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Self-Assembly and Induced Circular Dichroism in Dendritic Supramolecules with Cholesteric Pendant Groups

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Abstract: We report on the self-assembled solid-state structural features of self-assembled chiral supramolecules based on ionic complexation of chiral cholesteric pendant groups with achiral dendritic macromolecules and show that their optical activity exhibits a systematic change in the ultraviolet/visible light (UV–vis) absorption and enhancement in the circular dichroism (CD) signal, indicating the occurrence of supramolecular chirality, also referred to as induced circular dichroism (ICD). We construct a homologous series of complexes by varying systematically from 1 to 3 the generation of dendritic units contained in dendrons, dendrimers, and dendronized polymers. The structural properties of the complexes are investigated by means of small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Depending on the class of dendritic molecule and the generation, lamellar, columnar hexagonal, oblique columnar, and rectangular columnar phases can be found, with a direct correlation among the degrees of freedom of the dendritic macromolecules used and the level of order achieved in the self-assembled solid-state structures. The enhancement of the optical signals of these mesoscopic structures appears to be correlated with their order in the solid state. Complexes with the longest lattice correlation lengths also show the most enhanced CD signals. These results show the unique versatility of dendritic macromolecules as supramolecular templates capable of organizing low molecular weight chiral pendant units into a variety of solid-state structures with amplified optical properties.

Introduction

Noncovalent binding of side chains to polymer backbones is a powerful tool for designing polymer systems with complex topologies at the mesoscopic length scale.¹⁻³ By exploitation of the dynamic and reversible nature of physical bonds and the different energies that hold together side chains and polymers, as well as the multitudes of molecular architectures available for both the macromolecular templates and side chains, new materials with unprecedented properties can be created.⁴ The self-assembly behavior resulting from microphase separation occurring among noncovalently bound side chains and polymer backbones is an interplay between the immiscibility of pendant groups and the polymer backbone, the minimization of energy associated with creation of new interfaces, and the reduction of conformational entropy associated with restricted configurations of macromolecular backbones. If the side chains are mesogenic, an additional conformational driving force arises from the presence of liquid crystalline interactions. As a result of this complex behavior, these materials show properties inherent to both their polymeric nature and the liquid crystalline side groups.

Dendrons and dendrimers have a perfectly defined molecular architecture, in the sense that they possess 100% degree of branching, a fractal-like structure, and monodisperse molecular weights. As a consequence, they typically bear a large and defined number of functionalized groups in their outer shell. Their molecular conformations and properties are different from those of other macromolecules, since with increasing generation, they become larger and bulkier and contain an increasing number of peripheral units.⁵⁻⁹ On the other hand, dendronized polymers, that is, linear polymers with dendritic side chains attached to each individual repeat unit of a polymer backbone, combine features of both dendritic molecules and linear polymers.¹⁰⁻¹³ The polymer backbone may impose additional restrictions on the self-assembly process of the pendant dendritic side chains as compared to nonbonded dendrons and dendrimers.

ers. A thorough review of the self-organization and self-assembly of dendritic systems is available.

Liquid crystalline self-assembled materials have great potential in applications where dynamic and functional materials are required. Recently, we have shown that dendrons, dendrimers, and dendronized polymers can be used as efficient macromolecular templates to yield, via supramolecular self-assembly, nanostructured liquid crystalline polymers with unconventional solid-state structures. In these systems, the structure and period can be fine-tuned either by the dendron generation or by the size of the surfactants bound noncovalently to the dendron periphery. Most importantly, it was discovered that the columnar structures encountered in these supramolecular systems are “inverted” in the sense that the dendritic molecules occupy the continuous domains while the surfactants are confined in discrete domains: although these findings may appear counterintuitive given the natural curvature of the dendritic molecules, the inverted configuration has been univocally demonstrated both experimentally and theoretically.

