Preparation and Characterization of the Inclusion Complexes of Poly(dimethylsilane)s with Cyclodextrins

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ABSTRACT: β-Cyclodextrin (β-CD) and γ-cyclodextrin (γ-CD) formed inclusion complexes with poly(dimethylsilane)s (PSi) of various molecular weights to give crystalline compounds. However, α-cyclodextrin (α-CD) did not form complexes with PSi of any molecular weight. The yields of the β-CD−PSi inclusion complexes decreased with increasing molecular weight of PSi. In contrast, the yields of the γ-CD−PSi inclusion complexes increased with increasing molecular weight, reached a maximum at molecular weight of around 760, and gradually decreased at higher molecular weight. The chain-length selectivities are totally different between β-CD and γ-CD. The γ-CD−PSi inclusion complexes are stoichiometric 1:3 (γ-cyclodextrin:monomer unit of PS) compounds. The complexes were isolated and characterized by ^{1}H NMR, ^{13}C CP/MAS NMR, and X-ray diffraction studies. These results suggest that CDs form channel-type complexes with PSi. The optical properties were studied by ultraviolet absorption and fluorescence spectroscopy. The PSi main chain in the cavities of γ-CD takes an all-trans conformation.

Introduction

Cyclodextrins (CDs) are a series of cyclic oligosaccharides consisting of six to eight glucose units linked by α-1,4 linkages. They are called α-, β-, and γ-CD, respectively. They are known to form inclusion complexes with various low molecular weight compounds. Since the discovery of cyclodextrins, there have been many reports on complex formation of cyclodextrins with small molecules and ions.[1−5]

Previously, we reported that CDs form inclusion complexes with some organic polymers to give crystalline compounds with high selectivity. CDs form inclusion complexes not only with hydrophilic polymers but also with hydrophobic polymers. For example, α-CD formed complexes with poly(ethylene glycol)[6−8] and polyethylene (of MW > 1000)[9] and some polyesters.[10,11] β-CD gave complexes with poly(propylene glycol)[12,13] and polypropylene (of MW < 1000). γ-CD gave complexes with poly(methyl vinyl ether)[14,15] and polyisobutylene.[9,16,17] Other groups also reported complex formation between CDs and polyesters.[18−20] We reported the preparation of a polyrotaxane in which many α-CDs are threaded onto a polymer chain.[21−23] Wenz et al. also reported α-CDs threaded on a polyamine.[24] All the complexes mentioned above are main-chain polyrotaxanes composed of CDs and organic polymers.

Recently, some inorganic polymers have attracted much attention because they have excellent features such as resistance to heat and certain chemicals. However, most of them are decomposed by oxidation, hydrolysis, and acid−base reactions. Silicon-containing polymers are exceptionally thermally and chemically stable.[25−27]

Polyorganosiloxanes form a class of commercially important materials known as silicones. Poly(dimethylsiloxane) (PDMS) is the most common of the industrial silicone polymers. PDMS is unique because, despite high heat stability, it is an oily material. Polysilanes (Figure 1) have also been known as a series of silicon-containing inorganic polymers and are a new class of polymers, which may now be approaching commercialization, in which the polymer chain is made up entirely of silicon atoms, which allow significant delocalization of electrons along the polymer chain.[25−29] Delocalization of σ-electrons in polysilanes is apparent from ultraviolet absorption spectra. The polymers show characteristic strong electronic absorption bands usually in the range of 250−350 nm.[25−29] Polysilanes are insulators but become semiconducting upon treatment with oxidizing agents such as SbF_5 or AsF_5.[30]

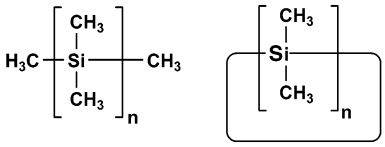

Figure 1. Structures of poly(dimethylsilane)s.

Recently, much attention has been focused on the design and construction of nanometer scale structures based on supramolecular noncovalent assemblies between organic compounds and inorganic materials called "organic−inorganic hybrids". However, these hybrids do not have strictly regulated structures. When inclusion complexes of CDs with silicon-containing polymers are formed, they are new organic−inorganic hybrids with exact stoichiometric relationships. Previously, we have found that β-CD and γ-CD formed complexes with poly(dimethylsiloxane) (PDMS), a typical inorganic polymer, and that the chain-length selectivities between β-CD and γ-CD are reversed.[31,32] This paper describes the preparation and characterization of inclusion complexes of CDs with poly(dimethylsilane)s (PSis).[33]

Results and Discussion

Preparation of Poly(dimethylsilane)s (PSis). Poly(dimethylsilane)s (PSis) were prepared starting from trimethylchlorosilane and dimethyldichlorosilane by Wurtz-type reductive polymerization.[25−29] The average molecular weights (MWs) of the *n*-hexane-soluble part of various PSi samples were determined by UV−vis

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Table 1. Results of the Complex Formation between CDs and Poly(dimethylsilane)s

PSi	$\overline{M_n}$ [a]	$\overline{DP}$ of PSi	λ_{max} of PSi (nm)	yield (%)[b]/stoichiometry[c] α-CD	*β*-CD	*γ*-CD
PSi90	88	1		21/0.55	8.8/0.24	2.7/0.61
PSi50	146	2	197.0	0	25/1.9	64/1.9
PSi200	204	3	215.5	0	5.4/1.3	73/2.2
PSi320	320	5	252.0	0	2.6/1.8	27/3.8
PSi440	436	7	264.5	0	0	59/3.0
PSi550	552	9	277.5	0	0	64/3.0
PSi610	610	10	279.5	0	0	58/3.0
PSi670	668	11	283.5	0	0	87/3.3
PSi780	784	13	286.5	0	0	57/6.1
PSi960	958	16	289.0	0	0	8.9/8.0

[a] Calculated from UV−vis spectra. [b] Based on PSi. [c] Molar ratio of monomer units of PSi to CD (calculated from ^{1}H NMR spectra).

spectroscopy and ^{1}H NMR spectroscopy.[34] Table 1 shows the average MWs of PSis obtained in this reaction.

Complex Formation of CDs with PSis. When PSis (colorless oil or white solid) were added to aqueous solutions of *β*-CD (diameter of the cavity: 0.70 nm) or *γ*-CD (diameter of the cavity: 0.85 nm) and the mixture was stirred at room temperature for a week, the heterogeneous solutions became turbid, and the complexes were formed as crystalline precipitates. However, α-CD only formed a complex with tetramethylsilane ($n = 1$). Table 1 shows the results of the complex formation between CDs and PSi. *β*-CD and *γ*-CD formed complexes with PS, although α-CD did not give complexes with PS of any molecular weight, except for tetramethylsilane ($n = 1$). The cavities of *β*-CD and *γ*-CD are large enough to accommodate PSi. However, the α-CD cavity (diameter of the cavity: 0.45 nm) is too small for PSi to penetrate due to steric hindrance by dimethyl groups on the main chain. Tetramethylsilane was partially included by α-CD and precipitated as a crystalline complex from aqueous solution. These results indicate that the relative sizes of the cavities of cyclodextrins to the cross-sectional area of the polymers are important in the complex formation of polymers with cyclodextrins. Thus, cyclodextrins recognize the diameter of polymer chains. These phenomena are similar to those of the complex formation of CDs with poly(dimethylsiloxane) (PDMS).[31,32]

When PSis were added to the solution of CDs in DMF and DMSO, the mixture did not change and no precipitate was formed. This result indicates that hydrophobic interaction is also important to form complexes of CDs with PSi.

