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Host–Guest Systems

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Helical Folding in a Helical Channel: Chiroptical Transcription of Helical Information through Chiral Wrapping**

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The helical structure is one of the most significant motifs in macromolecules. In nature, helical structures are often found in biomacromolecules and appear to play a critical role in biological phenomena such as molecular recognition and information storage. This is exemplified by the double helix of DNA and the α helix of proteins,[1] and some synthetic polymers also adopt a helical conformation.[2] Recently, the design and synthesis of macromolecules with a helical structure has attracted a great deal of interest as a result of their relationship to life sciences as well as their potential applications in materials science.[3] Herein, we show that linear oligosilanes acting as axle guest molecules within the internal helical channel of a polymer can be induced to form a preferential helical conformation. The helical sense of the guest molecules is then controlled by wrapping with either the left-handed or the right-handed helical conformation of the host polymer. The system presented herein offers a new approach in the field of helical expression in molecular and macromolecular systems.[4]

To explore the possibility of "helix-in-helix" supramolecular architecture, we have chosen host–guest combinations of linear polysaccharides and oligosilanes (Figure 1). One of the polysaccharides used is amylose, which is composed of α-1,4-linkages between D-glucopyranose residues. Amylose adopts a left-handed helical conformation and forms inclusion complexes as a result of hydrophobic interactions with guest molecules confined within the helical cavity.[5] The helical dimensions of amylose can be adjusted according to the size of the guest. The other polysaccharide examined was schizophyllan (SPG), which is composed of β-1,3-linkages between glucose units (β-1,3-glucan) and adopts a right-

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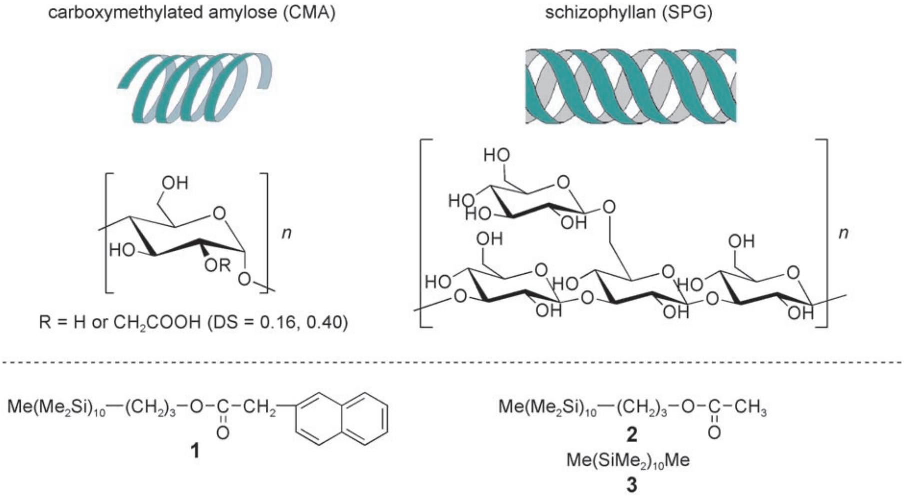

Figure 1. Combinations of host–guest complexation for linear polysaccharides and oligosilanes.

handed triple helix in nature.[6] On the other hand, oligosilanes **1**–**3**, used as the axle guests, are unique molecules that exhibit absorption in the UV region as a result of σ conjugation along the main chain. The absorption behavior of σ-conjugated systems is extremely sensitive to the conformation.[7] This sensitivity is exemplified by the behavior of helical poly- or oligosilanes in response to the chiral stimulus of their optically active substituents.[8] This allowed us to study photophysical properties that are dependent on the conformation of the main chain. Several reports have addressed control of the conformation of oligosilanes,[9] for example, by inclusion of a macrocyclic molecule (with α-1,4-glucopyranose units) into cyclodextrins.[10] Recently, we found the induction of a preferential helical-sense conformation in oligosilanes that are located within the internal cavity of cyclodextrins.[11]

Molecular mechanics was used to study models of the complexes at hand.[12] The minimum-energy structure of the simple model complex formed by the interaction between permethyldodecasilane and an amylose fragment that contains 16 repeating α-1,4-D-glucopyranose units is illustrated in Figure 2. The amylose fragment is shown to adopt a left-handed helical conformation by wrapping around the oligosilane axle. In the helical cavity created by the amylose wrapping, the oligosilane main chain assumes a helical conformation with a Si–Si torsion angle of about 165°.

