether, and 3,4-bis[*p*-(*n*-dodecan-1-yloxy)benzyloxy]benzyl ether first-generation monodendrons (minidendrons) were synthesized. The short nomenclature used for these monodendrons is identical to that employed in previous publications for AB_3 3,4,5-trisubstituted benzyl ether monodendrons.[3a,7,15a] Scheme 1 outlines their synthesis and reports the yields of the pure compounds and their theoretical molecular masses. On the top of this scheme are shown the structures of (*3,4,5-3,4*)12G2-X ($X = CO_2CH_3$), (A−X),[15a] (*3,4,5-3,5*)12G2-X ($X = CO_2CH_3$), (B−X),[15a] $(3,4)^2$12G2-X ($X = CO_2CH_3$), (C−X),[15a] (*4-3,4,5*)-12G1-X ($X = CO_2CH_3$,[16] CH_2OH[7a]), (D−X), and (*4-3,4*)-12G1-X ($X = CO_2CH_3$,[15a] CH_2OH[7c]), (E−X) that were reported previously from our laboratory. The second line from Scheme 1 shows the convergent synthesis[1b] of 3,4-disubstituted series of monodendrons together with reaction conditions and yields. The synthetic method used involves the quantitative reduction

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[3] (a) Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539. (b) Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. S. K. *Science* **1997**, *278*, 449.

[4] Yeardley, D. J. P.; Ungar, G.; Percec, V.; Holerca, M. N.; Johansson, G. *J. Am. Chem. Soc.* **2000**, *122*, 1684.

[5] (a) Percec, V.; Johansson, G.; Heck, J.; Ungar, G.; Batty, S. V. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1411. (b) Percec, V.; Heck, J. A.; Tomazos, D.; Ungar, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2381. (c) Percec, V.; Heck, J.; Tomazos, D.; Falkenberg, F.; Blackwell, H.; Ungar, G. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2799. (d) Percec, V.; Tomazos, D.; Heck, J.; Blackwell, H.; Ungar, G. *J. Chem. Soc., Perkin Trans. 2* **1994**, 31. (e) Johansson, G.; Percec, V.; Ungar, G.; Abramic, D. *J. Chem. Soc., Perkin Trans. 1* **1994**, 447. (f) Tomazos, D.; Out, G.; Heck, J. A.; Johansson, G.; Percec, V.; Möller, M. *Liq. Cryst.* **1994**, *16*, 509. (g) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855.

[6] Percec, V.; Ahn, C.-H.; Bera, T. K.; Ungar, G.; Yeardley, D. J. P. *Chem. Eur. J.* **1999**, *5*, 1070.

[7] (a) Percec, V.; Cho, W.-D.; Mosier, P. E.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc* **1998**, *120*, 11061. (b) Percec, V.; Cho, W.-D.; Möller, M.; Prokhorova, S. A.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **2000**, *122*, 4249. (c) Percec, V.; Cho, W.-D.; Ungar, G. *J. Am. Chem. Soc.* **2000**, *122*, 10273.

[8] Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *Angew. Chem.* **2000**, *112*, 1661.; *Angew. Chem., Int. Ed.* **2000**, *39*, 1597.

[9] Naylor, A. M.; Goddard, W. A., III; Kiefer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339.

[10] Percec, V.; Chu, P.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc*. **1995**, *117*, 11441.

[11] Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* **1998**, *391*, 161.

[12] Yin, R.; Zhu, Y.; Tomalia, D. A.; Ibuki, H. *J. Am. Chem. Soc.* **1998**, *120*, 2678.

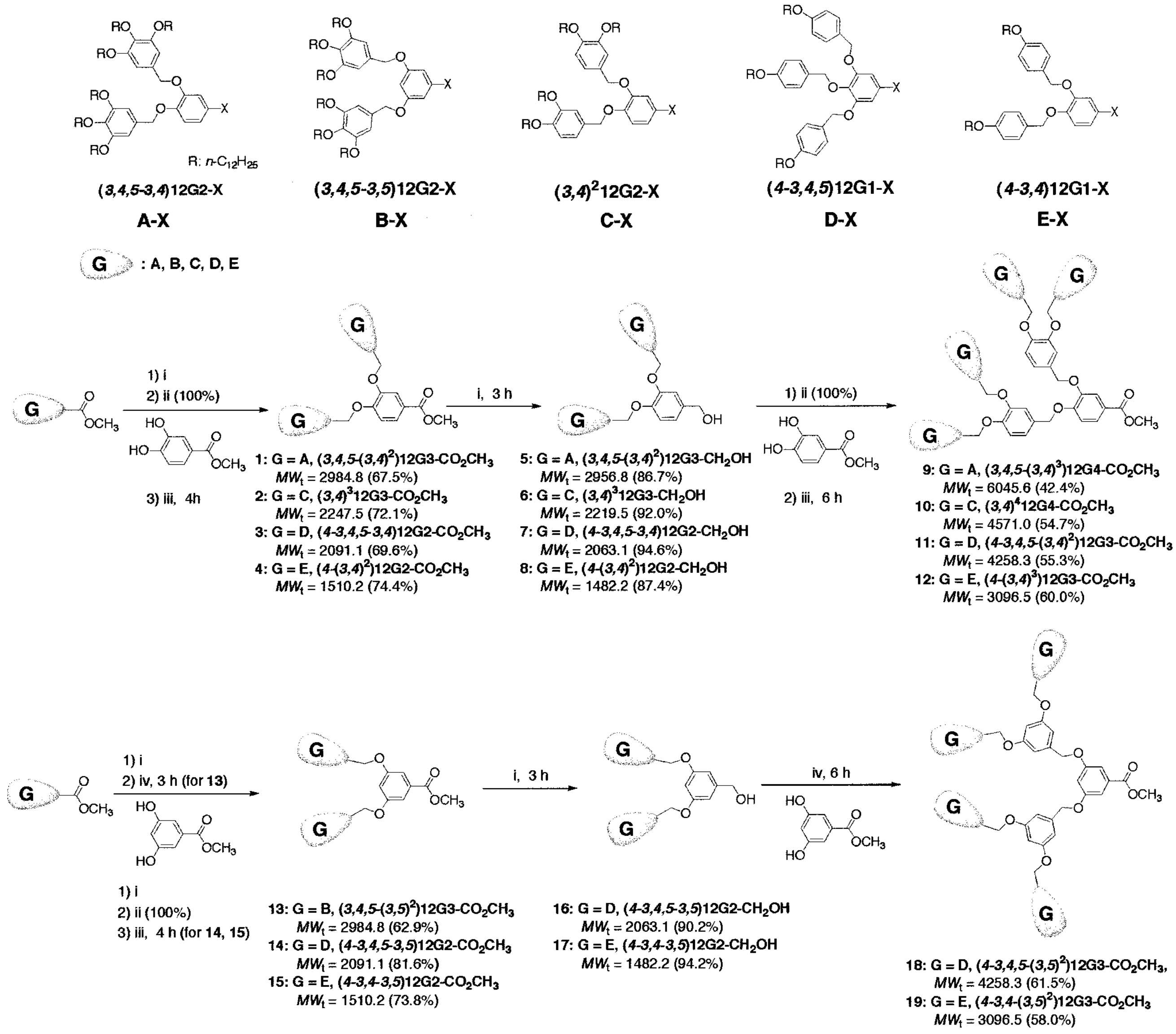
[13] Ungar, G.; Percec, V.; Holerca, M. N.; Johansson, G.; Heck. J. *Chem. Eur. J.* **2000**, *6*, 1258.

[14] Percec, V.; Ahn, C.-H.; Barboiu, B. *J. Am. Chem. Soc.* **1997**, *111*, 12978.

[15] (a) 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. (b) Percec, V.; Schlueter, D.; Ungar, G.; Cheng, S. Z. D.; Zhang, A. *Macromolecules* **1998**, *31*, 1745. (c) Prokhorova, S. A.; Sheiko, S. S.; Möller, M.; Ahn, C.-H.; Percec, V. *Macromol. Rapid Commun.* **1998**, *19*, 359. (d) Prokhorova, S. A.; Sheiko, S. S.; Ahn, C.-H.; Percec, V.; Möller, M. *Macromolecules* **1999**, *32*, 2653. (e) Prokhorova, S. A.; Sheiko, S. S.; Mourran, A.; Azumi, R.; Beginn, U.; Zipp, G.; Ahn, C.-H.; Holerca, M. N.; Percec, V.; Möller, M. *Langmuir* **2000**, *16*, 6862. (f) Percec, V.; Holerca, M. N. *Biomacromolecules* **2000**, *1*, 6.

[16] (a) Malthête, J.; Tinh, N. H.; Levelut, A. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1548. (b) Malthête, J.; Collet, A.; Levelut, A. M. *Liq. Cryst.* **1989**, *5*, 123.

Scheme 1. Synthesis of Libraries of Constitutional Isomeric 3,4- and 3,5-Disubstituted Benzyl Ether-Based Monodendrons



Reagents and conditions: (i) $LiAlH_4$, THF, 20 °C; (ii) $SOCl_2$, DTBMP, CH_2Cl_2, 20 °C; (iii) K_2CO_3, DMF, THF, 70 °C; (iv) DEAD, PPh_3, THF, 20 °C.

(followed by TLC, NMR) of the first- or second-generation methyl benzoate monodendron with $LiAlH_4$ in THF at 20 °C followed by the quantitative chlorination of the resulted benzyl alcohol into the corresponding benzyl chloride with $SOCl_2$ in CH_2Cl_2 in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP)[17] proton trap. The quantitative chlorination and the absence of decomposition during the chlorination process were determined by a combination of NMR, TLC, and HPLC. The reaction solvent was distilled in a rotary evaporator and the benzyl chloride derivative was used immediately in the etherification step. The etherification of methyl 3,4-dihydroxybenzoate with the monodendritic benzyl chloride was performed in various mixtures of DMF and THF in the presence of K_2CO_3 at 70 °C. The quantitative etherification was established by a combination of NMR, TLC, and HPLC analyses. It is essential that $SOCl_2$ and CH_2Cl_2 are of the highest commercial purities and are used from freshly opened containers. Additional experimental details of this synthetic procedure are available in the previous publications from our laboratory.[7,15a]

The synthesis of the series of 3,5-disubstituted benzyl ethers is shown on the last line of Scheme 1. Although they can be synthesized by the same method as the one used for the preparation of 3,4-disubstituted benzyl ether, the presently described monodendrons were synthesized by replacing the Williamson etherification with the Mitsunobu etherification.[8,18] Eight out of the 19 monodendrons containing a methyl benzoate group in their focal point, prepared according to the methods outlined in Scheme 1, were hydrolyzed with KOH in a mixture of EtOH and THF at reflux and after the neutralization of the reaction mixture with dilute CH_3COOH yielded the corresponding monodendrons containing a carboxylic acid at their focal point (Scheme 2).