Effects of Molecular Weight on Complex Formation. Table 1 shows the yields of the complexes of CDs with PSi of various molecular weights. Figure 2 shows the yields of the complexes as a function of the molecular weight of PSi. The yields are based on the starting amount of CD and the stoichiometry of CD to PSi as described below, using aqueous solutions of CD and PSi (1 equiv monomer unit to CD). The yields of the complexes of PS with *γ*-CD increased with increasing the molecular weight of PS, reached a maximum at around MW = 670, and then decreased. The yields of the complexes of PDMS with *β*-CD also decreased with increasing the molecular weight of PDMS. The chain-length selectivities were reversed. PDMSs were oily materials over the whole molecular weight region; however, most of PSis were white solids and difficult to disperse in water. Thus, the complex formation between CD and PSi is difficult due to the low dispersity of PSi in water. *γ*-CD formed inclusion complexes with PSis of high molecular weights (MW > 1000). However, the solubility of PSis with high molecular weights to common organic solvents is very poor. *β*-CD formed complexes with PSis with low molecular weights. The *β*-CD cavity is too small to diffuse onto a long PSi chain and interacts strongly with PSi through van der Waals interactions. α-CD did not form the complexes with PSi of any molecular weight, except for tetramethylsilane.

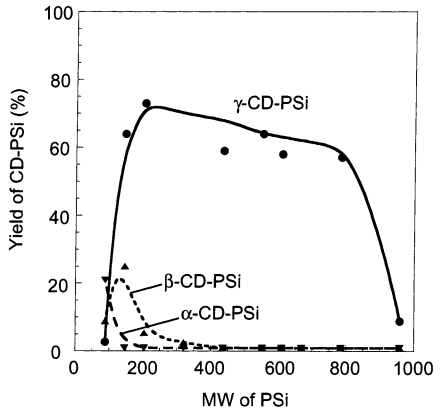

Figure 2. Yields of CD−PSi complex as a function of the molecular weight of PSi.

Stoichiometries. The complex formation of *γ*-CD with PSi was studied quantitatively. The yield of the complexes of *γ*-CD with PSi increases with an increase in the amount of PS added to the aqueous solution of *γ*-CD, until the saturation was observed. This saturation behavior suggests that the complex formation is stoichiometric. The complexes were isolated by centrifugation and filtration, washed with tetrahydrofuran to remove nonincluded PSi, dried, then washed with water to remove uncomplexed CD, and dried again. We calculated the mole ratio of PDMS to *γ*-CD in the complex. Comparing the integral of the peak of C_1H (*γ*-CD) and that of the methyl group on PSi, three monomer units were found to bind to a *γ*-CD molecule. The mole ratios of the complexes (Si monomer unit/*γ*-CD) are three in the range of MW = 400−1000, which is similar to those obtained in the cases of CD−PDMS complexes, i.e., included main-chain atoms of guest polymer was three (Si−O−Si or O−Si−O).[31,32] The length of three Si monomer units (ca. 6.9 Å) corresponds to the depth of the *γ*-CD (ca. 7.0 Å) cavity.

Properties. The inclusion complexes were thermally stable. TG curves of the complexes (Figure 3) show that they decompose above 300 °C. The complexes were insoluble in water. When the complexes were added to boiling water, they decomposed into CD aqueous solution and white PSi particles floated on the surface. The addition of urea, which is thought to affect hydrogen

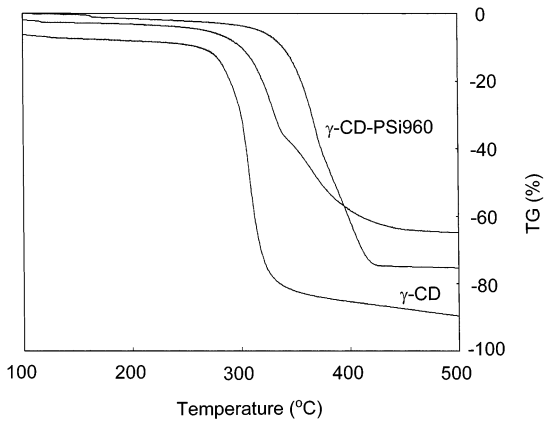

Figure 3. TG curves of γ-CD, PSi960, and γ-CD−PSi960 complex (in N_2, rate: 10 °C/min).

bonds, to the suspension of the γ-CD−PSi complex with heating resulted in solubilization of the complexes in water. This result indicates that hydrogen bonding between CDs plays an important role in stabilizing the complex. The complexes of CDs with low molecular weight of PS are soluble in pyridine, but the solubility of the complexes decreased with increasing PS molecular weight (MW > 1000). The X-ray powder diffraction studies show that all of the complexes are crystalline. When the CD−PSi complex was heated to 600 °C in inert atmosphere, about 40% of a charcoal-like residue remained.

Inclusion Modes of the Complexes. β-CD−PSi and γ-CD−PSi complexes are crystalline. Saenger and Harata reported that the crystal structures of CD complexes are classified mainly into three types: channel type, cage type, and layer type.[35−38] The powder X-ray diffraction patterns for β-CD, β-CD−*p*-nitroacetanilide complex, and β-CD−PSi complexes were measured. The β-CD−*p*-nitroacetanilide complex was found to adopt a head-to-head channel-type structure in which β-CD molecules are stacked along a *p*-nitroacetanilide axis to form a cylinder.[10,38] The reflection peaks of β-CD−PSi complexes are similar to those of the β-CD−*p*-nitroacetanilide complex and different from those of β-CD. These results suggest that β-CD−PSi complexes form head-to-head channels. Figure 4 shows the powder X-ray diffraction patterns of γ-CD, γ-CD−PPG complex, and γ-CD−PSi complexes. The γ-CD−PPG complex was found to adopt a head-to-head channel-type structure in which γ-CD molecules are stacked along a PPG axis to form a cylinder. The reflection peaks of γ-CD-PSi complexes are similar to those of the γ-CD−PPG complex and different from those of γ-CD. These results suggest that γ-CD−PSi complexes form head-to-head channels.

