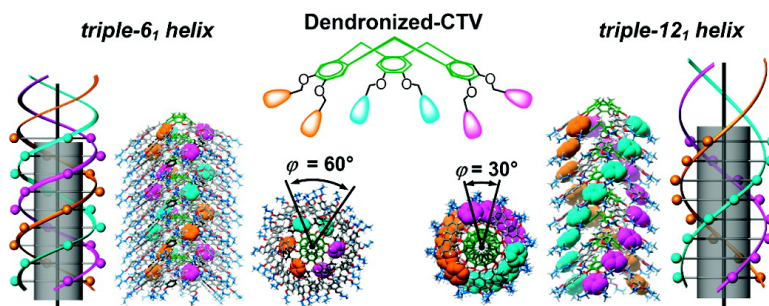


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J. Am. Chem. Soc., **2008**, 130 (44), 14840-14852 • DOI: 10.1021/ja806524m • Publication Date (Web): 09 October 2008

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Molecular Structure of Helical Supramolecular Dendrimers

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Abstract: The molecular structure of helical supramolecular dendrimers generated from self-assembling dendrons and dendrimers and from self-organizable dendronized polymers was elucidated for the first time by the simulation of the X-ray diffraction patterns of their oriented fibers. These simulations were based on helical diffraction theory applied to simplified atomic helical models, followed by Cerius2 calculations based on their complete molecular helical structures. Hundreds of samples were screened until a library containing 14 supramolecular dendrimers and dendronized polymers provided a sufficient number of helical features in the X-ray diffraction pattern of their oriented fibers. This combination of techniques provided examples of single- 9_2 and -11_3 helices, triple- 6_1 , -8_1 , -9_1 , and -12_1 helices, and an octa- 32_1 helix that were assembled from crownlike dendrimers, hollow and nonhollow supramolecular crownlike dendrimers, hollow and nonhollow supramolecular disklike dendrimers, and hollow and nonhollow supramolecular and macromolecular helicene-like architectures. The method elaborated here for the determination of the molecular helix structure was transplanted from the field of structural biology and will be applicable to other classes of synthetic helical assemblies. The determination of the molecular structure of helical supramolecular assemblies is expected to provide an additional level of precision in the design of helical functional assemblies resembling those from biological systems.

Introduction

During the first half of the previous century experimental results suggested that functional biomolecules may have a well-defined atomic composition and a fixed spatial structure rather than being random aggregates of atomic and molecular units that would preclude crystallization. As a consequence, complex biological macromolecules have been shown to exhibit nonisotropic X-ray scattering.¹ Their structural analysis was accelerated by Pauling's suggestion of a possible helical structure of filamentous proteins.² Pauling's idea initiated the demand for a method to perform the structural analysis of a fibrous helix. Prior to the development of the theory required for this analysis, a quasi-planar ribbonlike conformation was assigned to the X-ray diffraction (XRD) pattern obtained from fibers of helical peptides.³ In 1952 Cochran, Crick, and Vand (CCV) reported the helical diffraction theory elaborated for the interpretation of the XRD patterns obtained from helical protein fibers.⁴ The CCV publication was used immediately to reinterpret and propose an α -helix for the previous incorrect interpretation³ of the structure of the fibrous peptides,⁴ of other

proteins folding in single-, double- and triple-helical structures and to demonstrate that the globular proteins are also constructed from α -helices and other secondary structures.⁵ The helical diffraction theory⁴ was unexpectedly important in solving many other helical macromolecules of biological origin and of their complexes including collagen,^{6a} amylose triacetate,^{6b} DNA,⁷ tobacco mosaic virus (TMV),⁸ bacterial flagellar filament,⁹ and many others. The application of this theory to the elucidation of the helical structure of complex biological molecules was reviewed.¹⁰

One of the significant contributions of the CCV theory⁴ to nonbiological molecules was the elucidation of the helical

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structure of carbon nanotubes.¹¹ The first group of nonbiological macromolecules that exhibited helical structures in their crystal state were stereoregular synthetic polymers.¹² However, by contrast with biological macromolecules, due to their fast conformational dynamics they exhibit only short helical fragments in solution.^{12b} Synthetic polymers containing bulky side groups,¹³ helicates,^{14a-c} single- and double-stranded helical polymers^{14c,k} and other foldamers,^{14d-j} and many classes of supramolecular assemblies,¹⁵ including crown-shape^{15q} and discotic^{15c,d,m,n,r,s} molecules, helicenes,^{15t} supramolecular den-

drimers,¹⁶ and self-organizable dendronized polymers,¹⁷ exhibit helical structures that are persistent, just like biological assemblies,^{7,8} in bulk and in solution. However, only mono-disperse helicates^{14a-c} and some foldamers^{14g,j} form single crystals of the quality required for the determination of their helical structure. The other compounds had their helical structure suggested mostly by circular dichroism (CD). CD experiments provide limited information on the helical structure and are susceptible to errors during their interpretation.¹⁸ From this

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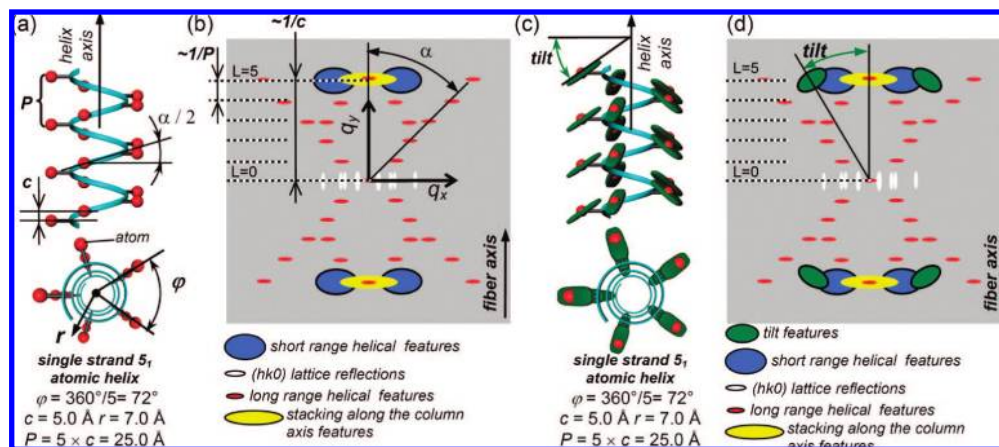


Figure 1. Diffraction by a helical fiber: (a) a 5_1 single-strand atomic helix and its structural parameters; (b) the simplified representation of the fiber diffraction generated for the structure from a by using the helical diffraction theory; (c) a 5_1 single-strand atomic helix model generated from tilted groups of atoms and its structural parameters; (d) the simplified representation of the fiber diffraction generated for the structure from b by using the helical diffraction theory.

group of macromolecules and supramolecular assemblies only crown-shaped^{15q} and discotic molecules,^{15r,s,u} supramolecular dendrimers,¹⁶ and self-organizable dendronized polymers¹⁷ form oriented fibers that were analyzed by XRD experiments. However, with few exceptions^{15u,16p} the XRD pattern obtained from their oriented fibers did not exhibit the sufficient number of helical features required to apply the helical diffraction theory to the analysis of the structure of helical assemblies. This paper reports the use of a combination of helical diffraction theory⁴ applied to the simulation of atomic helix and simulation of the molecular models to the analysis of oriented fibers generated from helical supramolecular dendrimers and self-organizable dendronized polymers. The results of this study will provide the molecular structure of the helix and will endow an entry into the mechanism of assembly of helical supramolecular dendrimers.

Results and Discussion

Diffraction by a Helical Fiber. The utility and the simplicity of the helical diffraction theory⁴ is best described by the following comment of Crick and Kendrew,^{19a} “Armed with the appropriate theory it is often possible to recognize the helical nature of a fiber structure at a glance, and sometimes to specify the main parameters of the helix and its subunits with very little trouble indeed”, and by the statement of Crick when referring to the discovery of DNA,^{19b} “it did mean that I had the expertise at my fingertips”.

Figure 1 illustrates the most important parameters generated by the helical diffraction theory⁴ applied to a 5_1 single-strand helix generated from atoms or atomic helix (Figure 1a) and groups of atoms that are tilted (Figure 1c). The XRD pattern generated by the helical structure from Figure 1a is outlined in Figure 1b, while a schematic pattern of the helical structure from Figure 1c is shown in Figure 1d. Both diffraction patterns exhibit a St Andrew’s cross, shown in red, made of the first maxima of the squared Bessel functions in the four quadrants. The St Andrew’s cross pattern indicates a long-range helical order. The α angle between the meridian and the cross and the rising slope of the helix are related to the helix radius r . The narrower is the angle α , the larger is the radius r of the helix. The pitch of the helix P is determined by the distance between the long-range helical features forming the cross. The atoms forming the helix in Figure 1a can be replaced with a tilted group of atoms, such as, for example, a tilted phenyl group,

shown in green with a red dot in Figure 1c. This group gives the diffraction features colored in green from Figure 1d. The tilt angle of this group vs the helix axis (Figure 1c) is shown in green on the schematic XRD pattern from Figure 1d. The diffraction features colored in blue in Figure 1b,d refer to short-range helical order. The diffraction features corresponding to the long-range stacking correlations along the helix axis are shown in yellow.

The discussion based on the schematics from Figure 1 helps us to estimate qualitatively the simplest examples of molecular helices generated from atoms and at the same time to visualize the difficulties encountered during the interpretation of a low-resolution XRD pattern. For example, when the pattern does not show the long-range helical cross that is marked in red, the tilt marked in green and the short-range helical features marked in blue can be assigned as column-to-column correlation features. The latter is in most cases considered less probable due to the larger degree of freedom of the alkyl groups from the periphery of the supramolecular columns. Moreover, in the case of columnar hexagonal packing such correlations are frustrated by the lattice symmetry. Therefore, all structures to be discussed in this report were selected to self-organize in columnar hexagonal (Φ_h) lattices.