In our experiments, we used partially carboxymethylated amylose (CMA), with DS = 0.16 or 0.40 (DS = the degree of carboxymethyl substitution) to increase the solubility of the resulting inclusion complex in water. In a typical preparation of the inclusion complex, a mixture of decasilane **1** (30 mg, 3.7×10^{-2} mmol) and CMA (DS = 0.16, 150 mg, 8.5×10^{-1} mmol glucose unit) in water (20 mL) was dispersed ultrasonically for 5 min and then stirred at room temperature for 8 days. The precipitate was collected by centrifugation and dried under vacuum to give the **1**–CMA complex (32 mg, 18 %), which was slightly soluble in water (up to concentrations of ≈ 10^{-4} M).[13] In agreement with the model structure, the **1**–CMA inclusion complex exhibited CP MAS (cross-polarization magic-angle spinning) ^{13}C NMR and the MASGHD (magic-angle spinning gate ^{1}H decoupled) ^{29}Si NMR signals that arose from CMA and the incorporated oligosilane chain.[14] A powder X-ray diffraction study demonstrated that the reflection pattern was very similar to that reported for a complex of γ-cyclodextrin (a macrocyclic molecule consisting of eight α-1,4-glucopyranose units), which exhibits a channel-type structure.[11,15] These studies suggest that the amylose is probably adopts a 8_1-helical structure (eight α-D-glucopyranose resides per turn) with a cross-section diameter of 8.5–9 Å to fit to the sequential size of the dimethylsilylene units of **1** (≈ 6 Å).

As was envisioned, and reinforced by the molecular mechanics calculations, decasilane **1** is indeed located in a helical channel and confined by CMA wrapping. The absorption and CD spectra provided information on the conformation of the oligosilane main chain within the channel (Figure 3). Thus, the absorption spectrum of a **1**–CMA complex (DS = 0.40) in water, at room temperature, exhibits an absorption maximum at 280 nm owing to the conjugated Si backbone σ–σ* transition ($\varepsilon = 1.1\times10^{4}\,\text{M}^{-1}\,\text{cm}^{-1}$).[16,17] In the CD spectrum, the complex displays an intense positive CD signal in the absorption region of the oligosilane ($\Delta\varepsilon = 2.56\,\text{mol}^{-1}\,\text{dm}^{3}\,\text{cm}^{-1}$ at 275 nm). Decasilane **1** does not give rise to any CD signals because of an equal mixture of enantiomeric twisted or helical conformers. However, in the helical channel of CMA, the decasilane **1** is induced to adopt a preferential helical conformation as a result of diastereoselective complexation with the chiral host. In this case, the main chain assumes a predominantly transoid conformation with a Si–Si torsion angle of 160–175° (15/7 helix).[18,19] The dissymmetry ratio, g_{abs} ($=\Delta\varepsilon/\varepsilon$), is usually used to characterize helical structures, such as right- and left-handed helix populations. The dissymmetry ratio for the **1**–CMA complex, $g_{\text{abs}} = 2.3\times10^{-4}$, is of the same order of magnitude ($1\text{–}2\times10^{-4}$) as that observed for a range of polysilanes with optically pure substituents that adopt a preferential screw sense.[20]

SPG also acts as a helical host polymer.[21] Decasilane **1**, in the presence of SPG, exhibits an absorption maximum at 284 nm ($\varepsilon = 1.1\times10^{4}\,\text{M}^{-1}\,\text{cm}^{-1}$) that is attributable to the σ–σ* transitions of the oligosilane main chain (Figure 3). In the CD spectrum, an induced CD signal is observed in the same region ($\Delta\varepsilon = -2.88\,\text{mol}^{-1}\,\text{dm}^{3}\,\text{cm}^{-1}$ at 282 nm). This signal is indicative of **1** being induced to assume a preferential helical conformation by complexation with SPG. The CD signal of the **1**–SPG complex is slightly red shifted relative to that of the **1**–CMA (DS = 0.40) complex. This shift is presumably associated with the pitch of the helical conformation of **1**. Such a pitch is induced when **1** is confined by the helices of the polysaccharide host molecules, as the pitch and the diameter of the host helices are different.[22,23] Interestingly, complexation of **1** with SPG, which conforms to a right-handed helix in water, induces a negative CD signal, whereas complexation