The increase in the size of these two series of constitutional isomeric monodendrons could be monitored by their HPLC and GPC traces since the chromatograms are well separated (Figure 1). The difference between the theoretical and experimental molecular weights (relative to polystyrene standards) is due to the difference between the hydrodynamic volume of polystyrene and of the monodendrons and agrees with previous results from our laboratory.[3]

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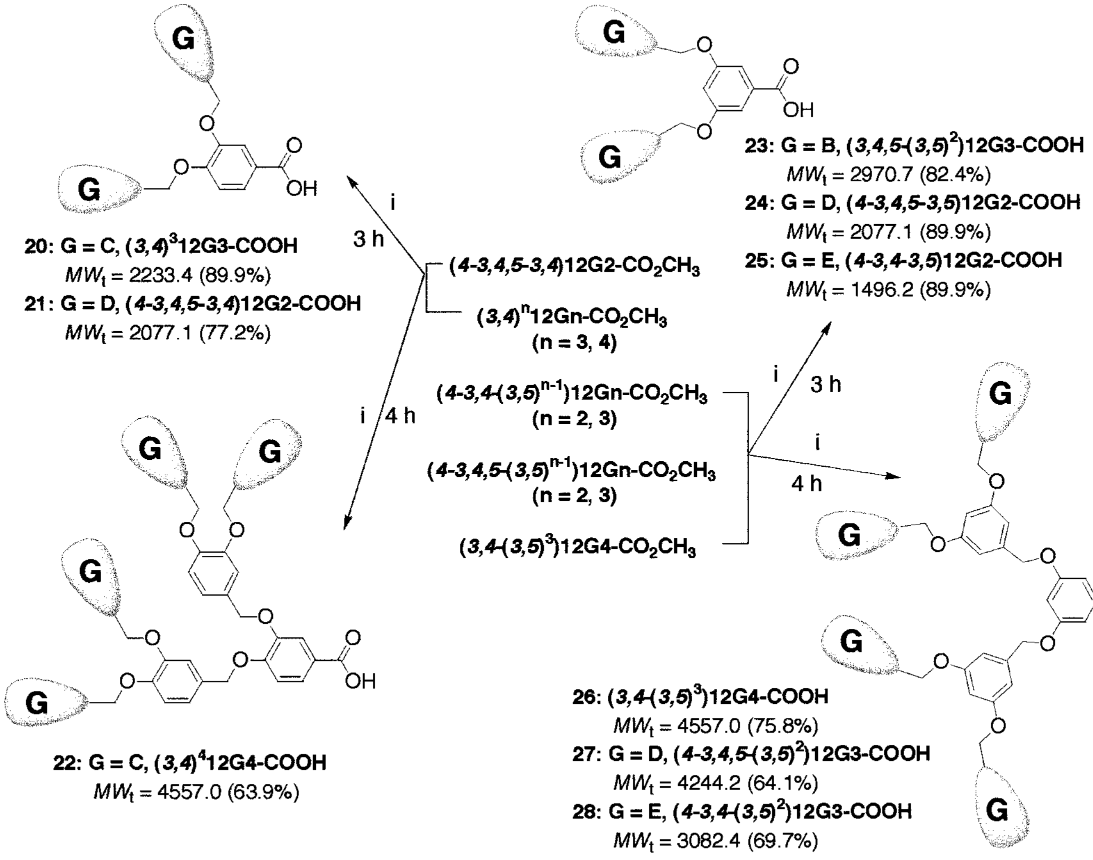
(17) Anderson, A. G.; Stang, P. J. *J. Org. Chem.* **1976**, *41*, 3034.

(18) (a) Mitsunobu, O. *Synthesis* **1981**, 1. (b) Hughes, D. L. *Org. React.* **1992**, *42*, 335. (c) Höger, S. *Synthesis* **1997**, 20.

Scheme 2. Synthesis of 3,4- and 3,5-Disubstituted Benzyl Ether-Based Monodendrons Containing Carboxylic Acid in Their Focal Point



***Reagents and conditions*:** (i) KOH, EtOH, THF, reflux, 50% aqueous CH$_3$COOH.

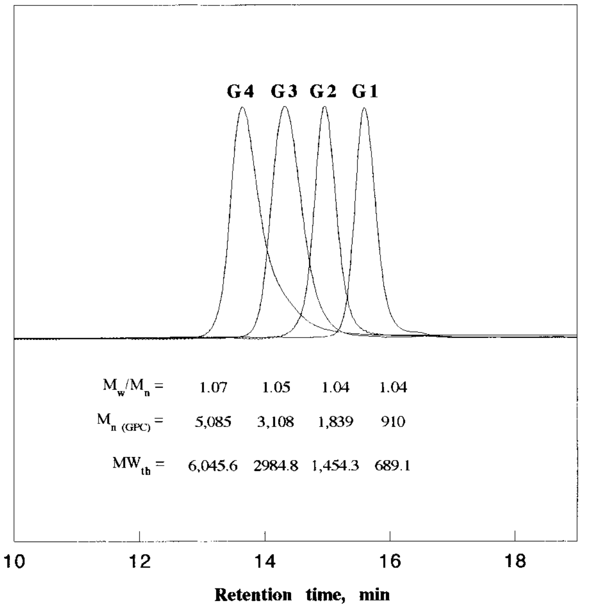
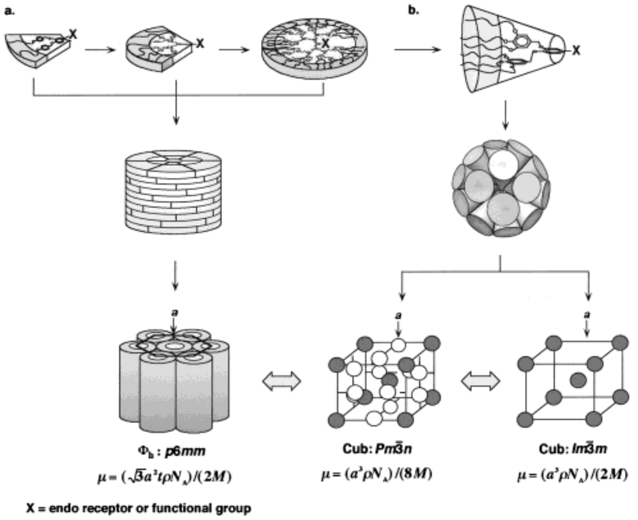


Figure 1. GPC traces with M_n and M_w/M_n values determined by GPC with polystyrene standards for (3,4,5-(3,4)$^{n-1}$)12G*n*-CO$_2$CH$_3$ with $n = 1-4$.

Scheme 3. Schematic Representation of (a) the Self-Assembly of Building Blocks Based on Flat Tapered and Disc-Shaped Monodendrons into Supramolecular Cylindrical Dendrimers and Their Subsequent Self-Organization in a *p*6*mm* Hexagonal Columnar (Φ_h) Lattice and (b) the Self-Assembly of the Conical Monodendrons into Supramolecular Spherical Dendrimers and Their Subsequent Self-Organization in *Pm*$\bar{3}$*n* and *Im*$\bar{3}$*m* Cubic (Cub) Lattices



Structural and Retrostructural Analysis of Supramolecular Dendrimers. The structural analysis of supramolecular dendrimers self-assembled in bulk from these two libraries of monodendrons was carried out by a combination of DSC, TOPM, and XRD experiments according to standard methods elaborated in our laboratory for the 2-D hexagonal columnar *p*6*mm*[5h] and 3-D cubic *Pm*$\bar{3}$*n*[3a] and *Im*$\bar{3}$*m*[4] lattices. The retrostructural analysis of these lattices was performed by using the values of the lattice dimensions and of the densities (ρ_{20}) of the supramolecular dendrimers. This procedure is outlined in Scheme 3 and is described in more detail in previous

Table 1. Theoretical and Experimental Molecular Weights Determined by GPC and Thermal Transitions of 3,4-Disubstituted Monodendrons

monodendron	MW$_t$	M_n (GPC)	M_w/M_n (GPC)	thermal transitions (°C) and corresponding enthalpy changes (kcal/mol)^a heating	cooling
(*3,4,5*)12G1-CO$_2$CH$_3$	689.1	910	1.04	k^b 44 (23.2) i^c k 23 (15.9) i	i 4 (15.5) k
(*3,4,5-3,4*)12G2-CO$_2$CH$_3$	1454.3	1839	1.04	k 40 (15.34) k 48 (5.03) i k −5 (1.86) T_g^{e} 9 Cub 40 (1.63) i	i 33 (1.77) Cub^d−13 (2.62)^f k
(*3,4,5-*(*3,4*)^2)12G3-CO$_2$CH$_3$	2984.8	3108	1.05	k 40 (25.94) Cub 69 (0.54) i k −22 (10.00) T_g 21 Cub 69 (0.57)^f i	i 57 (0.41)^f Cub −23 (4.85) k
(*3,4,5-*(*3,4*)^3)12G4-CO$_2$CH$_3$	6045.6	5085	1.07	k −2 (21.36)^f k 56 (33.03) Cub 94 (0.56) i k −18 (19.45) T_g 34 Cub 94 (0.72) i	i 73 (0.48) Cub −23 (12.15) k
(*3,4*)12G1-CH$_2$OH	476.8	830	1.02	k 12 (4.23) k 53 (16.06) i k 37 (0.53) −k 39 (2.32) k 52 (14.26) i	i 27 (10.91) k
(*3,4*)^{2}12G2-COOH	1071.7	1567	1.05	k 2 (0.31) k 88 (0.54) −k 97 (3.34) k 108 (17.58) Cub 119 (0.47) i −k 86 (4.63) k 108 (22.68) Cub 118 (0.54) i	i 114 (0.40) Cub 67 (17.04) k
(*3,4*)^{3}12G3-COOH	2233.4	2767	1.05	k 70 (11.56) Cub 178 (2.94) i k −10 (2.27) T_g 39 Cub 155 (2.17) i	i 153 (2.33) Cub −15 (4.84) k
(*3,4*)^{4}12G4-COOH	4557.0	4563	1.07	k −14 (16.61) T_g 41 Cub 194 (2.50) i k −11 (2.33) T_g 36 Cub 168 (0.97) i	i 165 (0.91) Cub −17 (6.92) k
(*4-3,4,5*)12G1-COOH	993.5	1498	1.02	k 47 (17.05)^f −k 58 (1.31) k 70 (11.82) Φ_h 145 (3.97) i k 43 (15.10)^f Φ_h 140 (3.71) i	i 136 (3.77) Φ_h^{g} 36 (15.43) k
(*4-3,4,5-3,4*)12G2-CO$_2$CH$_3$	2091.1	2852	1.05	k −9 (2.41) k 51 (23.21) Cub 119 (6.51) i k −27 (13.05) Cub 119 (4.96)^i	i 114 (4.83) Cub −26 (13.11) k
(*4-3,4,5-3,4*)12G2-COOH	2077.1	2868	1.05	k 1 (5.85)^f k 39 (2.56) k 78 (8.55) Cub 178 (4.74) i k −18 (3.73) T_g 31 k 62 (2.51) k 113 (0.08) Cub 178 (0.37) i	i 167 (0.11) Cub 51 (1.22) T_g^{g} 22 −22 (3.11) k
(*4-3,4,5-*(*3,4*)^2)12G3-CO$_2$CH$_3$	4258.3	4879	1.07	k −24 (13.92) −k 14 (14.24) k 24 (1.36) k 64 (2.12) Cub 153 (1.46) i k −25 (28.57) Cub 152 (1.08) i	i 143 (0.84) Cub 22 (0.17) k −28 (7.01) k
(*4-3,4*)12G1-CO$_2$CH$_3$	717.0	930	1.04	k 4 (1.96) k 60 (12.57) k 99 (4.87) i k 7 (1.64) k 55 (3.22) Φ_h 60 (2.03) i	i 54 (1.92) Φ_h 2 (2.51) k
(*4-3,4*)12G1-COOH	703.0	967	1.05	k −9 (9.89) Φ_h 125 (18.17) i k −9 (1.19) Φ_h 125 (19.22) i	i 114 (1.00) Φ_h 110 (15.37) Φ_h −15 (0.75) k
(*4-*(*3,4*)^2)12G2-CO$_2$CH$_3$	1510.2	2068	1.05	k 55 (14.39) Cub 162 (7.46) i k −17 (2.25) Cub 158 (6.04) i	i 153 (6.89) Cub −18 (3.12) k
(*4-*(*3,4*)^3)12G3-CO$_2$CH$_3$	3096.5	3872	1.07	k −2 (23.17) k 61 (1.53) Cub 211 (11.83) Cub 221 (11.35) i k −20 (14.83) Cub 205 (20.13)^f i	i 211 (6.61) Cub −22 (6.75) k

[a] Data from the first heating and cooling scans are on the first line, and data from the second heating are on the second line. [b] k = crystalline. [c] i = isotropic. [d] Cub = $Pm\bar{3}n$ cubic lattice. [e] T_g = glass transition temperature. [f] Sum of enthalpies from overlapped peaks. [g] Φ_h = *p*6*mm* hexagonal columnar lattice.