Helical supramolecular dendrimers may have more than one region of high electron density even within the same layer of the helix. At the same time different molecular helical structures, for example a single-strand 5_1 helix (Figure 2a) and a triple-strand 15_1 helix (Figure 2b), can generate similar diffraction patterns. The only difference between the two fiber patterns generated by the structures from Figure 1 or 2 is a scaling of the layer line maxima position in the q_x direction, if the r and c parameters are identical. In the following subchapters we will select from our previous studies^{16,17} and from a new example reported for the first time here, representative examples of dendrons and dendrimer conformations, supramolecular dendrimer architectures and dendronized polymers that self-assemble into helical structures. Their helical structures will be simulated via the helical diffraction theory applied to their simplified helical atomic model and via Cerius2 simulations based on their helical molecular model. This structural analysis process will provide for the first time access to the molecular structure of helical supramolecular dendrimers. When the helical structures will resemble models available in the literature that are generated from related or unrelated building blocks, they will be compared with the structures reported here.

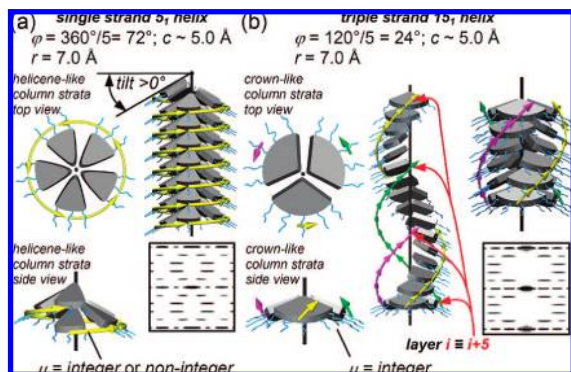
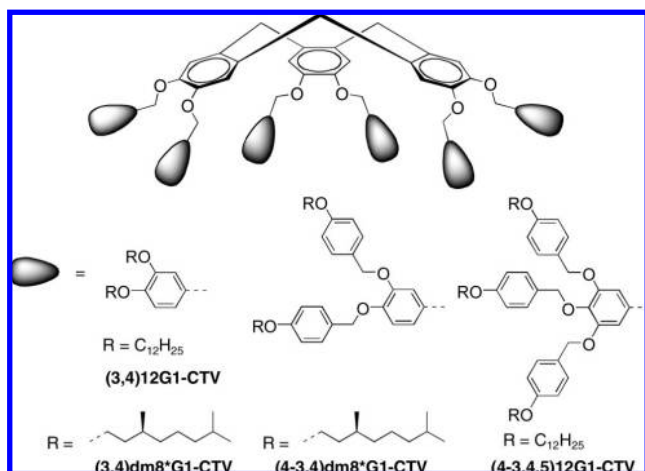


Figure 2. Helical packing of dendrons in a helicene-like column cross-section architecture and its 5_7 helical structure (a), and in a crownlike architecture and its 15_7 helical structure (b). In a the dendron tilt angle is shown; in b a 3-fold symmetry layer packed in a triple-strand 15_7 helix exhibits a similar diffraction pattern as a single-strand 5_7 helix from a, with the helical features scaled in the q_x direction as shown in the two atom-based simulations.

Scheme 1. Dendronized Cyclotrimeratrylene (CTV) Derivatives



Dendronized Cyclotrimeratrylenes as Models for Crownlike Dendrons, Dendrimers, and Supramolecular Dendrimers. Cyclotrimeratrylene (CTV) containing alkyl side groups and their corresponding derivatives exhibit a crown conformation that self-assembles in pyramidal columns.^{15q,20} Some of them were shown to form helical structures.^{15q,20} Therefore, we selected the CTV core to synthesize dendronized CTV molecules that are expected to provide a model for crownlike conformations. Scheme 1 shows the structure of the CTV molecules containing six symmetrically attached self-assembling dendrons containing nonchiral and respectively chiral alkyl groups. Their synthesis is presented in the Supporting Information. Powder and fiber small- and wide-angle

XRD experiments were used in all structural analysis experiments to calculate the lattice dimensions and the internal helical structure of the column. The fiber XRD experiments were carried out on oriented fibers, with a diameter of 0.7 mm, that were produced with a miniextruder described in Scheme SS1 of the Supporting Information. All fibers were well-oriented (Supporting Information Figure SF4). A combination of theoretical simulations was used to reconstruct the helical structure generated from atoms via helical diffraction theory⁴ and by Cerius2 for the entire molecular model of the helix. These simulations were used to fit the wide- and small-angle fiber XRD patterns (Figure 3) obtained for all the dendronized CTV molecules from Scheme 1, in their columnar hexagonal lattice, that exhibit internal order (Φ_h^{i0}).^{16e-1}

The 3-fold rotational symmetry of the hexasubstituted CTV (Figure 3d) mediates the helical arrangement of the supramolecular column. Four helical layer lines (L) were observed in the case of (3,4)12G1-CTV (Figure 1a). The fourth helical layer line exhibits the 4.8 Å strong meridional helical or π -stacking feature along the helix axis. This was assigned to the $c = 4.8 \text{ \AA}$ helix parameter from Figure 1a (Figure 3a). The simulation of the triple- 12_1 atomic helix fiber pattern that takes into account the 3-fold rotational symmetry of (3,4)12G1-CTV from Figure 3d is shown in Figure 4b. The helical molecular model and triple- 12_1 atomic helix model used in this simulation are shown in Figures 5a,c and 3a. A helical structure generated from the “forced-flat” conformation of (3,4)12G1-CTV (Figure 4d) was simulated with the Cerius2 (Figure 4a). The helical structure generated from the crown conformation of the same dendronized CTV (Figure 4e) was simulated via the triple- 12_1 helical atomic model (Figure 4b), while the molecular model was simulated by Cerius2 (Figure 4c). The experimental and simulated helical layer lines and intensity profiles of all structures reported are available in Supporting Information Table ST4.

The simulation of the helical structure generated from the crown conformation via Cerius2 (Figures 4c and 5c) fit all off-meridional principal maxima including the one observed on the fourth helical layer line from the original XRD pattern (Figure 3a) marked with green dotted lines. The green marked features from Figures 3a and 4c are missing from the fourth helical layer of the XRD pattern simulated from the forced-flat conformation (Figure 4d) of the same dendronized molecule (Figure 4a). This analysis concludes that the green dotted diffraction features from the original XRD pattern (Figure 3a) correspond to dendron tilt correlations (Figures 1d and 4c). The molecular model of (3,4)12G1-CTV used to simulate the XRD pattern from Figure 4c has a tilt angle of 34° . This value is in agreement with the value obtained from the original XRD pattern (Figures 3a and 4f) and with that of the conformation of CTV.²⁰ A dendron tilt conformation is also suggested by the relatively small value of the column diameter ($a = D_{\text{col}} = 37.5 \text{ \AA}$) assembled from (3,4)12G1-CTV. Therefore, the analysis discussed here provided access to the assignment of the off-meridional diffuse diffraction features that correspond to the dendron tilt correlations (Figure 1d in green) and eliminates their potential confusion with short-range helical diffraction features (Figure 1d in blue).

The XRD fiber patterns of (3,4)dm8*G1-CTV and (4-3,4)dm8*G1-CTV from Scheme 1 are shown in Figure 3b,c. The simulation of the molecular model shown in Figure 5a by Cerius2 gives an identical pattern for (3,4)nG1-CTV with $n = 12$ and dm8* (Scheme 1). This XRD pattern is shown in Figure 5c. The triple- 12_1 helical atomic model of (3,4)nG1-CTV and its simulation by the helical diffraction theory are shown in the white inset of Figure 5c. The molecular and atomic models (Figure 5d) of the helical structure of (4-3,4)dm8*G1-CTV from

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- (20) (a) Collet, A. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: New York, 1996; Vol. 6, pp 281–303. (b) Collet, A. *Tetrahedron* **1987**, *43*, 5725–5759. (c) Malthête, J.; Collet, A. *Nouv. J. Chim* **1985**, *9*, 151–153. (d) Zimmermann, H.; Poupko, R.; Luz, Z.; Billard, J. Z. *Naturforsch.* **1985**, *40a*, 149–160. (e) Malthête, J.; Collet, A. *J. Am. Chem. Soc.* **1987**, *109*, 7544–7545. (f) Poupko, R.; Luz, Z.; Spielberg, N.; Zimmermann, H. *J. Am. Chem. Soc.* **1989**, *111*, 6094–6105. (g) Lesot, P.; Merlet, D.; Sarfati, M.; Courtieu, J.; Zimmermann, H.; Luz, Z. *J. Am. Chem. Soc.* **2002**, *124*, 10071–10082. (h) Zimmermann, H.; Bader, V.; Poupko, R.; Wachtel, E. J.; Luz, Z. *J. Am. Chem. Soc.* **2002**, *124*, 15286–15301.

