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Induction of optical activity in oligosilanes within the internal cavity of cyclodextrins†

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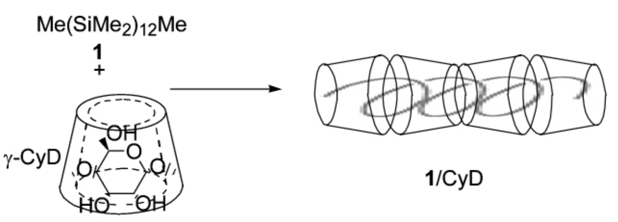
The first example of induced optical activity of oligosilanes within the internal cavity of γ-cyclodextrins is reported.

Recently, controlling the helical structure of macromolecules has been the subject of intense study,[1] because these polymers could be useful as potential chiral selectors for separation and catalysis, and especially as chiroptical materials for switching and in memory devices. Some synthetic polymers can adopt a helical-screw conformation. Polysilanes or oligosilanes with helical structure are particularly interesting because the unusual photophysical and electronic properties of polysilanes and oligosilanes are attributable to σ-conjugation along the main chain, and hence are extremely sensitive to the conformation.[2] Some approaches to controlling the conformation of polysilanes have been reported.[3] For example, polysilanes can adopt a preferential helical-sense conformation when substituted with optically active side chains[4] or end groups.[5] Another approach is provided by the non-covalent interaction of the polymer with optically active molecules[6] or solvent.[7]

Cyclodextrins (CyDs) are macrocyclic molecules consisting of six to eight α-1,4-glucose units.[8] They have a large intramolecular cavity with a cylindrical shape and the inside of the cavity is hydrophobic in nature. This provides CyDs with an important ability to form inclusion complexes with small molecules and linear polymers.[9,10] The inside of the cavity of CyDs further affords a chiral environment for the guest molecules,[11] because CyDs consist of optically active D-glucose units.

We report here the first example of induced optical activity of oligosilanes within the internal cavity of γ-CyDs.[12] The oligosilanes, with well-defined structures, are typical fundamental models for polysilanes. This system can lead to a preferential helical-sense induction of the oligosilane chain. Very recently, inclusion complexes of γ-CyDs with poly(dimethylsilane)[13] and permethyldecasilane[14] have been reported. In these cases, however, the induction of optical activity in the main chain inside the CyDs has not been demonstrated.

The inclusion complex **1**–CyD was prepared by mixing permethyldodecasilane (**1**, $Me(SiMe_2)_{12}Me$) with an aqueous solution of γ-CyD (in the mole ratio dodecasilane : γ-CyD of 1 : 10) at room temperature for several days (Scheme 1).‡ In this case, the size of dimethylsilylene units in the main chain fits into the diameter of the γ-CyD cavity (8.5 Å). The resulting complex **1**–CyD was slightly soluble in water. The molar ratio of **1** to γ-CyD, estimated by ^1H NMR (pyridine-d_5), was 1 : 4. The composition is compatible with the length of three dimethylsilylene units and the depth of the γ-CyD cavity (7 Å). Spectroscopic studies supported the structure of the inclusion complex **1**–CyD. In the CPMAS ^{13}C NMR spectrum, sharp signals of the γ-CyD relative to that of free γ-CyD were observed, indicating that the γ-CyD adopts a symmetric conformation. A powder X-ray diffraction (XRD) study showed that **1**–CyD was crystalline and the pattern was totally different from that of free γ-CyDs. The reflection peaks are similar to that of the reported complex of γ-CyD with a channel-type structure.[15,16] These results indicate that a 4 : 1 inclusion complex of γ-CyD with permethyldodecasilane is formed.



Scheme 1

It is interesting that the dodecasilane locates an optically active environment in the inclusion complexes. The UV spectra provided information on the conformation of the oligosilane main chain. Fig. 1 shows the UV spectrum of **1**–CyD in H_2O at room temperature. The complex **1**–CyD in H_2O exhibited an absorption maximum at 303 nm (Table 1, entry 1), while permethyldodecasilane in 3-methylpentane at room temperature showed an absorption maximum at 286 nm (entry 2), where the main chain adopts a random-coil conformation. The absorption at 303 nm of **1**–CyD is identical to the absorption of permethyldodecasilane **1** in 3-methylpentane at 77 K (302 nm, entry 3),[17] where the main chain assumes either an *anti* conformation or a *transoid* conformation with the dihedral angles of around 180° and 160–175° (15/7 helix) for the Si tetrads, respectively.[18,19] Under these conditions, the dodecasilane within the internal cavity of γ-CyD has the chance to adopt a preferential helical-sense conformation. Fig. 1 shows the circular dichroism (CD) spectrum in H_2O of **1**–CyD. The complex **1**–CyD actually exhibited a bisignate CD signal at about 305 nm. The induced CD band coincides with the absorption spectrum. This clearly indicates that the optical

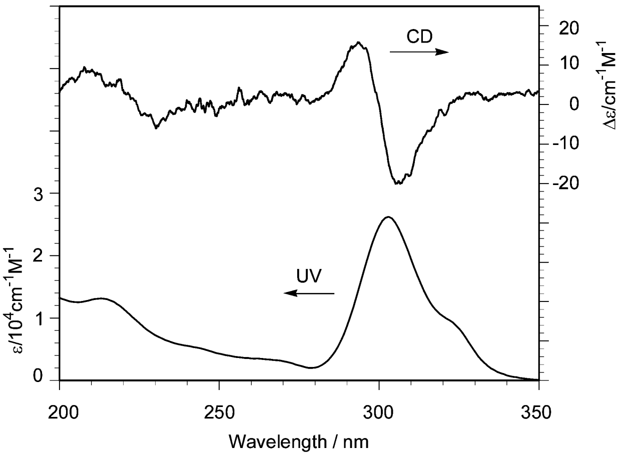


Fig. 1 UV absorption spectrum and circular dichroism (CD) of complex **1**–CyD in H_2O.