publications.[3a,4,5h] The DSC traces of all monodendrons are available in Figures 1−3 of the Supporting Information. The experimental transition temperatures and the corresponding enthalpy changes for the series of 3,4-disubstituted monodendrons are reported in Table 1, while the corresponding data for the 3,5-disubstituted monodendrons are listed in Table 2. On the optical polarized microscope, hexagonal columnar phases exhibit a focal conic texture (Figure 2), and therefore, this phase can be qualitatively discriminated from cubic phases that are optically isotropic. The analysis of the XRD results was carried out only for the *p*6*mm*,[5h] $Pm\bar{3}n$,[3a] and $Im\bar{3}m$[4] lattices that where previously understood from structural and model of self-assembly points of view. Selected examples of diffractograms that are characteristic of these three lattices are shown in Figure 3, together with their recording temperature. The *d*-spacings of the hexagonal columnar (Φ_h) and cubic (Cub) lattices of both libraries of compounds are collected in Table 3. The lattice dimensions (a), the experimental densities (ρ_{20}), the experimental diameter of the columnar or spherical supramolecular dendrimer (D), the number of monodendrons per unit cell (μ') for the $Pm\bar{3}n$ lattice, and the number of monodendrons per spherical dendrimer (μ) for the $Pm\bar{3}n$ lattice or per 4.7 Å[19] column stratum of the *p*6*mm* lattice are reported in Table 4 for the series of 3,4-disubstituted monodendrons and in Table 5 for the series of 3,5-disubstituted monodendrons. An additional and important parameter reported in Tables 4 and 5 is the planar angle (α') that represents the projection of the solid angle, α (where $\alpha = 4\pi/\mu$), of the conical and tapered monodendrons (where $\alpha' = \alpha/2 = 2\pi/\mu$).[7c] The results from Tables 4 and 5 were used to generate the mechanisms of self-assembly illustrated in Scheme 4 for the series of 3,4-disubstituted monodendrons and in Scheme 5 for the 3,5-disubstituted monodendrons. For comparison purposes, Scheme 6 compiles the structural analysis of the complete library of 3,4,5-trisubstituted benzyl ether monodendrons that was previously reported from our laboratory.[3a,7a−c] In addition, the values of α' that were previously reported only for one monodendron[7c] are now included for all of them in Scheme 6.

Let us discuss first the series of 3,4-disubstituted monodendrons summarized in Scheme 4. The largest generation monodendron is shown on top of each column of this scheme. The fragment corresponding to the structure of the first, second, third, and fourth generation of the monodendrons is marked with a dotted line on the structure of the largest generation. The dotted line is made with a color that corresponds to the generation number (i.e., $n = 1$ (blue), $n = 2$ (red), $n = 3$ (green), etc). In

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(19) Ungar, G.; Abramic, D.; Percec, V.; Heck, J. A. *Liq. Cryst.* **1996**, *21*, 73.

Table 2. Theoretical and Experimental Molecular Weights Determined by GPC and Thermal Transitions of 3,5-Disubstituted Monodendrons

monodendron	MW_t	M_n (GPC)	M_w/M_n (GPC)	thermal transitions (°C) and corresponding enthalpy changes (kcal/mol)[a] heating	cooling
(*3,4,5*)12G1-COOH	675.1	934	1.06	k 60[b] (14.90) i[c] k 59 (14.30) i	i 33 (14.1) k
(*3,4,5-3,5*)12G2-COOH	1440.3	2193	1.04	k −8 (2.60) k 65 (19.68)[d] i k 15 (1.91)[d] −k 25 (1.96) k 39 (5.28) −k 47 (0.72) −k 58 (1.20) i	i 19 (8.86)[d] k
(*3,4,5*-(*3,5*)^2)12G3-COOH	2970.7	4078	1.08	k −8 (2.60) k 55 (37.26) Cub[e] 92 (0.98) i k −5 (12.29) Cub 93 (0.99) i	i 87 (0.98) Cub −11 (14.69) k
(*3,4*)12G1-CH_2OH	476.8	830	1.02	k 12 (4.23) k 53 (16.06) i k 37 (0.53) −k 39 (2.32) k 52 (14.26) i	i 27 (10.91) k
(*3,4-3,5*)12G2-CH_2OH	1057.7	1663	1.04	k 65 (18.54) −k 69 (0.37) k 76 (5.47) i k 61 (12.91) i	i 49 (1.24) Φ_h[f] 37 (8.72) k
(*3,4-3,5*)12G2-COOH	1071.7	1673	1.04	k 69 (21.82) i k 14 (3.02) Φ_h 68 (3.94) i	i 63 (4.00) Φ_h 5 (2.45) k
(*3,4*-(*3,5*)^2)12G3-CO_2CH_3	2247.5	3216	1.07	k −5 (3.55) k 39 (12.56) k 45 (2.33) k 50 (0.86) i k −4 (4.01) Φ_h 45 (5.22) i	i 39 (2.55) Φ_h 27 (2.06) k
(*3,4*-(*3,5*)^3)12G4-CO_2CH_3	4571.0	5998	1.09	k 15 (72.96)[d] k 42 (4.38) Φ_h 66 (1.09) i k −12 (18.92) Φ_h 66 (1.06) i	i 58 (0.86) Φ_h −18 (14.95) k
(*4-3,4,5*)12G1-COOH	993.5	1498	1.02	k 47 (17.05)[d] −k 58 (1.31) k 70 (11.82) Φ_h 145 (3.97) i k 43 (15.10)[d] Φ_h 140 (3.71) i	i 136 (3.77) Φ_h 36 (15.43) k
(*4-3,4,5-3,5*)12G2-CO_2CH_3	2091.1	3104	1.05	k 54 (36.82) −k 66 (9.23) k 82 (0.22) i k −19 (7.95) Φ_h 71 (2.13) i	i 66 (2.15) Φ_h −23 (7.62) k
(*4-3,4,5*-(*3,5*)^2)12G3-CO_2CH_3	4258.3	5876	1.08	k −12 (39.64) k 60 (8.35) Φ_h 109 (3.63) i k −17 (44.15) Φ_h 108 (3.37) i	i 103 (3.72) Φ_h −22 (21.79) k
(*4-3,4*)12G1-CO_2CH_3	717.0	930	1.04	k 4 (1.96) k 60 (12.57) k 99 (4.87) i k 7 (1.64) k 55 (3.22) Φ_h 60 (2.03) i	i 54 (1.92) Φ_h 2 (2.51) k
(*4-3,4*)12G1-COOH	703.0	967	1.05	k −9 (9.89) Φ_h 125 (18.17) i k −9 (1.19) Φ_h 125 (19.22) i	i 114 (1.00) Φ_h 110 (15.37) Φ_h −15 (0.75) k
(*4-3,4-3,5*)12G2-CO_2CH_3	1510.2	2325	1.04	−k −15 (4.89) k 52 (1.31) k 77 (6.27)[d] 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
(*4-3,4-3,5*)12G2-CH_2OH	1482.2	2356	1.04	k 0 (3.57) k 73 (8.52) Φ_h 133 (3.28) i k −12 (6.75) k 85 (0.23) k 94 (1.63) Φ_h 133 (3.16) i	i 128 (3.09) Φ_h 36 (0.13) k −19 (2.52) k
(*4-3,4-3,5*)12G2-COOH	1496.2	2320	1.05	k −5 (4.75) k 58 (0.53) Φ_h 159 (2.70) i k −10 (9.92) k 84 (0.30) Φ_h 150 (1.81) i	i 146 (2.68) Φ_h −15 (5.95) k
(*4-3,4*-(*3,5*)^2)12G3-CO_2CH_3	3096.5	4506	1.07	k −6 (15.96) Φ_h 130 (4.73) i k −11 (9.76) Φ_h 130 (4.95) i	i 126 (4.72) Φ_h −15 (6.48) k
(*4-3,4*-(*3,5*)^2)12G3-COOH	3082.4	4518	1.07	k −4 (29.16) k 151 (0.39) Φ_h 189 (2.91) i[g]	

[a] Data from the first heating and cooling scans are on the first line, and data from the second heating are on the second line. [b] k = crystalline. [c] i = isotropic. [d] Sum of enthalpies from overlapped peaks. [e] Cub = $Pm\bar{3}n$ cubic lattice. [f] Φ_h = *p*6*mm* hexagonal columnar lattice. [g] Decompostion after first heating.

each column, next to the generation number (*n*) is shown the shape of the supramolecular dendrimer self-assembled from the monodendron with the corresponding *n*. Under the shape of each supramolecular dendrimer, the following data are provided: the functionality X from the focal point of the monodendron for which the structural analysis was reported, the temperature of the XRD experiment in °C (data in parentheses), the lattice dimension (*a* in Å), the diameter of the supramolecular cylindrical or spherical supramolecular dendrimer (*D* in Å), the number of monodendrons (μ) that self-assemble into a spherical supramolecular dendrimer or in a 4.7 Å cross section of the cylindrical supramolecular dendrimer, and the projection of the solid angle (planar angle, α' in degrees) of the monodendron.

Methyl 3,4,5-tris(*n*-dodecan-1-yloxy)benzoate [(*3,4,5*)12G1-CO_2CH_3], methyl 3,4-bis(*n*-dodecan-1-yloxy)benzoate [(*3,4*)-12G1-CO_2CH_3], and their corresponding carboxylic acids form crystal structures that were not yet elucidated, and therefore, they are not shown in Schemes 4 and 5. (*3,4,5*-(*3,4*)$^{n-1}$)12G*n*-X and (*3,4*)^{n}12G*n*-X with $n = 2-4$ self-assemble into spherical supramolecular dendrimers that self-organize in a $Pm\bar{3}n$ lattice. By increasing the generation number, *n*, and therefore the size, the number of monodendrons, μ, that self-assemble in a sphere decreases and the diameter, *D*, of the supramolecular dendrimer increases. However, the increase of the diameter does not correspond to the theoretical increase in the length of the monodendron expected for two extended conformations of the benzyl ether repeat unit i.e., 6.0 Å × 2 = 12.0 Å. This dependence is determined by the increase of the planar projection of the solid angle (α') of the monodendron with the increase of the generation number (*n*).[7c,13] For the case of (*3,4,5*-(*3,4*)$^{n-1}$)-12G*n*-X with $n = 2-4$, the diameter increases from 52.8 to 54.2 Å and to 55.0 Å, while α' increases from 11.6 to 22.5° and to 45.0°. This doubling of α' at each higher generation is generated by the simultaneous reduction in half of the number of monodendrons (μ) that self-assemble in a supramolecular sphere. A much larger increase in diameter is observed for the series (*3,4*)^{n}12G*n*-X with $n = 2-4$, i.e., starting from 51.8−59.6 Å to 69.4 or 64.3 Å (the last two values are dependent on the temperature at which the XRD experiment was carried out). This trend is due to a lower increase in α' (from 8.6−12.0° to 15.7° or 19.0° depending on temperature) that is generated by a higher number of monodendrons that self-assemble in a sphere (μ) and subsequently a lower decrease of μ by increasing the generation number. Therefore, according to these two series of monodendrons, for the same internal repeat unit, it is the unit from the periphery of the monodendron that determines the size