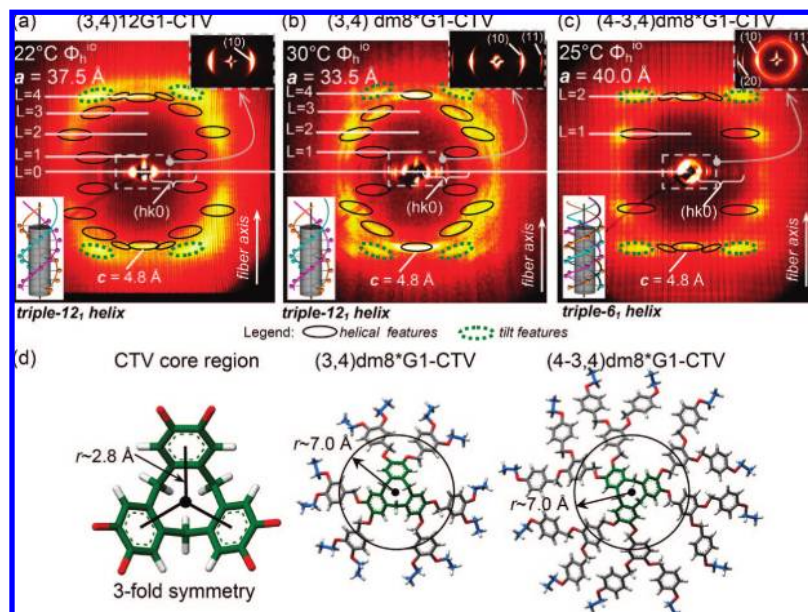


Figure 3. Wide-angle XRD patterns collected from the helical assemblies generated from oriented fibers of dendronized CTV at the indicated temperatures (a–c) and schematic of the dendronized CTV structures (d). In all cases: the calculated helix radii $r = 7.0 \pm 1.0$ Å, the layer thickness along the column axis $c = 4.8$ Å, and L indicates the helical layer line order. In a–c the lower left insets depict the schematic of the identified model of the atomic helix. The top right insets present the small angle oriented fiber XRD patterns.

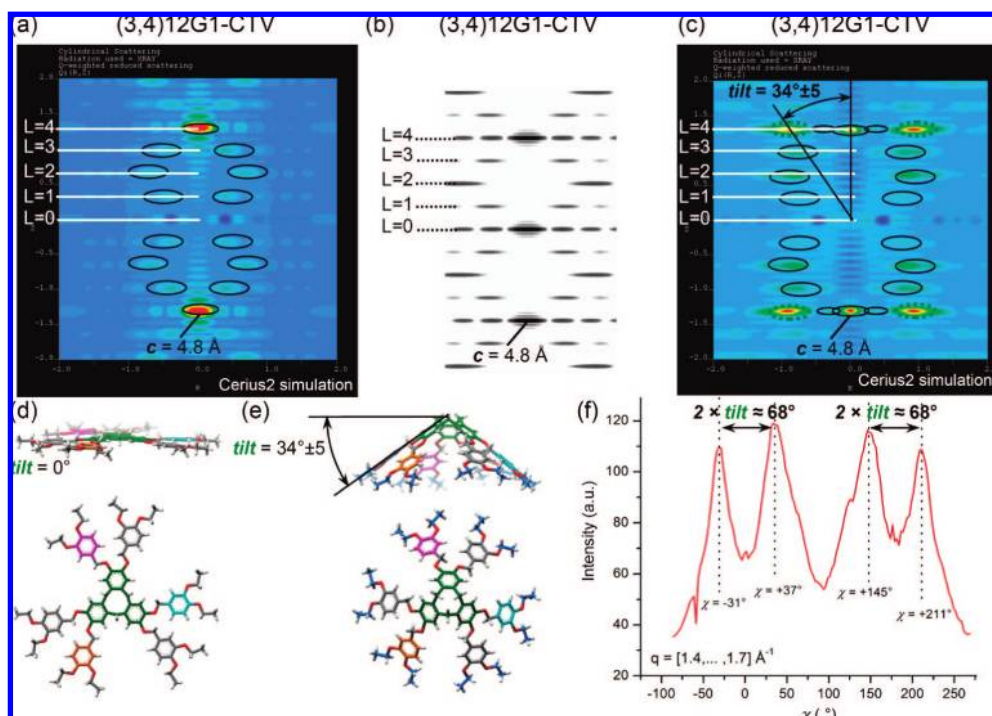


Figure 4. Cerius2 fiber pattern simulations of the helical assemblies based on the forced-flat (a, d) and the crownlike (c, e) architectures generated by (3,4)12G1-CTV. Theoretical fiber pattern simulation based on a triple-strand helical distribution of atoms shown in Figure 5c (b). Azimuthal angle χ versus intensity plot of the fiber pattern from Figure 3a (f).

Figure 5b,d were simulated by Cerius2 and by the CCV theory and are shown in Figure 5d and in its white inset.

The fiber XRD pattern obtained for (4-3,4,5)12G1-CTV in its Φ_h^{10} phase is shown in Figure 6a. The triple-6_l atomic helical (Figure 6c) and the molecular (Figure 6d) models of its helical structure were simulated in Figure 6b and in its white inset.

The wide-angle XRD pattern from Figure 6a shows a significantly larger average layer thickness ($c = 5.7$ Å) for this

CTV molecule when compared with the value of $c = 4.8$ Å observed for the cases of (3,4)12G1-CTV, (3,4)dm*G1-CTV, and (4-3,4)dm8*G1-CTV (Figure 3a–c). The steric constraints created by the larger dendron attached to the periphery of (4-3,4,5)12G1-CTV increase the layer spatial separation along the column and helix axis. The intramolecular aromatic interactions shown in Figure 6d are also responsible for the higher value of the dendron tilt. Table 1 summarizes the structure of the triple-

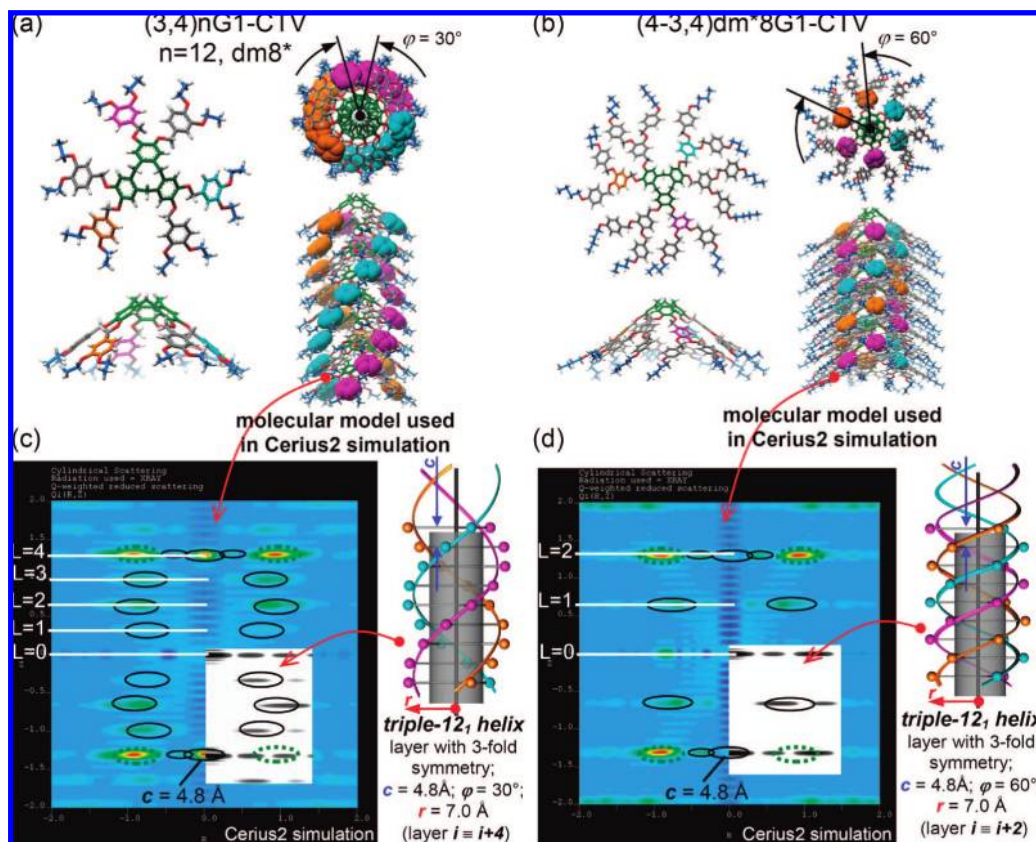


Figure 5. Cerius2 simulations of the molecular models: single-layer and column top and side views (a, b). Simulated XRD oriented fiber patterns as calculated from Cerius2 (blue background) and from the shown atomic multistrand triple helix (the overlaid lower right quadrant, white inset) (c, d). The hypotheses that the outer (3,4) or (4-3,4) aromatic rings form a structure with 6-fold symmetry failed in fitting the experimental data, as based on the performed Cerius2 simulations.

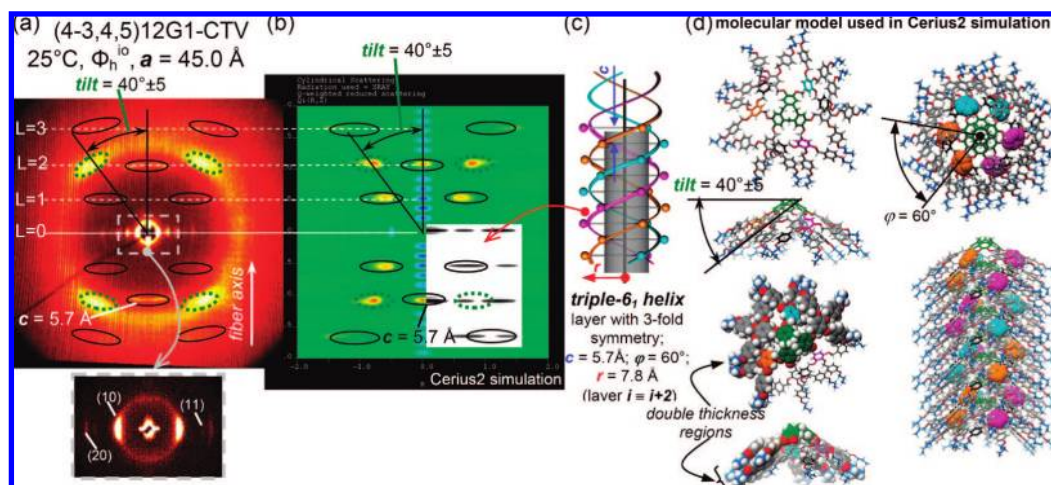


Figure 6. Experimental (a) and Cerius2 simulated wide-angle oriented fiber XRD of the molecular models of the helical structure generated from (4-3,4,5)12G1-CTV (b); theoretical atomic helix model used for the CCV simulation (c); molecular models of (4-3,4,5)12G1-CTV (d). The inset in a depicts the fiber alignment in small-angle XRD; L = helical layer line order. In d a combined space-filling and stick view of the helical structure illustrates the intramolecular aromatic interactions localized at the periphery of the crowded (4-3,4,5) aromatic region, in agreement with the larger value of the average layer separation ($c = 5.7 \text{ \AA}$ for (4-3,4,5)12G1-CTV vs $c = 4.8 \text{ \AA}$ for (3,4)12G1-CTV or (4-3,4)dm8*G1-CTV).

strand helix obtained for the four CTV derivatives discussed above and the parameters of their helix calculated from the two sets of simulations.