In side-chain polymers, chiral pendant groups attached to a racemic or achiral polymer backbone may induce a chiral conformation in the polymer. This “chirality driving force” can be utilized in supramolecular host–guest systems where chiral guest molecules induce chirality in an achiral host or vice versa. Work for “memorizing”, that is, freezing the chiral conformation of host molecules when the chiral guest molecules are removed from the complex, was pioneered by Yashima et al. in polymer solutions. Since then the memory effect has been shown to function in many supramolecular systems. Relatively small molecules, polymers, and supramolecular assemblies among others can act as a host. The phenomenon is not only limited to solutions; for example, chirality memorizing thin films and gels have been studied. In addition to chirality sensing and optically active materials, the memory effect can be utilized in, for example, stereoselective catalysis. In self-assembly dendritic systems, the introduction of chiral elements to dendritic molecules results in chiral molecular assemblies among others can act as a host. The phenomenon is not only limited to solutions; for example, chirality memorizing thin films and gels have been studied. In addition to chirality sensing and optically active materials, the memory effect can be utilized in, for example, stereoselective catalysis. In what follows, we present the structural results of the complexes by each individual dendritic class.
Dendrons. Dendrons are the smallest molecules used in this study. They are also the basic building blocks of the other dendritic molecules studied in this paper. Figure 1a shows a TEM image of the first-generation dendron complex (DD1-Chol). The morphology is clearly lamellar, which is also confirmed by the evenly spaced SAXS peaks shown in Figure 1b. The period of the lamellar spacing is 4.8 nm according to SAXS, which agrees well with 4.9 nm given by TEM analysis. The high-magnification inset in Figure 1a reveals the presence of undulations in the lamellar phase.

The second-generation dendron complex DD2-Chol has columnar morphology, in which the cylinders are organized in a hexagonal lattice, as clearly shown in the corresponding TEM image in Figure 2a. The hexagonal arrangement of the columns is also confirmed by SAXS. In the diffractogram shown in Figure 2b, the scattering peaks are spaced as 1:√3:2:√7:3:√12:√13, which is a characteristic feature of hexagonal systems. The lattice parameter \( a \) is extracted to be 9.0 nm, which is consistent with the 8.9 nm measured in TEM.

The atypical structure factor of the diffractogram in Figure 2b, with the second Bragg reflection being the most intense, also suggests nontrivial hexagonal columnar packing. A similar scattering profile has been recently reported by Merlet-Lacroix et al.\(^\text{(45)}\) in core–shell hexagonally packed cylinders based on another class of dendritic supramolecular ionic complexes.

Dendrimers, Dendrons, Dendronized Polymers (DP\(n\)), and Cholesteryl Sulfate Unit Used in the Present Study

\(^\text{a}\) Only third-generation molecules are entirely drawn; the corresponding first and second generations (excluding ammonium charges) are highlighted in blue and green, respectively. X identifies the cholesteryl sulfate sodium salt unit already dissociated from the Na\(^+\) counterion and is highlighted in red.

consistent with this self-assembly model is schematically shown in Figure 3. To find out whether the low electron density cylinder cores actually correspond to empty space, a separate Brunauer–Emmett–Teller (BET) analysis was carried out. This analysis, however, demonstrated that these samples are compact and they do not exhibit any porosity. The measured adsorption and desorption isotherms (see Supporting Information) were of type III, which is characteristic for nonporous or macroporous materials. The pore volume calculated by the BET method was below 0.01 cm$^3$/g.

The third-generation dendron is the largest and bulkiest of the dendrons discussed here. The structure of its cholesteryl complex DD3$^-\text{Chol}$, while poor in long-range order, is similar to the second-generation complex DD2$^-\text{Chol}$ as seen in the TEM image shown in Figure 4. However, the positions of SAXS peaks of the complex do not coincide with a regular columnar hexagonal pattern, which suggests an alternative packing structure of the cylinders or simply a more distorted lattice.

A possible structure that could explain the features seen in both TEM images and SAXS diffractograms is the oblique columnar structure. Its lattice vectors and parameters are shown in Figure 5. The unit cell of the oblique columnar structure is defined by two lattice parameters $a$ and $b$ and an angle $\gamma$. In order to find the lattice parameters for the third-generation dendron complex, a simple method for fitting the scattering peak positions based on work by Zhou et al.\textsuperscript{49} was used. Although the method does not allow fitting of the intensity of the experimental curve with the effective structure factors, it enables one to compare the peak positions. The model assumes a simple total scattering intensity

$$I(q) = \langle \sum_{h,k} I_{hk}(q - ha^* - kb^*) \rangle_{\text{spherical}} = \sum_{h,k} \frac{1}{4\pi q_{hl}} I_{hl}(q - q_{hl})$$

(1)

where $\langle \cdots \rangle_{\text{spherical}}$ denotes a spherical average, $q$ is the magnitude of the scattering vector $\mathbf{q}$, $I_{hl}$ is the scattering intensity from the two-dimensional scattering plane defined by the indices $h$ and $k$, $a^*$ and $b^*$ are the reciprocal lattice vectors, and $q_{hl}$ is the magnitude of the scattering vector from the $(hk)$ plane.

