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Chirality Control in Oligothiophene through Chiral Wrapping

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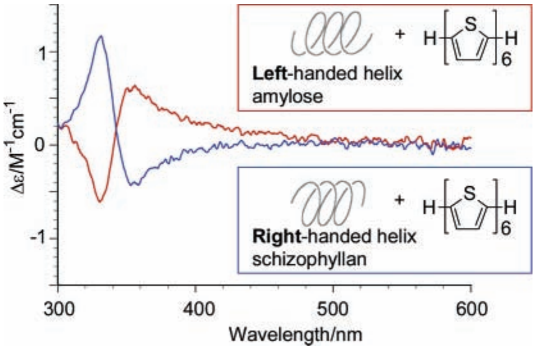
ABSTRACT



Mixing oligothiophenes and polysaccharides, such as amylose and schizophyllan, affords novel inclusion complexes, in which oligothiophene guests adopt twisted conformation in the chiral channel created by left- or right-handed helical wrapping with the polysaccharide host polymers, leading to optical activity.

The control of the chirality of molecules is one of the most intriguing research fields in chemistry. In recent years, the design and synthesis of optically active polymers and oligomers has attracted considerable interest because of their potential applications as chiral selectors for separation, catalysts, and adsorbents, and especially as chiroptical materials for switching and in memory devices.[1] Among optically active polymeric materials,[2] π-conjugated polymers and oligomers are interesting. For example, polythiophenes and oligothiophenes are a class of the most important conjugated polymeric materials of prominent semiconducting and optoelectronic properties and have been widely studied.[3] In particular, α-sexithiophene (6T) and its derivatives have been employed as the active layer in organic electronic devices.[4] Some optically active polythiophenes and oligothiophenes with chiral substituents have been reported.[5,6] They exhibit optical activity in the $\pi-\pi^*$ transition region derived from the main chain chirality in the circular dichroism (CD).

In this report, we show that oligothiophenes within the internal helical channel of a polymer can be induced to display optical activity, where the chirality is controlled by wrapping with either the left-handed or the right-handed helical sense conformation of the host polymer. The present system offers optically active supramolecular insulated wires.[7−10]

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A number of polysaccharides adopting ordered helical conformations have been reported, and some of them have been demonstrated as receptors capable of accommodating guest molecules in the internal helical cavities. We have examined amylose and schizophyllan (SPG) as host polymers, as shown in Figure 1. Amylose, composed of α-1,4-linkages between D-glucopyranose residues, adopts a left-handed helical conformation and forms inclusion complexes as a result of hydrophobic interactions with guest molecules confined within the helical cavity.[11] In our experiments, we used partially carboxymethylated amylose (CMA) with DS = 0.36 (DS = the degree of carboxymethyl substitution) to increase the solubility of the resulting inclusion complex in water.[12,13] Schizophyllan (SPG) is composed of β-1,3-linkages between glucose units (β-1,3-glucan) and adopts a right-handed triple helix in water but a single random-coil conformation in DMSO.[14] The unique structural motif stimulated us to employ these polysaccharides as the chiral host molecule. Recently, we found the induction of a preferential helical conformation to the main chain of oligosilanes within the helical channel of amylose and SPG, where the helical sense of the guest molecules is controlled by wrapping with either the left- or the right-handed helical sense conformation of the host polymer.[15] Shinkai and co-workers also reported the supramolecular chiral complex between SPG and water-soluble polythiophene.[16]

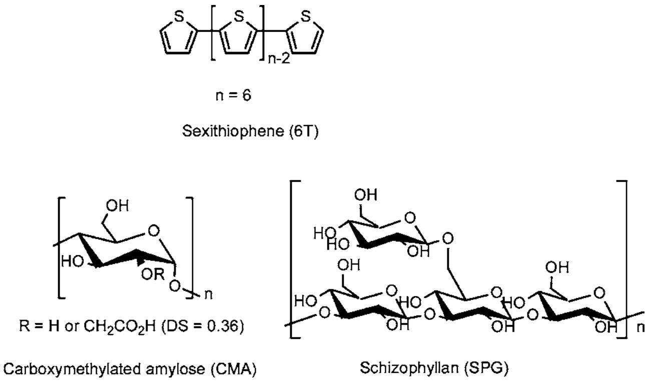

Figure 1. Chemical structures of guest (6T) and host (CMA and SPG) compounds.