The comparison of the helix parameters of the supramolecular columns self-assembled from these crownlike CTV derivatives demonstrates the role of the molecular structure of the dendron to the helical assembly (Figure 7). The 3-fold rotational

symmetry of the CTV derivatives mediates the helical arrangement by minimizing the empty space and by maximizing their aromatic interactions. An architectural-dependent specific translation and rotation of the adjacent layers reduces the free energy of the supramolecular column via the schematic mechanism outlined in Figure 7. The molecular structure of the dendron, via its solid angle, controls the rotation angle φ . A “sharper”

Table 1. Summary of the Wide-Angle Oriented Fiber Data of the Dendronized CTV Crownlike Structures

dendrimer	T (°C)	helix type	c^a (Å)	ξ^b (Å)	ξ/c^c	φ^d (deg)	r^e (Å)	helical pitch (Å)	dendron tilt (deg)
(3,4)12G1-CTV	22	triple-strand- 12_1	4.8	195	40	30	7.0	19.2 ± 0.5	34 ± 5
(3,4)dm8*G1-CTV	30	triple-strand- 12_1	4.8	240	50	30	7.0	19.4 ± 0.5	29 ± 5
(4-3,4)dm8*G1-CTV	25	triple-strand- 6_1	4.8	250	50	60	7.0	9.6 ± 0.5	33 ± 5
(4-3,4,5)12G1-CTV	25	triple-strand- 6_1	5.7	175	30	60	7.8	11.4 ± 0.5	40 ± 5

^a Helix parameter c . ^b Correlation length of the c helical feature calculated from the diffraction full width at half-maxima (fwhm): $\xi = 2\pi/\text{fwhm}$. ^c Estimate of the helical correlation length along the column axis converted in number of layers (column strata). ^d Helix parameter φ . ^e Helix radius r .

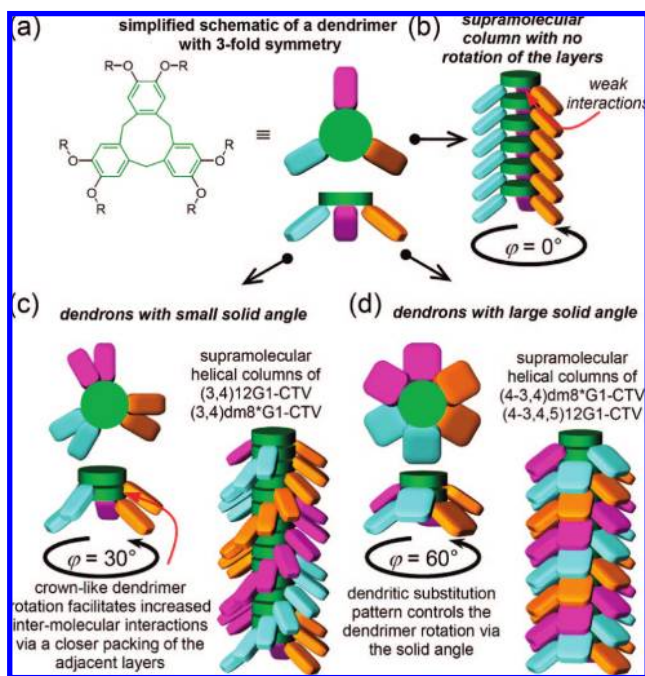


Figure 7. Mechanism of helical self-assembly by the crownlike architectures with 3-fold symmetry: (a) CTV–dendrimer simplified schematic; (b) self-assembled supramolecular columns with no rotation of the adjacent layers that are not filling the space and therefore are not in the minimum free energy conformation due to the tilt of the aromatic core; (c, d) helix parameter control by dendron architecture via its solid angle.

dendron or a dendron with a smaller solid angle²¹ attached to the CTV core generates a smaller rotational angle φ than a “wider” dendron or a dendron with a larger solid angle. The aromatic core region of the crown acts as the helix “interlock”. This process is illustrated in Figure 7. These cooperative intra- and intermolecular interactions determine the tilt and the helix parameters of the supramolecular helical column self-assembled from crownlike dendrimers.

A direct comparison of the helical organization in bulk and in solution for the chiral dendronized CTV (3,4)dm8*G1-CTV reveals that the long-range helical correlations demonstrated in the oriented fiber XRD experiments (Figures 3 and 5 and Table 1) translate into a strong ellipticity observed in the CD spectra recorded in the solvophobic solvent dodecane (Figure 8).

The presence in the CD spectra of the two Cotton effects with opposite signs at 200 and 240 nm, respectively, demonstrate the helical self-assembly in solution. The ellipticity maxima of the (3,4)dm8*G1-CTV spectra are at least two to three times more intense than those observed for other self-assembled dendritic structures.^{16e–i} Dendritic structures with the chiral center localized in the aromatic region would be expected to provide an even

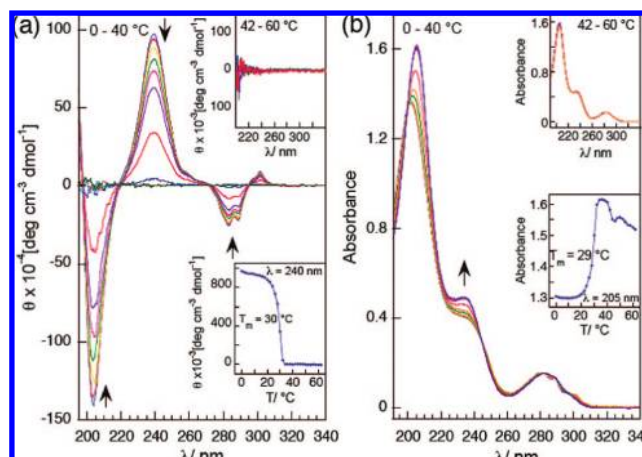
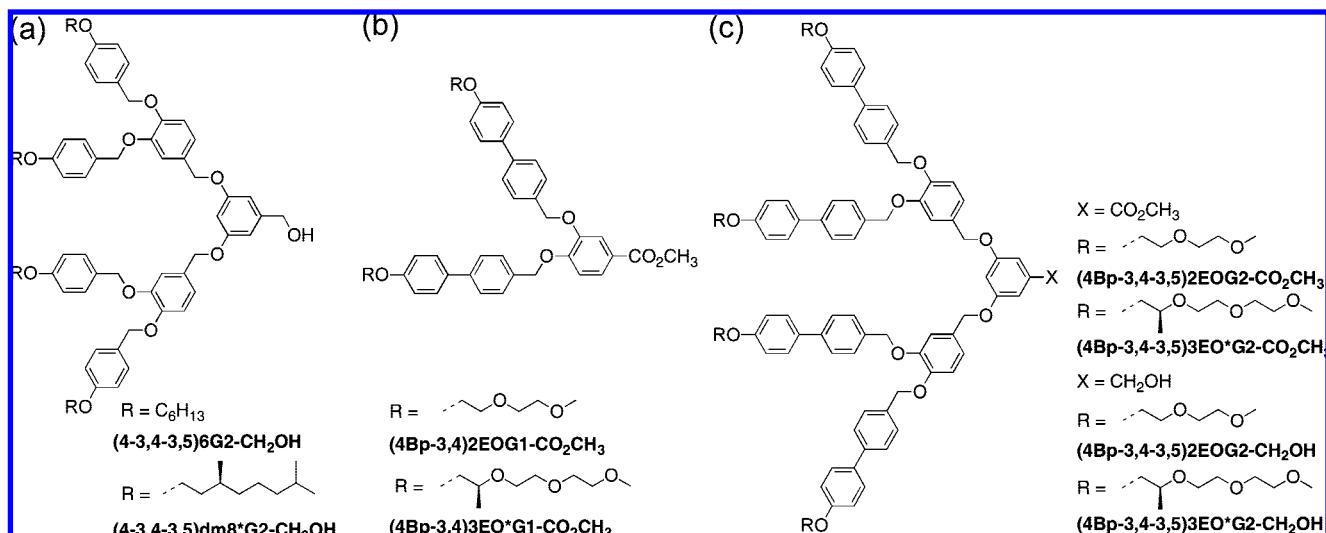


Figure 8. Temperature dependence CD (a) and UV (b) spectra of (3,4)dm8*G1-CTV in dodecane (6.0×10^{-5} M). Arrows indicate trends upon increasing temperature; the lower insets depict changes in molecular ellipticity and absorbance as a function of temperature; the upper right insets illustrate the Cotton effects associated with the molecular solution of the supramolecular dendrimers.

stronger optical rotation due to a better correlation between the units. The fact that the CD signal of (3,4)dm8*G1-CTV is more intense, even though the chiral center is located in the alkyl groups from the dendron periphery, suggests that the chiral centers only select the handedness of a racemic supramolecular helix. This mechanism is supported by the similar helical packing of the chiral (3,4)dm8*G1-CTV and the achiral (3,4)12G1-CTV in their Φ_h^{i0} phase (Figures 3–5). This similarity demonstrates that for these structures the chiral centers play the primary role of selecting the handedness of the helix and that otherwise they have little influence on the supramolecular helical self-assembly process. Nevertheless, a small amplification of the optical activity cannot be excluded, especially since the bulk data indicate a slight increase of the helical correlation length, ξ , for the dendronized CTV structures with a chiral center in comparison with the achiral derivatives (ξ values are listed in Table 1). This result is in line with other results reported from our laboratory.¹⁷ⁱ