For the oblique columnar structure assumed here

$$q_{hl} = \frac{2\pi}{\sin \gamma} \sqrt{\frac{h^2 + \frac{2hk \cos \gamma}{ab} + \frac{k^2}{b^2}}}{a^2}$$

(2)

We chose the individual scattering intensities $I_{hl}$ to be of Gaussian peak shape with predefined width and normalized height. Therefore, details like crystallite sizes, lattice distortions, and...
or device factors that make the widths of the peaks dependent on the scattering vector are not included in the model. The algorithm works as follows: starting from initial lattice parameters \( a \) and \( b \) and angle \( \gamma \), the Nelder–Mead simplex method is used to minimize the sum of squared differences between Lorentz-corrected peak positions in the experimental data and the corresponding peak positions in calculated \( \mathbf{I} \). During computations, the indices \( h \) and \( k \) were limited in the range \([-5 \ldots +5]\), because considering higher indices did not affect the results. As can be seen in Figure 5, hexagonal columnar structure is a special case of oblique columnar where \( a = b \) and \( \gamma = 120^\circ \). Since the TEM images of DD3–Chol are similar to those of the second-generation complex, we expect to find lattice parameters close to the values of the hexagonal morphology, namely, \( a \approx b \) and \( \gamma \approx 120^\circ \). This is indeed the case: the fitting algorithm gives lattice parameters \( a = 9.9 \text{ nm} \), \( b = 8.8 \text{ nm} \), and \( \gamma = 124^\circ \). The Bragg reflections are correctly reproduced as can be seen in Figure 6. In the measured data, the highest deviation in peak intensities arises, as expected, in the second Bragg reflection, as a consequence of the nonconventional form factor of the core–shell-type cylinders.45 Also, the parameters are consistent with TEM analysis in which \( a \) and \( b \) are approximately \( 8 \sim 9 \text{ nm} \). Therefore, we infer that the structure is of the oblique columnar type.

Dendrimers. The dendrimer molecules are formed by attaching three dendrons together from their focal points, and accordingly, they have three times the functional peripheral groups of the corresponding dendron generation. Thus, it is not
a surprise to find some analogies between the morphologies of the dendrimer and the dendron complexes. A first difference, however, arises when the first-generation homologous complexes are compared: while in the case of DD1–Chol a lamellar phase is found (Figure 1), in the case of DM1–Chol (see Figure 7a) a structure similar to the columnar morphologies of the higher-generation dendron complexes is observed. The second-generation homologous dendrons and dendrimers cases (Figures 2 and 7b, respectively) are more directly comparable. In transmission electron microscopy, DM2–Chol appears again as a core–shell-like columnar structure with light coronas, and a central spot within dark cylinders can be observed (see the inset in Figure 7b). However, the structure is not as well ordered as DD2–Chol and the micrographs are reminiscent of the DD3–Chol complex where the oblique columnar morphology was observed. Indeed, SAXS peak positions suggest a similar morphology for both DM1–Chol and DM2–Chol. Therefore, the same fitting procedure as described for DD3–Chol was used to resolve the lattice parameters from the SAXS data for the DM1–Chol and DM2–Chol complexes. The diffractograms and fitted intensities are shown in Figure 7. The fitting procedure results in lattice parameters $a = 10.2$ nm, $b = 9.0$ nm, and $\gamma = 124^\circ$ for both DM1–Chol and DM2–Chol. Thus, the generation does not seem to considerably affect the lattice parameters. Tentatively, these results can be explained with a more pronounced tilt of DM2–Chol “dislike” complexes with respect to the main columnar axis as compared to DM1–Chol complexes, yielding virtually identical lattice parameters.

The third-generation dendrimer complex DM3–Chol, the largest of the dendrimers, shows a microphase-separated state distinguishingly different from the first- and second-generation dendrimers. The structure has very short-range order, as revealed by both TEM and the SAXS diffractogram (Figure 8). A broad SAXS peak centered at $1.27$ nm$^{-1}$ corresponds to a period of $4.9$ nm, which is consistent with the “wormlike” structure with the 4.7 nm period observed in TEM.

Taken together, the SAXS and TEM data for the dendrimer complexes reveal a decreased level of order when compared to the homologous dendron complex series. The reasons for such a decreased structural order in the solid state have to be searched on the topological restrictions imposed on three dendrons when connected into a single dendrimer: it is evident that this results in a restriction of the original $3^3$ degrees of freedom of the three dendrons’ focal points to $3^2$ degrees of freedom of the single core of the dendrimer. These topological restrictions might very well explain the reduced order achieved by the dendrimer complexes in the solid state when compared with the dendrons. This argument will be further reinforced by the study of the dendronized polymer complexes presented in what follows.

