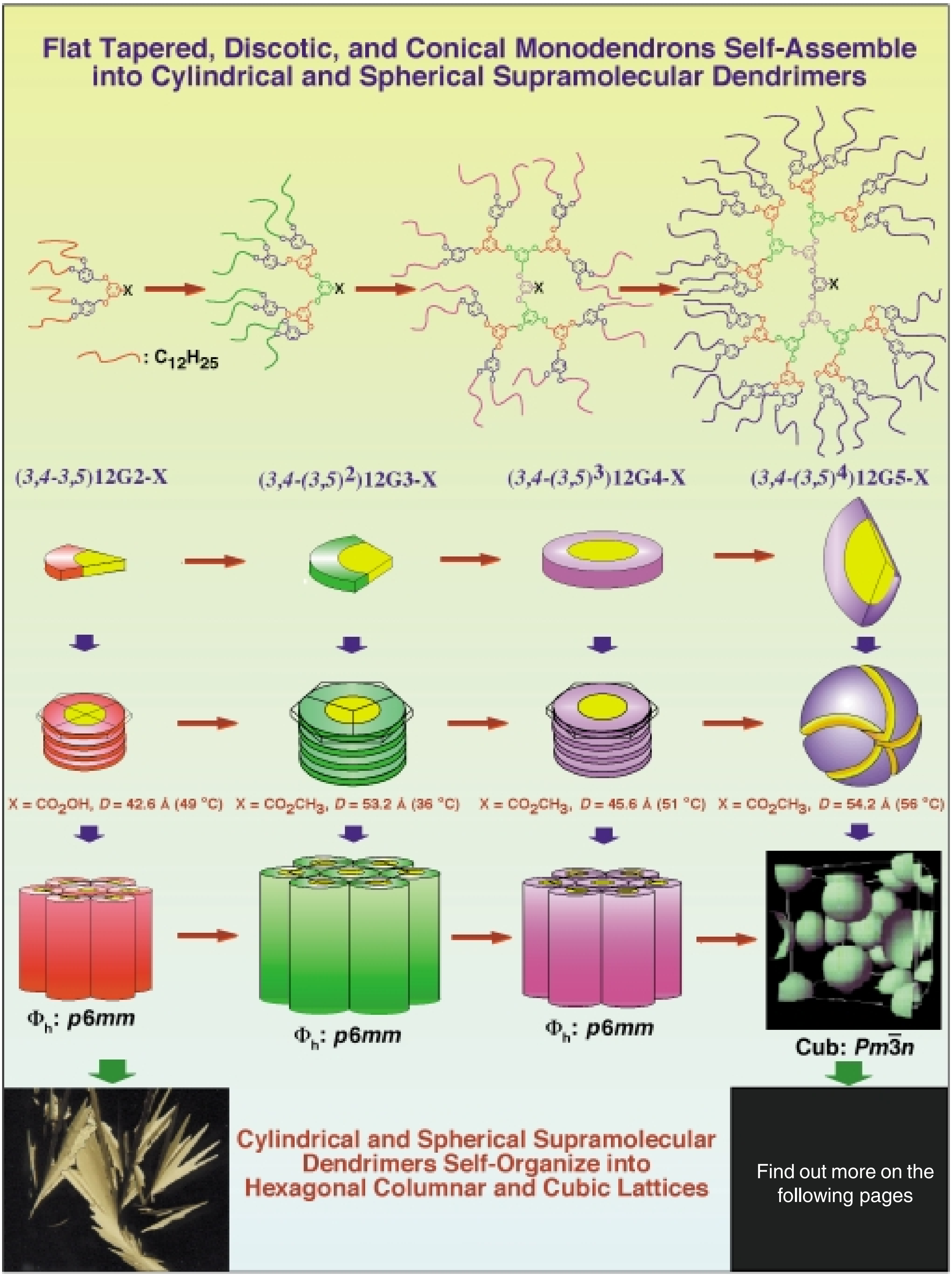

Flat Tapered, Discotic, and Conical Monodendrons Self-Assemble into Cylindrical and Spherical Supramolecular Dendrimers

Cylindrical and Spherical Supramolecular Dendrimers Self-Organize into Hexagonal Columnar and Cubic Lattices