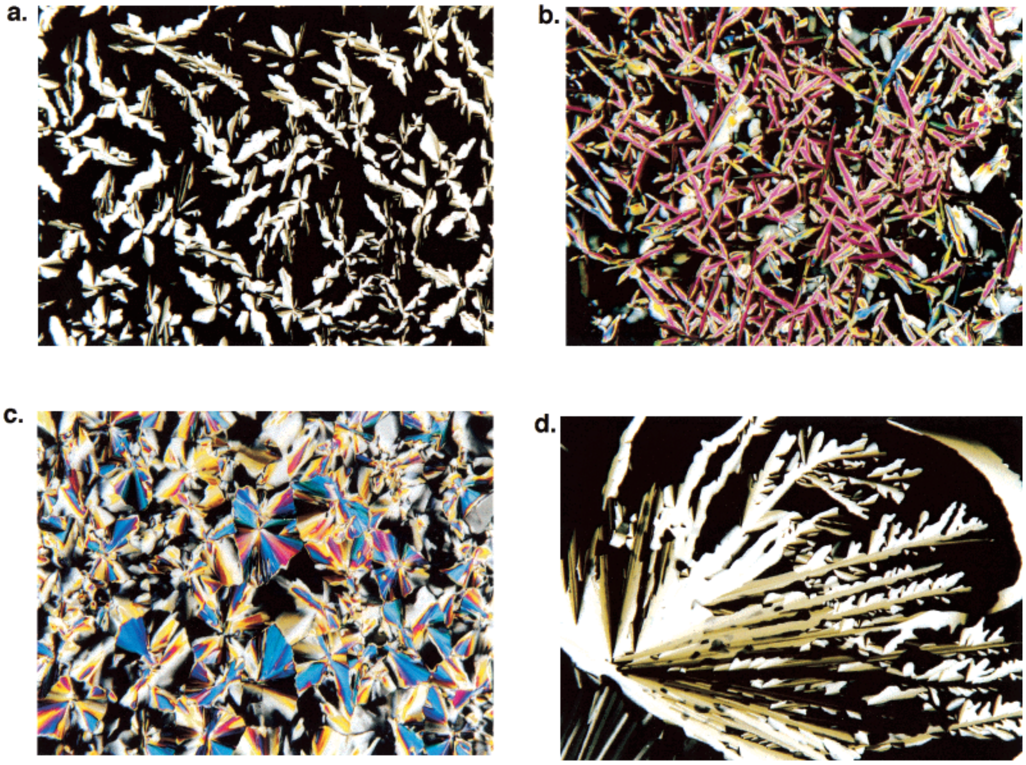


Figure 2. Representative optical polarized texture exhibited by the hexagonal columnar (Φ_h) mesophase of (a) (*4-3,4*)12G1-CO_2CH_3 obtained upon cooling from 99 to 61.3 °C at 1 °C/min, (b) (*4-3,4*-(*3,5*)^2)12G3-CO_2CH_3 obtained upon cooling from 133 to 130.3 °C at 10 °C/min, (c) (*4-3,4,5-3,5*)12G2-CH_2OH obtained upon cooling from 101 to 85.3 °C at 1 °C/min, and (d) (*4-3,4,5*-(*3,5*)^2)12G3-CO_2CH_3 obtained upon cooling from 109 to 108.2 °C at 1 °C/min.

of the supramolecular dendrimer and of its monodendrons as well as the dependence of μ, α', and D on generation number. From the analysis of these two series of monodendrons, we can conclude that the attachment of a 3,4-bis(*n*-dodecan-1-yloxy)-benzyl ether unit on the periphery provides a series of monodendrons that have a lower solid angle and a larger increase of their diameter as a function of n than the similar series containing the 3,4,5-tris(*n*-dodecan-1-yloxy)benzyl ether unit on the periphery.

The replacement of 3,4,5-tris(*n*-dodecan-1-yloxy)benzyl ether and 3,4-bis(*n*-dodecan-1-yloxy)benzyl ether from the periphery of (*3,4,5*-(*3,4*)$^{n-1}$)12G*n*-X and (*3,4*)^{n}12G*n*-X monodendrons with 3,4,5-tris[*p*-(*n*-dodecan-1-yloxy)benzyloxy]benzyl ether and, respectively, 3,4-bis[*p*-(*n*-dodecan-1-yloxy)benzyloxy]-benzyl ether groups provides the (*4-3,4,5*-(*3,4*)$^{n-1}$)12G*n*-X and (*4*-(*3,4*)^n)12G*n*-X series of monodendrons that are illustrated in the last two columns of Table 4. By contrast to the two series shown in the first two columns of Scheme 4 the first-generation monodendrons of the last two series self-assemble into cylindrical supramolecular dendrimers. The planar projection of the solid angle of (*4-3,4*)12G1-X (α') is lower than that of (*4-3,4,5*)-12G1-X. Simultaneously, the diameter of the supramolecular dendrimers generated from (*4-3,4*)12G1-X is larger than that of the supramolecular dendrimer generated from (*4-3,4,5*)12G1-X. At the transition from generation 1 to 2, both supramolecular dendrimers change their shape from cylindrical to spherical, and subsequently, their corresponding monodendrons change their shape from tapered to conic. This shape change is in agreement with theoretical predictions[9] and with previous results from our laboratory.[7a,8] Therefore, we can conclude that the molecular architecture of the unit from the periphery of the monodendron determines the dependence of the solid angle of the monodendron and the diameter of supramolecular dendrimer on generation number for the case of both cylindrical and spherical supramolecular dendrimers. The trend observed for the case of tapered monodendrons and cylindrical supramolecular dendrimers is continued at higher generations for conical monodendrons and spherical supramolecular dendrimers; i.e., (*4*-(*3,4*)^n)12G*n*-X with $n = 2$ and 3 exhibit lower α' and higher diameter than the series (*4-3,4,5*-(*3,4*)$^{n-1}$)12G*n*-X with $n = 2$ and 3.

Scheme 6 summarizes the structural data of the library of AB_3 monodendrons functionalized on their periphery with the same units as the AB_2 library described in Scheme 4. At first sight, these two libraries seem to represent a mirror image of each other. A more detailed analysis reveals two major differences. In the case of (*4-3,4,5*-(*3,4*)$^{n-1}$)12G*n*-X from the AB_2 library, the change in shape occurs at the transition from generation 1 to 2, while for the case of the AB_3 library for (*4*-(*3,4,5*)^n)12G*n*-X, an identical change in shape takes place at the transition from generation 2 to 3. All monodendrons of the AB_3 library (Scheme 6) have larger α' values and consequently their supramolecular dendrimers have lower diameters than the supramolecular dendrimers of the AB_2 library (Scheme 4).

Let us now compare the two constitutional isomeric libraries based on 3,4- and 3,5-disubstituted AB_2 internal repeat units shown in Schemes 4 and 5. At first sight, the shapes of these supramolecular dendrimers are completely different. This is expected since we are comparing the physical properties of two libraries of constitutional isomeric compounds. Since physical properties of chemical compounds are determined by their conformation, shape, and crystal structure, we have expected differences between these two constitutional isomeric libraries. However, we could not predict the dramatic difference observed here. In Scheme 5, we see a single spherical supramolecular dendrimer, i.e., corresponding to (*3,4,5*-(*3,5*)$^{n-1}$)12G*n*-X. The series (*3,4*-(*3,5*)$^{n-1}$)12G*n*-X was reported previously[8] and is shown here for comparison. Both (*3,4*-(*3,5*)$^{n-1}$)12G*n*-X and (*4-3,4,5*-(*3,5*)$^{n-1}$)12G*n*-X series follow a similar trend; i.e., by

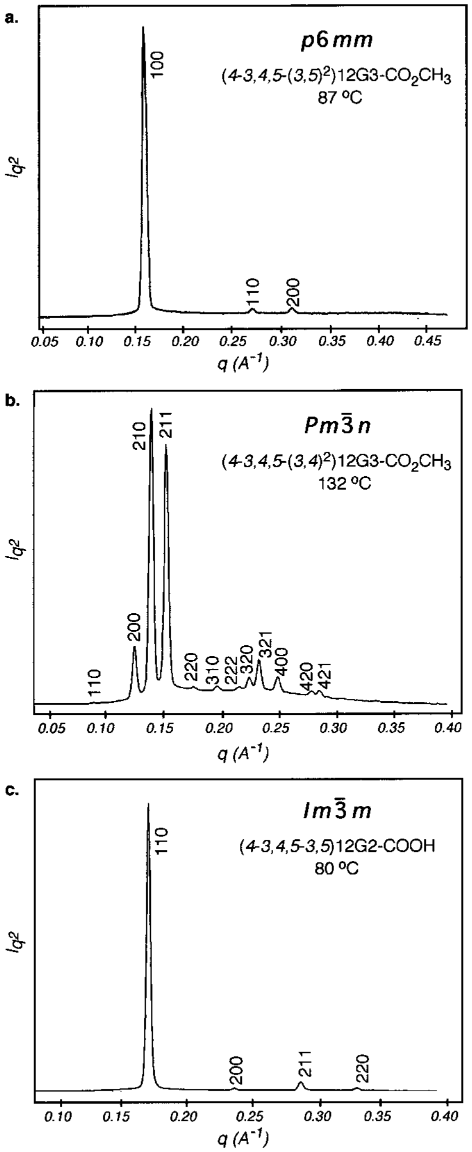


Figure 3. X-ray diffractograms of (a) the *p*6*mm* 2-D lattice exhibited by (*4-3,4,5-*(*3,5*)^2)12G3-CO_2CH_3 at 87 °C, (b) the *Pm*$\bar{3}$*n* 3-D lattice exhibited by (*4-3,4,5-*(*3,4*)^2)12G3-CO_2CH_3 at 132 °C, and (c) the *Im*$\bar{3}$*m* 3-D lattice exhibited by (*4-3,4,5-3,5*)12G2-COOH at 80 °C.

increasing the generation number, the monodendrons change their shape from a quarter of a disk to a third of a disk and subsequently exhibit the shape of a disklike molecule. In both series, there is a very small increase in the diameter of the supramolecular cylindrical dendrimer followed by a decrease when the supramolecular cylinder is generated from monodendritic disks. The last series of monodendrons from this library, i.e., (*4-3,4-*(*3,5*)$^{n-1}$)12G*n*-X, increases the number of monodendrons forming a 4.7 Å cross section of a cylinder from μ = 12 (at $n = 1$) to $\mu = 5$ (at $n = 2$) and to $\mu = 3$ (at $n = 3$). However, even if the values of α' increase with the increase in the generation number, the diameter of the supramolecular cylindrical dendrimers changes very little. This is partially because the X-ray experiments were performed at higher temperatures for higher generations. At higher temperatures, the diameter of the supramolecular dendrimer shrinks.[13] However, this low increase in diameter is due to a combination of higher temperature and small increase in size with *n*. In addition to the striking and unpredictable structural differences between these two constitutional isomeric libraries of AB_2 monodendrons, there are several additional rewarding events that are exhibited by the monodendrons and supramolecular dendrimers marked in the boxes in Scheme 5. They will be discussed in the next subchapter.

Supramolecular Dendrimers Exhibiting Reversible Shape Changes. (*3,4,5-*(*3,5*)$^{n-1}$)12G*n*-X with $n = 2$ and 4 self-assemble into supramolecular dendrimers with unknown shapes and subsequently self-organize in lattices that were not yet elucidated.

(*3,4-*(*3,5*)^3)12G4-CO_2CH_3 ($n = 4$ in second column of Scheme 5) has a disklike shape that self-assembles in supramolecular cylinders. The corresponding monodendron containing a carboxylic acid in its focal point; i.e., (*3,4-*(*3,5*)^3)12G4-COOH exhibits a conical shape that self-assembles into a spherical supramolecular dendrimer (Scheme 7a). Therefore, the cleavage of the methyl ester group from the focal point of this monodendron induces a change in monodendron shape from discotic to conical and a supramolecular dendrimer shape change from cylindrical to spherical (Scheme 7a). Simultaneously, a change in lattice from the 2-D *p*6*mm* to the 3-D *Pm*$\bar{3}$*n* occurs. A similar shape change is observed for (*4-3,4,5-*(*3,5*)^2)12G3-CO_2CH_3 and (*4-3,4,5-*(*3,5*)^2)12G3-COOH (Scheme 7b). This demonstrates that discotic monodendrons containing a carboxylic acid rather than an ester in their focal point have the ability to change the shape from disk to cone. The cleavage of an ester to a carboxylic acid can be triggered via various mechanisms, and therefore, the concept elaborated here can provide strategies to design externally regulated supramolecular objects.

The most unexpected result is exhibited by (*4-3,4,5-3,5*)12G2-CO_2CH_3 and (*4-3,4,5-3,5*)12G2-COOH (Scheme 7c). The former monodendron exhibits a tapered shape that is the equivalent of a third of a disk. Its carboxylic acid homologue has a conelike shape. However, although the conical monodendron self-assembles in a spherical supramolecular dendrimer, its lattice does not have a *Pm*$\bar{3}$*n* symmetry as all previous cases of (*4-3,4,5-*(*3,5*)^2)12G3-COOH and (*3,4-*(*3,5*)^3)12G4-COOH exhibit, but it has an *Im*$\bar{3}$*m* symmetry. The possibility of a bicontinuous structure for the *Im*$\bar{3}$*m* lattice was eliminated in a previous publication.[4] In the meantime, TEM and electron density calculations have definitively confirmed that the *Im*$\bar{3}$*m* lattice is generated from spherical objects. This work will be published in due time.

