

**Synthesis and crystal structure of double-three ring (D3R)-
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Synthesis and crystal structure of double-three ring (D3R)-type cage siloxanes modified with dimethylsilanol groups

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The controlled assembly of molecular building blocks enables the rational design of nanomaterials. In this study, two types of cage-type oligosiloxanes with double-three ring (D3R) structures are modified with dimethylsilanol groups to form supramolecular assemblies. One is the siloxane cage derived from Si(OEt)₄ (denoted as the Q₆ cage), and the other is the organosiloxane cage derived from (EtO)₃Si-CH₂-Si(OEt)₃ (denoted as the T₆ cage). The syntheses of the silanol-modified cages are performed in two steps: i) dimethylsilylation of the corner Si–O[−] groups on the Q₆ and T₆ cages to introduce Si–H groups and ii) subsequent oxidation of the Si–H groups to Si–OH groups. Dimethylsilylation of the cages is conducted at much lower temperatures (−94 and −78 °C for Q₆ and T₆ cages, respectively) than those used for conventional silylation, which is the key to suppressing the deterioration of the unstable D3R structure. The subsequent oxidation of the Si–H groups proceeds successfully, and the crystallization of these molecules is induced by the hydrogen bonds of the silanol groups. The crystal structure of the Q₆ cage modified with dimethylsilanol groups can be regarded as a layered structure with tetrahydrofuran between the layers. In contrast, the T₆ cage modified with dimethylsilanol groups assembled to form a more densely-packed structure with no included solvent molecules. The differences between the crystal structures are discussed in terms of the shape of the cages. The insight into the effect of the shape of the cage on its assembly behavior will lead to the designable synthesis of crystalline siloxane-based materials.

Introduction

Cage siloxanes are polyhedral molecules that are composed mainly of silicon and oxygen atoms. These molecules have many characteristics that make them useful as building blocks to construct siloxane-based nanomaterials, such as their rigid structures and the ability to attach a variety of functional groups at their corners.¹ In particular, the construction of porous materials from cage siloxanes is expected to be a useful method for tuning the structural properties and composition of the porous materials. Many porous materials have been prepared by connecting cage siloxanes via C–C,² Si–O–Si,³ Si–O–C,⁴ and Si–C⁵ bond formation reactions. Cage siloxanes are normally linked randomly to form amorphous materials,^{2b, 2f} though periodicity can be obtained by utilizing rigid organic linkers^{2b, 2f} or by the self-assembly of amphiphilic derivatives.^{2d, 3b, 3c}

Recently, we found that double-four ring (D4R) siloxanes with dimethylsilanol groups assembled to form a porous crystal via hydrogen bonds (H-bonds) between the silanol groups and the subsequent linking of the silanol groups by silylation with trichlorosilane.⁶ While silanol groups are typically regarded as being only intermediates of the formation of Si–O–Si bonds from Si–O–C bonds via hydrolysis and condensation reactions, in our method, silanol groups played an important role in arranging and connecting the molecules based on their ability to act as both H-bond donors and acceptors, and to form Si–O–Si bonds by various reactions.⁷ This method opened a new route for the synthesis of porous crystals via soft chemical processes. This finding prompted us to further investigate the fundamental chemistry of the assembly of cage-type siloxanes via H-bonds. To increase the structural variety of such porous crystals, it is important to determine the relationship between the molecular structure and the resulting crystal structure. In particular, the shape of the cage is expected to have a strong influence on the crystal structure, as the number of functional groups on the cage corners and the direction, in which they point, is different for each cage shape. Therefore, our interest is focused on the use of other cage siloxanes with different structures.

The syntheses of various types of cage siloxanes, such as those with D3R, D4R, double-five ring (D5R), and double-six ring (D6R) structures, have been reported.^{1a} Among these cages, D3R siloxanes are quite interesting as building blocks because of their unique prismatic shape with distorted trisiloxane rings, which are rarely present in conventional siloxane-based