Solid-state ^{13}C NMR studies (such as ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR) give information about macrocyclic conformation of CDs. The ^{13}C shifts of the C-1 and C-4 resonance of CDs reflect the dihedral angles around the α-1,4-glycosidic linkage. The ^{13}C shifts of C-6 resonance are related to the conformation about the C-5−C-6 bond. Figure 5 shows the ^{13}C CP/MAS NMR spectra of γ-CD and γ-CD−PS complexes. The ^{13}C resonances of C(1) and C(4) of γ-CD gave multiplet lines because of the asymmetric glucopyranosyl conformations. However, the ^{13}C signals of C(1) and C(4) of γ-CD−PSi complexes gave sharp singlets, showing that the γ-CD takes symmetric cyclic

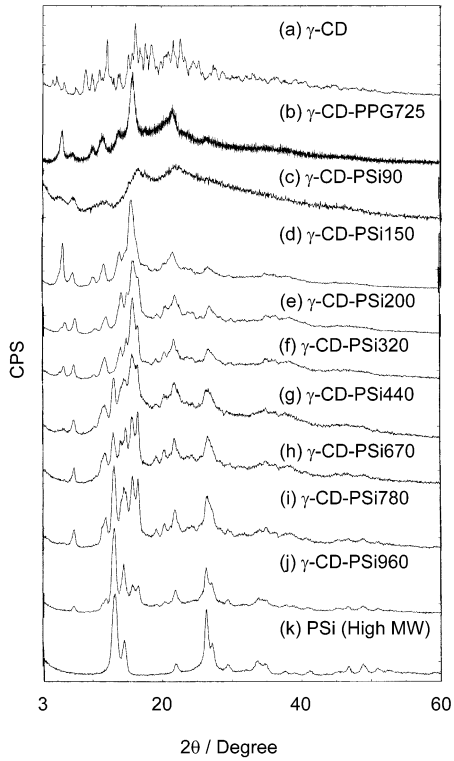

Figure 4. Powder X-ray diffraction patterns for (a) γ-CD, (b) γ-CD−PS90, (c) γ-CD−PSi150, (d) γ-CD−PSi200, (e) γ-CD−PSi320, (f) γ-CD−PSi440, (g) γ-CD−PSi670, (h) γ-CD−PSi780, (i) γ-CD−PSi960, and (j) PSi (high MW) (40 kV, 100 mA, Cu Kα, at RT).

conformation. These results of solid-state ^{13}C NMR analysis support that CDs form channel-type complexes with PSi.

Molecular model studies show that the PSi chain is able to penetrate the γ-CD cavity, while the PSi chain cannot pass through the α-CD cavity, owing to the hindrance of the dimethyl groups on the main chain. The hindrance of the dimethyl groups makes PSi difficult to penetrate β-CD cavities. These views are in accordance with our results that γ-CD formed a complex with PSi but α-CD did not form complexes with PS. Model studies further indicate that the single cavity accommodates three monomer units. Figure 6 shows a proposed structure of the complex of PSi with γ-CD.

Optical Properties. Although PSis do not have any chromophore on their side chain, they show a strong absorption band in the ultraviolet region and strong emission band in the near-ultraviolet region because of delocalization of σ-electrons along the polymer chain.[28,29] When PSi is added to a aqueous CD solution, the reaction mixture becomes turbid and gives white crystalline precipitates. When the reaction mixtures are diluted sufficiently, the CD−PSi inclusion complexes are solubilized in water. Here we discuss the interactions between CDs and PSis in dilute aqueous solutions and compare them to the solid state. Preparations of samples are as follows: PSis were dissolved in *n*-hexane, and *n*-hexane was evaporated. Then, the aqueous CD solution was added and agitated vigorously for 7 days. Figure 7 shows the UV spectra of dilute aqueous solution of the γ-CD−PSi inclusion complex (10-fold excess of γ-CD compared to PSi monomer unit) and PS in *n*-hexane. PSi730 showed a typical absorption band maximum at 284 nm in *n*-hexane at room temperature, attributed to the $\sigma-\sigma^*$ transition. In the case of dilute

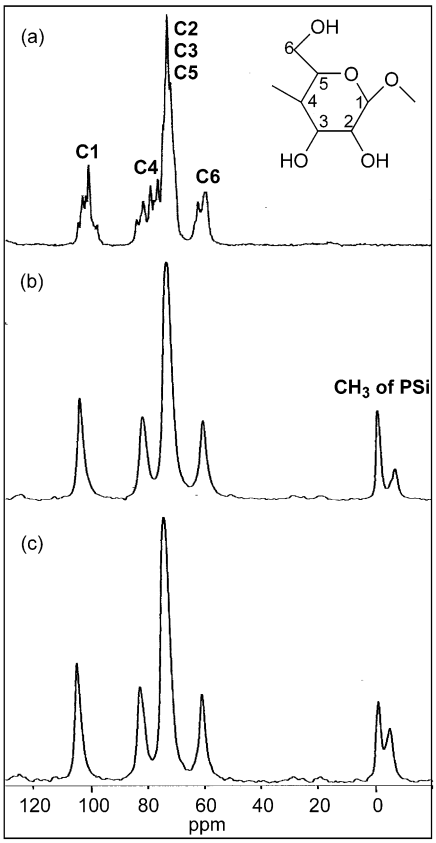

Figure 5. The 75.6 MHz ^{13}C CP/MAS NMR spectra of (a) γ-CD, (b) γ-CD−PSi150, and (c) γ-CD−PSi320 complexes at room temperature.

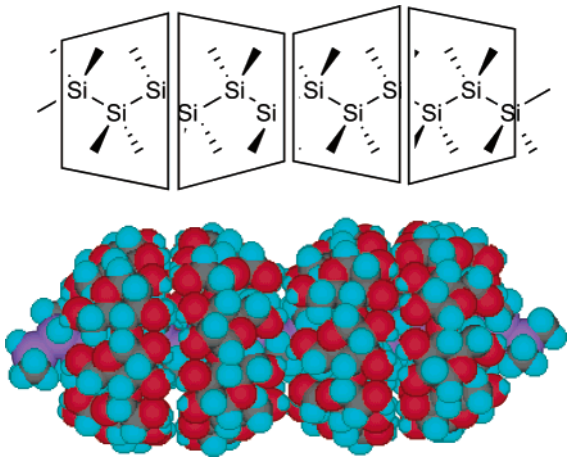

Figure 6. Proposed structure of γ-CD−PSi inclusion complex.

aqueous solution of the γ-CD−PSi inclusion complex, λ_{max} was strongly red-shifted to 301 nm. This λ_{max} value was equal to that of PSi730 in *n*-hexane at 77 K and in the solid state, taking the all-trans conformation.[39,40] Thus, PSi730 in the inclusion complexes were supposed to take the all-trans conformation.

Figure 8 shows the change of UV spectra of γ-CD−PSi730 on addition of γ-CD. On the addition of γ-CD, λ_{max} of PSi730 was red-sifted significantly. These results suggested that the conformation of PSi backbone became an all-trans conformation more completely on the addition of γ-CD.

Figure 9 shows the fluorescence spectra of dilute aqueous solution of the γ-CD−PSi inclusion complex (γ-CD 10-fold excess over the Si monomer unit) and PSi in *n*-hexane. The fluorescence spectra of the aqueous solution of the γ-CD−PS730 inclusion complexes excited at 280 nm show that the emission maximum was red-shifted by 10 nm. These results also show that effective conjugation length is enlongated on the inclusion into γ-CD cavities.