Scheme 8 shows the two examples discovered so far of supramolecular dendrimers that exhibit thermally induced shape changes. The first is (*4-3,4,5-3,5*)12G2-CH_2OH (Scheme 8a), and the second is (*4-3,4,5-*(*3,5*)^2)12G3-COOH (Scheme 8b). The first one is based on a monodendron that changes its shape from a third of a disk to a cone above 87 °C, and during this process, the supramolecular dendrimer changes its shape from cylindrical to spherical while the corresponding lattice transforms from a *p*6*mm* to a *Pm*$\bar{3}$*n* symmetry. The second example of thermally induced shape change is shown in Scheme 8b. It is based on a disklike monodendron that at a higher temperature than 151 °C (Tables 6−8) becomes conical. The lattice symmetries of these two examples are identical, i.e., *p*6*mm* for the cylindrical supramolecular dendrimer and *Pm*$\bar{3}$*n* for the spherical supramolecular dendrimer. Other functionalities at the focal point of these two monodendrons do not provide molecules and supramolecules that undergo thermal reversible shape changes. Another interesting feature of the thermally induced phase and shape transition is that the low-temperature *p*6*mm* lattice is 2-D while the high-temperature *Pm*$\bar{3}$*n* phase is 3-D. According to thermodynamic principles, this is an example of re-entrant phase transition, since usually the phase at higher temperature should have a lower symmetry.

Table 3. Measured *d*-Spacings of the *p6mm* Hexagonal Columnar and $Pm\bar{3}n$ Cubic Lattices Generated by Selected Examples of 3,4- and 3,5-Disubstituted Monodendrons

monodendron	T (°C)	lattice	d_{100} (Å)	d_{110} (Å)	d_{200} (Å)	d_{210} (Å)	d_{211} (Å)	d_{220} (Å)	d_{310} (Å)	d_{222} (Å)	d_{320} (Å)	d_{321} (Å)	d_{400} (Å)	d_{420} (Å)	d_{421} (Å)
(3,4,5-3,4) 12G2-CO_2CH_3	32	$Pm\bar{3}n$			42.6	38.0	34.5					22.8	21.3		
(3,4,5-(3,4)^2)12G3-CO_2CH_3	58	$Pm\bar{3}n$		62.3	43.7	38.7	35.3	31.0	27.7	25.3	24.3	23.3	21.8	19.5	19.0
(3,4,5-(3,4)^2)12G3-CO_2CH_3	70	$Pm\bar{3}n$		62.7	44.6	39.7	36.0	31.0	28.1	25.7	24.7	23.8	22.3	19.8	19.3
(3,4,5-(3,5)^2)12G3-COOH	89	$Pm\bar{3}n$			37.0	33.1	30.3	26.2	23.5	21.3	20.5	19.8	18.5		
(3,4)^{2}12G2-COOH	112	$Pm\bar{3}n$			42.4	37.7	34.2	29.6	26.7			22.6	21.1	18.8	18.3
(3,4)^{3}12G3-COOH	145	$Pm\bar{3}n$			48.3	42.9	39.0	33.9	30.5			25.7	24.0	21.4	20.9
(3,4)^{4}12G4-COOH	95	$Pm\bar{3}n$			55.8	50.1	45.6					29.9	28.0		
	160	$Pm\bar{3}n$			52.0	46.3	42.1		32.7			27.8	26.0		
(3,4-3,5)12G2-CH_2OH	49	*p6mm*	36.9	21.5	18.3										
(3,4-3,5)12G2-COOH	66	*p6mm*	38.0	21.5	18.6										
(3,4-(3,5)^2)12G3-CO_2CH_3	36	*p6mm*	45.7	26.6	23.1										
(3,4-(3,5)^3)12G4-CO_2CH_3	51	*p6mm*	39.4	22.8	19.8										
(4-3,4,5)12G1-COOH	87	*p6mm*	35.4		17.7										
(4-3,4,5-3,4)12G2-CO_2CH_3	112	$Pm\bar{3}n$			49.1	43.8	40.1	34.8	31.2	28.5	27.4	26.5	24.9	22.2	21.7
(4-3,4,5-3,4)12G2-COOH	140	$Pm\bar{3}n$			45.8	40.9	37.6	32.5	29.1	26.6	25.7	24.8	23.2	20.6	20.2
(4-3,4,5-(3,4)^2)12G3-CO_2CH_3	117	$Pm\bar{3}n$		73.3	51.6	46.3	42.2	36.5	32.6	29.8	28.6	27.5	25.8	23.0	22.5
	132	$Pm\bar{3}n$		71.6	50.7	45.4	41.5	35.8	32.1	29.2	28.1	27.0	25.3	22.6	22.1
	142	$Pm\bar{3}n$		70.7	49.8	44.7	40.8	35.2	31.4	28.7	27.6	26.6	24.9	22.2	21.6
(4-3,4,5-3,5)12G2-CO_2CH_3	60	*p6mm*	40.5		20.4										
	70	*p6mm*	40.0		20.0										
(4-3,4,5-(3,5)^2)12G3-CO_2CH_3	87	*p6mm*	40.0	23.0	19.9										
	97	*p6mm*	39.2	22.7	19.6										
(4-3,4)12G1-CO_2CH_3	57	*p6mm*	49.7	28.9	24.9										
(4-3,4)12G1-COOH	77	*p6mm*	46.6												
(4-(3,4)^2)12G2-CO_2CH_3	89	$Pm\bar{3}n$			58.5	52.5	47.9	41.6	37.1	33.9	32.5	31.3	29.3		
(4-(3,4)^3)12G3-CO_2CH_3	176	$Pm\bar{3}n$			60.4	54.1	49.4	42.7	38.2	34.9	33.5	32.3	30.2		
(4-3,4-3,5)12G2-CO_2CH_3	100	*p6mm*	49.0	28.4	24.6	18.5									
(4-3,4-3,5)12G2-CH_2OH	80	*p6mm*	46.0		23.0										
(4-3,4-3,5)12G2-COOH	100	*p6mm*	45.6	26.3	22.9										
(4-3,4-(3,5)^2)12G3-CO_2CH_3	100	*p6mm*	49.8	29.0	25.1										
(4-3,4-(3,5)^2)12G3-COOH	147	*p6mm*	45.2	26.2	22.8	17.2									

Table 4. Structural Characterization of Supramolecular Dendrimers Self-Assembled from Selected Examples of 3,4-Disubstituted Monodendrons

monodendron	T (°C)	lattice	$\langle d_{100}\rangle$[a] (Å)	a (Å)	ρ_{20}[c] (g/cm^3)	D (Å)	μ'[f]	μ	α'[i] (deg)
(3,4,5-3,4) 12G2-CO_2CH_3	32	$Pm\bar{3}n$		85.1[b]	0.98	52.8[d]	250	31[g]	11.6
(3,4,5-(3,4)^2)12G3-CO_2CH_3	58	$Pm\bar{3}n$		87.3[b]	0.96	54.2[d]	129	16[g]	22.5
(3,4,5-(3,4)^3)12G4-CO_2CH_3	70	$Pm\bar{3}n$		88.7[b]	0.97	55.0[d]	67	8[g]	45.0
(3,4)^{2}12G2-COOH	112	$Pm\bar{3}n$		83.5[b]	1.02	51.8[d]	334	42[g]	8.6
(3,4)^{3}12G3-COOH	145	$Pm\bar{3}n$		96.0[b]	1.01	59.6[d]	241	30[g]	12.0
(3,4)^{4}12G4-COOH	95	$Pm\bar{3}n$		111.8[b]	1.01	69.4[d]	187	23[g]	15.7
	160	$Pm\bar{3}n$		103.7[b]	1.01	64.3[d]	149	19[g]	19.0
(4-3,4,5)12G1-COOH	87	*p6mm*	35.4	40.9[a]	1.02	40.9[e]		4[h]	90.0
(4-3,4,5-3,4)12G2-CO_2CH_3	112	$Pm\bar{3}n$		98.7[b]	1.03	61.2[d]	285	36[g]	10.0
(4-3,4,5-3,4)12G2-COOH	140	$Pm\bar{3}n$		92.2[b]	1.03	57.2[d]	234	29[g]	12.4
(4-3,4,5-(3,4)^2)12G3-CO_2CH_3	117	$Pm\bar{3}n$		103.2[b]	1.00	64.0[d]	155	19[g]	19.0
	132	$Pm\bar{3}n$		101.3[b]	1.00	62.8[d]	147	18[g]	20.0
	142	$Pm\bar{3}n$		99.6[b]	1.00	61.8[d]	140	18[g]	20.0
(4-3,4)12G1-CO_2CH_3	57	*p6mm*	49.9	57.6[a]	1.05	57.6[e]		12[h]	30.0
(4-3,4)12G1-COOH	77	*p6mm*	46.6	53.8[a]	1.04	53.8[e]		11[h]	32.7
(4-(3,4)^2)12G2-CO_2CH_3	89	$Pm\bar{3}n$		117.3[b]	0.99	72.8[d]	637	80[g]	4.5
(4-(3,4)^3)12G3-CO_2CH_3	176	$Pm\bar{3}n$		120.9[b]	1.05	75.0[d]	361	45[g]	8.0

[a] *p6mm* hexagonal columnar lattice parameter $a = 2\langle d_{100}\rangle/3^{1/2}$; $\langle d_{100}\rangle = (d_{110} + 3^{1/2}d_{110} + 4^{1/2}d_{200} + 7^{1/2}d_{200})/4$. [b] $Pm\bar{3}n$ cubic lattice parameter $a = (2^{1/2}d_{110} + 4^{1/2}d_{200} + 5^{1/2}d_{210} + 6^{1/2}d_{211} + 8^{1/2}d_{220} + 10^{1/2}d_{310} + 12^{1/2}d_{222} + 13^{1/2}d_{320} + 14^{1/2}d_{321} + 16d_{400} + 20^{1/2}d_{420} + 21^{1/2}d_{421})/12$. [c] ρ_{20} = experimental density at 20 °C. [d] Experimental spherical diameter $D = 2\sqrt[3]{3a^3/32\pi}$. [e] Experimental column diameter $D = 2\langle d_{100}\rangle/3^{1/2}$. [f] Number of monodendrons per unit cell $\mu' = (a^3N_A\rho)/M$. [g] Number of monodendrons per $Pm\bar{3}n$ spherical dendrimer $\mu = \mu'/8$. [h] Number of monodendrons per 4.7 Å column stratum $\mu = (3^{1/2}N_AD^2t\rho)/2M$ (Avogadro's number $N_A = 6.022\,045 \times 10^{23}$ mol^{-1}, the average height of the column stratum $t = 4.7$ Å, and M = molecular weight of monodendron). [i] Projection of the solid angle for tapered and conical monodendron $\alpha' = 360/\mu$ (deg).

The monodendrons and supramolecular dendrimers that undergo shape changes either via the change of the functionality of their focal point or by temperature are expected to generate novel technological applications. At the same time, they provide an elegant demonstration of the *quasi-equivalence*[11] of these dendritic building blocks.

