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Solvophobically and Metal-Coordination-Driven Chirality Induction in Poly(*m*-phenylenedisilanylene)

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The helical structure is one of the most significant motifs in macromolecules. It can exist in either a right- or left-handed twist sense and displays optical activity. In recent years, the design and synthesis of polymers and oligomers with helical structures have been an active area of research. Among optically active macromolecules, conjugated polymers and oligomers are particularly interesting because of their potential applications as chiral selectors for separation, sensors, catalysts, adsorbents, and especially as chiroptical materials for switching and memory devices.[1] Accordingly, quite a few publications have reported the synthesis and properties of optically active π-conjugated polymers such as poly(phenylacetylene)s and poly(thiophene)s.[2] A dynamic folding of oligo(*m*-phenyleneethynylene)s in polar solvents from a random coil to a helical conformation resulting from a solvophobic interaction has also been reported.[3,4] Alternatively, σ-conjugated polymers, polysilanes, induce optical activity as a result of chiral stimuli.[5] However, the synthesis of chiral $\sigma-\pi$ conjugated polymers, composed of an alternating arrangement of organosilicon and π-electron units in the backbone, is limited.[6] We are interested in $\sigma_{(Si-Si)}-\pi$ conjugated polymers because these conjugated polymers usually show unique photophysical properties due to the interaction of the Si−Si σ-bonding orbital with the π^*-orbital of the conjugated unit, $\sigma_{(Si-Si)}-\pi$ conjugation.[7] Here, we report that poly(*m*-phenylenedisilanylene) with a chiral tri(ethylene glycol) side chain, **1**, displays optical activity arising from solvophobic and metal-coordination interactions. In this system, the polymer is successfully applied to metal guest sensing or detection to display optical activity. This is the first example of optically active $\sigma_{(Si-Si)}-\pi$ conjugated polymers.

We designed the $\sigma-\pi$ conjugated polymer **1**, in which a disilane unit is linked to a *m*-phenylene having a chiral tri(ethylene glycol) side chain. Polymer **1** was prepared by a conventional sodium coupling of chlorosilane **2** having a chiral tri(ethylene glycol) chain in toluene, as shown in Scheme 1.[8] After the polymerization, the desired polymer was purified by preparative GPC. The yield of polymer **1** was 28%, and the number-averaged molecular weight (M_n) was estimated at 8.5 $\times$ 10^3 ($M_w/M_n = 1.5$), using GPC with polystyrene standards. Polymer **1** was soluble in various organic solvents such as tetrahydrofuran, hexane, chloroform, and methanol but not in water. The structure was confirmed by NMR spectroscopy.[9]

Scheme 1. Synthesis of Poly(*m*-phenylenedisilanylene), 1

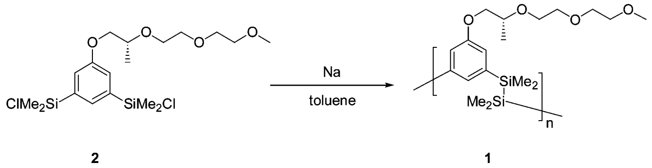

Figure 1 shows the absorption and circular dichroism (CD) spectra of **1** in dichloromethane and methanol. In the absorption spectra, polymer **1** in dichloromethane and also in methanol shows absorption at 289 nm ($\epsilon = 3800$ cm^{-1} M^{-1}) and 296 nm ($\epsilon = 3700$ cm^{-1} M^{-1}), ascribed to the $\sigma-\pi$ conjugation of the main chain.[10] The photoluminescence spectra of **1** in dichloromethane and methanol are also almost the same (Figure 8S). These spectral features suggest that the polymer does not undergo a conformational transition depending on the solvent. In the CD spectra, however, the polymer in dichloromethane shows almost no Cotton effect but in methanol shows a positive Cotton effect from the main chain ($\Delta\epsilon = 0.17$ cm^{-1} M^{-1} at 295 nm).[11] Further, absorption and CD spectral studies on changing in-solvent composition were performed (Figure 9S). Again, polymer **1** in dichloromethane shows almost no ellipticity. However, upon addition of methanol to the dichloromethane solution of the polymer, a new CD signal appears at around 290 nm in the CD spectra, while no change is observed in the absorption spectra. The Cotton effect increases gradually with increasing methanol content.[12] In addition, the induced chirality in methanol is observed even at 60 °C, showing only a 20% decrease in the CD intensity as compared with the original value observed at room temperature (Figure 10S). These results indicate that the polymer in methanol, which is a "good" solvent for the tri(ethylene glycol) side chain but not for the main chain, adopts the biased twist sense of the helical conformations to display optical activity.[13]

Recently, a dynamic structural change, induced by internal or external physical or chemical stimuli, in molecular and supramolecular systems has attracted significant interest.[14] In this context, it is interesting to note that polymer **1** is induced to twist the sense bias of the helical conformation even in dichloromethane when complexed with appropriate metal ions.[15−17] For example, addition of Li$^+$ to a dichloromethane solution of **1** results in the appearance of a positive Cotton effect, while the absorption band decreases slightly (Figure 2 and Figure 12S).[12,18] On addition of either Na$^+$ or K$^+$, however, a negative Cotton effect is observed, whereas the intensity of the absorption

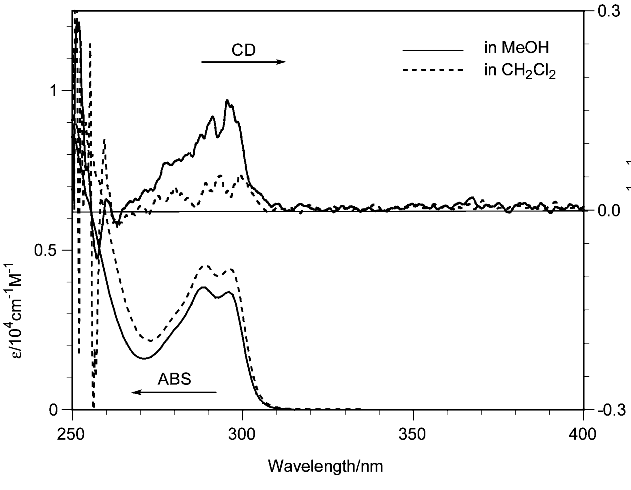

Figure 1. Absorption and CD spectra of **1** in dichloromethane (dotted line) and methanol (solid line).