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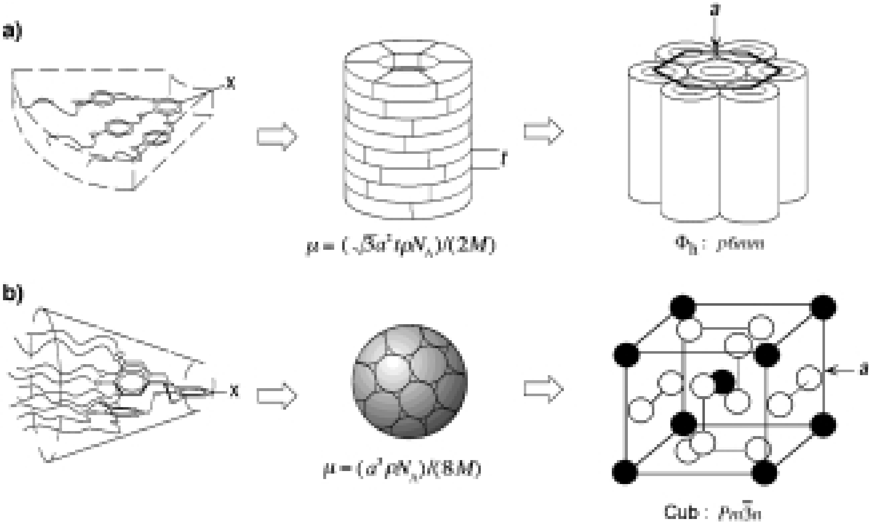
From Molecular Flat Tapers, Discs, and Cones to Supramolecular Cylinders and Spheres using Fréchet-Type Monodendrons Modified on their Periphery**

Virgil Percec,* Wook-Dong Cho, Goran Ungar, and Duncan J. P. Yeardley

Dendritic building blocks are one of the most powerful architectural motifs for the construction of complex molecular, macromolecular, and supramolecular functional nanosystems that have the potential to generate many novel technological applications.[1] We have elaborated a rational approach to the design, synthesis, and structural analysis of dendritic building blocks. These blocks self assemble into cylindrical or spherical supramolecular dendrimers, that in turn semiorganize into a hexagonal columnar *p6mm*[2] or cubic *Pm*$\bar{3}$*n*[3a] liquid-crystalline (LC) lattices, respectively (Scheme 1). The analysis of these lattices by X-ray diffraction (XRD) experiments provides access to the determination of the shape and size of the dendritic building blocks. Subsequently, these blocks are employed in the synthesis of cylindrical or spherical macromolecular objects[4] with controlled internal structures, that self-organize into similar lattices. More complex objects, able to self-organize into various superlattices,[5] were also developed from these dendritic building blocks. Cylindrical macromolecules that do not self-organize to hexagonal columnar lattices[6a–c] or self-organize to a nematic LC phase[6d] were also reported.

Presently we are elucidating the principles that govern the control of the shape and size of self-assembling monodendrons and, through their architecture, the shape and size of their supramolecular and macromolecular dendritic forms. Toward this end, we are investigating libraries of self-assembling monodendrons which differ in their: minidendron architecture on the periphery;[2a, 3a, 7] internal repeat unit architectures;[8] generation number;[7] core functionalities;[4a,b] core multiplicities;[2a, 3a] and so forth.



Scheme 1. Schematic representation of a) the self-assembly of flat, tapered monodendrons into a supramolecular cylindrical dendrimer and their subsequent self-organization to a hexagonal columnar *p6mm* (Φ_h) LC lattice, and b) the self-assembly of conical monodendrons into a supramolecular spherical dendrimer and their subsequent self-organization in the cubic *Pm*$\bar{3}$*n* (Cub) LC lattice. For explanation on the calculation of μ, see Table 2; $t = 4.7$ Å. X = endoreceptor or functional group.

In this communication, we report the attachment of the first generation 3,4-bis(*n*-dodecan-1-yloxy)benzyl ether monodendron (that is, minidendron[5]) to the periphery of Fréchet-type dendritic repeat units (3,5-disubstituted benzyl ethers) to produce a class of hybrid self-assembly monodendrons. The first five generations of these monodendrons exhibit the largest diversity of monodendron and supramolecular dendrimer shapes reported to date. Particularly interesting for the design of novel architectural motifs, lattices, and superlattices is that the fourth generation includes the first monodendron that exhibits a disclike shape.