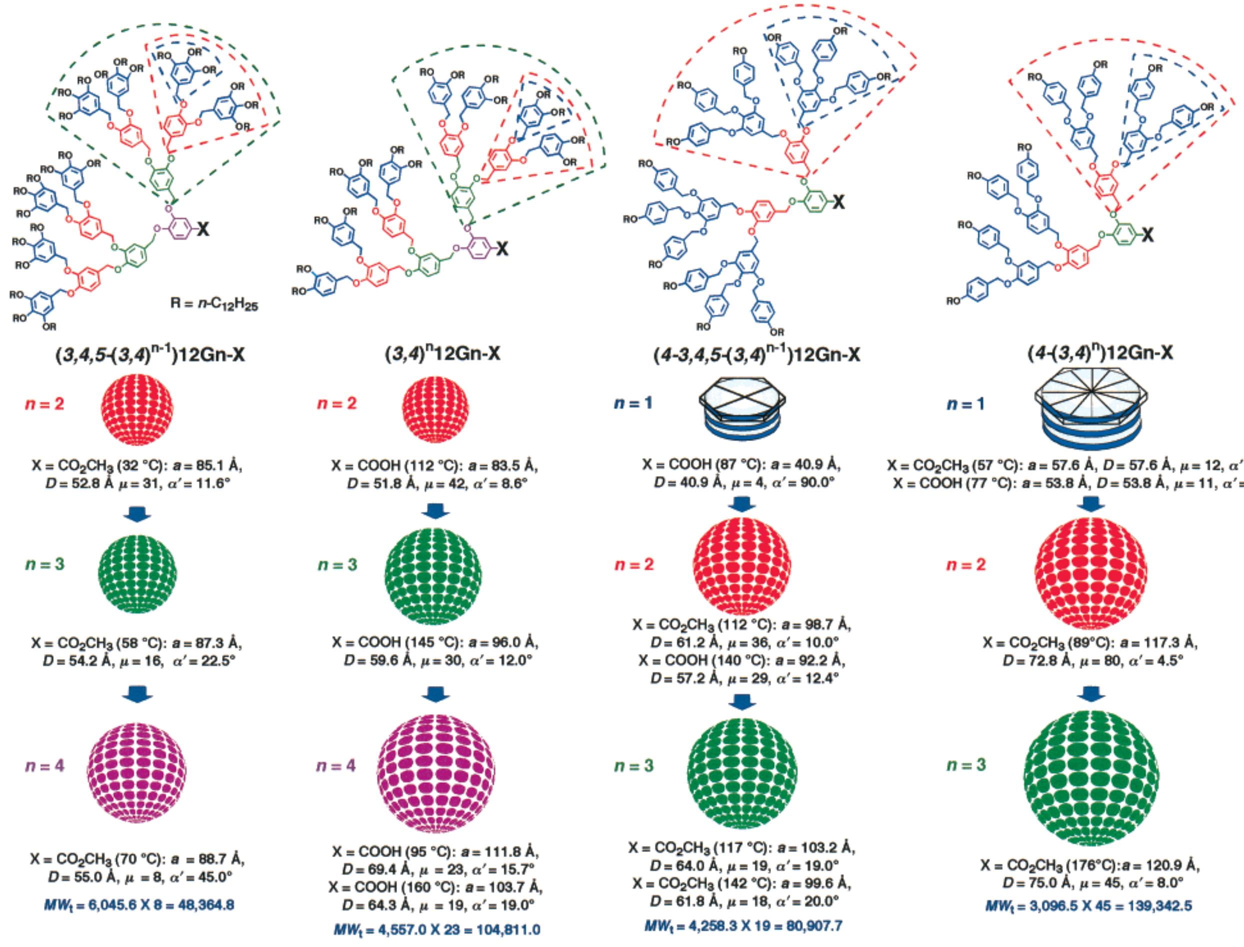
At present we do not understand the design principles for the synthesis of additional monodendrons that undergo reversible shape changes. Nevertheless, several structural particularities that favor shape changes can be obtained by the inspection of Schemes 5, 7, and 8. These schemes indicate that the monodendrons that undergo shape changes by chemical modification

Table 5. Structural Characterization of Supramolecular Dendrimers Self-Assembled from Selected Examples of 3,5-Disubstituted Monodendrons

monodendron	T (°C)	lattice	$\langle d_{100}\rangle^a$ (Å)	a (Å)	$\rho_{20}{}^c$ (g/cm^3)	D (Å)	$\mu'^{\,f}$	μ	$\alpha'^{\,i}$ (deg)
(*3,4,5*-(*3,5*)^2)12G3-COOH	89	$Pm\bar{3}n$		74.1^b	0.97	46.0^d	80	10^g	36.0
(*3,4*-*3,5*)12G2-CH$_2$OH	49	*p6mm*	36.9	42.6^a	0.99	42.6^e		4^h	90.0
(*3,4*-*3,5*)12G2-COOH	66	*p6mm*	37.5	43.3^a	1.02	43.3^e		4^h	90.0
(*3,4*-(*3,5*)^2)12G3-CO$_2$CH$_3$	36	*p6mm*	46.0	53.1^a	1.01	53.1^e		3^h	120.0
(*3,4*-(*3,5*)^3)12G4-CO$_2$CH$_3$	51	*p6mm*	39.5	45.6^a	0.99	45.6^e		1^h	360.0
(*4*-*3,4,5*)12G1-COOH	87	*p6mm*	35.4	40.9^a	1.02	40.9^e		4^h	90.0
(*4*-*3,4,5*-*3,5*)12G2-CO$_2$CH$_3$	60	*p6mm*	40.7	47.0^a	1.02	47.0^e		3^h	120.0
	70	*p6mm*	39.9	46.1^a	1.02	46.1^e		3^h	120.0
(*4*-*3,4,5*-(*3,5*)^2)12G3-CO$_2$CH$_3$	87	*p6mm*	39.9	46.1^a	1.02	46.1^e		1^h	360.0
	97	*p6mm*	39.2	45.3^a	1.02	45.3^e		1^h	360.0
(*4*-*3,4*)12G1-CO$_2$CH$_3$	57	*p6mm*	49.9	57.6^a	1.05	57.6^e		12^h	30.0
(*4*-*3,4*)12G1-COOH	77	*p6mm*	46.6	53.8^a	1.04	53.8^e		11^h	32.7
(*4*-*3,4*-*3,5*)12G2-CO$_2$CH$_3$	100	*p6mm*	49.1	56.7^a	1.00	56.7^e		5^h	72.0
(*4*-*3,4*-*3,5*)12G2-CH$_2$OH	90	*p6mm*	46.0	53.1^a	1.06	53.1^e		5^h	72.0
(*4*-*3,4*-*3,5*)12G2-COOH	100	*p6mm*	45.7	52.8^a	1.03	52.8^e		5^h	72.0
(*4*-*3,4*-(*3,5*)^2)12G3-CO$_2$CH$_3$	100	*p6mm*	50.1	57.9^a	1.04	57.9^e		3^h	120.0
(*4*-*3,4*-(*3,5*)^2)12G3-COOH	147	*p6mm*	45.4	52.4^a	1.04	52.4^e		2^h	180.0

[a] *p6mm* hexagonal columnar lattice parameter $a = 2\langle d_{100}\rangle/3^{1/2}$; $\langle d_{100}\rangle = (d_{110} + 3^{1/2}d_{110} + 4^{1/2}d_{200} + 7^{1/2}d_{200})/4$. [b] $Pm\bar{3}n$ cubic lattice parameter $a = (2^{1/2}d_{110} + 4^{1/2}d_{200} + 5^{1/2}d_{210} + 6^{1/2}d_{211} + 8^{1/2}d_{220} + 10^{1/2}d_{310} + 12^{1/2}d_{222} + 13^{1/2}d_{320} + 14^{1/2}d_{321} + 16^{1/2}d_{400} + 20^{1/2}d_{420} + 21^{1/2}d_{421})/12$. [c] ρ_{20} = experimental density at 20 °C. [d] Experimental spherical diameter $D = 2\sqrt[3]{3a^3/32\pi}$. [e] Experimental column diameter $D = 2\langle d_{100}\rangle/3^{1/2}$. [f] Number of monodendrons per unit cell $\mu' = (a^3N_A\rho)/M$. [g] Number of monodendrons per $Pm\bar{3}n$ spherical dendrimer $\mu = \mu'/8$. [h] Number of monodendrons per 4.7 Å column stratum $\mu = (3^{1/2}N_AD^2t\rho)/2M$ (Avogadro's number $N_A = 6.022\,045 \times 10^{23}$ mol^{-1}, the average height of the column stratum t = 4.7 Å, and M = molecular weight of monodendron). [i] Projection of the solid angle for tapered and conical monodendron $\alpha' = 360/\mu$ (deg).

Scheme 4. Retrostructural Analysis of Supramolecular Dendrimers Self-Assembled from AB$_2$ 3,4-Disubstituted Monodendrons



at their focal point or by temperature are based on molecules that display either a disklike shape or a tapered shape that is the equivalence of a third of a disk. The functionality that favors a disklike monodendron and a cylindrical supramolecular dendrimer is noninteracting, i.e., ester, while the functionality that stabilizes a conical monodendron and a spherical supramo-

Scheme 5. Retrostructural Analysis of Supramolecular Dendrimers Self-Assembled from AB_2 3,5-Disubstituted Monodendron

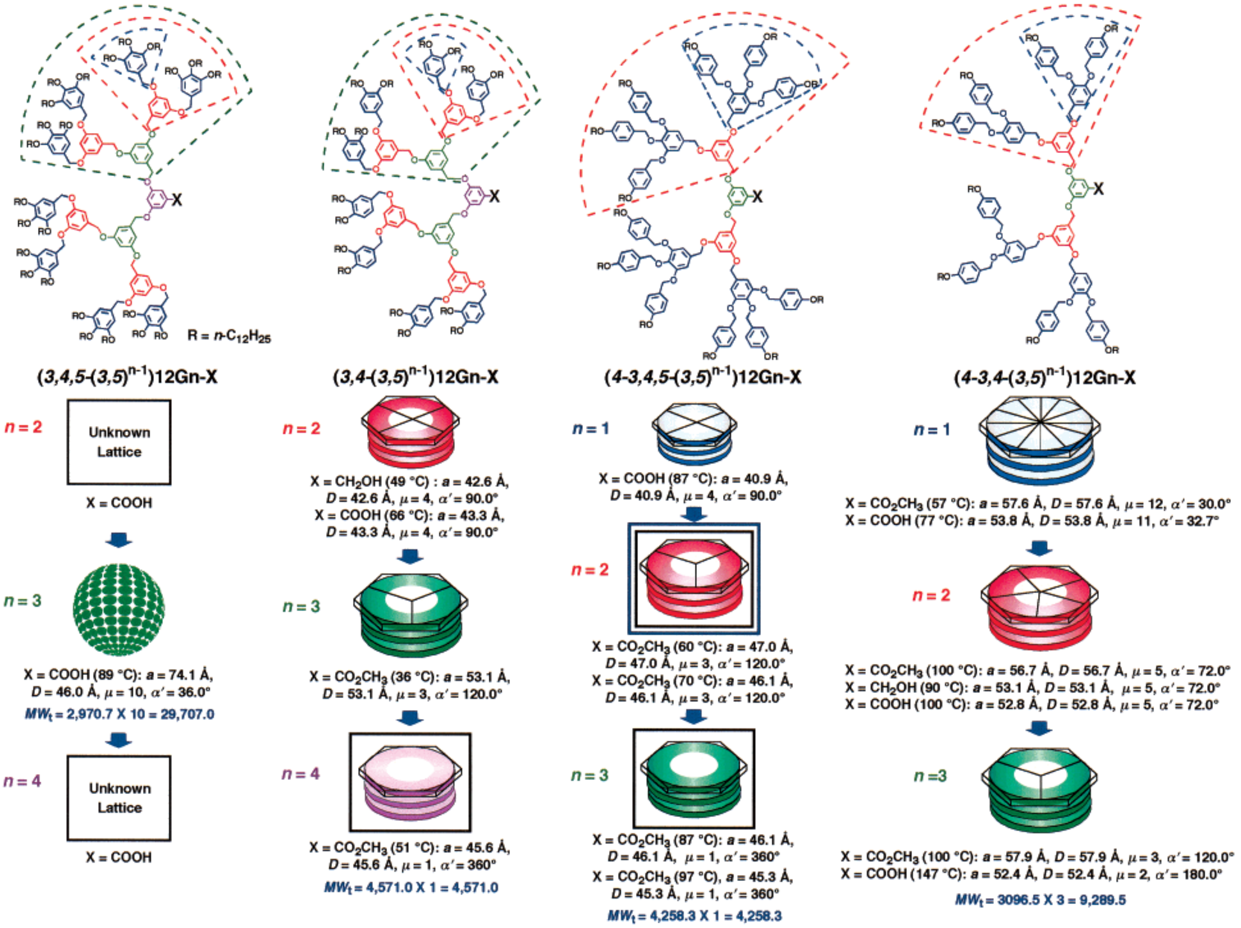


Table 6. Theoretical and Experimental Molecular Weights Determined by GPC and Thermal Transitions of the Monodendrons that Self-Assemble into Supramolecular Dendrimers Which Exhibit Reversible Shape Changes