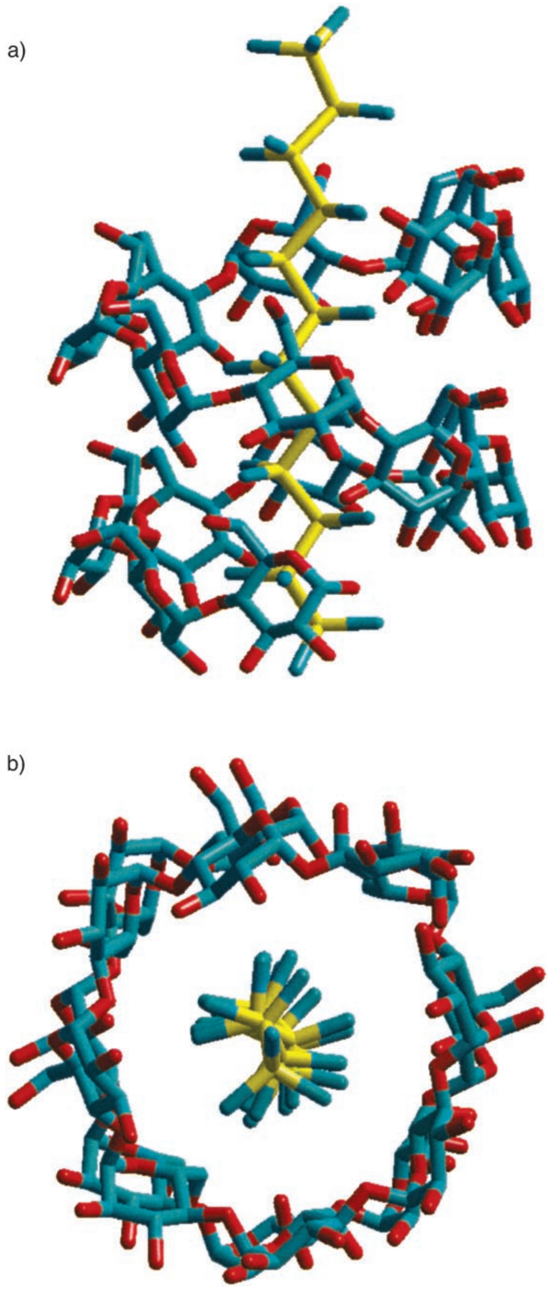

Figure 2. Energy-minimized models based on the AMBER force field for an inclusion complex of $Me(SiMe_2)_{12}Me$ with an amylose fragment containing 16 repeating α-1,4-D-glucopyranose residues: a) side view and b) top view. Carbon, oxygen, and silicon atoms are shown in blue, red, and yellow, respectively. The hydrogen atoms have been omitted for clarity.

with CMA adopts a left-handed helical conformation in water and induces a positive CD signal (see above). Thus, the helical sense of the guest molecule is dependent on, and can be controlled by, the helical sense of the host polymer.

The time course of the absorption and CD spectra of a mixture of **1** and CMA revealed the progress of the folding process. The inclusion complex, generated in situ by mixing **1** and CMA in water for 40 h, showed an absorption maximum at 279 nm and a positive Cotton effect. However, the

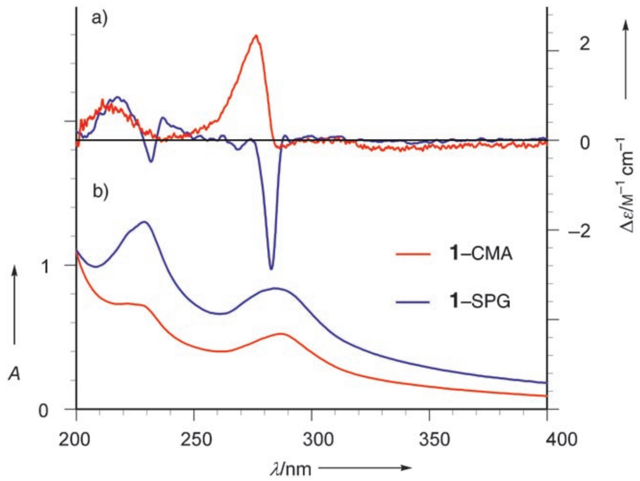

Figure 3. a) CD and b) absorption spectra of **1**–CMA (red line) and **1**–SPG (blue line) in water.