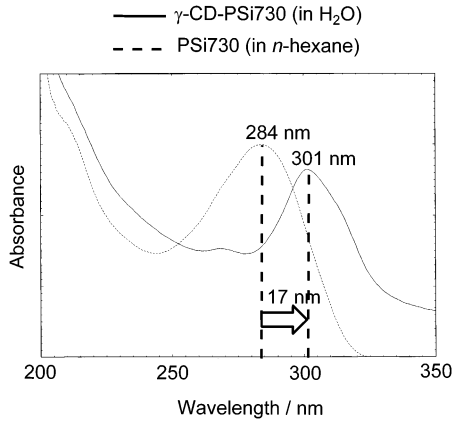

Figure 7. UV spectra of PSi730 (in *n*-hexane, [PSi730] = 5.30×10^{-6} M) and γ-CD−PS730 inclusion complex (in H_2O, [γ-CD] = 6.05×10^{-4} M, [PSi730] = 5.30×10^{-6} M, [Si unit] = 6.36×10^{-5} M, stirred at RT).

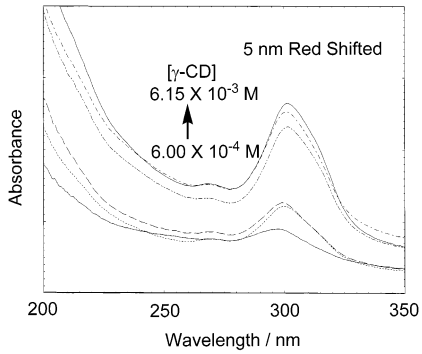

Figure 8. UV spectra of γ-CD−PSi730 (in H_2O, [γ-CD] = 6.00×10^{-4}−6.15×10^{-3} M, [PS730] = 5.30×10^{-5} M, [Si unit] = 6.36×10^{-4} M, stirred at RT).

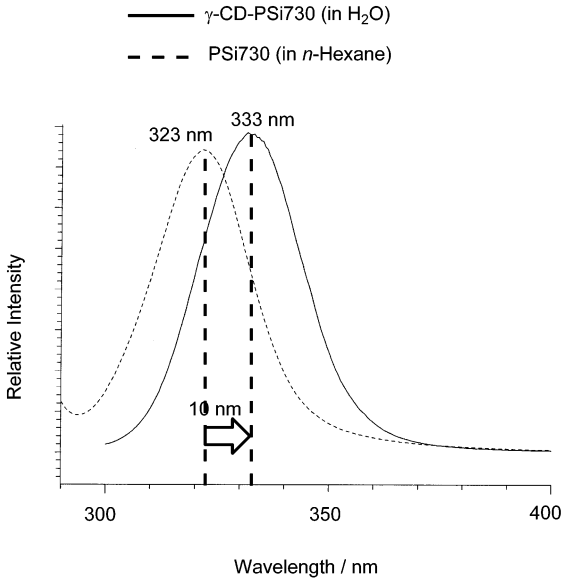

Figure 9. Fluorescence spectra of PSi730 (in *n*-hexane, [PSi730] = 5.30×10^{-6} M) and γ-CD−PSi730 inclusion complex (in H_2O, [γ-CD] = 6.05×10^{-4} M, [PSi730] = 5.30×10^{-6} M, [Si unit] = 6.36×10^{-5} M, λ_{ex} = 280 nm, stirred at RT).

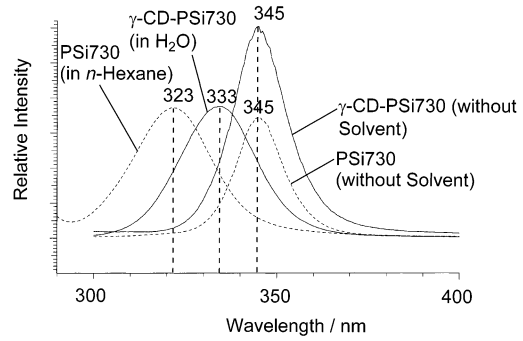

Figure 10. Fluorescence spectra of γ-CD−PSi730 (in H_2O and without solvent, [γ-CD, in H_2O] = 6.05×10^{-4} M, [PSi730, in H_2O] = 5.30×10^{-6} M, [Si unit, in H_2O] = 6.36×10^{-5} M).

Scheme 1

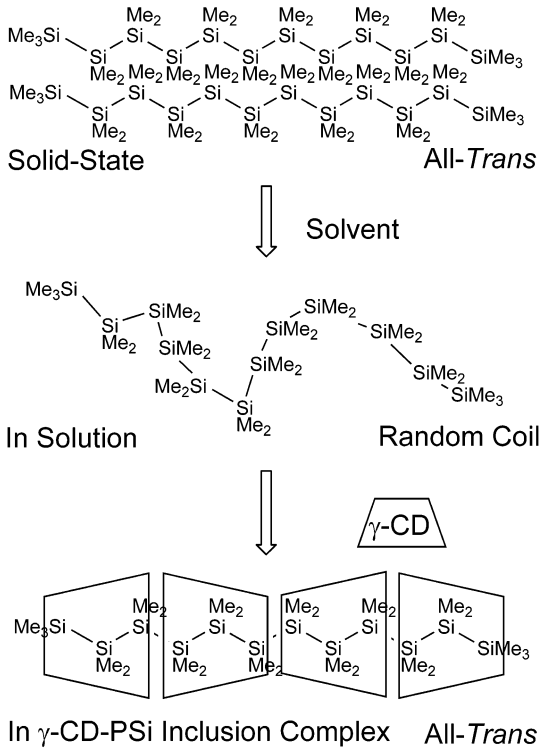

Figure 10 shows comparison of fluorescence spectra of the inclusion complexes of γ-CD−PSi730 in solution and without solvent. As mentioned above, in the case of dilute aqueous solution of γ-CD−PSi730 inclusion complex, the maximum of emission was red-shifted by 10 nm. In the solid-state, however, the maximum of emission did not change before and after the formation of the inclusion complex. These results suggested that the main chain of PSi takes an all-trans conformation in the absence of solvent and in the cavities of the γ-CD−PSi inclusion complex (Scheme 1). Figure 11 shows comparison of the UV spectra of the absorption maximum of the inclusion complex of Psi730 with methylated γ-CDs and γ-CD oligomers linked by epichlorohydrin were smaller than that of γ-CD. The conformation of PS backbones was regulated in the γ-CD cavities.

Formation of the Charge-Transfer Complex.[41,42] Figure 11 shows the UV−vis spectrum of the aqueous solution of the γ-CD−PSi inclusion complex (γ-CD 10-fold excess over the Si monomer unit) in the presence of 7,7,8,8-tetracyano-1,4-quinodimethane (TCNQ), well-known as a strong electron acceptor. TCNQ did not dissolve alone in water. However, when a large excess of γ-CD was added, TCNQ was solubilized in aqueous solution. The broad absorption band appeared at 647 nm, and the aqueous solution changed to light blue (Figure 11).