Scheme 2 describes the synthesis of the first five generations of monodendrons **(*3,4*-(*3,5*)$^{n-1}$)12G*n*-X** (generation number $n = 1-5$) by using our previously reported synthetic procedure.[3a, 7] Details of their synthesis and characterization, by ^{1}H and ^{13}C NMR, HPLC, GPC, elemental analysis, differential scanning calorimetry (DSC), XRD and thermal-optical polarized microscopy (TOPM), by our standard procedures[3a, 7] are available in the Supporting Information and in Tables 1 and 2. The synthesis and characterization of **(*3,4*)12G1-X** (**X** = CO_2CH_3,[9a,b] CH_2OH,[9c,d] CH_2Cl[4b]) and of **(*3,4-3,5*)12G2-X** (**X** = CO_2CH_3, COOH)[4b] have been reported. Table 1 summarizes the most representative analytical results and the phase behavior of selected supramolecular dendrimers obtained by a combination of DSC, TOPM (Figure 1), and XRD.

Scheme 3 illustrates the mechanism of self-assembly over four monodendron generations, the lattice dimensions *a* [Å], the number of monodendrons (μ) forming the cross-section of thickness *t* ($t = 4.7$ Å) of a supramolecular cylinder or of a supramolecular sphere (Scheme 1), and their diameter *D* [Å]. The temperature at which the XRD analysis was performed is

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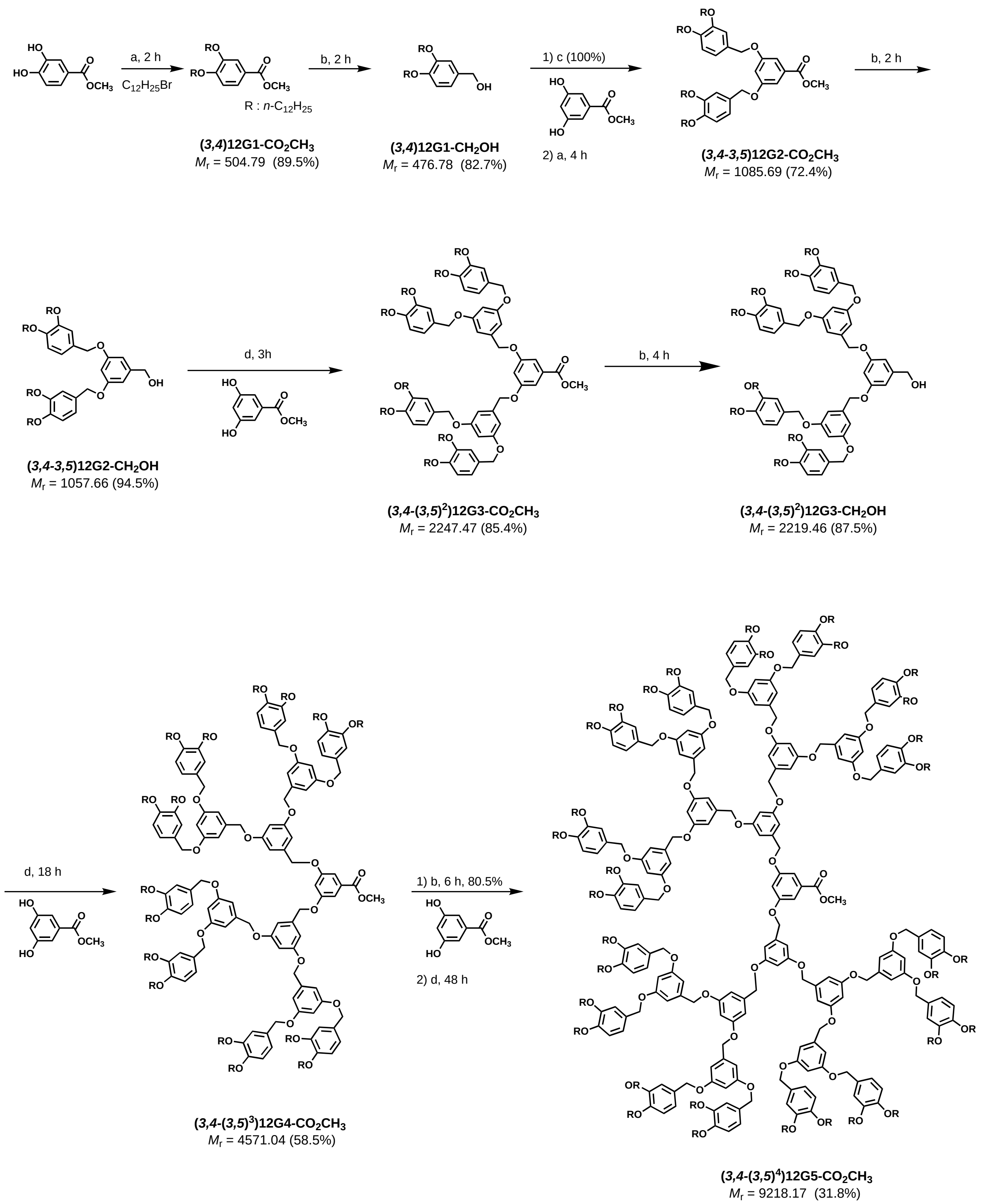