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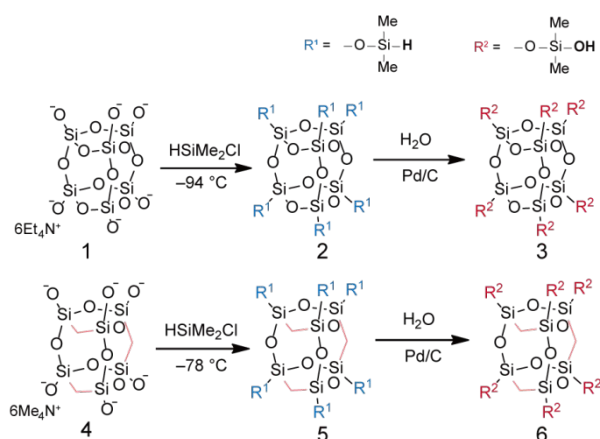
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materials. Interestingly, two kinds of D3R cages have been reported; one is composed solely of Si–O–Si linkages (denoted as the Q₆ cage), while the other is composed of both Si–O–Si and Si–CH₂–Si linkages (denoted as the T₆ cage).⁸ The differences between the bond angles and lengths of the Si–O–Si and Si–CH₂–Si linkages should result in slight differences in the cage shapes and in the directions of the dimethylsilanol groups on the corners, which in turn should result in different crystal structures. Therefore, a comparison of their crystal structures could provide information regarding the molecular factors that influence the supramolecular-assembly of cage siloxanes.

Q₆ cages with corner Si–O[−] groups (**1** and **4**, respectively, in Scheme 1) are easily obtained by the hydrolysis and condensation of Si(OEt)₄ or SiO₂ in the presence of tetraethylammonium (TEA) hydroxide.⁹ However, there have been only a few reports of the introduction of silyl groups on D3R siloxanes^{9–10} since the first report in 1980.^{9a} This can be attributed to the low stability of the D3R structures due to the strained Si–O–Si bonds; this low stability is evidenced by the fact that silica zeolites containing D3R units have never been found.¹¹ A modified silylation method is therefore required to suppress the deterioration of the D3R structure.

Herein, we report the synthesis of Q₆ and T₆ cages modified with dimethylsilanol groups (**3** and **6**, respectively, in Scheme 1). These molecules were synthesized from **1** and **4** by silylation to form dimethylsilylated derivatives (**2** and **5**, respectively), followed by oxidation of the Si–H groups (Scheme 1). Although deterioration of **1** and **4** inevitably occurred when conventional silylation methods were used, we found that dimethylsilylation at low temperature was quite effective for the preservation of the unstable D3R cages. In addition, **3** and **6** were crystallized via H-bonds between the silanol groups. The presence or absence of Si–CH₂–Si linkages induced different orientations of the silanol groups, which in turn resulted in the formation of different crystal structures with different H-bond networks.



Scheme 1 Synthesis of a Q₆ cage (**3**) and T₆ cage (**6**) with dimethylsilanol groups. Red lines indicate Si–CH₂–Si bonds.

Results and discussion

Synthesis and crystal structure of the dimethylsilanol-modified Q₆ cage (**3**)

The Q₆ cage **1** was synthesized according to the method reported by Hoebbel *et al.*,^{9a} but we were unable to reproduce the preparation of crystals of **1**. Therefore, **1** was silylated by adding a TEA–silicate solution of **1** directly to chlorodimethylsilane at −94 °C using a liquid N₂–acetone bath. The ¹H nuclear magnetic resonance (NMR) spectrum of the product showed signals that were assigned as SiCH₃ (0.27 ppm) and SiH groups (4.75 ppm), which were used to determine the progress of the silylation reaction and the retention of the Si–H groups (Figure S1†). The ²⁹Si NMR spectrum of the product (Figure S2†) mainly showed M¹ (Me₂HSi(OSi)) and Q⁴ (Si(OSi)₄) signals at 0.11 ppm and −99.03 ppm, respectively. Small M¹ and Q⁴ signals at −1.4 ppm and −108.63 ppm, respectively, corresponding to the dimethylsilylated D4R siloxane,¹² were also observed. This impurity was removed by recrystallization after the Si–H groups were converted into Si–OH groups.

It should be noted here that dimethylsilylation of **1** at room temperature resulted in the formation of a large amount of by-products. ²⁹Si NMR and matrix-assisted laser desorption/ionization time of flight (MALDI TOF) mass spectra (Figure S3†) suggested that these side products were mainly formed by the oxidation of Si–H groups and cleavage of Si–O–Si bonds. The former side reaction can be attributed to the presence of a relatively large amount of water in the highly basic solution of **1**. The latter side reaction, i.e., cleavage of the three-membered rings in **1**, was probably due to the strained Si–O–Si bonds. Generally, the silylation of silicate species using chlorosilanes is performed at a temperature of 0 °C or higher. This is the first report to demonstrate that low-temperature reaction can effectively achieve the silylation of relatively labile silicate oligomers without structural deterioration. This method is also expected to be effective for other labile silicates.