Dendronized Polymers. The dendronized polymers studied here are formed by polymerizing the dendron molecules from their focal point. As they are the largest and bulkiest class of molecules in this study, it comes as no surprise that the dendronized polymers exhibit the least ordered structures. In the TEM images the three dendronized polymer generations DP1–Chol, DP2–Chol, and DP3–Chol, a microphase-separated wormlike structure can be identified as shown in the insets of Figure 9. All three generations have two scattering maxima in their SAXS diffractograms. Again, the separation of the scattering peak positions does not fit with conventional hexagonal or lamellar patterns. Since there are only two distinguishable scattering peaks, a fit based on the method used previously with the oblique columnar structures would not be justified because of its three independent parameters. Therefore, we interpret the structures to be of the rectangular columnar type where $\gamma = 90^\circ$ and $a \neq b$. For rectangular columnar structure

\[ q_{ib} = 2\pi \sqrt{\frac{k^2}{a^2} + \frac{k^2}{b^2}} \]  \hspace{1cm} (3)

This structure has been also found in a previous study for the same dendronized polymers complexed with lipids and is
not uncommon in other helical supramolecular systems.50 Fitting to the SAXS peaks gives computed intensities shown along with the measured data in Figure 9. The parameters resulting from the fitting for first-generation dendronized polymer complex (DP1−Chol) are \(a = 5.4\) nm and \(b = 3.3\) nm and for the second-generation complex (DP2−Chol), \(a = 5.6\) nm and \(b = 3.8\) nm. These values are consistent with TEM analysis, which shows structures of approximately 5 nm in size for DP1−Chol and DP2−Chol, and are very similar to the lattice parameters reported for the rectangular phases found in supramolecular dendronized polymer−lipid complexes.17 The difference between the lattice vector lengths of these two dendritic polymers is due to the higher generation and thus larger dendritic side chains of DP2−Chol. The trend continues with the third-generation dendronized polymer: fitting gives lattice parameters \(a = 7.4\) nm and \(b = 4.3\) nm, while TEM gives a period of approximately 7 nm.

The poor order observed in the dendronized polymer systems can be rationalized once more in terms of the topological restrictions imposed by the spatial arrangement of dendron−cholesteryl moieties in the solid state, once these are attached to a common backbone. In this case, any three consecutive dendrons along the backbone not only are attached covalently through their focal point to a common polymer backbone but also have the focal points aligned along the same linear contour length. Because the consecutive grafting distances are fixed, the only degree of freedom remaining is the position of grafting along the polymer backbone. In other words, for any \(n\) dendrons, the degrees of freedom of the corresponding focal points are \(3 ^{n} - 3 \times 1 \rightarrow n \times 3\) when going from dendrons → dendrimers → dendronized polymers.

It is to be expected that further topological bond restrictions occurring in both dendrimers and dendronized polymers will additionally reduce the possible packing configurations with respect to the free dendron systems, further depressing the ordering of the corresponding solid-state complexes.

The different dendritic complexes and their structures as revealed by SAXS and TEM analysis are summarized in Table 1.

### Circular Dichroism.

The ultraviolet/visible light spectrum and circular dichroic signal were acquired from drop-cast films for each individual complex and compared with the corresponding noncomplexed dendritic macromolecule and the cholesteryl sulfate sodium salt. The noncomplexed dendrons, dendrimers, and dendronized polymers absorbed light in the ultraviolet wavelengths with a maximum absorption at approximately 210 nm but did not show significant optical activity in the CD region. The film of chiral cholesteryl sulfate sodium salt had an absorption maximum in the UV region and showed a single minimum value in the CD at approximately 200 nm. All dendritic complexes showed enhanced optical activity with complex CD spectra. Figure 10b compares the UV−vis spectra of the noncomplexed first-generation dendron, the cholesteryl sulfate sodium salt, and their complex (DD1−Chol). Note that the detector was saturated at wavelengths below approximately 210 nm. The corresponding CD signals are shown in Figure 10a. As can be observed, the CD signal appears to be uncorrelated with that of the chiral cholesteryl sulfate sodium salt, with the presence of additional and distinct CD peaks that are not characteristic of the cholesteryl unit alone. This clearly indicates the presence of supramolecule-induced chirality, or induced circular dichroism (ICD). Figure 10 panels d and f show

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**Table 1. Structures of Dendron, Dendrimer, and Dendronized Polymer Cholesteryl Sulfate Sodium Salt Complexes**