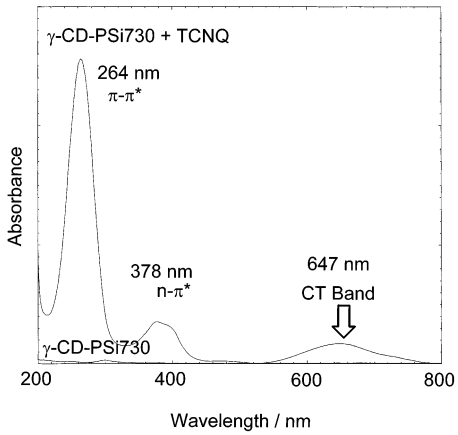

Figure 11. UV spectra of γ-CD−PSi730 and γ-CD−PSi730 + TCNQ (in H_2O, [γ-CD] = 6.05×10^{-4} M, [PSi730] = 5.30×10^{-6} M, [Si unit] = 6.36×10^{-5} M, stirred at RT).

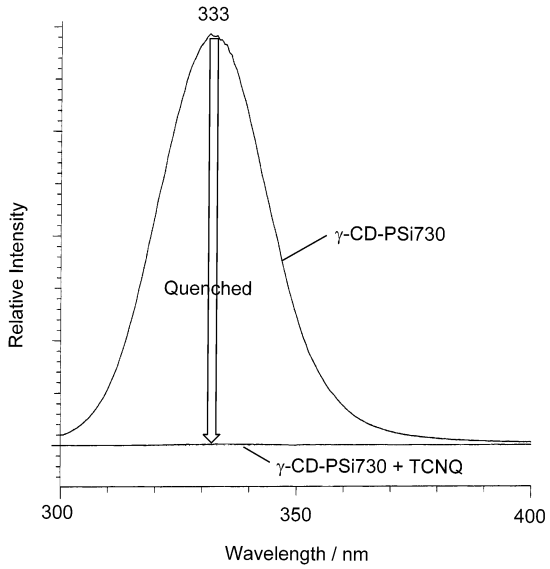

Figure 12. Fluorescence spectra of γ-CD−PSi730 and γ-CD−PSi730 + TCNQ (in H_2O, [γ-CD] = 6.05×10^{-4} M, [PSi730] = 5.30×10^{-6} M, [Si unit] = 6.36×10^{-5} M, λ_{ex} = 280 nm, stirred at RT).

These results indicate the formation of the charge-transfer complex between PS730 (electron donor) and TCNQ (electron acceptor) in the cavities of γ-CD in aqueous solution (Figure 13).

Complex Formation of CDs with PSicyc6. When dodecamethylcyclohexasilane (PSicyc6) was added to aqueous solution of γ-CD and stirred at room temperature for a week, the heterogeneous solution became turbid, and the complex was formed as crystalline precipitate in 61% yield. However, α-CD and β-CD did not form complexes with PSicyc6. The cavity of γ-CD is large enough to bind PSicyc6. However, the cavities of α-CD and β-CD are too small for PSicyc6 to include due to steric hindrance. The complex was isolated by centrifugation and filtration, washed with tetrahydrofuran

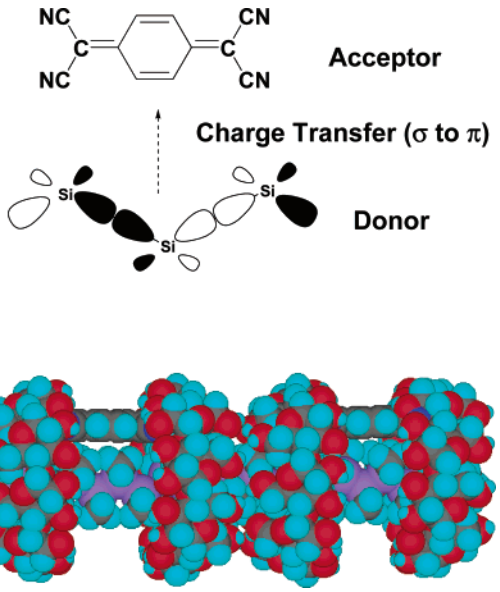

Figure 13. Proposed structure of ternary inclusion complex.

to remove nonincluded PSicyc6, then washed with water to remove uncomplexed CD, and dried again. The mole ratio of the γ-CD−PSicyc6 complex was calculated by comparing the integral of the peak C_1H of γ-CD and that of the methyl group of PSicyc6 in the ^1H NMR spectrum of the complex in pyridine-d_5. The mole ratio of the complex was 1:1 (γ-CD:PSicyc6). The inclusion complex was thermally stable. TG analysis showed that PSicyc6 sublimed over 100 °C, but the complex decomposed above 300 °C. The powder X-ray diffraction and the ^{13}C CP/MAS NMR spectroscopy of γ-CD-PSicyc6 complex showed PSicyc6 was included in the cavity of γ-CD. The proposed structures of the inclusion complex are shown in Figure 14.

Conclusions

In conclusion, β-CD and γ-CD formed crystalline inclusion complexes with PSi, and α-CD did not form complexes with PSi. These complexes were novel organic−inorganic hybrids that are strictly regulated on the nanometer scale. The chain-length selectivities are totally different between β-CD and γ-CD. The stoichiometry of γ-CD-PS inclusion complexes is 1:3 (γ-CD:Si monomer unit). The powder X-ray diffraction and the solid-state ^{13}C NMR show that the solid-state structures of γ-CD−PSi inclusion complexes were *pseudo*-polyrotaxane type with many γ-CD threaded on the PSi main chain. The optical properties of γ-CD−PSi inclusion complexes were studied by ultraviolet absorption and fluorescence spectroscopy. Since the absorption maximum and the emission maximum of the PS of the inclusion complex are red-shifted significantly, the PSi main chain in the cavities of γ-CD takes an all-trans conformation. PSi (electron donor) and TCNQ (electron acceptor) formed the charge-transfer complex in the cavities of γ-CD in aqueous solution.

Experimental Section

Materials. α-Cyclodextrin (α-CD) and γ-cyclodextrin (γ-CD) were kindly supplied by Nihon Shokuhin Kako Co., Ltd. β-Cyclodextrin (β-CD) was obtained from Tokyo Kasei Kogyo Co., Ltd. Cyclodextrins were used after drying under vacuum at 80 °C. Dichlorodimethylsilane and chlorotrimethylsilane were purchased from Tokyo Kasei Kogyo Co. Ltd. and used after distillation under Ar flow. Sodium was purchased from Nacalai Tesque Inc. Poly(dimethylsilane)s were prepared by published methods using melted sodium.