In a typical preparation of the complex, a mixture of 6T (20 mg, 4.0×10^{-2} mmol) and CMA (156 mg, 0.85 mmol glucose unit, $M_n = 5.8 \times 10^4$, $M_w/M_n = 1.7$) in DMSO (2 mL) was dispersed ultrasonically for 2 min and was added to water (18 mL) and subsequently sonicated for 5 min. The mixture gradually changed in color from brownish-red to yellow. The resulting solution was stirred at room temperature for 10 days.[17] The orange precipitated product was collected by centrifugation and washed with water and then with THF. The residue was dried under vacuum to give the 6T/CMA complex as orange powder (138 mg, 86%), which was characterized by a variety of spectroscopic techniques.[18] In the CPMAS ^{13}C NMR spectrum, the 6T/CMA inclusion

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(17) When monitoring with UV−vis and CD spectra, the complex of 6T and CMA was formed in a few hours after ultrasonic dispersion. The intensity of the absorption and CD increased slightly for a few days, and then reached a constant value, although the material partially precipitated during the complexation. See Supporting Information.

complex displayed the signals of the thiophene ring with those of CMA units (Figure 2). The powder X-ray diffraction pattern showed a peak at 2θ (Cu Kα) of about 20°, similar to that reported for a complex of β-cyclodextrin, a macrocyclic molecule consisting of seven α-1,4-glucopyranose units, exhibiting a channel-type structure.[19] These studies suggest that the amylose is probably in the 7_1-helical structure (seven α-D-glucopyranose resides per turn), with a cross-section diameter of 7 Å to fit to the sequential size of the thiophene units. The ratio of the 6T/CMA complex was determined by the elemental analysis. On the basis of the helical pitch of CMA with 7_1 helix and the molecular length of 6T, the molar ratio of CMA:6T is approximately 2:3.

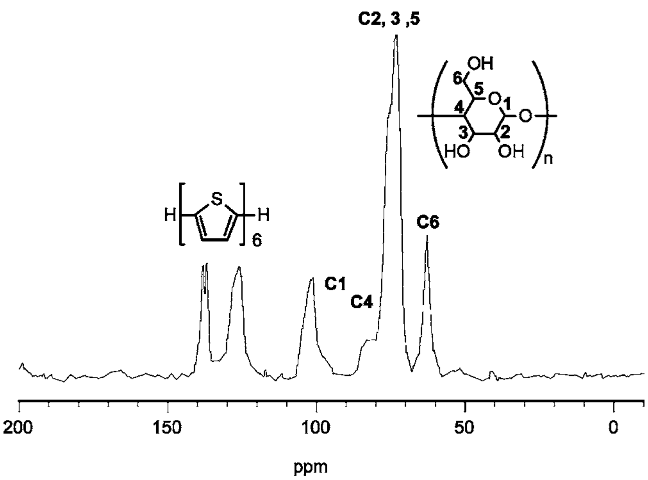

Figure 2. CPMAS ^{13}C NMR spectra of the 6T/CMA complex.