<table>
<thead>
<tr>
<th>type of complex</th>
<th>structure</th>
<th>lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrons</td>
<td></td>
<td></td>
</tr>
<tr>
<td>generation 1</td>
<td>lamellar</td>
<td>(a = 4.4) nm</td>
</tr>
<tr>
<td>generation 2</td>
<td>hexagonal columnar</td>
<td>(a = b = 9.0) nm, (\gamma = 120^\circ)</td>
</tr>
<tr>
<td>generation 3</td>
<td>oblique columnar</td>
<td>(a = 9.9) nm, (b = 8.8) nm, (\gamma = 124^\circ)</td>
</tr>
<tr>
<td>Dendrimers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>generation 1</td>
<td>oblique columnar</td>
<td>(a = 10.2) nm, (b = 9.0) nm, (\gamma = 124^\circ)</td>
</tr>
<tr>
<td>generation 2</td>
<td>oblique columnar</td>
<td>(a = 10.2) nm, (b = 9.0) nm, (\gamma = 124^\circ)</td>
</tr>
<tr>
<td>generation 3</td>
<td>microphase-separated</td>
<td>(4.7) nm</td>
</tr>
<tr>
<td>Dendronized Polymers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>generation 1</td>
<td>rectangular columnar</td>
<td>(a = 5.4) nm, (b = 3.3) nm</td>
</tr>
<tr>
<td>generation 2</td>
<td>rectangular columnar</td>
<td>(a = 5.6) nm, (b = 3.8) nm</td>
</tr>
<tr>
<td>generation 3</td>
<td>rectangular columnar</td>
<td>(a = 7.4) nm, (b = 4.3) nm</td>
</tr>
</tbody>
</table>

\(^{*}\) Lattice parameters for the oblique columnar and rectangular columnar structures are based on the fitting procedure described in the paper.

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the UV–vis absorbance for the second- and third-generation dendron complexes (DD2–Chol and DD3–Chol), Figure 10 panels c and e give the corresponding CD signals, showing again the presence of ICD in the solid state. The CD spectra for all the other complexes investigated are given in the Supporting Information. While the effect is not as pronounced as with dendron complexes, they also exhibited ICD. It turns out to be challenging to correlate the exact CD signal with the solid-state structures observed for the various complexes, but clearly induced circular dichroism occurs in each individual complex with a systematic change in their CD signal. In general, it was observed that the first-generation complexes had more pronounced CD signals, and the higher molecular weight dendritic classes (dendrimers and dendronized polymers) had a lower ICD effect than dendrons. This suggests that molecular mobility in the dendritic complexes and the final level of order achieved in the solid state can play a major role on the establishment of macromolecular chirality. Irrespective of the architecture of the complexes, all columnar phases may be assumed to adopt a helical arrangement similar to that disclosed in Figure 3, which is responsible for the observed macromolecular chirality. The occurrence of induced circular dichroism in the lamellar phases (DD1–Chol) can be thought to arise from chirality-induced undulations of the lamellae, consistent with what is shown in the inset of Figure 1a.

**Conclusions**

Ionic complexation of chiral cholesteric pendant groups with dendritic macromolecules such as dendrons, dendrimers, and dendronized polymers leads to self-organizing microphase-separated structures as a consequence of the segregation of the cholesteric pendant groups and the dendritic core. Depending on the kind of dendritic molecule and the generation, (i) lamellar, (ii) columnar hexagonal, (iii) oblique columnar, (iv) rectangular columnar, and (v) short-range ordered microphase-separated morphologies are observed by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) studies. A general trend is that the level of order achieved in the solid state is directly correlated with the degrees of freedom of the dendritic macromolecular template used. Accordingly, the order in self-assembled structures of the complexes in the solid state is found to decrease when going from dendron → dendrimer.
dendronized polymer complexes. A particular feature of the columnar systems, which can be revealed by TEM, is that the dendritic molecules are positioned in such a way that the cholesteric units occupy the column shells while the focal points of the dendrons and dendrimers are in the center of the columns. This structural feature differs from the topological organization found in inverted columnar phases obtained by the same dendritic macromolecules complexed with smaller and softer sulfate alkyl tail nonchiral surfactants, inferring the role of volume fraction, rigidity, and chirality in the molecular packing of the complexes in the solid state. Finally, the columns are dense and do not exhibit a central cavity as demonstrated by porosity measurements (BET).

Compared to the noncomplexed dendritic molecules, optical activity in the solid state showed a change in ultraviolet/visible light (UV–vis) absorption and a systematic increase in the CD signal, indicating the occurrence of supramolecular chirality induced by the complexation of the achiral dendritic molecules with the chiral cholesteric moieties. Enhancement of the optical signals appear to be correlated with the order of the structure in the solid state, because complexes that exhibit the highest structural order in the solid state also show the most enhanced CD signal.

