Induction of Optical Activity in Oligosilanes by Chiral Wrapping with *β*-1,3-Glucan (Schizophyllan)

Takanobu Sanji,* Nobu Kato, and Masato Tanaka*
Chemical Resource Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503

(Received May 27, 2005; CL-050693)

Linear oligosilanes form inclusion complexes with schizophyllan to induce a preferential helical conformation within the chiral environment constructed by wrapping with schizophyllan.

Recently, controlling the helical structure of macromolecules has attracted a great deal of interest.[1] The helical structures are often found in biomacromolecules like DNA[2] and protein[3] and appear to play critical roles in biological phenomena such as molecular recognition and information storage as exemplified. Some synthetic polymers also adopt a helical conformation even in solution and new approaches to synthesizing polymers with a helical conformation have been carried out.[4,5]

Among the synthetic polymers with the helical sense, polysilanes are particularly interesting because of their unique electronic and photophysical properties. The unique properties are attributed to the σ-conjugation occurring along the main chain, and hence, extremely sensitive to the polymer conformation.[6] Polysilanes, which induce a preferential helical conformation when substituted with optically active side chains[7] or end groups,[8] allow us to study the photophysical properties in connection with the conformation of the polymer main chain. Oligosilanes with well-defined structures are typical fundamental models for polysilanes, and several reports have addressed controlling the conformation of oligosilanes.[9]

We have recently reported the first example of the induction of a preferential helical conformation in oligosilanes within the internal cavity of cyclodextrins.[10] We extend this approach to linear polysaccharides as host molecules, which can wrap the guest molecules. Schizophyllan (SPG, β-1,3-glucan), one of polysaccharides, is composed of β-1,3-linkages between glucose residues, where the repeating units consist of three β-1,3-glucose units with one β-1,6-glucose side chain linked at every third main chain glucose (Chart 1).[11] SPG adopts a right-handed triple helix (t-SPG) in nature. The unique structural motif of SPG stimulated us to employ as the chiral host molecule for complexing with oligosilanes. Here we show that oligosilanes could form inclusion complexes with SPG to induce a preferential helical conformation within the chiral environment constructed by wrapping with SPG. Very recently, Shinkai and co-workers reported the supramolecular chiral complex between SPG and polythiophene.[12]

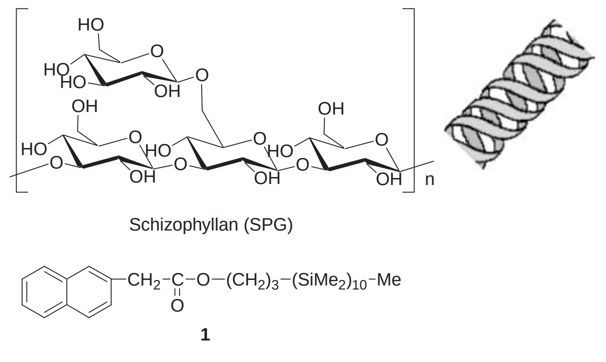

Chart 1. Chemical structure of schizophyllan and the oligosilane **1**.

The oligosilane **1** was employed as a guest molecule. In a typical preparation of the complex, a mixture of the decasilane **1** (0.25 mg, 3.1×10^{-4} mmol) and SPG (0.80 mg, 1.2×10^{-3} mmol per 4 glucose units, $Mw = 1.5\text{–}4.0 \times 10^5$) in water (3.2 mL) was dispersed ultrasonically for 5 min and then stirred at room temperature for 2 h. The decasilane **1** was insoluble in water, but **1** in the presence of SPG was soluble in water, and hence, the spectroscopic properties of the complex in water could be successfully determined. The absorption and circular dichroism (CD) spectra provide information on the conformation of the oligosilane main chain. Thus, in the UV spectrum, a mixture of **1** and SPG in H_2O at room temperature exhibits an absorption maximum at 284 nm ($\varepsilon = 1.1 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$) (Figure 1), ascribable to the σ–σ^* transition of the oligosilane main chain. In the circular dichroism (CD) spectrum, **1** in the presence of SPG displays a sharp negative induced CD band in the absorption region of the σ–σ^* transitions of the oligosilane ($\Delta\varepsilon = -2.88\ \mathrm{M^{-1}\,cm^{-1}}$ at 282 nm), while **1** itself does not show CD signals. This clearly indicates that the decasilane **1** in the presence of SPG is induced to assume a preferential one-handed helical conformation leading to the observed optical activity by complexation with SPG, where the main chain of **1** assumes a predominantly *transoid* conformation with an Si tetrad dihedral angle of 160–175° (15/7 helix),[13] The dissymmetry ratio, g_{abs} ($=\Delta\varepsilon/\varepsilon$), is usually used to characterize helical struc-

