Monodendrons synthesized by a convergent method and dendrimers prepared by a divergent method or by the covalent or supramolecular assembly of monodendrons to a multiple molecular or macromolecular core are valuable building blocks used in the construction of object-like nanosystems with novel functions and properties. Recently, we have elaborated a novel approach to the design, shape, and size analysis of self-assembling monodendrons and self-organizable supramolecular and macromolecular dendrimers (Scheme 1). This strategy involves the quantitative analysis by X-ray diffraction (XRD) of the thermotropic liquid crystalline (LC) 2-D hexagonal columnar P6mm and 3-D cubic Pm3m[12] and Pm3n[15] lattices self-organized from cylindrical and respectively spherical supramolecular dendrimers. These building blocks are subsequently employed in the construction of more complex functional architectural motifs.

This contribution reports the design, synthesis, and the structural analysis by XRD of the first spherical functional monodendron that self-organizes in a cubic Pm3n lattice. The direct visualization by scanning force microscopy (SFM) of the spherical monodendron both as a single molecule and in disordered monolayers is also reported. Previous examples of spherical dendritic objects self-organizable in a cubic lattice were obtained only by the self-assembly of conical and hemispherical monodendrons. Dendrimers obtained by a divergent synthesis, that have a spherical shape in solution but lack the shape perfection required for self-organization in a lattice, were also reported. Their spherical shape was estimated, in solution, by SAXS and TEM and on a surface by AFM or SPM.

Scheme 1. Self-assembly of Conical Monodendrons into Supramolecular Spherical Dendrimers and the Subsequent Self-Organization of the Supramolecular Dendrimers in a Pm3n Cubic Lattice

Scheme 2. Synthesis of (3,4-(3,4,5)n−1)12Gn-X (n = 1 to 5) Monodendrons and Determination of Shape and Size by XRD Analysis of the Pm3n Cubic Lattice

Design and Structural Analysis of the First Spherical Monodendron Self-Organizable in a Cubic Lattice

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Scheme 2 and Table 1 summarize the synthesis and the results of the structural analysis by a combination of differential scanning calorimetry (DSC), thermal optical polarized microscopy (TOPM), XRD, and SFM of the first five generations of (3,4-(3,4,5)n−1)12Gn-X (where n is the generation number, n = 1 to 5) monodendrons. The difference between the GPC and theoretical molecular weights of these monodendrons is in agreement with previously reported data, demonstrating the decrease in hydrodynamic volume with the increase of Gn. The Pm3n cubic lattice dimension (a, in Å), the diameter of the supramolecular or molecular dendritic sphere (D, in Å), the number of monodendrons (µ) that self-assemble into a sphere, the temperature at which the XRD analysis was performed, the functional group X, and the theoretical molar mass of the monodendron are also shown in

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Table 1. Theoretical and Experimental Molecular Weights Determined by GPC, Experimental Densities, and Thermal Transitions of Selected Examples of (3,4-(3,4,5))n12Gn-X (X = CH$_2$OH, COOH, and CO$_2$CH$_3$) Monodendrons

<table>
<thead>
<tr>
<th>Monodendron</th>
<th>$M_w$ (GPC)</th>
<th>$M_n$ (GPC)</th>
<th>$\rho^\circ$ (g/cm$^3$)</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3,4)12G1-CH$_2$OH</td>
<td>477</td>
<td>830</td>
<td>1.02</td>
<td>1.00</td>
<td>k$^\circ$ 12 (4.23) k 53 (16.06) i i 27 (10.91) k</td>
</tr>
<tr>
<td>(3,4,3,4,5)9G2-CH$_2$OH</td>
<td>1532</td>
<td>2069</td>
<td>1.04</td>
<td>1.00</td>
<td>k 37 (0.53) – k 39 (2.32) k 52 (14.26) i</td>
</tr>
<tr>
<td>(3,4-(3,4,5))412G3-COOH</td>
<td>4713</td>
<td>5067</td>
<td>1.07</td>
<td>0.99</td>
<td>k 0 (2.42) k 60 (39.14) Cub 133 (4.45) i i 128 (4.31) Cub 15 (20.49) k</td>
</tr>
<tr>
<td>(3,4-(3,4,5))412G5-CO$_2$CH$_3$</td>
<td>3273</td>
<td>3540</td>
<td>1.06</td>
<td>0.98</td>
<td>k 42 (18.32) Cub 133 (4.30) i k 9 (7.42) k 12 (6.84) k 131 (15.74) k</td>
</tr>
</tbody>
</table>

* Densities were measured at 20 °C. ° Data from the first DSC heating and cooling scans are on the first line, and data from the DSC second heating are on the second line. ° k = crystalline. ° Cub = Cubic Pm3n. ° Decomposition after first heating.