Measurements. ^1H NMR spectra were recorded at 270 MHz on a JEOL EX-270 NMR spectrometer and at 400 MHz on a JEOL GSX-400 spectrometer at 30 °C. Chemical shifts were referenced to the solvent value (δ = 7.19 ppm for pyridine-d_5 and δ = 7.26 ppm for chloroform-d). ^{13}C NMR spectra were measured at 100.5 MHz on a JEOL GSX-400 spectrometer at 30 °C. Chemical shifts were referenced to the solvent value (δ = 77.0 ppm for chloroform-d and δ = 123.5 ppm for pyridine-d_5). ^{13}C CP/MAS and ^{13}C PST/MAS NMR spectra were measured at 75.6 MHz on a Chemagnetics JMN-CMX300W spectrometer with a sample spinning rate of 4.0 kHz at room temperature. Chemical shifts were referenced to external hexamethylbenzene (δ = 17.36 ppm). Powder X-ray diffraction patterns were taken using Cu Kα irradiation with a Rigaku RAD-ROC X-ray diffractometer (voltage, 40 kV; current, 100 mA; scanning speed, 3°/min). FT-IR measurements were performed on a JASCO FT/IR-410 spectrometer. Gel permeation chromatography determination was carried out with Tohso CCP&8010 system (columns: G3000HXL and G2000HXL). TG/DTA measurements were carried out with a Seiko EXSTAR6000 TG/DTA system. Absorption spectra were recorded on a Shimadzu UV2500 PC spectrometer at room temperature. Fluorescence spectra were recorded on a HITACHI F-2500 spectrometer at room temperature.

Preparation of the Inclusion Complexes of Poly(dimethylsilane) with CDs. α-CD−PSi Complexes. PSi (Si monomer unit: 5.0×10^{-4} mol) was put into a tube. A saturated aqueous solution of α-CD (14.7 mL) containing 486 mg of α-CD (5.00×10^{-4} mol) was added at room temperature. The mixture was stirred for a week and then allowed to stand overnight at room temperature. The precipitated product was collected by centrifugation, dried under vacuum, then washed with THF and dried under vacuum, and washed with water and dried under vacuum to give the α-CD−PSi complex. The results are summarized in Table 1.

α-CD−PSi90. Yield: 184 mg, 21%. ^1H NMR (pyridine-d_5, 270 MHz): δ 5.55 (*d*, 6H, C_1H of α-CD), 4.71 (*t*, 6H, C_3H of α-CD), 4.43 (*m*, 18H, C_5H and C_6H of α-CD), 4.29 (*m*, 6H, C_2H of α-CD), 4.05 (*m*, 6H, C_4H of α-CD), −0.014 (*s*, 12H, methyl H of PSi). FT-IR (KBr, cm^{-1}): 3398 (s, ν_s, O−H), 2929 (m, ν_s, C−H), 1249 (w, ν_{as}, Si−C), 1154, 1078, 1031 (s, ν_s, C−O), 862 (ν_s, Si−C). Anal. Calcd for $(C_{36}H_{60}O_{30})_{1.8}(C_6H_{18}OSi_2)_{1.0}(H_2O)_{5.1}$: C, 42.82; H, 6.79. Found: C, 42.81; H, 6.84.

***β*-CD−PSi Complexes.** PSi (Si monomer unit: 5.0×10^{-4} mol) was put into a tube. A saturated aqueous solution of β-CD (30.7 mL) containing 568 mg of β-CD (5.00×10^{-4} mol) was added at room temperature. The mixture was stirred for a week and then allowed to stand overnight at room temperature. The precipitated product was collected by centrifugation, dried under vacuum, then washed with THF and dried under vacuum, and washed with water and dried under vacuum to give the β-CD−PSi complex. The results are summarized in Table 1.

***β*-CD−PSi90.** Yield: 217 mg, 8.8%. ^1H NMR (pyridine-d_5, 270 MHz): δ 5.68 (*d*, 7H, C_1H of β-CD), 4.83 (*t*, 7H, C_3H of β-CD), 4.54 (*m*, 21H, C_5H and C_6H of β-CD), 4.30 (*m*, 7H, C_2H of β-CD), 4.15 (*m*, 7H, C_4H of β-CD), −0.014 (*s*, 12H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3364 (ν_s, O−H), 2926 (ν_s, C−H), 1254 (ν_{as}, Si−C), 1156, 1080, 1030 (ν_s, C−O), 860 (ν_s, Si−C). Anal. Calcd for $(C_{42}H_{70}O_{35})_{1.1}(C_6H_{18}OSi_2)_{1.0}(H_2O)_{12}$: C, 42.77; H, 6.55. Found: C, 42.79; H, 6.79.

***β*-CD−PSi150.** Yield: 83.8 mg, 25%. ^1H NMR (pyridine-d_5, 270 MHz): δ 5.69 (*d*, 7H, C_1H of β-CD), 4.79 (*t*, 7H, C_3H of β-CD), 4.50 (*m*, 21H, C_5H and C_6H of β-CD), 4.31 (*m*, 7H, C_2H of β-CD), 4.15 (*m*, 7H, C_4H of β-CD), 0.091 (*s*, 18H, methyl H of PSi). FT-IR (KBr, cm^{-1}): 3377(ν_s, OH), 2942 (ν_s, CH), 1246 (ν_{as}, Si−C), 1157, 1080, 1030 (ν_s, CO), 838 (ν_s, Si−C). Anal. Calcd for $(C_{42}H_{70}O_{35})_{1.1}(C_8H_{24}O_2Si_3)_{1.0}(H_2O)_{3.6}$: C, 42.70; H, 7.11. Found: C, 42.69; H, 7.08.

***β*-CD−PSi200.** Yield: 28.3 mg, 5.4%. ^1H NMR (pyridine-d_5, 270 MHz): δ 5.69 (*d*, 7H, C_1H of β-CD), 4.83 (*t*, 7H, C_3H of β-CD), 4.54 (*m*, 21H, C_5H and C_6H of β-CD), 4.31 (*m*, 7H, C_2H of β-CD), 4.15 (*m*, 7H, C_4H of β-CD), 0.192, 0.159, 0.133 (*m*,

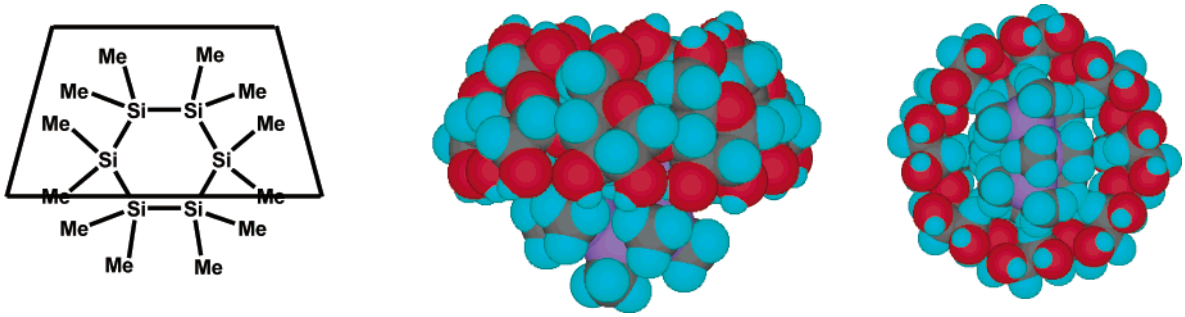

Figure 14. Proposed structures of γ-CD−PSicyc6 inclusion complex.