monodendron	MW_t	M_n (GPC)	M_w/M_n (GPC)	thermal transitions (°C) and corresponding enthalpy changes (kcal/mol)[a] heating	cooling
(*3,4*-(*3,5*)^3)12G4-CO_2CH_3	4571.0	5998	1.09	k[b] 15 (72.96) k 42 (4.38) Φ_h[c] 66 (1.09) i[d] k −12 (18.92) Φ_h 66 (1.06) i	i 58 (0.86) Φ_h −18 (14.95) k
(*3,4*-(*3,5*)^3)12G4-COOH	4557.0	5778	1.09	k −10 (11.52) k 39 (38.97) Cub[e] 109 (1.48) i k −9 (10.58) Cub 109 (1.25) i	i 104 (1.39) Cub −14 (11.87) k
(*4-3,4,5-3,5*)12G2-CO_2CH_3	2091.1	3104	1.05	k 54 (36.82) −k 66 (9.23) k 82 (0.22) i k −19 (7.95) Φ_h 71 (2.13) i	i 66 (2.15) Φ_h −23 (7.62) k
(*4-3,4,5-3,5*)12G2-CH_2OH	2063.1	3155	1.05	k −18 (0.22) k 57 (13.72)[f] Φ_h 87 (0.50) Cub 101 (0.22) i[f] k −18 (4.14) T_g[g] 28 Φ_h 87 (0.59) Cub 101 (0.18) i	i 90 (0.05) Cub 74 (0.68) Φ_h −24 (3.73) k
(*4-3,4,5-3,5*)12G2-COOH	2077.1	3134	1.05	k 35 (168.4)[f] Cub[h] 196 (0.64) i k −19 (21.02) k 75 (3.34) Cub[h] 165 (0.86) Cub[h] 195 (0.50) i	i 181 (0.17) Cub 64 (1.30) k −22 (8.28) k
(*4-3,4,5*-(*3,5*)^2)12G3-CO_2CH_3	4258.3	5876	1.08	k −12 (39.64) k 60 (8.35) Φ_h 109 (3.63) i k −17 (44.15) Φ_h 108 (3.37) i	i 103 (3.72) Φ_h −22 (21.79) k
(*4-3,4,5*-(*3,5*)^2)12G3-COOH	4244.2	5737	1.08	k −12 (31.89) k 51 (3.54) Φ_h 151 (0.21) Cub 164 (0.44) i k −21 (23.35) Φ_h 151 (2.03) Cub 164 (3.05) i	i 152 (0.29) Cub 119 (0.33) Φ_h 88 (0.32) T_g 40 −24 (16.37) k

[a] Data from the first heating and cooling scans are on the first line, and data from the second heating are on the second line. [b] k = crystalline. [c] Φ_h = *p*6*mm* hexagonal columnar lattice. [d] i = isotropic. [e] Cub = $Pm\bar{3}n$ cubic lattice. [f] Sum of enthalpies from overlapped peaks. [g] T_g = glassy transition temperature. [h] Cub = $Im\bar{3}m$ cubic lattice. The $Im\bar{3}m$ to $Im\bar{3}m$ transition from the second heating scan of (*4-3,4,5-3,5*)12G2-COOH represents a discontinuous change in the XRD intensity of the same symmetry.

lecular dendrimer requires interactions by H-bonding. In addition, the molecules that undergo shape changes as a function of temperature always have an H-bonding functionality in their focal point. Although extensive modeling experiments are in progress in various laboratories,[20,21] we currently do not understand why the present supramolecular dendrimers self-organize mostly in a $Pm\bar{3}n$ lattice. Examples of small polyphilic molecules that exhibit transitions between columnar and various cubic phases are available in the literature.[23] However, in this case,[23] the authors claim that the type of the mesophase is

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(20) Cagin, T.; Wang, G.; Martin, R.; Goddard, W. A., III, in preparation.
(21) Ziherl, P.; Kamien, R. D. *Phys. Rev. Lett.* **2000**, *85*, 3528.

Scheme 6. Retrostructural Analysis of Supramolecular Dendrimers Self-Assembled from AB_3 3,4,5-Trisubstituted Monodendron

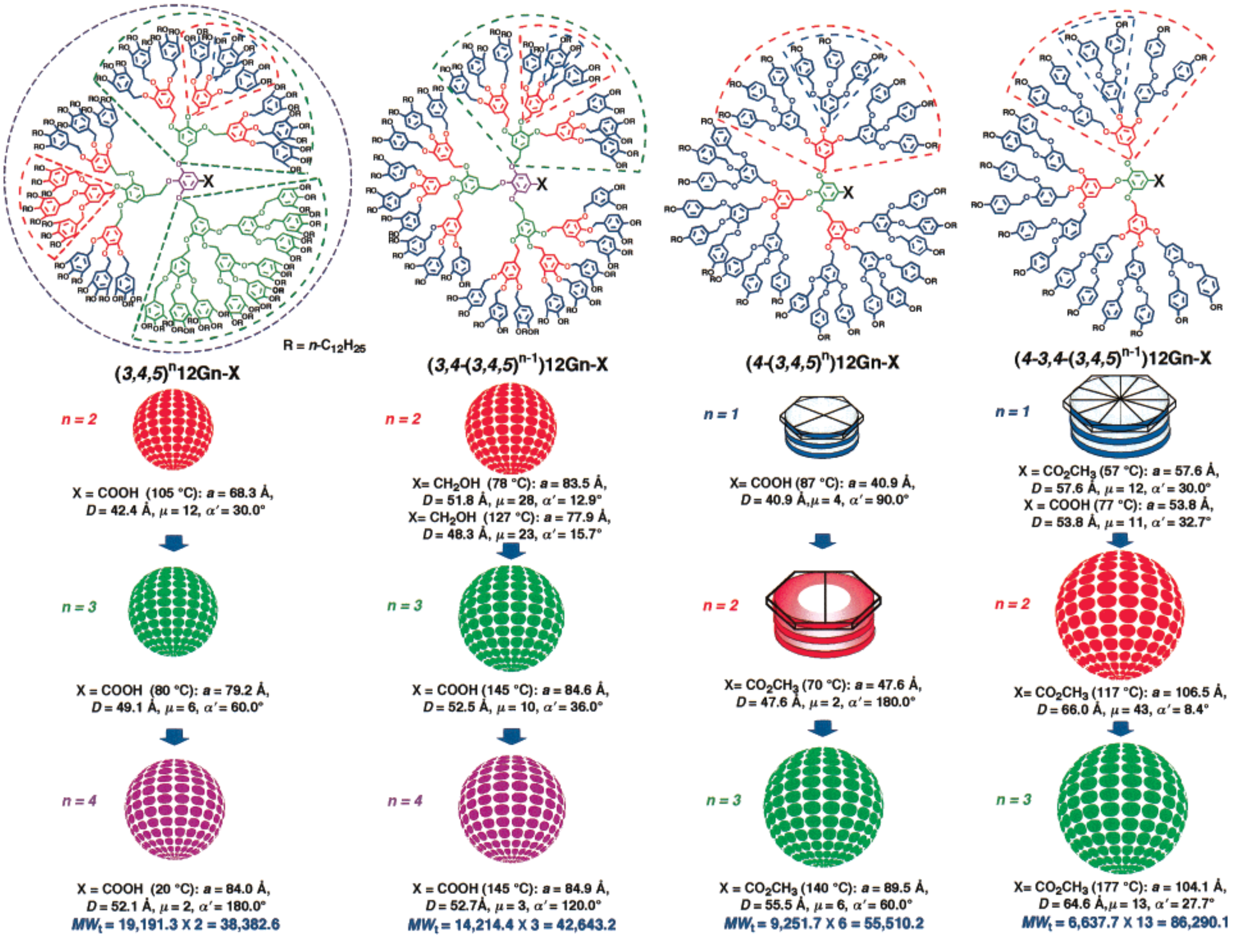

Table 7. Measured d-Spacings of the $p6mm$ Hexagonal Columnar, $Pm\bar{3}n$, and $Im\bar{3}m$ Cubic Lattices Generated by the Monodendrons that Self-Assemble into Supramolecular Dendrimers Which Exhibit Reversible Shape Changes

monodendron	T (°C)	lattice	d_{100} (Å)	d_{110} (Å)	d_{200} (Å)	d_{210} (Å)	d_{211} (Å)	d_{220} (Å)	d_{310} (Å)	d_{222} (Å)	d_{320} (Å)	d_{321} (Å)	d_{400} (Å)	d_{420} (Å)	d_{421} (Å)
$(3,4\text{-}(3,5)^3)$12G4-CO_2CH_3	51	$p6mm$	39.4	22.8	19.8										
$(3,4\text{-}(3,5)^3)$12G4-COOH	97	$Pm\bar{3}n$	39.4	62.5	44.6	40.0	36.6	31.7	28.4	25.8	24.8	24.0	22.4		
$(4\text{-}3,4,5\text{-}3,5)$12G2-$CO_2CH_3$	60	$p6mm$	40.5		20.4										
	70	$p6mm$	40.0		20.0										
$(4\text{-}3,4,5\text{-}3,5)$12G2-$CH_2OH$	67	$p6mm$	40.4	23.3	20.2										
	92	$Pm\bar{3}n$			43.6	39.0	35.7	31.0	27.6	25.2	24.2	23.3	21.8	19.5	19.0
$(4\text{-}3,4,5\text{-}3,5)$12G2-COOH	80	$Im\bar{3}m$		38.5	27.2		22.1	19.1							
	120	$Im\bar{3}m$		36.3	25.7		20.9	18.1							
$(4\text{-}3,4,5\text{-}(3,5)^2)$12G3-$CO_2CH_3$	87	$p6mm$	40.0	23.0	19.9										
	97	$p6mm$	39.2	22.7	19.6										
$(4\text{-}3,4,5\text{-}(3,5)^2)$12G3-COOH	137	$p6mm$	39.7												
	155	$Pm\bar{3}n$			43.9	39.3	35.9	31.0	27.8						

determined by the principles of classic lyotropic liquid crystals. In our case, the dendritic architectural effect provides a more complex and unique phase behavior.

Conclusions

Two constitutional isomeric libraries of AB_2-based self-assembling monodendrons containing 3,4-dibenzyl ether and 3,5-dibenzyl ether internal repeat units and four different minidendritic repeat units on their periphery were synthesized. The structural and retrostructural analysis of their corresponding supramolecular dendrimers have demonstrated that the shapes of the supramolecular dendrimers and of their monodendritic building blocks are completely different; i.e., while the supramolecular dendrimers derived from 3,4-dibenzyl ether monodendrons are spherical, most the supramolecular dendrimers derived from 3,5-dibenzyl ether monodendrons are cylindrical. As a consequence, the monodendritic building blocks of the 3,4-disubstituted series have a conelike shape while those of 3,5-disubstituted series have a shape that corresponds to a fragment of a disk or a disklike shape. In addition, the 3,4-dibenzyl ether-based library resembles the 3,4,5-tribenzyl ether library reported previously from our laboratory.[3a,7] The major