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Supporting Information Available: Descriptions of experimental methods, materials and synthesis; transmission electron micrographs of the dendronized polymer complexes (DP1–Chol, DP2–Chol, DP3–Chol); circular dichroism and ultraviolet/visible light spectra of the dendrimer complexes (DM1–Chol, DM2–Chol, DM3–Chol) and the dendronized polymer complexes (DP1–Chol, DP2–Chol, DP3–Chol); and nitrogen adsorption and desorption isotherms of the second-generation dendron complex (DD2–Chol). This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information for

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Experimental

Materials

The detailed synthesis of dendrons\textsuperscript{1,2}, dendrimers\textsuperscript{1,2} and dendronized polymers\textsuperscript{3,4} is described elsewhere and will not be discussed here (see Scheme S1 for chemical details). Synthesis of the third generation dendrimer is new and details are given in the following section. Cholesteryl sulfate sodium salt (Sigma-Aldrich) was used as received. The dendritic molecules and cholesteryl sulfate sodium salt were dissolved separately in mixtures of 1-propanol (approx. 15 w-%) and deionized water (Milli-Q) with pH adjusted between 3 and 4 by HCl (Fluka). The weight fraction was less than 0.2 % for cholesteryl sulfate sodium salt and 1-2 % for the dendritic molecules in the solutions. The solutions were mixed in ratios for which the molar amount of cholesteryl sulfate corresponds to the amount of the NH\textsubscript{2} peripheral groups of the dendritic molecules. The mixing yielded a cloudy dispersion. The
dispersions were successively centrifuged for 20 minutes at 6000 rpm and at a temperature of +4 °C. The precipitates were left to dry overnight. Further drying was done in a vacuum oven (10⁻² mbar) for three days at room temperature. The complexes based on dendrons were labeled as DD1-Chol, DD2-Chol, DD3-Chol, dendrimers as DM1-Chol, DM2-Chol, DM3-Chol and dendronized polymers as DP1-Chol, DP2-Chol, DP3-Chol, for generations 1, 2 and 3, respectively. The dried complexes were annealed for one to three days in chloroform vapor at +60 °C in closed bottles. Thermal annealing at temperatures above the glass transitions of all compounds turned out not to be of practical use since most of these complexes degraded at relatively low temperatures. However, some samples, especially DD2-Chol could withstand temperatures up to 120 °C in a high vacuum oven which further improved its structural order.

**Synthesis of DM3**

![Scheme S1](image)

Scheme S1. Reagents and conditions: a) 1, 2, HOBt, EDC, DMF/MeOH, -20°C, 36 h, (30 %); b) 3a, TFA, 36 h, (88%)

Compounds 1 and 2 were synthesized according to literature methods. Other reagents were purchased from Aldrich, Across or Fluka. Triethylamine (TEA) was refluxed over Na.
N-Hydroxybenzotriazole (0.315 g, 2.33 mmol) was added to a solution of acid 2 (5 g, 1.94 mmol) in dry DMF (200 mL) at room temperature. After 10 min N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (0.49 g, 2.56 mmol) was added at -20°C, and the reaction mixture was stirred until the hydrochloride was dissolved completely (ca. 4 h). Then a solution of TEA (0.49 g, 4.87 mmol) and 1 (0.20 g, 0.325 mmol) in methanol (10 mL) was added dropwise at -10°C. The resulting mixture was warmed to room temperature and stirred for 36 h. Solvent was removed in vacuo and residue again dissolved in DCM and then washed with aqueous NaHCO₃ and brine. The organic layer was dried with magnesium sulphate and
the solvent removed in vacuo. Three successive chromatographic separations (silica gel, DCM/MeOH 25/1, 15/1 and CHCl3/MeOH 7:1) gave 3a as colorless foam (698 mg, 30 %). Rf = 0.31 (DCM/MeOH 10/1) ; M.p. = 117 – 118 °C ; 1H NMR : d = 1.42 (s, 216 H; Boc), 1.88, 2.01, 2.06 (m, 90 H; CH3), 3.21, 3.51 (t, 90 H; CH2NH), 3.89 (m, 90 H; PhOCH2), 4.90, 5.18 (br, 24 H; NH), 5.93 (s, 3 H; Ph core), 6.38 (t, 9 H; Ph), 6.46 (t, 12 H; Ph), 6.86 (dd, 18 H; Ph), 6.92 (dd, 24 H; Ph), 7.73, 7.85 (t, 21 H; NH) ppm. ; 13C NMR: d = 28.42 (C(CH3)3), 28.93, 29.48 (CH2), 37.77 (CH2N), 65.72, (OCH2), 79.19 (C(CH3)3), 94.36 (Ph core), 104.29, 105.82, 136.45, 156.21, 159.75 (Ar), 159.85 (CONH), 167.62 (CO) ppm. ; MALDI-TOF: m/z (rel-%) 7979.46 (30) [M + Na]+, 7995.15 (25) ([M + K]+; elemental analysis (%) calcd. for C308H597N45O114 (7956.44): C 61.59, H 7.56, N 7.92; found: C 60.37, H 7.39, N 7.55.