Scheme 2. Synthesis of **(*3,4*-(*3,5*)$^{n-1}$)12G*n*-X** (**X** = CO_2CH_3, CH_2OH, and CH_2Cl) monodendrons. a) k_2CO_3, DMF, 70° C; b) $LiAlH_4$, THF, 20° C; c) $SOCl_2$,CH_2Cl_2, DMF (cat.); d) diethylazodicarboxylate (DEAD), PPh_3, THF, 20° C.

presented in parentheses in the same Scheme and also in Table 2.

The results from Tables 1, 2, and Scheme 3 can be summarized as follows. The first generation monodendron **(*3,4*)12G1-X** (**X** = CO_2CH_3, CH_2OH) (that is, minidendron), that was used to functionalize the periphery of the later generations of monodendrons, is crystalline (Table 1). The second, third, and fourth generation monodendrons self-

Table 1. Theoretical and experimental (GPC) molecular masses, experimental densities,[a] and thermal transitions of selected monodendrons ***(3,4-(3,5)*$^{n-1}$)12G*n*-X** (**X** = CH_2OH, COOH, CO_2CH_3).

Monodendron	M_r	M_n (GPC)	M_w/M_n (GPC)	ρ_{20}[a] [g cm^{-3}]	Thermal transition [°C] and corresponding enthalpy change [kcal mol^{-1}]	
					heating[b]	cooling
***(3,4)*12G1-CO_2CH_3**	504.79	829	1.01	1.01	1) k −2 (0.92) k 16 (2.93) k 54 (17.13) i 2) k 38 (1.16) −k 41 (3.69) k 54 (16.95) i	i 22 (13.58) k
***(3,4)*12G1-CH_2OH**	476.78	796	1.01	1.01	1) k 12 (4.23) k 53 (16.06) i 2) 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**	1057.68	1663	1.04	0.99	1) k 65 (18.54) −k 69 (0.37) k 76 (5.47) i 2) k 61 (12.91) i	i 49 (1.24) Φ_h 37 (8.72) k
***(3,4-3,5)*12G2-COOH**	1071.66	1673	1.04	1.02	1) k 69 (21.82) i 2) k 14 (3.02) Φ_h[c] 68 (3.94) i	i 63 (4.00) Φ_h 5 (2.45) k
***(3,4-(3,5)*^{2})12G3-CO_2CH_3**	2247.47	3216	1.07	1.01	1) k −5 (3.55) k 39 (12.56) k 45 (2.33) k 50 (0.86) i 2) 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**	4571.04	5998	1.11	0.99	1) k 15 (72.96) k 42 (4.38) Φ_h 66 (1.09) i 2) k −12 (18.92) Φ_h 66 (1.06) i	i 58 (0.86) Φ_h −18 (14.95) k
***(3,4-(3,5)*^{4})12G5-CO_2CH_3**	9218.17	8638	1.09	0.99	1) k −6 (41.47) k 46 (11.79) Cub[d] 67 (3.79) i 2) k −5 (34.85) T_g 36 Cub 59 (1.61) Cub 66 (1.40) i	i 57 (0.42) Cub −11 (36.61) k

[a] Densities were measured at 20 °C. [b] 1) Data from the first heating and cooling scans; 2) data from the second heating scan. [c] Φ_h = Hexagonal-columnar *p6mm* LC phase. [d] Cub = Cubic $Pm\bar{3}n$ LC phase.