Scheme 2. Both their synthesis and structural analysis were carried out as reported previously for the first four generations of (3,4,5)-(3,4,5)$^{n-1}$12Gn-X and the first three generations of (4-(3,4,5)$^{n-1}$12Gn-X monodendrons. (3,4-(3,4,5)$^{n-1}$12Gn-X represents the third series from a library of self-assembling monodendrons based on 3,4,5-trisubstituted AB$_3$ benzyl ether repeat units. They are functionalized on the periphery with 3,4-bis(n-dodecan-1-yl)oxy)benzyl ether groups. (3,4,5)-(3,4,5)$^{n-1}$12Gn-X series is functionalized on the periphery with 3,4,5-tris(n-dodecan-1-yl)oxy)benzyl ether, and while the series (4-(3,4,5)$^{n-1}$12Gn-X contains 3,4,5-tris[p-(n-dodecan-1-yl)oxy]benzyloxy]benzyl ether groups on the periphery.

The rational for the selection of the series of experiments described in Scheme 2 is as follows. The analysis of (3,4,5)-(3,4,5)$^{n-1}$12Gn-X and (4-(3,4,5)$^{n-1}$12Gn-X demonstrated that for the same internal repeat unit the shape and size of the monodendron is determined by the structure of the first generation monodendron attached on the periphery. The fourth generation monodendron (3,4,5)-(3,4,5)$^{5}$12G4-COOH has a hemispherical shape and a theoretical molar mass of 19 191. Attempts to synthesize its fifth generation did not succeed due to the low molar concentration of its X group and the steric hindrance induced by its shape. The third generation of (4-(3,4,5)$^{5}$12G3-CO$_2$CH$_3$ has a shape that is equivalent with a sixth of a sphere and a theoretical molar mass of 9252. Therefore, two additional generations would have been required to accomplish a spherical monodendron. This would have produced an even larger molar mass and similar steric constrains as (3,4,5)-(3,4,5)$^{5}$12G4-X. Therefore, we have advanced the hypothesis that the experiments summarized in Scheme 2 could alleviate some of these problems since this series of monodendrons would be expected to have shapes, sizes, and molar masses between those of the two series reported previously.

The results presented in Scheme 2 can be summarized as follows. (3,4)12G1-X (not shown in Scheme 2) is only crystalline. Twenty three (3,4,3,4,5)12G2-CH$_2$OH monodendrons and respectively 10 (3,4,5)-(3,4,5)$^{5}$12G3-COOH monodendrons self-assemble into a sphere. Therefore, we hypothesize that each has a conical shape. Only three (3,4,3,4,5)$^{5}$12G4-COOH monodendrons of molar mass 12414 are required to self-assemble into a sphere. Finally, a single (3,4,3,4,5)$^{5}$12G5-CO$_2$CH$_3$ monodendron forms a sphere. This functional single monodendron–single sphere has a single X functionality isolated in its core (Scheme 2). The most significant difference between a spherical monodendron and a spherical dendrimer is that the last one does not have a single functional group in its core.

According to the results outlined in Scheme 2, a single (3,4,3,4,5)$^{5}$12G5-CO$_2$CH$_3$ monodendron of theoretical molar mass 42 731, most probably the largest synthesized so far, exhibits a spherical shape when the molecule is self-organized in a cubic Pm3n lattice. The most intriguing question is what is the shape of this molecule in a disordered assembly or as a single molecule? Does it display the same shape as in its Pm3n lattice? Single molecules and dissolved molecules within islands of several hundred were visualized by SFM on mica (Figure 1). Within islands, the average diameter of the molecule is 60 Å, and the average height is 50 Å (Figure 1a). These results are in excellent agreement with the diameter determined by XRD in a lattice (57 Å). If we consider that the resolution of the SFM is ±5 Å, these data may suggest that on a surface, a monolayer of densely packed monodendrons could adopt only a slightly oblate spherical shape (Figure 1a). The average diameter of the single monodendron is 100 Å, and its height is 25 Å (Figure 1b). The distortion of the shape of the single monodendron on a surface is in agreement with previous reports. However, in these reports the dendrimers did not assemble into a lattice. Therefore, these authors could not offer information on the shape of the dendrimers within such a lattice. This distortion is most probably due to the interaction of the single monodendron with the surface and/or its soft structure. The most dramatic shape change reported so far is in spherical from in solution to “windscreen wiper” in a lattice. Experiments to quantitatively elucidate the similarities and differences between monodendrons in a lattice, in the disordered bulk state, in solution, and as single molecules together with the elaboration of novel single molecule-based functional nanosystems are in progress.

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Supporting Information Available: Reaction schemes, experimental procedures, analytical data, tables with characterization results, and references (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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