1,3,5-Tris(3-(3,5-bis(3-(3,5-bis(3-aminoproxy)benzamido) propoxy)benzamido)propoxy)benzamide)propoxy)benzene tetrakisocosatrifluoracetate (DM3)

To an 3a (0.5 g, 0.062 mmol), 10 mL of neat TFA (15.23 g, 133.6 mmol) was added. After stirring for 24 h, 10 mL of methanol was added and mixture was left stirring for 12 h. Evaporation of solvent without further purification gave brownish liquid DM3 (0.45 g, 88 %) ; 1H NMR (CD3OD) : d = 2.02, 2.10 (m, 90 H; CH2), 3.12, 3.29, 3.51 (m, 90 H; CH2NH), 3.97, 4.00, 4.08 (m, 90 H; PhOCH2), 6.00 (s, 3 H; Ph core), 6.56 (t, 9 H; Ph), 6.67 (t, 12 H; Ph), 6.93 (dd, 18 H; Ph), 6.99 (dd, 24 H; Ph), 8.00, 8.52, (t, 21 H; NH) ppm. ; 13C NMR (CD3OD): d = 28.30, 30.19 (CH2), 38.40, 38.47, 38.55 (CH2N), 66.50, 67.19, 67.27 (OCH2), 94.36 (Ph core), 105.65, 105.74, 106.95, 107.19, 137.64, 137.80, 161.16, 161.55 (Ar), 169.72, 169.88 (CO) ppm. ; MALDI-TOF: m/z (rel-%) 5553.7 (100) [M – (24xCF3COOH)]+; elemental analysis (%) calcd. for C336H429N45O114F72 (8290.20): C 48.68, H 5.22, N 7.60; found: C 44.89, H 4.73, N 6.76.
Figure S0. 500 MHz $^1$H-NMR spectrum of the Boc protected 3a and deprotected DM3 dendrimer measured in CDCl$_3$ and CD$_3$OD respectively at 25°C. Note that the resonances of the deprotected are slightly shifted compared with those of the protected one due to structural differences and the different solvents used for these measurement (*: chloroform-d, #: water and §: methanol).
Figure S1. MALDI-TOF mass spectrum of 3a dendrimer with its corresponding Na and K molecular ion peaks.
Figure S2. 500 MHz 1H-NMR spectrum of the Boc protected 3a and deprotected DM3 dendrimer measured in CDCl3 and CD3OD respectively at 25°C. Note that the resonances of the deprotected are slightly shifted compared with those of the protected one due to structural differences and the different solvents used for these measurement (*. chloroform-d, #: water and §: methanol).
Ultra-violet/Visible Light Spectroscopy

Samples for Ultra-violet/visible light spectroscopy (UV-Vis) measurements were prepared as described above up to the centrifugation step. After centrifugation, the wet precipitates were frozen in liquid nitrogen and dried in a vacuum oven (10⁻² mbar). Quartz substrates were cleaned in 1:1:5 solution of hydrogen peroxide (30 % vol., Riedel-de Haën), ammonia (25 % vol., Riedel-de Haën) and deionized water at +70 °C for 10 minutes, rinsed, dried and finally kept under ultra-violet irradiation for 10 minutes. The freeze-dried complexes were dissolved in chloroform and drop-cast on the substrates. The reference samples, the pristine cholesteryl sulfate sodium salt and the dendritic macromolecules, were dissolved in ethanol (>99.5 % vol., Altia) and drop-cast. The absorption spectra were acquired using Perking Elmer Lambda 960 UV/Vis/NIR spectrophotometer.

Circular Dichroism

The same samples as for UV-Vis were used also for circular dichroism (CD) measurements. A clean quartz substrate was measured for background, which was subtracted from all measured spectra. The spectra were collected with JASCO J-750 CD spectrometer with a sensitivity of 100 mdeg using continuous scanning mode and a speed of 200 nm/min, data pitch of 1 nm, response time of 2 s and band width of 2.0 nm. Altogether four scans/sample were acquired and averaged on. The samples were rotated around the optical axis by 90° to rule out artifacts in the CD signals arising from samples’ anisotropy.