Supramolecular Crowns and Hollow Crowns Self-Assembled from Tapered Dendrons. For crownlike dendrimers with n -fold rotational axis of symmetry, ($n \geq 2$), it was demonstrated that the process of self-assembly into helical supramolecular columns is mediated by the intrinsic symmetry of the crown from the column stratum. In the case of the self-assembly of tapered dendrons, the column stratum is assembled from independent dendron units via noncovalent interactions. Consequently, the self-assembly process into helical structures involves a more complex mechanism than in the case of symmetric crownlike dendrimers. From the library of tapered dendritic alcohols (4-3,4-3,5)nG2-CH₂OH with $n = 1–16$, reported previously,¹⁶ⁱ we selected the dendron with $n = 6$ and synthesized a new dendritic molecule containing a chiral alkyl group on its periphery $n = \text{dm8}^*$ (Supporting Information; Scheme 2a). This library will provide one of the few examples of

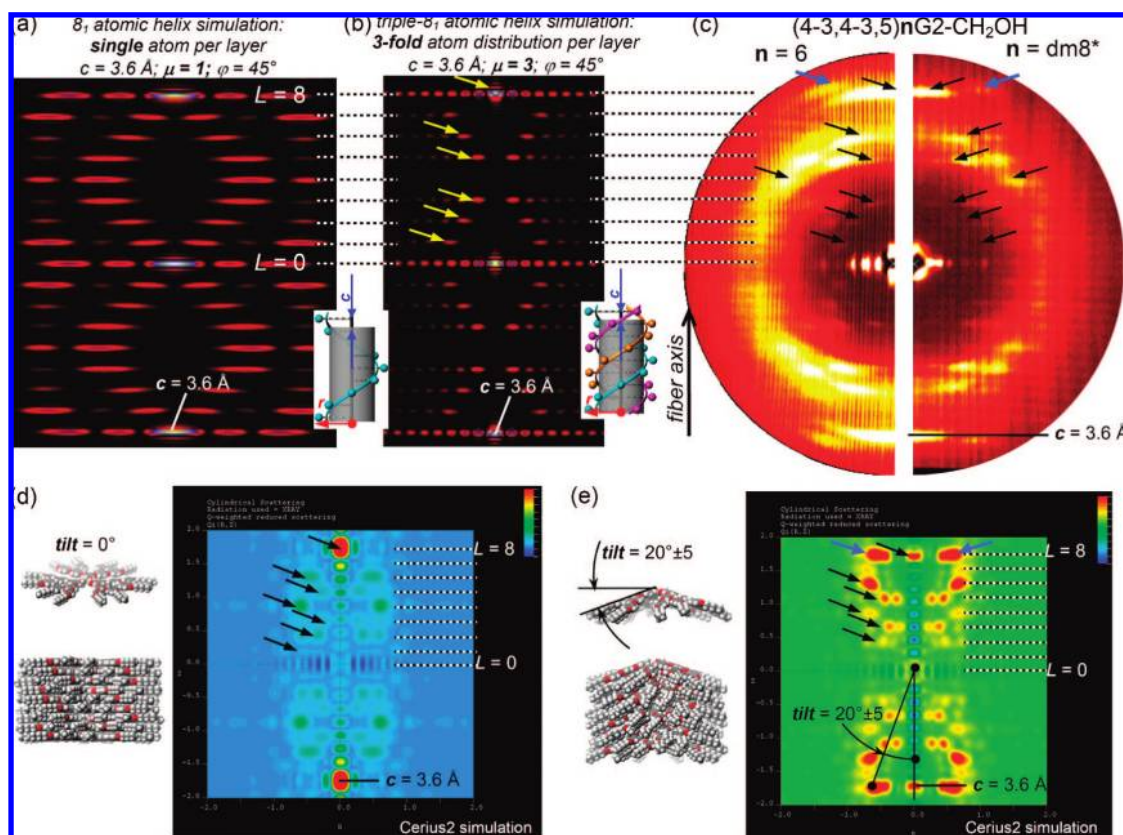
(21) Ungar, G.; Percec, V.; Holerca, M. N.; Johansson, G.; Heck, J. A. *Chem.–Eur. J.* **2000**, *6*, 1258–1266.

Scheme 2. Structures of Tapered Dendrons That Self-Assemble into Supramolecular Crownlike (a) and Disklike (b, c) Architectures

self-assembly of tapered dendrons into supramolecular helical structures via a column cross-section generated from a supramolecular crown (Figure 2b).

Figure 9c shows a side-by-side comparison of the wide-angle XRD patterns of oriented fibers obtained from the tapered dendritic alcohols **(4-3,4-3,5)*n*G2-CH₂OH** with $n = 6$ and **dm8***. The remarkable similarity of the two XRD fiber patterns implies that the addition of a chiral center in the system does not affect much the self-assembly process. In both fiber patterns, eight layer lines (L) were identified (Figure 9). On the eighth layer line there is a strong meridional maximum corresponding to a column stratum

spacing of $c = 3.6 \text{ \AA}$. The initial assignment of the packing was an 8_1 helix. The 8_1 atomic helical model with its simulated pattern is presented in Figure 9a. However, this model fails to fit the intensity profiles of the experimental helical layer lines generated from an atomic helix via the CCV theory. The lack of any intensity on the seventh layer line and the presence of a stronger intensity of the principal maxima on the third layer line (Figure 9c) suggest that the column stratum can have a 3-fold rotational symmetry. Indeed, the theoretical fiber pattern simulation based on a triple- 8_1 atomic helix fits most of the helical features (Figure 9b,c). The other cases considered were based on column strata with 2-fold,

**Figure 9.** Theoretical fiber pattern simulation for a single- 8_1 atomic helix (a) and a triple- 8_1 atomic helix (b). Wide-angle oriented fiber patterns collected for **(4-3,4-3,5)*n*G2-CH₂OH**, $n = 6$ and **dm8*** (c). Cerius2 fiber pattern simulations and the corresponding molecular models (d, e).

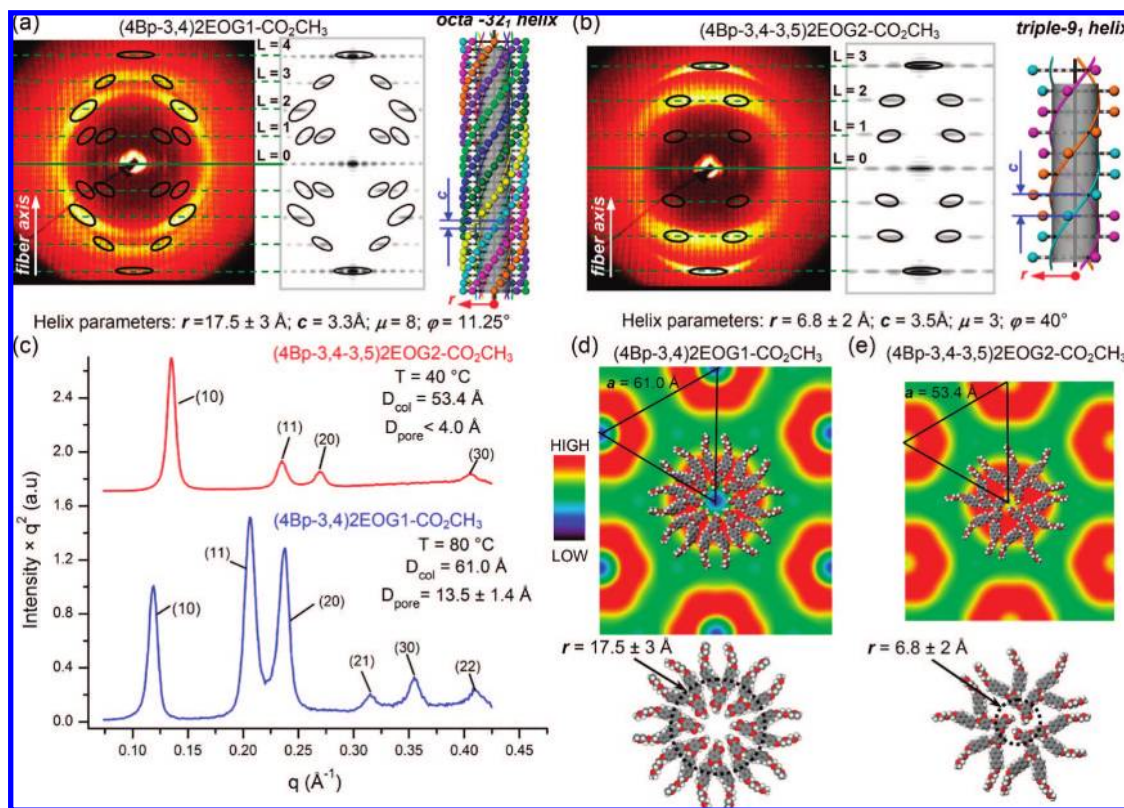


Figure 10. Comparison of the first and second generation supramolecular disk architectures assembled from hybrid dendritic esters: wide-angle oriented fiber patterns, simulated by the atomic helices shown on the right side (a, b); XRD powder diffraction plots (c); and corresponding electron density maps with overlaid molecular models (d, e).

4-fold, 5-fold, and 6-fold rotational symmetry. All of them failed to fit the experimental data.