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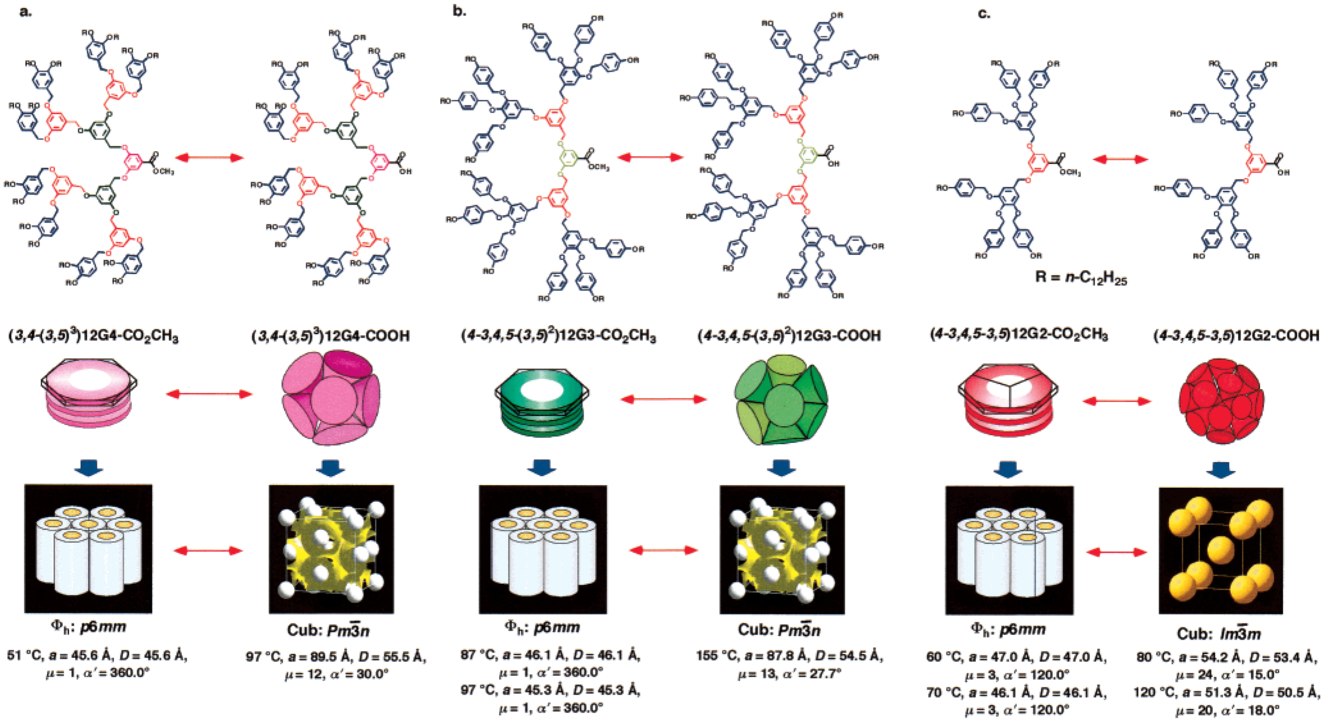
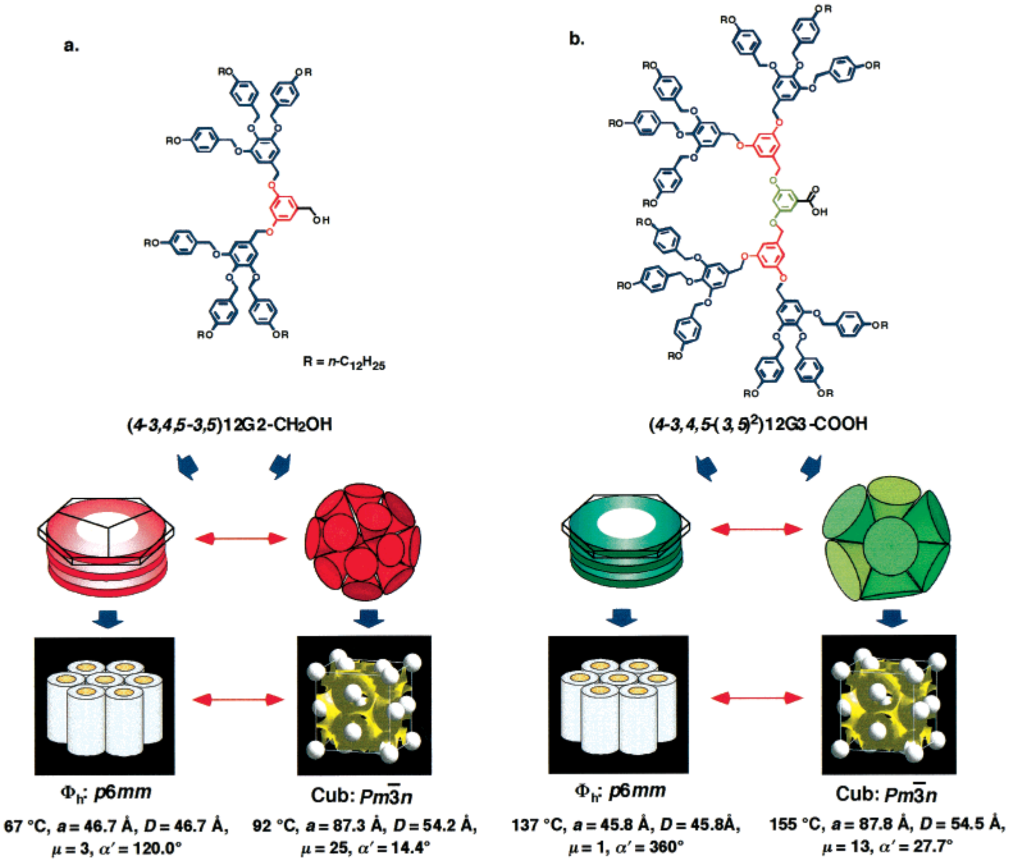
(22) (a) Percec, V.; Kawasumi, M. *Macromolecules* **1992**, *25*, 3843. (b) Percec, V.; Chu, P.; Kawasumi, M. *Macromolecules* **1994**, *27*, 4441.

(23) Borisch, K.; Diele, S.; Göring, P.; Kresse, H.; Tschierske, C. *J. Mater. Chem.* **1998**, *8*, 529.

Scheme 7. Reversible Shape Changes of Supramolecular Dendrimers via Molecular Recognition and Chemical Reactions



Scheme 8. Temperature-Induced Reversible Shape Change between Cylindrical and Spherical Supramolecular Dendrimers Self-Organized in a Lattice



difference between the 3,4-disubstituted and 3,4,5-trisubstituted constitutional isomeric libraries is the number of monodendritic building blocks that self-assemble in a supramolecular dendrimer. The 3,4,5-trisubstituted library has fewer monodendrons self-assembling in a supramolecular dendrimer than the 3,4-disubstituted-based library.

In all three libraries, the structure of the internal repeat unit determines the shape of the monodendron and of the supramo-

Table 8. Structural Characterization of Monodendrons that Self-Assemble into Supramolecular Dendrimers Which Exhibit Reversible Shape Changes

monodendron	T (°C)	lattice	$\langle d_{100}\rangle^a$ (Å)	a (Å)	$\rho_{20}{}^d$ (g/cm^3)	D (Å)	μ' ^{h}	μ	α' ^{l} (deg)
(*3,4*-(*3,5*)^3)12G4-CO_2CH_3	51	*p*6*mm*	39.5	45.6^a	0.99	45.6^e		1^i	360.0
(*3,4*-(*3,5*)^3)12G4- COOH	97	$Pm\bar{3}n$		89.5^b	1.00	55.5^f	95	12^j	30.0
(*4-3,4,5-3,5*)12G2-CO_2CH_3	60	*p*6*mm*	40.7	47.0^a	1.02	47.0^e		3^i	120.0
	70	*p*6*mm*	39.9	46.1^a	1.02	46.1^e		3^i	120.0
(*4-3,4,5-3,5*)12G2-CH_2OH	67	*p*6*mm*	40.4	46.7^a	1.01	46.7^e		3^i	120.0
	92	$Pm\bar{3}n$		87.3^b	1.01	54.2^f	196	25^j	14.4
(*4-3,4,5-3,5*)12G2-COOH	80	$Im\bar{3}m$		54.2^c	1.03	53.4^g	48	24^k	15.0
	120	$Im\bar{3}m$		51.3^c	1.03	50.5^g	40	20^k	18.0
(*4-3,4,5*-(*3,5*)^2)12G3-CO_2CH_3	87	*p*6*mm*	39.9	46.1^a	1.02	46.1^e		1^i	360.0
	97	*p*6*mm*	39.2	45.3^a	1.02	45.3^e		1^i	360.0
(*4-3,4,5*-(*3,5*)^2)12G3-COOH	137	*p*6*mm*	39.7	45.8^a	1.04	45.8^e		1^i	360.0
	155	$Pm\bar{3}n$		87.8^b	1.04	54.5^f	100	13^j	27.7

[a] *p*6*mm* hexagonal columnar lattice parameter $a = 2\langle d_{100}\rangle/3^{1/2}$; $\langle d_{100}\rangle = (d_{110} + 3^{1/2}d_{110} + 4^{1/2}d_{200} + 7^{1/2}d_{200})/4$. [b] $Pm\bar{3}n$ cubic lattice parameter $a = (2^{1/2}d_{110} + 4^{1/2}d_{200} + 5^{1/2}d_{210} + 6^{1/2}d_{211} + 8^{1/2}d_{220} + 10^{1/2}d_{310} + 12^{1/2}d_{222} + 13^{1/2}d_{320} + 14^{1/2}d_{321} + 16^{1/2}d_{400} + 20^{1/2}d_{420} + 21^{1/2}d_{421})/12$. [c] $Im\bar{3}m$ cubic lattice parameter $a = (2^{1/2}d_{110} + 4^{1/2}d_{200} + 6^{1/2}d_{211} + 8^{1/2}d_{220})/4$. [d] ρ_{20} = experimental density at 20 °C. [e] Experimental column diameter $D = 2\langle d_{100}\rangle/3^{1/2}$. [f] Experimental $Pm\bar{3}n$ spherical diameter $D = 2\sqrt[3]{3a^3/32\pi}$. [g] Experimental $Im\bar{3}m$ spherical diameter $D = 2\sqrt[3]{3a^3/8\pi}$. [h] Number of monodendrons per unit cell $\mu' = (a^3N_A\rho)/M$. [i] Number of monodendrons per 4.7 Å column stratum $\mu = (3^{1/2}N_AD^2t\rho)/2M$ (Avogadro's number $N_A = 6.022\,045 \times 10^{23}$ mol^{-1}, the average height of the column stratum $t = 4.7$ Å, and M = molecular weight of monodendron). [j] Number of monodendrons per $Pm\bar{3}n$ spherical dendrimer $\mu = \mu'/8$. [k] Number of monodendrons per $Im\bar{3}m$ spherical dendrimer $\mu = \mu'/2$. [l] Projection of the solid angle for tapered and conical monodendron $\alpha' = 360/\mu$ (deg).

lecular dendrimer. However, for the same internal repeat unit, the size of the monodendron and of the supramolecular dendrimer is determined by the structure of the repeat unit on their periphery. This result is in agreement with the first examples of monodendrons and hyperbranched polymers that self-organize in a lattice reported from our laboratory[10,22] and with related experiments reported from other laboratories.[24] The number of monodendrons that self-assemble in a supramolecular dendrimer determines the solid angle of the monodendron. The solid angle of the monodendron determines the shape of the monodendron and of the supramolecular dendrimer and ultimately the diameter of the supramolecular dendrimer. Regardless of the shape of the monodendron and of the supramolecular dendrimer, the solid angle of the monodendron increases with the increase of the generation number. Subsequently, the shape of the monodendron changes from a fragment of a disk to a disk, to a cone, to a half of a sphere, and ultimately to a sphere. As a consequence, the diameter of the supramolecular dendrimers self-assembled from AB_2 or AB_3 benzyl ether monodendrons with identical internal repeat units in each generation and different repeat units on their periphery seem to be limited to maximum 80 Å. This is because prior to the transition from a monodendritic fragment of a sphere to a monodendritic sphere,[7b] the increase in solid angle is very large and as a consequence the increase in diameter is very small. The library based on 3,5-disubstituted benzyl ethers provides the first example of *quasi-equivalent* monodendrons and supramolecular dendrimers that are able to change their shape in a reversible way both by the change of the functionality available at their focal point and by temperature. In addition, the same library provided the first example of a spherical supramolecular dendrimer that self-organizes in an $Im\bar{3}m$ lattice and several examples of monodendrons that self-assemble and subsequently self-organize into new lattices. The three libraries of self-assembling monodendrons discussed here provide building blocks required for the construction of functional supramolecular and single-molecule-based nanosystems. However, alternative design principles should be elaborated for the construction of monodendrons and supramolecular dendrimers of larger dimensions.

Experimental Section

The synthetic methods and techniques are similar to those used conventionally in our laboratory.[3a,7,8] They are presented in the Supporting Information.

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Supporting Information Available: Experimental procedures with characterization results and figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Baars, M. W. P. L.; Söntjens, S. H. M.; Fischer, H. M.; Peerlings, H. W. I.; Meijer, E. W. *Chem. Eur. J.* **1998**, *4*, 2456 and references therein.