Figure 3 shows the absorption and CD spectra of the 6T/CMA complex in a 10% DMSO aqueous solution.[20] In the absorption spectrum, the 6T/CMA complex exhibited an absorption maximum at 343 nm, while 6T in toluene at room temperature showed an absorption maximum at 400 nm. The significantly blue-shifted absorption suggests that 6T in the helical channel of CMA adopts a nonplanar conformation that has a limited conjugation path comprising only 2−3 thiophene repeat units along the backbone[21] upon complexation. The photoluminescence spectra of the complex are red-shifted (λ_{em} = 533 and 567 nm) with a large Stokes shift as compared to those of 6T in toluene (λ_{em} = 460 and 505 nm).[22−24] In the CD spectrum, the complex displays a bisignate induced CD (ICD) signal in the absorption region of 6T ($\Delta\epsilon_1 = 0.64$ M^{-1} cm^{-1} at 356 nm) along with the $\theta = 0$ crossing wavelength that basically coincides with the absorption maximum, while 6T itself does not show any CD signals because of it being an equal mixture of enantiomeric twisted or random conformers. This clearly indicates that 6T in the helical channel of CMA is induced to a preferential twisted conformation as a result of the diastereoselective complexation with the chiral host, leading to the optical activity.[25] Further, the complexes of induced chirality were stable even at 80 °C, showing only a 20% decrease in the CD intensity as compared with the original value observed at room temperature.[22]

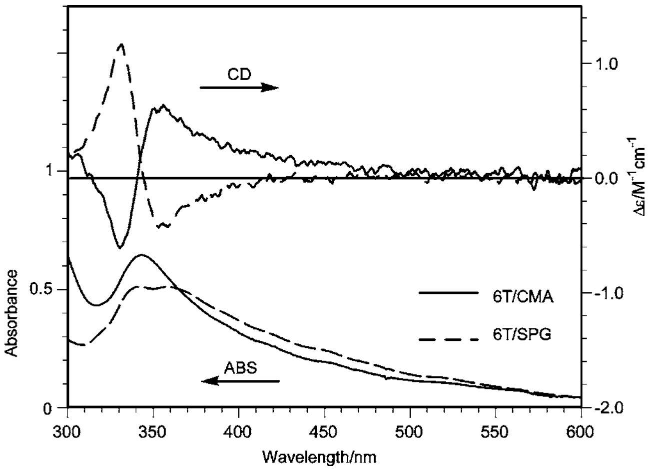

Figure 3. Absorption and CD spectra of 6T/CMA (solid line) and 6T/SPG (dashed line) in a 10% DMSO aqueous solution. [6T] = 1.0×10^{-4} M; [CMA] = 2.9×10^{-3} M; [SPG] = 2.1×10^{-4} M.

SPG also acts as a helical host polymer; 6T in the presence of SPG exhibits an absorption maximum at 342 nm ($\epsilon = 7.8 \times 10^3$ M^{-1} cm^{-1}), ascribed to the oligothiophene main chain (Figure 3).[26,27] In the photoluminescence spectra, when complexed with SPG, 6T displayed an emission at 534 and 567 nm. The SPG complex shows an ICD signal in the region similar to the region of the absorption ($\Delta\epsilon_1 = -0.43$ M^{-1} cm^{-1} at 358 nm). These spectroscopic features are almost the same as those observed with the 6T/CMA complex.[18]

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(18) The NMR measurement in solution was not possible because of its low solubility in H_2O and 10% DMSO aqueous solution (up to concentrations of ca. 10^{-4} M).

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(20) The spectroscopic study was usually carried out by in situ measurement for a mixture of 6T and CMA in a 10% DMSO aqueous solution.

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(23) These spectral features may suggest that 6T in the helical channel of CMA assumes a π-stacked ordered form. Because the helical dimensions of amylose can be adjusted according to the size of the guest, 6T can be partially aligned to a π-stacked interchain packing form. See ref 5 and Oguchi, T.; Yamasato, H.; Limmatvapirat, S.; Yonemochi, E.; Yamamoto, K. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 923−927. A detailed description of the structure of the complex by, for example, X-ray single-crystal analysis or SPM observation, requires further study.