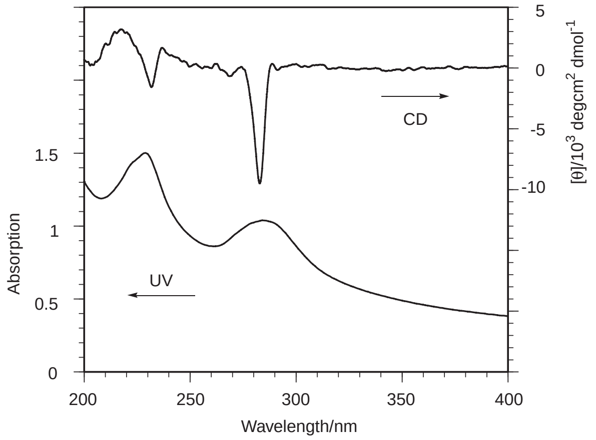

Figure 1. UV and CD spectra of **1** in the presence of SPG in H_2O.

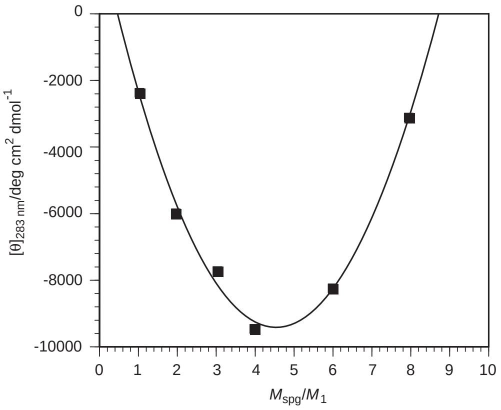

Figure 2. Job's plot upon mixing of **1** and SPG in H_2O, obtained by means of CD spectroscopy (M_{SPG}/M_1 vs [θ] at 283 nm).

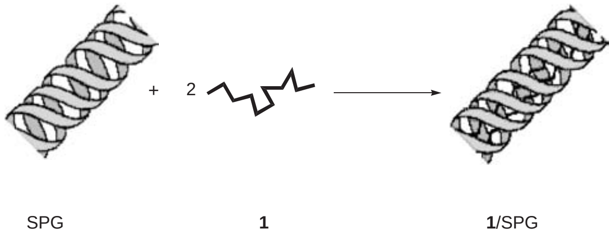

Figure 3. Schematic illustration of the chiral supramolecular complex formation between **1** and SPG.

tures such as right- and left-handed helix populations. The **1**/CyD complex has a g_{abs} of 2.6×10^{-4}. The value is the same order of magnitude ($1–2 \times 10^{-4}$) observed for a range of polysilanes with optically pure substituents which adopt preferential screw senses.[14,15] At present, the relationship between the sign of the Cotton effect in the CD spectrum and the screw-direction of the helix in the oligosilane chain is not clear.

The stoichiometry of the complex formation was determined by the CD titration measurement to discuss the supramolecular complex formation, as shown in Figure 2. The CD intensity increased with the addition of SPG to **1** in H_2O at the initial stage, but an inflection point was observed at $M_{spg}/M_1 = 4.5$ (M_{spg} and M_1 are the molar concentration of SPG and **1**, respectively). Based on the molecular length of **1** (2.8 nm) and the helical pitch of SPG with 6/1 helix (1.8 nm), the mole ratio of the glucose residues along the SPG main chain to the oligosilane **1** for the maximum complex formation is estimated at approximately 1.5. This indicates that the supramolecular complex forms between a triple helix of SPG and two molecules oligosilane **1**, in which **1** adopts the helical conformation (Figure 3), although a detailed description of the structure of the **1**/SPG complex by, for example, X-ray single crystal analysis or SPM observation requires further study. The triple helix SPG has enough space with the inner diameter of 1.75 nm[11] for fitting two oligosilane chains **1** with the cross section diameter of 6 Å into the cavity. Indeed, the **1**/SPG complex excited at 284 nm exhibited a dimer emission (400 nm) of the naphthyl groups,[16] as well as the local emission (330 nm) from both the naphthyl group and the oligosilane chain, indicating partial π–π stacking of the naphthyl groups stabilized in the helical channel of SPG. Thus, the triple helix SPG as a host molecule affords the chiral space and the hydrophobic interaction between the guest molecules and the internal hydrophobic surface of SPG is considered to be a major driving force for the complex formation.[17]

In conclusion, we have demonstrated the induction of helical conformation in oligosilane by wrapping with SPG. The present system is a new approach in the field of helical expression in molecular and macromolecular systems.