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† Electronic supplementary information (ESI) available: XRD, CPMAS ^{13}C NMR, and ^{29}Si NMR of **1**–CyD. See http://www.rsc.org/suppdata/cc/b3/b303771a/

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Table 1 Spectroscopic data for inclusion complex of permethyldodecasilane **1** and γ-cyclodextrin (**1**–CyD) in H_2O and **1** in 3-methylpentane

			CD			
			First Cotton		Second Cotton	
Entry	Compound (**1** : γ-CyD)^a	UV λmax/nm (ε/cm^{-1} M^{-1})	Sign	Δε/cm^{-1} M^{-1} (λmax/nm)	Sign	Δε/cm^{-1} M^{-1} (λmax/nm)
1	**1**–CyD (1 : 4)	303 (26 000)	−	20 (306)	+	16 (294)
2	**1**	286 (41 000)^b		—^{d}		—^{d}
3	**1**	302 (230 000)^c		—^{d}		—^{d}
4	**1**–CyD (1 : 3)	303 (9200)	−	5.4 (306)	+	3.5 (294)
5	**1**–CyD (1 : 2)	303 (6600)	−	3.9 (306)	+	1.9 (294)
6	**1**–CyD (1 : 1)	303 (7600)	−	0.8 (306)	+	1.2 (294)

^{a} Determined by ^{1}H NMR in pyridine-d_5. ^{b} In 3-methylpentane at room temperature. ^{c} In 3-methylpentane at 77 K. ^{d} Not optically active.

activity in the dodecasilane in the cavity of γ-CyD is induced in a preferential one-handed helical sense. The bisignate induced CD effect is considered to be characteristic of exciton coupling between closely situated transition dipole moments on neighboring segments in the chiral supramolecule.[20,21]

Interestingly, control of the magnitude of the optical activity appears to be possible, depending on the ratio of **1** to γ-CyD in the complexes. When the reaction was carried out using equimolecular amounts of **1** and γ-CyD, an inclusion complex in the mole ratio of **1** : γ-CyD of 1 : 1 was formed. The complex also exhibited an induced CD, but the intensity of the CD signal was smaller than that of the 1 : 4 inclusion complex. The ratio of **1** to γ-CyD in the complexes and the molar circular diachronic absorption (Δε) for the complex are summarized in Table 1. The intensity of the CD signal decreased with decreasing threading ratio.

In conclusion, we have demonstrated a new approach for the induction of optical activity in oligosilanes within the internal cavity of cyclodextrins. This provides a simple way to control the conformation of oligosilanes. This finding is important in view of further applications.

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Notes and references

‡ In a typical preparation of the inclusion complex of permethyldodecasilane **1** and γ-cyclodextrin, a mixture of permethyldodecasilane (50 mg, 6.0×10^{-2} mmol) and γ-cyclodextrin (1 g, 7.5×10^{-1} mmol) in 10 ml water was dispersed ultrasonically and then stirred at room temperature for a week. The white precipitated product was collected by centrifugation and washed with water and then with THF. The residue was dried under vacuum to give the inclusion complex **1**–CyD as a white powder (240 mg, 63%). The molar ratio of dodecasilane to γ-CyD, estimated by ^{1}H NMR (pyridine-d_5), was 1 : 4. **1**–CyD: a white powder; mp = 258 °C (decomp.); ^{1}H NMR (pyridine-d_5, 300 MHz) δ 0.19 (s, 18H), 0.26 (s, 12H), 0.33 (s, 12H), 0.37 (s, 12H), 0.38 (s, 12H), 0.39 (s, 12H), 4.09 (m, 8H × 4), 4.27 (m, 8H × 4), 4.38 (m, 24H × 4), 4.65 (t, J = 8.9 Hz, 8H × 4), 5.74 (d, J = 3.2 Hz, 8H × 4), 6.44 (s, 8H × 4), 7.70 (s, 16H × 4); solid-state CPMAS ^{13}C NMR (68 MHz) δ −2.1 (br), 61.1, 72.7, 73.6, 81.7, 83.0, 104.6; solid-state CPMAS ^{29}Si NMR (54 MHz) δ −42.9, −40.6, −36.8, −34.5, −14.4.

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18 The molar absorption coefficient of **1**–CyD was quite small, possibly due to aggregation resulting from poor solubility. We measured the UV spectra of the complex in concentrations ranging from 10^{-7} to 10^{-6} M or after filtration (0.45 μm pore size). The UV features were similar. However, aggregates of smaller size may be contributing.

19 Sakamoto *et al.* reported that the permethyldecasilane main chain in CyDs adopts the *anti* conformation. However, the oligosilane may also adopt a loose helical conformation under this set of conditions. In our case, the absorption spectrum of **1**–CyD showed a shoulder at longer wavelength to the side of the main absorption band. This absorption may be assigned to the *anti* conformation of the oligosilane main chain.

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21 The induction of optical activity presumably results from a monomolecular event of the complex with the dodecasilane **1** and CyDs. The γ-CyD has insufficient space (8.5–9 Å cavity diameter × 7 Å cavity depth) to fit two oligosilane chains **1** into the cavity. However, it is also possible that small aggregates of **1**–CyD may be contributing to the CD signals. The findings will be available in a future publication.