(24) The emission peaks of oligothiophene often show a shift to a longer wavelength in the interchain packing form.[4,5]

(25) It seems that the observed magnitude of the CD signal is rather week, suggesting incomplete inclusion of 6T or incomplete induction of the helical sense in the helical cavity of the amylose.

(26) The spectroscopic study was carried out by in situ measurement for a mixture of 6T and SPG in a 10% DMSO aqueous solution. In a typical experiment, a mixture of 6T (0.155 mg, 3.1×10^{-4} mmol) and SPG (0.40 mg, 6.2×10^{-4} mmol per 4 glucose units) in DMSO (0.3 mL) was dispersed ultrasonically for 2 min and added to water (2.7 mL) and subsequently sonicated for 3 min. The resulting solution was stirred at room temperature for 2 h and was subjected to spectroscopic measurement.

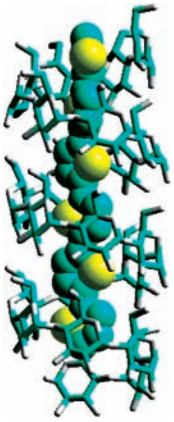

Figure 4. Energy-minimized model based on the AMBER force field for an inclusion complex of 6T with an amylose fragment containing 21 repeating α-1,4-D-glucopyranose residues. Carbon, oxygen, and sulfur atoms are shown in blue, gray, and yellow, respectively. The hydrogen atoms have been omitted for clarity.

However, we found that the chirality in the oligothiophenes is controlled by the helical sense of the host polymer. Very interestingly, the complex of 6T with a left-handed helical CMA displays the ICD signal with a positive sign for the first Cotton effect, but the complex of 6T with a right-handed helical SPG displays the ICD signal with a negative sign for the first Cotton effect. This indicates that 6T adopts a twisted conformation, but in opposite directions in the twisted-sense. The sign of the ICD pattern is related to a clockwise and anticlockwise twisted conformation, respectively.[5]

According to molecular mechanics for the simple model of 6T and an amylose fragment containing 21 repeating α-1,4-D-glucopyranose units,[28] the amylose fragment adopts a 7_1 left-handed helical conformation by wrapping around 6T as an axle (Figure 4). In the helical cavity created by the amylose wrapping, the 6T main chain assumes a twisted conformation. This is consistent with the view that 6T in the helical channel adopts the nonplanar conformation with the limited conjugation comprising only 2−3 thiophene repeating units, as deduced from the experimental result.

In conclusion, we have demonstrated the chirality control in oligothiophenes through helical wrapping with amylose and schizophyllan. The present system offers a new approach in the field of chiral expression in molecular and macromolecular systems to prepare conjugated supramolecular materials.

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Supporting Information Available: Experimental procedures, XRD data and an absorption and CD spectral change of 6T/CMA, photoemission spectra, and temperature-dependent CD spectra of 6T/CMA and 6T/SPG complexes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) To discuss the supramolecular complex formation, the stoichiometry of the complexation was determined by the CD titration measurement (Job plot). The stoichiometric ratio is found to be $M_{\mathrm{spg}}/(M_{\mathrm{spg}} + M_{6\mathrm{T}}) = 0.33$ and 0.83 (M_{spg} and $M_{6\mathrm{T}}$ are the molar concentration of SPG and 6T, respectively). On the basis of the molecular length of 6T and the helical pitch of SPG, the mole ratio of the glucose residues along the SPG main chain to 6T for the maximum complex formation is estimated at 2:1 and 2:2. SPG has enough space with the inner diameter of 1.75 nm for fitting two 6T into the cavity. The detail will be reported elsewhere.

(28) Monte Carlo searches for minimum energy conformations were performed using the HyperChem 7.5 and the AMBER force field. The spectroscopic features may suggested that 6T in the helical channel of CMA assumes a partially π-stacked interchain packing form, although the detail structure requires further study. At present the complex with 6T and the amylose fragments were examined as the simple model for the calculation.