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan (No. 16685004).

References and Notes

1 T. Nakano and Y. Okamoto, *Chem. Rev.*, **101**, 4013 (2001).

2 W. Saenger, "Principles of Nucleic Acid Structure," Springer-Verlag, New York (1984), Chap. 10 and 11.

3 G. E. Schulz and R. H. Schimer, "Principles of Protein Structure," Springer-Verlag, New York (1979), Chap. 5.

4 a) E. Yashima, K. Maeda, and Y. Okamoto, *Nature*, **399**, 449 (1999). b) H. Nakashima, J. R. Koe, K. Torimitsu, and M. Fujiki, *J. Am. Chem. Soc.*, **123**, 4847 (2001). c) P. Dellaportas, R. G. Jones, and S. J. Holder, *Macromol. Rapid Commun.*, **23**, 99 (2002).

5 a) A. Tanatani, M. J. Mio, and J. S. Moore, *J. Am. Chem. Soc.*, **123**, 1792 (2001). b) V. Berl, I. Huc, R. G. Khoury, M. J. Krische, and J.-M. Lehn, *Nature*, **407**, 720 (2000). c) S. H. Gellman, *Acc. Chem. Res.*, **31**, 173 (1998).

6 R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989).

7 a) M. Fujiki, *J. Am. Chem. Soc.*, **116**, 11976 (1994). b) M. Fujiki, *J. Am. Chem. Soc.*, **122**, 3336 (2000). c) J. R. Koe, M. Fujiki, and H. Nakashima, *J. Am. Chem. Soc.*, **121**, 9734 (1999).

8 K. Obata and M. Kira, *J. Am. Chem. Soc.*, **119**, 11345 (1997).

9 a) S. Mazières, M. K. Raymond, P. A. Raabe, and J. Michl, *J. Am. Chem. Soc.*, **119**, 6682 (1997). b) K. Tamao, H. Tsuji, M. Terada, M. Asahara, and S. Yamaguchi, *Angew. Chem., Int. Ed.*, **39**, 3287 (2000). c) I. El-Sayed, Y. Hatanaka, S. Onozawa, and M. Tanaka, *J. Am. Chem. Soc.*, **123**, 3597 (2001). d) K. Sakamoto, T. Naruoka, and M. Kira, *Chem. Lett.*, **32**, 380 (2003).

10 a) T. Sanji, A. Yoshiwara, H. Sakurai, and M. Tanaka, *Chem. Commun.*, **2003**, 1506. b) T. Sanji, M. Kato, and M. Tanaka, *Macromolecules*, **38**, 4034 (2005).

11 a) T. Yanaki, T. Norisuye, and M. Fujita, *Macromolecules*, **13**, 1462 (1980). b) C. T. Chuah, A. Sarko, Y. Deslandes, and R. H. Marchessault, *Macromolecules*, **16**, 1375 (1983). c) T. M. McIntire and D. A. Brant, *J. Am. Chem. Soc.*, **120**, 6909 (1998). d) K. Sakurai and S. Shinkai, *J. Am. Chem. Soc.*, **122**, 4520 (2000). e) M. Numata, T. Hasegawa, T. Fujisawa, K. Sakurai, and S. Shinkai, *Org. Lett.*, **24**, 4447 (2004). f) T. Hasegawa, S. Haraguchi, M. Numata, T. Fujisawa, C. Li, K. Kaneko, K. Sakurai, and S. Shinkai, *Chem. Lett.*, **34**, 40 (2005).

12 C. Li, M. Numata, A.-H. Bae, K. Sakurai, and S. Shinkai, *J. Am. Chem. Soc.*, **127**, 4548 (2005).

13 J. Michl and R. West, *Acc. Chem. Res.*, **3**, 821 (2000).

14 a) M. Fujiki, *J. Am. Chem. Soc.*, **116**, 6017 (1994). b) S. Toyoda and M. Fujiki, *Macromolecules*, **34**, 640 (2001).

15 The band widths of the absorption and the CD at 284 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.

16 K. Ueno, K. Takahashi, and T. Osa, *J. Chem. Soc., Chem. Commun.*, **1980**, 921.

17 Shinkai and co-workers reported that the retrieval process from the single helix structure to the triple helix structure of SPG in the DMSO/H_2O mixed solvent system is a requirement for the supramolecular complexation.[12] In our case, the supramolecular complex formation was carried out in H_2O alone and the triple helix structure of SPG could not be dissociated in to a single chain.

Published on the web (Advance View) July 16, 2005; DOI 10.1246/cl.2005.1144