The Cerius2 fiber pattern simulation based on the molecular model of a triple-strand δ_7 helix of a forced-flat disklike column cross-section, shown in Figure 9d, could also fit most of the experimental intensities of the helical layer lines, but failed to agree with the eighth layer line off-meridional secondary maxima. On the basis of the identification of the tilt feature for the crownlike CTV dendrimers presented in the previous section, the Cerius2 fiber pattern simulation based on the molecular model of a triple-strand δ_7 helix with $\sim 20^\circ$ tilted dendrons, presented in Figure 9e, fits the experimental intensity profile of all helical layer lines. Therefore, these tapered dendrons self-assemble into a helical column generated from cross-sections based on supramolecular crownlike strata.

It is important to remark that the systematic investigation of the wide-angle XRD patterns of the oriented fiber as a function of the number of methylenic units of the alkyl groups from the periphery of (4-3,4-3,5) n G2-CH₂OH dendron library (Supporting Information, Figure SF3) reveals a delicate balance between the self-assembly process into helical supramolecular column and the structure of the dendron. As the number of methylenic units in the alkyl groups increases from 6 to 8, the intensity profile of the fiber patterns remains unchanged, with the exception of the first two helical layer lines that are possibly too weak to be experimentally observed. However, an additional increase of n to 10 and 12 generates a gradual change of the intensity profile, and a reduced number of helical layer line features is observed. Most probably the increased degree of freedom provided to the aliphatic region by the longer alkyl chains, gradually affects the correlation length of the rotational symmetry along the column axis. However, the local packing of the aromatic region of the column strata is affected

to a smaller extent, as indicated by the presence of the third helical layer line in the fiber pattern obtained from the dendron with $n = 12$. In other words, as n increases, during the self-assembly process some degree of the helical correlation is conserved, especially in the aromatic core region, but the increased conformational freedom of the aliphatic periphery limits the extent of the helical packing to a smaller number of column strata and, therefore, generates a short-range helix.

Supramolecular Disklike and Hollow Disklike Architectures. Two architectures based on the first (Scheme 2b) and respectively second (Scheme 2c) generation hybrid dendrons with oligo(oxyethylene) groups replacing the alkyl groups from the periphery were synthesized, and their helical structure was analyzed. Their synthesis is described in the Supporting Information. The first and second generation dendritic esters from Scheme 2 self-assemble into Φ_h^{io} phases as demonstrated in the wide-angle oriented fiber patterns from Figures 10 and 11. A direct comparison of the lattice parameters, $a = 61.0 \text{ \AA}$ for (4Bp-3,4)2EOG1-CO₂CH₃ with $a = 53.4 \text{ \AA}$ for (4Bp-3,4-3,5)2EOG2-CO₂CH₃, together with the molecular models suggest that the first generation hybrid dendritic ester (4Bp-3,4)2EOG1-CO₂CH₃ self-assemble into a hollow Φ_h^{io} phase. This is not unexpected considering the fact that the first generation ester has a smaller solid angle than that of the second generation (4Bp-3,4-3,5)2EOG2-CO₂CH₃. The reconstructed electron density maps generated from their small-angle powder XRD (Figure 10c–e) together with the pore diameter calculated from the simulation of the powder diffraction peaks amplitudes^{16j} demonstrated that the (4Bp-3,4) n G1- hybrid dendritic esters self-assemble into a hollow Φ_h^{io} phase.

The octa-32₁ atomic helix (Figure 10a), the triple-9₁ atomic helix (Figure 10b) and the molecular models were simulated by the CCV theory and Cerius2 for the first and second generation of hybrid

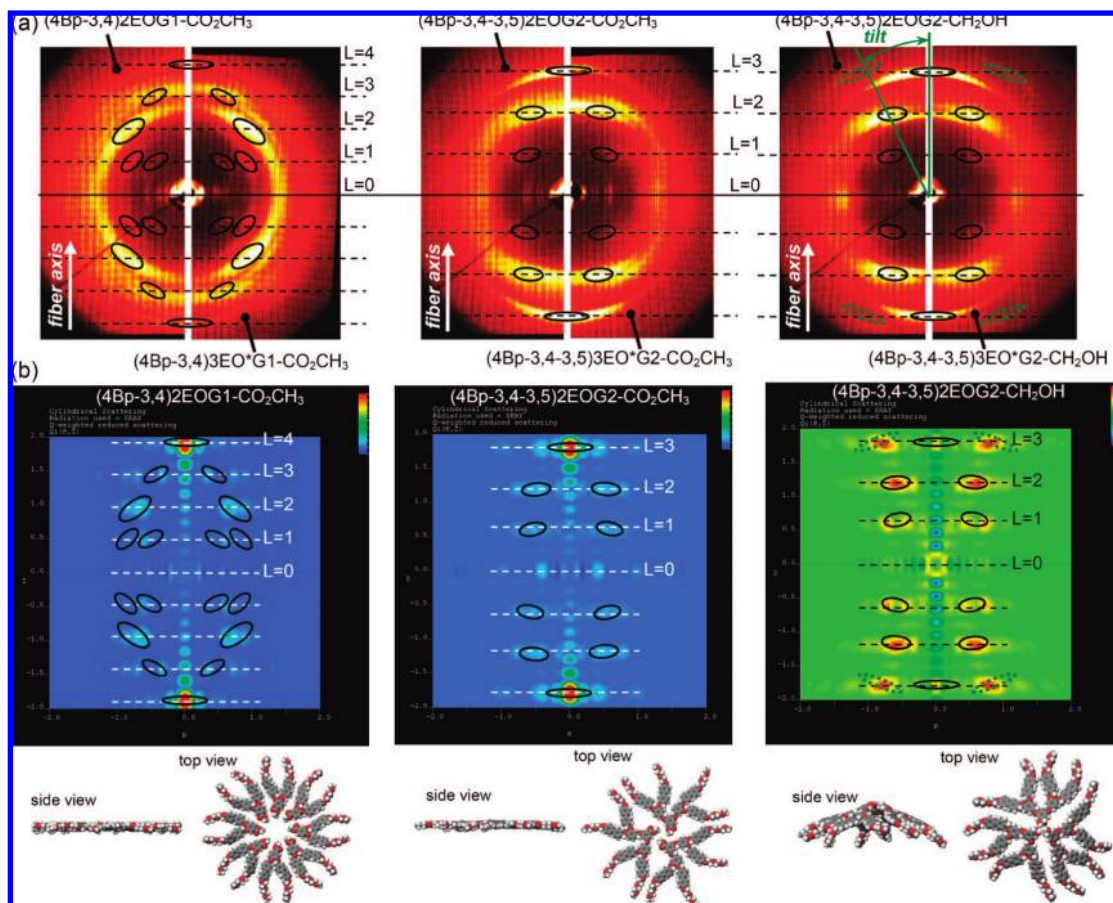


Figure 11. Oriented fiber diffraction patterns collected at wide angle from the achiral (left panels) and chiral (right panels) hybrid dendritic structures that generate hollowlike, nonhollow disklike, and crownlike architectures during helical column assembly (a). The corresponding Cerius2 fiber pattern simulations and the molecular models used (b).

dendrons (Figure 11). The fiber pattern simulations of **(4Bp-3,4)2EOG1-CO₂CH₃** and **(4Bp-3,4-3,5)2EOG2-CO₂CH₃** provide an indirect demonstration of the hollow center in the self-assembled columns of the first generation ester. This is based on the increase of the helix radius from 6.8 Å for **(4Bp-3,4-3,5)2EOG2-CO₂CH₃** to 17.5 Å for **(4Bp-3,4)2EOG1-CO₂CH₃** (Figure 10). The comparison of the wide-angle oriented fiber patterns collected from the assemblies of the achiral and chiral hybrid dendrons shown in Figure 11 demonstrate that **(4Bp-3,4)2EOG1-CO₂CH₃** self-assemble into a hollow disklike cross-section in its helical column (Figure 10a, Figure 11a,b), while **(4Bp-3,4-3,5)2EOG2-CO₂CH₃** assemble in a nonhollow disklike structure (Figure 10b, Figure 11a,b). These results also demonstrate that the dendritic structures template the helical self-assembly mechanism. The chiral stereocenters just select the handedness of the self-assembled chiral supramolecular columns, as suggested by the identical helical features of the chiral and achiral corresponding hybrid dendrons (Figure 9) and by their CD spectra in solvophilic solvent 1-octanol (Figure 12). Although the stereocenter of this dendron is attached in the flexible part of its apex (Scheme 2, Figure 12) rather than on its periphery (Figure 8, Scheme 1), a very strong amplification of chirality^{16c} is observed during its self-assembly in the helical column. As indicated by the same sign of all Cotton effects from Figures 8 and 12 the two helical columns have, as expected, the same handedness. However, no correlation between the CD spectra (Figures 8 and 12) and their triple-*12_l* helix (Figure 5a,c) or triple-*9_l* helix (Figure 10b) is possible at this time. This demonstrates the difficulty encountered with the assignment of a helical structure based on CD experiments alone.

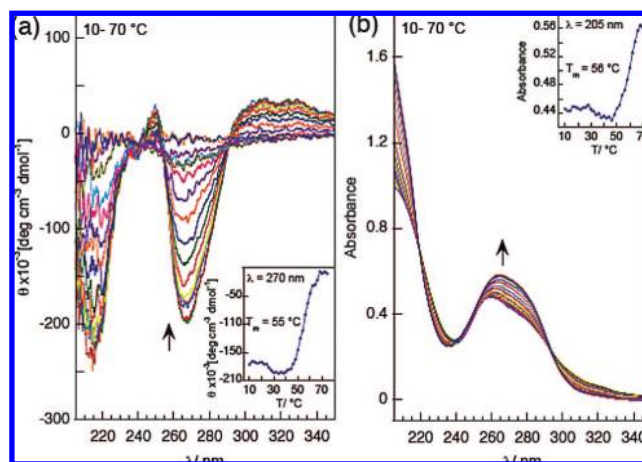


Figure 12. Temperature dependence CD (a) and UV (b) spectra of **(4Bp-3,4-3,5)3EO*G2-CO₂CH₃** in 1-octanol (7.4×10^{-5} M). Arrows indicate trends upon increasing temperature. The changes in molecular ellipticity and absorbance as a function of temperature are shown at the right insets.