Table 2. Structural characterization of supramolecular dendrimers from selected monodendrons ***(3,4-(3,5)*$^{n-1}$)12G*n*-X**.

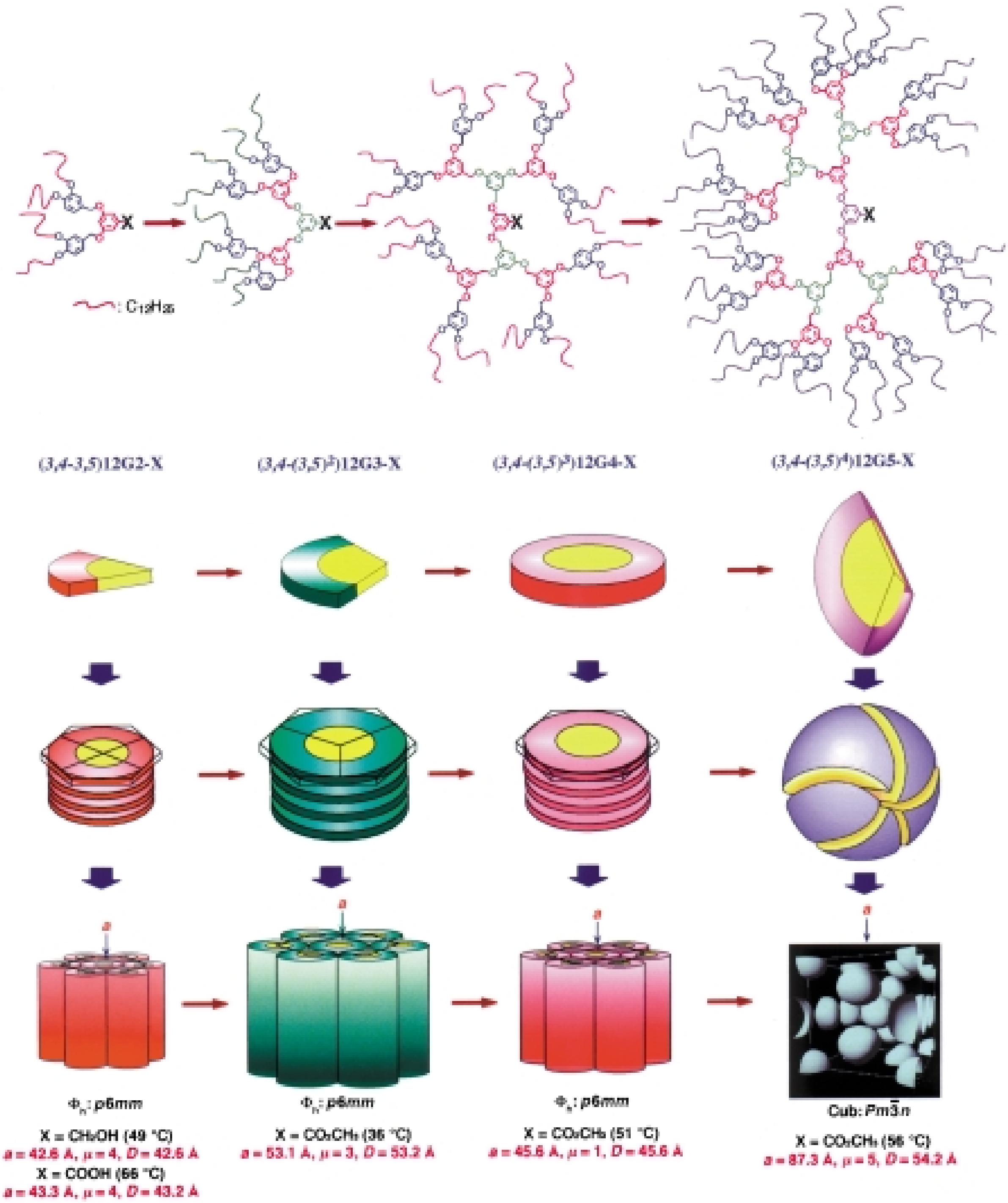
Monodendron	T [°C]	Lattice	$\langle d_{100}\rangle$[a]	$\langle d_{210}\rangle$[b]	a [Å]	R [Å]	μ'[g]	μ
***(3,4-3,5)*12G2-CH_2OH**	49	*p6mm*	36.9		42.6[c]	21.3[e]		4[h]
***(3,4-3,5)*12G2-COOH**	66	*p6mm*	37.5		43.3[c]	21.6[e]		4[h]
***(3,4-(3,5)*^{2})12G3-CO_2CH_3**	36	*p6mm*	46.0		53.1[c]	26.6[e]		3[h]
***(3,4-(3,5)*^{3})12G4-CO_2CH_3**	51	*p6mm*	39.5		45.6[c]	22.8[e]		1[h]
***(3,4-(3,5)*^{4})12G5-CO_2CH_3**	56	$pm\bar{3}n$		39.0	87.3[d]	27.1[f]	43	5[i]