absorption undergoes a bathochromic shift to 293 nm over a period of a month without a change in the sign of the Cotton effect.[24,25] This can be attributed to changes in the helical pitch of the oligosilane to accommodate the dimensions of the helical channel. However, as **1** is confined by amylose wrapping, progress is slow as a result of the steric constraint. The fluorescence spectrum of the **1**–CMA complex discloses the more detailed structure of **1** in the channel. Thus, the **1**–CMA (DS = 0.40) complex, when excited at 298 nm, exhibits a local emission at 330 nm from both the naphthyl group and the oligosilane chain and an emission for the dimer at 400 nm from the naphthyl groups.[26] Accordingly, oligosilane **1**, within the complex, is envisioned to have aligned in a head-to-head fashion with the stacking of the naphthyl groups within the helical amylose.

Finally, a similar wrapping with CMA (DS = 0.16) has also been found to proceed with **2** and **3** as the guest molecules (Figure 1). The resultant complexes exhibit a positive Cotton effect; however, the intensities of the signals are weak. We presume that further to the hydrophobic interactions between the guest molecules and the helical cavity as the major driving force for complex formation, hydrogen bonding and/or π–π interactions within the channel also play an important role in the formation or stabilization of the complex.

In summary, we have demonstrated helical induction of oligosilane by using peripheral wrapping with amylose and schizophyllan. This system is the basis for a new and simple concept of helical expression in molecular and macromolecular systems.

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[12] Monte Carlo searches for minimum-energy conformations were performed by using the HyperChem 7.5 and the AMBER force field.

[13] The NMR spectroscopic measurement was not possible because of the solubility of **1**–CMA in H_2O. A detailed description of the structure of the complex by, for example, X-ray single-crystal analysis or SPM observation requires further study.

[14] See Supporting Information.

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[17] Although the absorption overlapped with that of the naphthyl group chromophore, the molar extinction coefficient of the permethyldecasilane was much higher than that of naphthylacetic acid ($\varepsilon = 500\,\text{M}^{-1}\,\text{cm}^{-1}$ at 273 nm). The absorption of **1**, which occurs at around 290 nm, was ascribed to the oligosilane.

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[19] The band widths of the absorption and the CD at 280 nm look somewhat different, probably due to incomplete inclusion of the oligosilane into the cavity or incomplete induction of the helical sense in the cavity. The other conformation of the oligosilane in the complex may also induce a Cotton signal.

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[21] Very recently, Shinkai and co-workers reported on a supramolecular chiral complex with SPG and polythiophene, see; C. Li, M. Numata, A.-H. Bae, K. Sakurai, S. Shinkai, *J. Am. Chem. Soc.* **2005**, *127*, 4548 – 4549.

[22] The helical CMA composed of α-1,4-D-glucopyranose residues assumes a 6/1–8/1 helical pitch (0.8 nm) with a 0.5–0.8 nm inner diameter, whereas the helical SPG composed of β-1,3-glucose residues assumes a 6/1 helical pitch (1.8 nm) with 1.75 nm inner diameter.

[23] Very recently, we found the supramolecular complex forms between a triple helix of SPG and two molecules of oligosilane **1**; for the detailed structure of the **1**–SPG complex, see: T. Sanji, N. Kato, M. Tanaka, *Chem. Lett.* **2005**, *34*, 1144 – 1145.

[24] The degree of carboxymethyl substitution on the amylose (DS) affects the helix formation of the amylose, the complexation ability between guest molecules and amylose, as well as the solubility in water. We found that complex formation between CMA and the oligosilanes depends on the DS. In the case of CMA (DS = 0.16), the complex, which was monitored with UV and CD measurements, was formed in a few hours after ultrasonic dispersion. In the case of CMA (DS = 0.40), complex formation was quite slow. Once the complex was formed, however, it was stable for more than a few months without alteration in the UV absorption intensity or the sign of the CD signal. We also examined the pH dependence of the complex formation under buffered conditions. In the neutral (pH 7.0) and the basic (pH 9.2) buffer solution, the situation of complex formation was almost the same. In the acid buffer solution (pH 5.0), however, complex formation was hardly observed. Furthermore, the thermostability of the complex was examined. At 80 °C no Cotton effect was observed, thus indicating that the complex was not stable at high temperature. We thank a referee for valuable suggestions.

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