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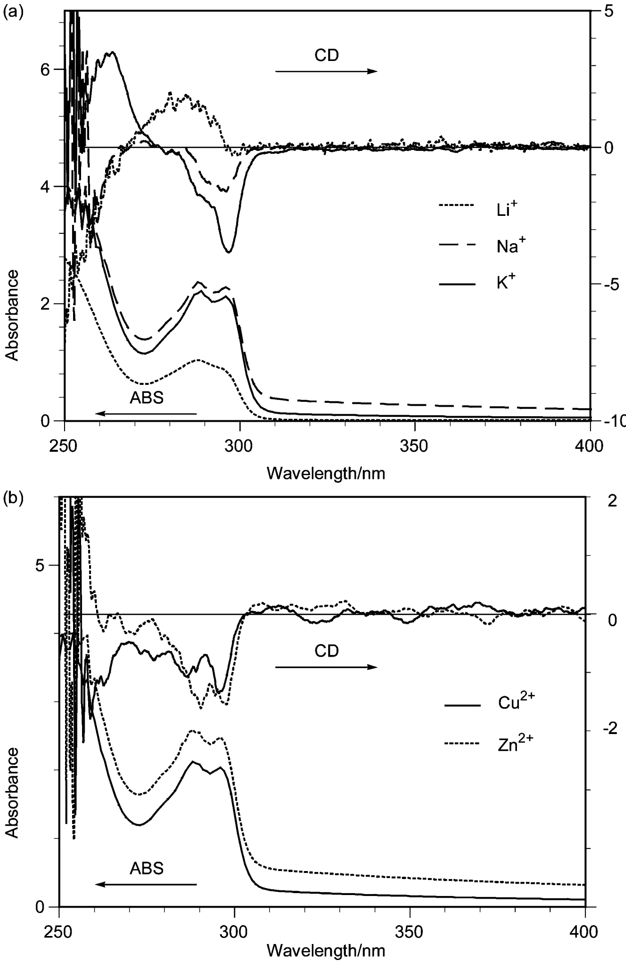

Figure 2. Absorption and CD spectra of **1** in dichloromethane in the presence of metal ions: (a) Li(OTf) (dotted line), Na(OTf) (dashed line), and K(OTf) (solid line); (b) Cu(OTf)$_2$ (solid line) and Zn(OTf)$_2$ (dotted line).

band does not change. This means the polymer assumes a helical conformation, the direction of which depends on the metal ion. On the other hand, very little Cotton effect is observed upon addition of Mg^{2+} or Ca^{2+} (Figure 13S), where the absorptions are almost the same as those observed for the complex with K$^+$. Further, polymer **1** displays a negative Cotton signal when complexed with Cu^{2+} or Zn^{2+}. Thus, interaction of the side chains with the metal ions is sensitive to the size and the coordination mode of the metal ions, and the complexation can play a role in induction of the selective twist sense bias of the helical conformation to display optical activity. Interestingly, polymer **1** reveals the reversibility of the metal-induced chirality: when the solution was washed with water to remove the metal ions, no CD signals were observed (Figure 14S).

In conclusion, we have demonstrated chirality induction in poly(*m*-phenylenedisilanylene) with solvophobic or metal−coordinate interaction, in which the helical conformations is biased. Despite polymer **1** having the flexible disilanylene units as compared with the related oligo(*m*-phenyleneethynylene)s,[3] **1** can adopt the biased twist sense of the helical conformations to display optical activity under the appropriate conditions. This system offers a new approach in the field of chiral expression in macromolecular systems and also the possibility of metal ion sensing.

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Supporting Information Available: Experimental procedures, absorption and CD spectra of **3** and **1** in a dichloromethane/methanol mixed solution, temperature-dependent CD spectra, fluorescence spectra, CD spectra in the presence of Mg$^+$ and Ca$^+$ ions, absorption and CD spectral changes by titration with K$^+$, and a summary of the photophysical properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) See Supporting Information.

(10) The extent of $\sigma-\pi$ conjugation in the main chain of **1** is limited based on the comparison of the absorption spectra of the monomeric compound. See Figure 7S.

(11) The CD signal being rather weak appears to suggest incomplete induction of the helical sense in **1**. The dissymmetry ratio, g_{abs} (= $\Delta\epsilon/\epsilon$), which is usually used to characterize helical structures, such as right- and left-handed helix populations, is 4.5×10^{-5} for **1**.

(12) The absorption and CD spectra after filtration (0.45 μm pore size) are almost the same as those before filtration, indicating that aggregation in methanol is ruled out. See Figure 11S.

(13) At the present stage, we cannot conclude that the polymer in dichloromethane exists in either a dynamic mixture of right- and left-handed twist senses of the helical conformations or a random conformation.

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(18) The spectral features may suggest that polymer **1** assumes a helical conformation with a shorter conjugation length when complexed with Li^+.

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