[a] $\langle d_{100}\rangle = (d_{100} + \sqrt{3}d_{110} + 2d_{200})/3$. [b] $\langle d_{210}\rangle = (\sqrt{2}d_{110} + \sqrt{4}d_{200} + \sqrt{5}d_{210} + \sqrt{6}d_{211} + \sqrt{8}d_{220})/5\sqrt{5}$. [c] Hexagonal columnar lattice parameter $a = 2\langle d_{100}\rangle/\sqrt{3}$. [d] Cubic lattice parameter $a = \sqrt{5}d_{210}$. [e] Column radius $R = \langle d_{100}\rangle/\sqrt{3}$. [f] Sphere radius $R = \sqrt[3]{(3a^3/32\pi)}$. [g] Number of monodendrons per unit cell $\mu' = (a^3\rho)/M$. [h] Number of monodendrons per cylinder stratum $\mu = (4\sqrt{3}N_AR^2t\rho)/2M$ (Avogadro's number $N_A = 6.022045 \times 10^{23}$ mol^{-1}, average height of the column stratum $t = 4.7$ Å, M = molecular mass of the monodendron). [i] Number of monodendrons per spherical dendrimer $\mu = \mu'/8$.

assemble into supramolecular cylinders which in turn self-organize in a hexagonal columnar *p6mm* LC lattice. Under the polarized microscope the texture of their LC phase shows a combination of large isotropic domains, characteristic of a homeotropic arrangement of the columns, and a focal conic, fan-shaped anisotropic texture (Figure 1).[2a, 7] An XRD analysis of these lattices (Scheme 1)[2a] demonstrates that ***(3,4-3,5)*12G2-X** (**X** = CH_2OH, COOH) have a flat, tapered shape equivalent to a quarter of a cross section of its supramolecular cylinder (D = 42.6, 43.2 Å, respectively; t = 4.7 Å). Monodendron ***(3,4-(3,5)*^{2})12G3-CO_2CH_3** also has a flat tapered shape. However, its size represents a third of a cross section of its supramolecular cylinder (D = 53.2 Å). The shape of ***(3,4-(3,5)*^{3})12G4-CO_2CH_3** is equivalent to an entire cross section of its supramolecular cylinder, that is, it is a disclike molecule (D = 45.6 Å). This is the first example of a monodendron that has a disclike shape. Monodendron ***(3,4-(3,5)*^{4})12G5-CO_2CH_3** is equivalent of a fifth of its supramolecular sphere (D = 54.2 Å). Under the polarized microscope the texture of the cubic phase, self-organized from the supramolecular spheres, is optically isotropic.

Previously, we reported the first examples of monodendrons and supramolecular dendrimers with a shape controlled by the generation number and quantitative analysis by XRD.[7a] This experiment demonstrated the validity of the theoretical prediction that the generation number should control the shape of the dendrimer.[7b] For this previous report, the transition from a supramolecular cylinder to a supramolecular sphere occurred by changing the shape of the monodendron directly, from that of a half disc to a sixth of a sphere without passing through a complete disc shape. The ability to create the disclike molecule ***(3,4-(3,5)*^{3})12G4-X** provides a general strategy for the synthesis of supramolecular columns with anisotropic surfaces. This synthesis hinges on the design of surface patterns with ***(3,4)*12G1-X** minidendrons functionalized with chemically dissimilar, flexible groups.