24H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3378 (ν_s, OH), 2934 (ν_s, CH), 1246 (ν_{as}, Si−C), 1157, 1080, 1030 (ν_s, CO), 840 (ν_s, Si−C). Anal. Calcd for $(C_{42}H_{70}O_{35})_{2.3}(C_{12}H_{36}O_4Si_5)_{1.0}(H_2O)_{16}$: C, 40.45; H, 7.08. Found: C, 40.90; H, 7.07.

***β*-CD−PSi320.** Yield: 8.5 mg, 2.6%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.69 (*d*, 7H, C_1H of β-CD), 4.79 (*t*, 7H, C_3H of β-CD), 4.54 (*m*, 21H, C_5H and C_6H of β-CD), 4.30 (*m*, 7H, C_2H of β-CD), 4.15 (*m*, 7H, C_4H of β-CD), 0.155, 0.143 (*m*, 36H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3397 (ν_s, OH), 2928 (ν_s, CH), 1247 (ν_{as}, Si−C), 1028 (ν_s, CO), 841 (ν_s, Si−C). Anal. Calcd for $(C_{42}H_{70}O_{35})_{2.8}(C_8H_{24}O_2Si_3)_{1.0}(H_2O)_{24}$: C, 39.67; H, 7.17. Found: C, 39.69; H, 7.17.

Preparation of γ-CD−PS Inclusion Complexes. PSi (Si monomer unit: 5.0×10^{-4} mol) was put into a tube. An aqueous solution of γ-CD (5.59 mL) containing 649 mg of γ-CD (5.00×10^{-4} mol) was added at room temperature. The mixture was supersonically agitated for about 15 min and then allowed to stand overnight at room temperature. The precipitated product was collected by centrifugation, dried under vacuum, then washed with THF and dried under vacuum, and washed with water and dried under vacuum to give the γ-CD−PSi complex. The results are summarized in Table 1.

γ-CD−PSi90. Yield: 29.8 mg, 2.7%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.72 (*d*, 8H, C_1H of γ-CD), 4.64 (*t*, 8H, C_3H of γ-CD), 4.38 (*m*, 18H, C_5H and C_6H of γ-CD), 4.28 (*m*, 8H, C_2H of γ-CD), 4.09 (*m*, 8H, C_4H of γ-CD), −0.012 (*s*, 12H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3399 (ν_s, O−H), 2929 (ν_s, C−H), 1248 (ν_{as}, Si−C), 1157, 1080, 1027 (ν_s, C−O), 862 (ν_s, Si−C). Anal. Calcd for $(C_{48}H_{80}O_{40})_{1.6}(C_6H_{18}OSi_2)_{1.0}(H_2O)_{5.8}$: C, 42.79; H, 6.69. Found: C, 42.78; H, 6.78.

γ-CD−PSi150. Yield: 279 mg, 64%. ^{1}H NMR (pyridine-d_5, 400 MHz): δ 5.72 (*d*, 8H, C_1H of γ-CD), 4.63 (*t*, 8H, C_3H of γ-CD), 4.37 (*m*, 18H, C_5H and C_6H of γ-CD), 4.27 (*m*, 8H, C_2H of γ-CD), 4.09 (*t*, 8H, C_4H of γ-CD), 0.079 (*s*, 18H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3389 (ν_s, O−H), 2931 (ν_s, C−H), 1246 (ν_{as}, Si−C), 1158, 1081, 1036 (ν_s, C−O), 837 (ν_s, Si−C). Anal. Calcd for $(C_{48}H_{80}O_{40})_{1.2}(C_8H_{24}O_2Si_3)_{1.0}(H_2O)_{4.5}$: C, 42.66; H, 6.93. Found: C, 42.72; H, 7.11.

γ-CD−PSi200. Yield: 298 mg, 73%. ^{1}H NMR (pyridine-d_5, 400 MHz): δ 5.72 (*d*, 8H, C_1H of γ-CD), 4.63 (*t*, 8H, C_3H of γ-CD), 4.39 (*m*, 24H, C_5H and C_6H of γ-CD), 4.27 (*m*, 8H, C_2H of γ-CD), 4.09 (*t*, 8H, C_4H of γ-CD), 0.181, 0.148, 0.122 (*m*, 24H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3388 ν_s, O−H), 2939 ν_s, C−H), 1246 ν_{as}, Si−C), 1158, 1080, 1026 ν_s, C−O), 837 ν_s, Si−C). Anal. Calcd for $(C_{48}H_{80}O_{40})_{1.4}(C_{12}H_{36}O_4Si_3)_{1.0}(H_2O)_{5.8}$: C, 42.51; H, 7.02. Found: C, 42.51; H, 7.18.

γ-CD−PSi320. Yield: 57.8 mg, 27%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.72 (*d*, 8H, C_1H of γ-CD), 4.63 (*t*, 8H, C_3H of γ-CD), 4.39 (*m*, 24H, C_5H and C_6H of γ-CD), 4.27 (*m*, 8H, C_2H of γ-CD), 4.10 (*t*, 8H, C_4H of γ-CD), 0.330, 0.250, 0.167 (*m*, 36H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3375 (ν_s, O−H), 2939 (ν_s, C−H), 1247 (ν_{as}, Si−C), 1157, 1080, 1025 (ν_s, C−O), 837 (ν_s, Si−C). Anal. Calcd for $(C_{48}H_{80}O_{40})_{1.3}(C_{22}H_{66}O_9Si_{10})_{1.0}(H_2O)_{9.9}$: C, 41.06; H, 7.39. Found: C, 41.07; H, 7.19.

γ-CD−PSi440. Yield: 141 mg, 59%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.72 (*d*, 8H, C_1H of γ-CD), 4.63 (*t*, 8H, C_3H of γ-CD), 4.38 (*m*, 24H, C_5H and C_6H of γ-CD), 4.27 (*m*, 8H, C_2H of γ-CD), 4.09 (*t*, 8H, C_4H of γ-CD), 0.345, 0.295, 0.178 (*m*, 48H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3377 (ν_s, O−H), 2944 (ν_s, C−H), 1248 (ν_{as}, Si−C), 1159, 1081, 1027 (ν_s, C−O), 834 (ν_s, Si−C). Anal. Calcd for $(C_{48}H_{80}O_{40})_{2.3}(C_{34}H_{102}O_{15}Si_{16})_{1.0}(H_2O)_{22}$: C, 40.69; H, 7.16. Found: C, 40.68; H, 7.08.