The molecular model simulations by Cerius2 provided the oriented fiber diffraction patterns that are summarized in Figure 11. These data illustrate the important role played by the addition of the H-bonding interactions. Both first and second generation hybrid dendritic esters self-assemble into helical supramolecular columns with disklike layers. In the case of the first generation hybrid dendritic alcohols, the H-bonding interactions significantly

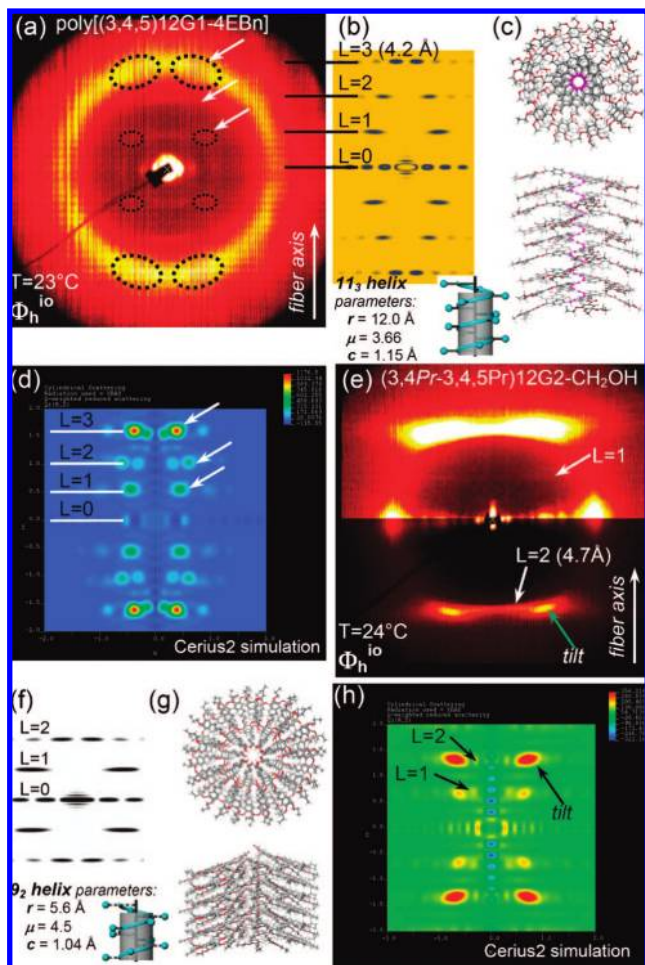
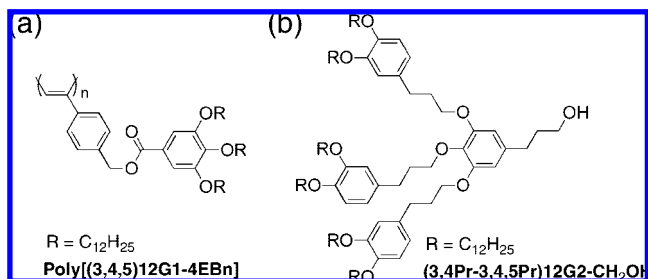


Figure 13. Wide-angle XRD fiber pattern obtained from **poly[(3,4,5)-12G1-4EBn]** (a); CCV simulation of atomic helical model (b). The molecular model of the helix (c), used in the Cerius2 simulation, is shown in d. Wide-angle XRD fiber pattern obtained from the assembly generated by **(3,4Pr-3,4,5Pr)12G2-CH₂OH** (e); CCV simulation of atomic helical model (f). The molecular model of the helix (g), used in the Cerius2 simulation, is shown in h. In e the lower half of the pattern has increased contrast to detail the second layer line features.

influenced the self-assembly process by generating smectic phases that will not be discussed here. In contrast, the second generation hybrid dendritic alcohol **(4Bp-3,4-3,5)2EOG2-CH₂OH** preserved most of the helical packing during self-assembly as observed for its ester apex substituted counterparts. The only difference observed is the presence of a dendron tilt correlation feature in the wide-angle oriented fiber diffraction patterns (Figure 11a,b, right column). It is most probable that the H-bonding interactions are strong enough to induce significant conformational changes and, therefore, change the supramolecular disklike conformation into a supramolecular dendritic crown. It is also remarkable that the self-assembly process into supramolecular helical columns of the **(4-3,4-3,5)*n*G2-CH₂OH** dendritic architecture was just slightly influenced by the structural changes in the alkyl and aromatic peripheral region. This is supported by the relatively small changes of the layers rotational angle φ and of the dendron tilt angle: $\varphi = 45$ and 20° dendron tilt angle for the **(4-3,4-3,5)*n*G2-CH₂OH** (Figure 9) to $\varphi = 40$ and 26° dendron tilt angle for the **(4Bp-3,4-3,5)2EOG2-CH₂OH** (Figure 11).

Supramolecular and Macromolecular Helicene-like Architectures. Figure 13 provides two representative oriented fiber patterns that were selected to exemplify the case of a helicene-

Scheme 3. Structures of Dendronized Polymer and of Self-Assembling Dendron That Generate Supramolecular Helicene-like Architectures



like dendronized polymer **poly[(3,4,5)12G1-4EBn]**^{17j} (Figure 13a–c, Scheme 3a) and from the self-assembling tapered dendron **(3,4Pr-3,4,5Pr)12G2-CH₂OH**^{16l} (Figure 13d–g, Scheme 3b). The general signature for this model of helical self-assembly is the absence of any stacking feature along the column or helix axis in the fiber XRD pattern of the oriented fibers in the region located at the average layer separation. The approximate value for this feature is expected to be between 3.6 and 5.7 Å, depending on the molecular structure of the unit. In the case of the *cis*-**poly[(3,4,5)12G1-4EBn]** (Figure 13a–d and Scheme 3a), the folding of the *cis*-transoidal backbone conformation into a single-strand *cis*-cisoidal helix is induced by the assembly of the dendron into a helical column. Consequently, each **(3,4,5)12G1-** dendron attached to the *cis*-poly(phenylacetylene) backbone is translated and rotated in such a way that it accommodates, via a cooperative process, a minimum free energy conformation of the dendron-backbone system. The identification of the single-*11₃* helical packing for **poly[(3,4,5)12G1-4EBn]** is an approximate solution for the experimental fiber pattern shown in Figure 13a and is based on matching both the simulation of the *11₃* atomic helix by the CCV theory and of the molecular model by Cerius2 (Figure 13b–d). The approximation of the fiber pattern simulation rises from the way the number of dendrons per average thickness of the column stratum was estimated by matching the experimental density.¹⁶

A similar single-strand *9₂* helical packing was identified via the atomic helix simulation (Figure 13f) and by the simulation of the molecular model (Figure 13h) and fit the oriented fiber pattern of the supramolecular dendrimer self-assembled from **(3,4Pr-3,4,5Pr)12G2-CH₂OH** (Scheme 3b). The separation of the tilt feature from the helical features on the second layer line uses the general procedure established in the previous sections. The assignment of the fiber pattern intensity profile to a single-strand *9₂* helix is again approximate since it is based on the estimated number of dendrons per average thickness of the column stratum.

Molecular Structure of Helical Supramolecular Dendrimers and Self-Organizable Dendronized Polymers. Figure 14 uses atomic helical models to summarize the diversity of helical structures discovered in this study by the investigation of the library of self-assembling dendrons and dendrimers and of self-organizable dendronized polymers. The investigation of the supramolecular helical structures generated from dendronized CTV crownlike architectures established a general methodology for the identification and separation of the dendron tilt feature, when it is located at the average thickness of the column stratum. Single-*9₂*, single-*11₃*, triple-*6₁*, triple-*12₁*, triple-*8₁*, triple-*9₁*, and octa-*32₁* atomic helical structures were discovered by the simulation of the fiber

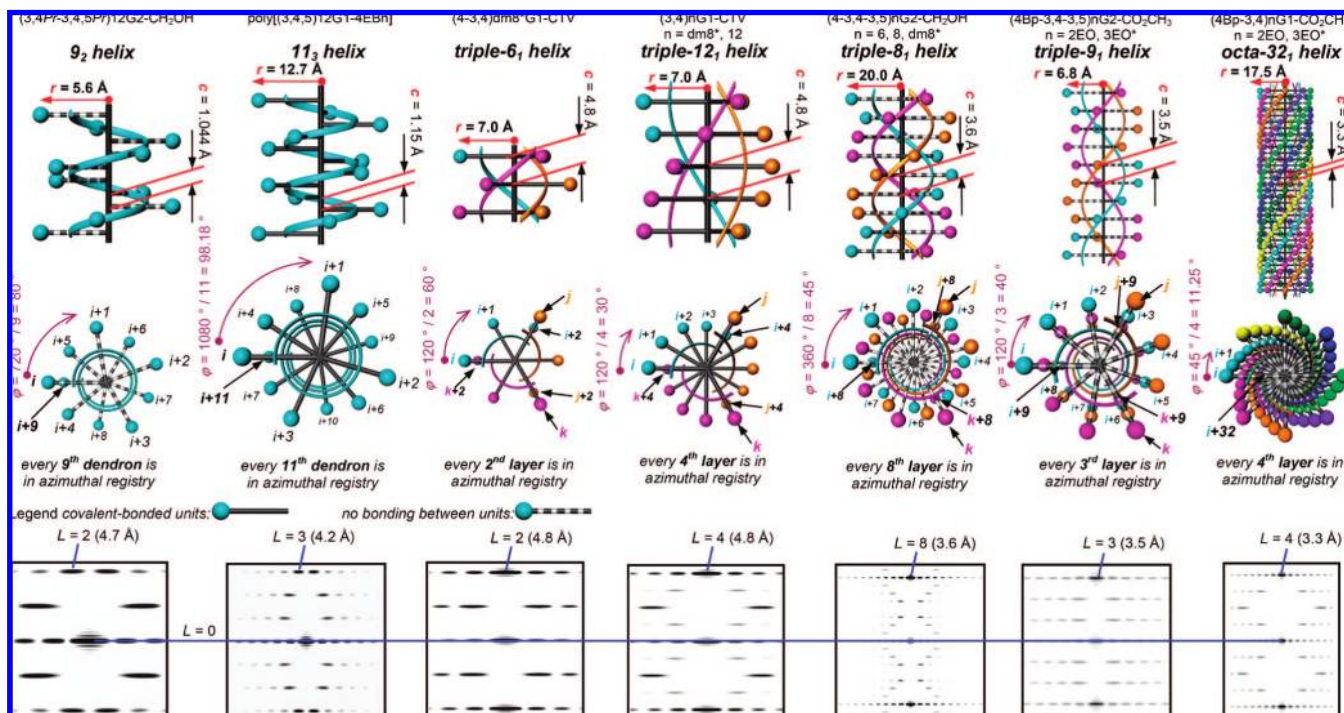


Figure 14. Single- and multistrand atomic models of the helices identified in the supramolecular helical columns self-assembled from dendrons, dendrimers, or self-organizable dendronized polymers.