Finally, the results reported here can contribute in a quantitative way to some of the most interesting applications



Scheme 3. XRD analysis of supramolecular cylindrical and spherical dendrimers self-assembled from **$(3,4\text{-}(3,5)^{n-1})12Gn\text{-}X$** monodendrons. Variables: a [Å] is the lattice parameter; D [Å] is the diameter of the supramolecular columnar or spherical dendrimer; μ is the number of monodendrons forming the 4.7 Å cross-section of a supramolecular cylindrical of spherical supramolecular dendrimer; the temperature [°C] of the XRD experiments in given in parentheses.

that are widely pursued with Fréchet-type monodendrons and dendrimers. For example, several research groups are exploiting these dendritic building blocks to explore concepts based on various site isolation strategies and controlled microenvironments in both the solution and bulk states. Such site isolation is expected to occur during the shape transition to a globular structure.[10] Elegant experiments by Fréchet et al.[10] and Aida et al.[11] have demonstrated that, in solution, this shape transition occurs during the development of the monodendron from generation three to four, although the extent of site isolation continues to increase from generation four to five.[11] The fifth generation monodendron adopts a globular shape in the bulk state.[12] The results from Scheme 3 support all previous reports.[10, 11, 12] If X in the **$(3,4\text{-}(3,5)^{n-1})12Gn\text{-}X$** monodendron represents the site to be isolated, the site-isolating globular shape begins at generation five in the solid state but at generation four in a dilute solution. This occurs for reasons of conformational flexibility,

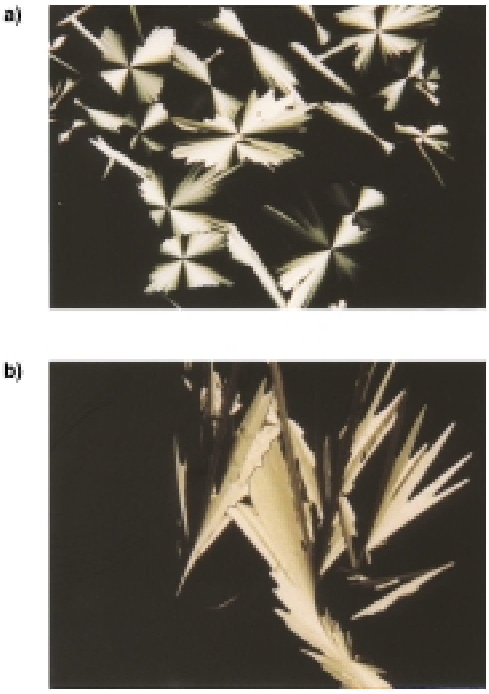


Figure 1. Representative thermal-optical polarized microscopy pictures showing the textures of the hexagonal columnar (Φ_h) mesophases of a) **(*3,4–3,5*)12G2-CH$_2$OH** upon cooling from 76 °C to 54.9 °C at 1 K min^{-1}; and b) **(*3,4*-(*3,5*)^2)12G3-CO$_2$CH$_3$** obtained upon cooling from 50 °C to 45.1 °C at 1 K min^{-1}.

as the disclike molecule **(*3,4*-(*3,5*)^3)12G4-X** can adopt a globular shape in solution. The extent of site isolation will increase from the fourth to the fifth and higher generations.

These results suggest synthetic methods that place X in the center of a single spherical monodendron. Such a molecule would generate an ideal site-isolation mechanism both in the bulk and in solution.

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Nickel-Catalyzed Cross-Coupling of Aryl Chlorides with Aryl Grignard Reagents**

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Christian W. K. Gstöttmayr, and
Wolfgang A. Herrmann*

Dedicated to Professor Wilhelm Keim
on the occasion of his 65th birthday

The Grignard cross-coupling mediated by nickel and palladium catalysts[1, 2] represents a useful synthetic approach to biaryls, terphenyls, and oligoaryls which are important

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