Small Angle X-ray Scattering

Small-angle X-ray scattering (SAXS) spectra were acquired on a device consisting of Bruker MICROSTAR microfocus rotating anode X-ray source with Montel Optics (Cu Kα radiation, λ = 1.54 Å). The beam was further collimated to a radius of approximately 0.5 mm at the sample position using four sets of JJ X-Ray four blade slits. Sample-to-detector distance
of 45 cm was used. The scattering intensities were measured using a 2-D area detector (Bruker HiStar). The magnitude of the scattering vector \( q \) is given by \( q = 4\pi \sin(\theta)/\lambda \), where \( 2\theta \) is the scattering angle. About 0.1 mm thick samples were maintained between two Mylar sheets.

**Transmission Electron Microscopy**

Transmission electron microscopy (TEM) was carried out using Jeol JEM-3200FSC field emission microscope. The operating voltage was 300 kV. The images were acquired in bright field mode with Gatan Ultrascan 4000 CCD camera. Specimen temperature was maintained at -187 °C during the imaging. Additionally some of the samples were imaged at room temperature using FEI Tecnai 12 microscope equipped with Gatan Ultrascan 1000 CCD camera. This microscope was operated at 120 kV. Thin sections (~70 nm) were cut at -60 °C by Leica Ultracut UTC microtome using a 25° Diatome diamond knife. The sections were collected on 300 mesh lacey carbon grids. The samples were stained in vapor of 0.5 % RuO₄ stabilized aqueous solution (Electron Microscopy Sciences) for five minutes. RuO₄ selectively stains the aromatic rings present in the dendritic molecules of the complexes which confers them a dark contrast in the TEM micrographs. Structure periodicities and lattice parameters were calculated using the peak positions of Fourier transform spectra of the micrographs.

**BET Porosity Analysis**

Pore volume and surface area of the sample were analyzed using static volumetric nitrogen adsorption at temperature of liquid nitrogen (-196 °C). For this task, Coulter Omnisorp 100CX apparatus was used. Before adsorption measurement the sample was evacuated at 100 °C for three hours to remove the possible adsorbed molecules from sample surface. The measurement was started in vacuum and adsorption isotherm of nitrogen was measured by increasing the pressure of nitrogen around the sample up to 0.95 % of nitrogen saturated
vapor pressure on that temperature. After adsorption nitrogen was desorbed from the surface by gradually lowering the pressure. The adsorption and desorption isotherms were then used to calculate the pore volume of the sample using BET equation.

Transmission electron microscopy (TEM) images

Figure S3. Transmission electron micrograph of the first generation dendronized polymer complex DP1-Chol.

Figure S4. Transmission electron micrograph of the second generation dendronized polymer complex DP2-Chol.
Figure S5. Transmission electron micrograph of the third generation dendronized polymer complex DP3-Chol.

Ultra-violet/Visible Light (UV-Vis) Spectra and Circular Dichroism Signals

Figure S6. (a) Ultra-violet/visible light absorption spectrum and (b) circular dichroism signal of the first generation dendrimer (black circles) and its complex DM1-Chol (solid line).
Figure S7. (a) Ultra-violet/visible light absorption spectrum and (b) circular dichroism signal of the second generation dendrimer (black circles) and its complex DM2-Chol (solid line).

Figure S8. (a) Ultra-violet/visible light absorption spectrum and (b) circular dichroism signal of the third generation dendrimer (black circles) and its complex DM3-Chol (solid line).

Figure S9. (a) Ultra-violet/visible light absorption spectrum and (b) circular dichroism signal of the first generation dendronized polymer (black circles) and its complex DP1-Chol (solid line). Measurement data in the $\lambda < 207$ nm range is not shown due to CD detector saturation.
Figure S10. (a) Ultra-violet/visible light absorption spectrum and (b) circular dichroism signal of the second generation dendronized polymer (black circles) and its complex DP2-Chol (solid line).

Figure S11. (a) Ultra-violet/visible light absorption spectrum and (b) circular dichroism signal of the third generation dendronized polymer (black circles) and its complex DP3-Chol (solid line). Measurement data in the $\lambda < 197$ nm range is not shown due to CD detector saturation.
BET Porosity Analysis

Figure S12. Gas adsorption (red circles) and desorption (blue squares) isotherms for the second generation dendron complex (DD2-Chol). The pore volume calculated using BET method is below 0.01 cm$^3$/g.

References