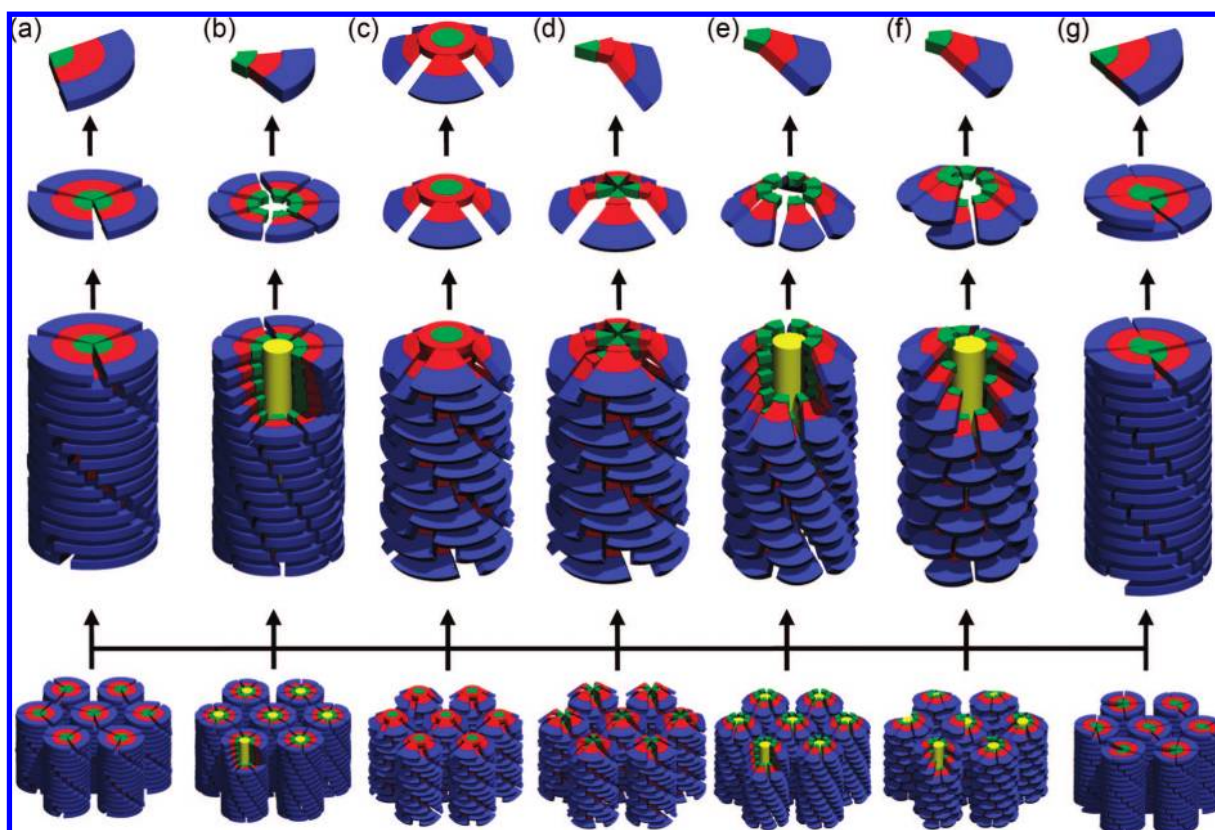


Figure 15. Mechanism of assembly of helical supramolecular dendrimers.

pattern of supramolecular dendrimers and self-organizable dendronized polymers analyzed by the helical diffraction theory.

The schematic representation of the molecular models generated by the cross-section of the columns during the self-assembly

of the helical supramolecular dendrimers and dendronized polymers is outlined in Figure 15. For simplicity, a single handedness is shown in Figure 15 although both can be selected by different stereocenters. Racemic or nonchiral building blocks provide, depending on the persistence length of the column,

intracolumnar inversions of the helix sense or mixtures of left and right handed columns.

The conformations of the dendron that generate the most fundamental columnar architectures are shown on the first two horizontal lines from Figure 15. Column a shows the formation of supramolecular disks by the assembly of tapered dendrons. Truncated dendrons producing hollow supramolecular disks are shown in column b from Figure 15. The supramolecular disks resemble classic examples of discotic molecules^{22a–e} that generate columnar liquid crystalline assemblies and are of interest for organic electronic materials.^{22a,c} Although single crystal quality fibers were drawn from discotic liquid crystals,^{22a} they provided mostly liquid-like intracolumnar order,^{22a,e} with one notable exception where a helical structure was observed^{15r} and analyzed by helical diffraction theory.^{15u} The hollow supramolecular disklike assembly from column b of Figure 15 resembles literature examples of disklike molecules generated from shape persistent macrocycles decorated with alkyl groups.^{22f,g} No fiber XRD analysis is available on these molecules.^{22f,g} Column c from Figure 15 outlines the structure of crownlike dendrimers, while columns d and e are generated from supramolecular crowns and supramolecular hollow crowns. The crown dendrimers reported here resemble examples of CTV-crowns that generate pyramidal liquid crystals.^{15g,20} This class of liquid crystals was shown previously to form helical pyramidal columns.^{15g} However, the previous level of analysis was limited to the suggestion of a helical structure.^{15g} The results reported here on dendronized CTV support the conformation proposed previously for the case of a crownlike dendron.^{16p} The architectures shown in columns f and g of Figure 15 are supramolecular and macromolecular helicene-like. Helicenes are ortho-condensed rings that owe their asymmetry, conformation, and chirality to intramolecular overcrowding.²³ Their helical structure was determined by single crystal XRD experiments.²³ Helicenes functionalized with alkyl side groups form helical columnar liquid crystals.^{15t,23e,g–i} Although liquid crystal helicenes are of interest for potential applications^{23g} only powder XRD analysis was performed on their helical columnar structures.^{23h,i} The supramolecular helicenes reported here are most probably the first examples of dynamic nonrigid helicene-like architectures generated by self-assembly rather than intramolecular overcrowding. Therefore, most of the architectures forming the cross-section of the helical columns from Figure 15 seem to be general and were previously encountered in discotic, pyramidal, helicene-based liquid crystals and in helical peptides. However, the only molecular structures that generate all of them are self-assembling dendrons or dendrimers and self-organizing dendronized polymers. These architectures create a helical structure

via rotation along their column axis (Figure 15). Although from a chemical point of view the reason for this rotation can be generated by a combination of minimum free volume and maximum nonbonding interactions, theoretical physics arguments continue to be debated.²⁴

Conclusions

A library of self-assembling dendrons, dendrimers, and self-organizable dendronized polymers forming helical supramolecular architectures was analyzed by a combination of simulation of their fiber XRD patterns, by the helical diffraction theory applied to atomic helical models, and by Cerius2 applied to their molecular models. This library that contains 14 supramolecular dendrimers and dendronized polymers that exhibit a sufficient number of helical features in their X-ray diffraction patterns obtained from oriented fibers was selected by screening several hundred of supramolecular dendrimers. This combination of structural analysis methods was transplanted from structural biology and generated for the first time access to the molecular structure of helical supramolecular dendrimers. Examples of single- 6_1 , - 9_2 , and - 11_3 helices, triple- 8_1 , - 9_1 , and - 12_1 helices, and an octa- 32_1 helix generated from disklike, crownlike, and helicene-like molecular, macromolecular, and supramolecular hollow and nonhollow dendritic architectures were demonstrated. These structures are expected to provide new entries in the molecular design of supramolecular dendrimers and of their derived functions. The molecular structural details of the helical supramolecular dendrimers generated by the simulation of their XRD fiber patterns based on the helical diffraction theory bring for the first time a level of molecular information related to that available in helical biologic macromolecules and in helical biological assemblies. This method is applicable to many other classes of synthetic macromolecular structures^{13–15,20} and is expected to facilitate the design of the helical supramolecular functional systems including dendritic systems^{16,17} at the molecular level. At the same time this work will provide access to a molecular level structural analysis in dendritic supramolecular systems²⁵ approaching that currently encountered in biological systems.

Acknowledgment. Financial support by the National Science Foundation (Grants DMR-0548559 and DMR-0520020) and the P. Roy Vagelos Chair at Penn is gratefully acknowledged. We thank Professor G. Ungar from the University of Sheffield, U.K. for helpful discussions.

Supporting Information Available: Experimental synthetic procedures with complete spectral, structural, and retrostructural analysis and the complete ref 17j. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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