γ-CD−PSi550. Yield: 163 mg, 64%. ^{1}H NMR (pyridine-d_5, 400 MHz): δ 5.49 (*d*, 8H, C_1H of γ-CD), 4.38 (*t*, 8H, C_3H of γ-CD), 4.17 (*m*, 24H, C_5H and C_6H of γ-CD), 4.03 (*m*, 8H, C_2H of γ-CD), 3.95 (*t*, 8H, C_4H of γ-CD), 0.349, 0.308, 0.210 (*m*, 60H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3398 (ν_s, OH), 2940 (ν_s, CH), 1249 (ν_{as}, Si−C), 1158, 1081, 1025 (ν_s, CO), 760 (ν_s, Si−C). Anal. Calcd for $(C_{48}H_{80}O_{40})_{3.0}(C_{52}H_{156}O_{24}Si_{25})_{1.0}(H_2O)_{12}$: C, 41.83; H, 7.10. Found: C, 41.81; H, 7.22.

γ-CD−PSi610. Yield: 141 mg, 58%. ^{1}H NMR (pyridine-d_5, 400 MHz): δ 5.49 (*d*, 8H, C_1H of γ-CD), 4.38 (*t*, 8H, C_3H of γ-CD), 4.17 (*m*, 24H, C_5H and C_6H of γ-CD), 4.04 (*m*, 8H, C_2H of γ-CD), 3.96 (*t*, 8H, C_4H of γ-CD), 0.355, 0.301, 0.211 (*m*, 66H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3407 (ν_s, O−H), 2927 (ν_s, C−H), 1249 (ν_{as}, Si−C), 1159, 1081, 1026 (ν_s, C−O), 796 (ν_s, Si−C). Anal. Calcd for $(C_{48}H_{80}O_{40})_{3.3}(C_{52}H_{156}O_{24}Si_{25})_{1.0}(H_2O)_{20}$: C, 41.32; H, 7.11. Found: C, 41.32; H, 7.16.

γ-CD−PSi670. Yield: 198 mg, 87%. ^{1}H NMR (pyridine-d_5-chloroform-*d* 2:1 v/v, 400 MHz): δ 5.48 (*d*, 8H, C_1H of γ-CD), 4.38 (*t*, 8H, C_3H of γ-CD), 4.17 (*m*, 24H, C_5H and C_6H of γ-CD), 4.15 (*m*, 8H, C_2H of γ-CD), 3.95 (*t*, 8H, C_4H of γ-CD), 0.349, 0.241, 0.210 (*m*, 72H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3388 (ν_s, O−H), 2941 (ν_s, C−H), 1248 (ν_{as}, Si−C), 1158, 1028 (ν_s, C−O), 759 (ν_s, Si−C). Anal. Calcd for $(C_{48}H_{80}O_{40})_{3.7}(C_{52}H_{156}O_{24}Si_{25})_{1.0}(H_2O)_{18}$: C, 41.80; H, 7.02. Found: C, 41.79; H, 7.06.

γ-CD−PSi780. Yield: 79.1 mg, 57%. ^{1}H NMR (pyridine-d_5-benzene-d_6 3:1 v/v, 400 MHz): δ 5.72 (*d*, 8H, C_1H of γ-CD), 4.64 (*t*, 8H, C_3H of γ-CD), 4.39 (*m*, 24H, C_5H and C_6H of γ-CD), 4.26 (*m*, 8H, C_2H of γ-CD), 4.08 (*t*, 8H, C_4H of γ-CD), 0.458, 0.429, 0.319, 0.244 (*m*, 84H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3410 (ν_s, O−H), 2950 (ν_s, C−H), 1261 (ν_{as}, Si−C), 1158, 1080, 1027 (ν_s, C−O), 757 (ν_s, Si−C). Anal. Calcd for $(C_{48}H_{80}O_{40})_{4.3}(C_{52}H_{156}O_{24}Si_{25})_{1.0}(H_2O)_{21}$: C, 39.79; H, 7.61. Found: C, 39.79; H, 7.61.

γ-CD−PSi960. Yield: 22.2 mg, 8.9%. ^{1}H NMR (pyridine-d_5, 400 MHz): δ 5.72 (*d*, 8H, C_1H of γ-CD), 4.64 (*t*, 8H, C_3H of γ-CD), 4.38 (*m*, 24H, C_5H and C_6H of γ-CD), 4.28 (*m*, 8H, C_2H of γ-CD), 4.09 (*t*, 8H, C_4H of γ-CD), 0.381, 0.347, 0.229, 0.198 (*m*, 102H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3386 (ν_s, O−H), 2949 (ν_s, C−H), 1248 (ν_{as}, Si−C), 1158, 1080, 1028 (ν_s, C−O), 746 (ν_s, Si−C). Anal. Calcd for $(C_{48}H_{80}O_{40})_{2.0}(C_{52}H_{156}O_{24}Si_{25})_{1.0}(H_2O)_{19}$: C, 40.07; H, 7.76. Found: C, 40.02; H, 8.36.

Preparation of Dodecamethylcyclohexasilane (PSicyc6). Dodecamethylcyclohexasilane (PSicyc6) was prepared starting from dimethyldichlorosilane by Wurtz-type reductive oligomerization using an excess amount of lithium. PSicyc6 was purified by sublimation at 100 °C in vacuo and recrystallization twice from *n*-hexane/ethanol. Characterization of PSicyc6 was carried out by ^{1}H/^{13}C/^{29}Si NMR and ultraviolet absorption spectroscopy.

Preparation of γ-CD−PSicyc6 Inclusion Complex. PSicyc6 179 mg (5.13×10^{-3} mol) was put into a tube. An aqueous solution of γ-CD (5.59 mL) containing 649 mg of γ-CD (5.00×10^{-4} mol) was added at room temperature. The mixture was stirred vigorously for a week and then allowed to stand overnight at room temperature. The precipitated product was collected by centrifugation, dried under vacuum, then washed

with THF and dried under vacuum, and washed with water and dried under vacuum to give the γ-CD−PSicyc6 complex.

γ-CD−PSicyc6. Yield: 501 mg, 61%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.72 (*d*, 8H, C_1H of γ-CD), 4.63 (*t*, 8H, C_3H of γ-CD), 4.39 (*m*, 18H, C_5H and C_6H of γ-CD), 4.27 (*m*, 8H, C_2H of γ-CD), 4.09 (*m*, 8H, C_4H of γ-CD), 0.216 (*s*, 36H, methyl H of PS). FT-IR (KBr, cm^{-1}): 3411 (ν_s, O−H), 2929 (ν_s, C−H), 1248 (ν_{as}, Si−C), 1158, 1080, 1027 (ν_s, C−O), 845 (ν_s, Si−C). Anal. Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_{12}H_{36}Si_6)_{1.0}(H_2O)_{3.5}$: C, 42.16; H, 7.25. Found: C, 42.15; H, 7.03.

Calculation of Yields and Stoichiometries by ^{1}H NMR. The yields were calculated from the intensity ratio of the peaks at 5.73−5.69 ppm derived from C_1H of CD and 0.35−0.10 ppm derived from the methyl proton of PSi. The stoichiometry, which means the ratio between CD and monomer units of polymer, was calculated by the same manner as the determination of yield.

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