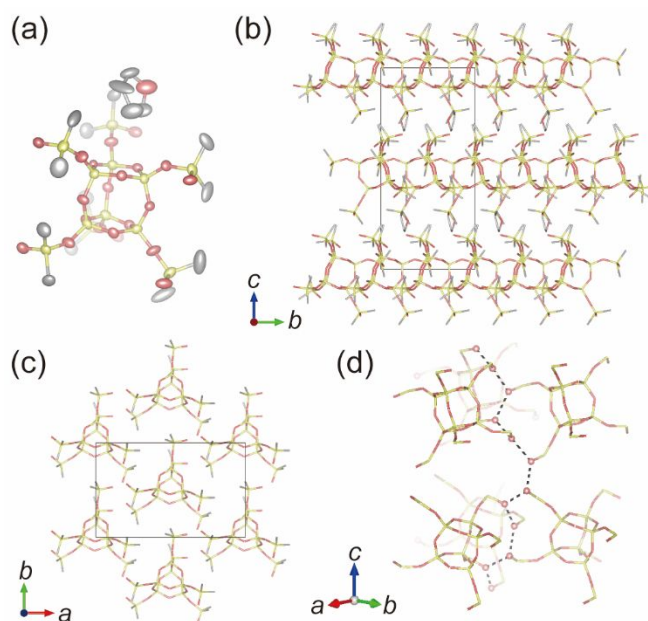


Figure 1 (a) Molecular structures of **3** and THF obtained by single crystal X-ray structural analysis. The ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for

clarity. (b,c) Crystal structure of **3** viewed along the (b) [100] and (c) [001] directions. Hydrogen atoms are omitted for clarity. (d) The linear hydrogen-bonding network formed by the silanol groups of **3**. Dashed lines indicate hydrogen bonds. Methyl groups are omitted for clarity. Atom colors: Yellow: Si, red: O, and gray: C.

The conversion of the Si–H groups into Si–OH groups was achieved without any noticeable side reactions (Figure S4a[†]), and compound **3** was isolated by recrystallization from a tetrahydrofuran (THF)–toluene–hexane solution to obtain aggregated block-shaped crystals (Figure S5[†]). The ¹H NMR spectrum of **3** showed signals corresponding to SiOH and SiMe groups (Figure S6[†]). The ²⁹Si NMR spectrum (Figure S4b[†]) showed a D¹ (Me₂(HO)Si(OSi)) signal (−10.76 ppm) and Q⁴ signal from the silylated Q₆ cage (−99.94 ppm). These spectra did not contain signals attributable to SiH groups, indicating the almost quantitative formation of **3**.

Single crystal X-ray structural analysis of the obtained crystal was conducted. The crystal had a monoclinic lattice with the space group *Cc*, and contained THF molecules in a 1:1 ratio (**3**:THF) (Figure 1a). These THF molecules were included within the crystalline lattice with two probable orientations (Figure S7[†]). The crystal structure was essentially layered, and the constituent layers were arranged in parallel along the *ab* plane (Figure 1b). The molecules of **3** were arranged in a base-centered lattice within the plane (Figure 1c). The distances between adjacent silanol groups ranged from 2.69 to 2.72 Å, indicating that all the silanol groups formed H-bonds. Monosilanol molecules modified with various organic groups have been reported to form various H-bond arrangements, such as trimeric,¹³ tetrameric,¹⁴ and hexameric^{6, 14a, 15} rings and linear structures.^{6, 16} In this case, the H-bonds connected the modified D3R cages to form layers (Figure 1d) and also crossed the layers to form a linear arrangement, resulting in a three-dimensional extended framework in the crystal structure.

In order to visualize the apparent pores within the crystal of **3**, that is, the space occupied by the THF molecules, the Connolly surface (the surface of the field that is accessible to the probe sphere) of the crystal (shown in Figure S8[†] as the molecular surface colored in blue) was calculated using a hypothetical spherical probe with a diameter of 0.4 nm. The calculation revealed that the diameter of the closed spherical pores was ca. 0.6 nm.

In our previous report, we prepared crystals of dimethylsilanol-modified D4R siloxanes from a THF–1,3,5-trimethylbenzene (TMB) solution,⁶ and found that they assembled into a pillared layer structure. In contrast, **3** did not crystallize when THF and TMB were used as solvents. The difference in the crystal structures can be attributed to the differences in the D3R and D4R structures and the H-bond networks of the silanol groups. While the silanol groups of the D4R siloxane formed cyclic hexameric and octameric H-bond networks containing both inter- and intra-molecular H-bonds, those of **3** formed a linear network. The differences in the H-bond networks can be attributed to the different distances between adjacent silanol groups on the cage corners. The distance between the adjacent oxygen atoms attached directly to the cage of the D4R siloxane was estimated to be 0.48 nm;

this value was shorter than the value of 0.52 nm estimated for **3** (Figure S9[†]). This difference is due to the distorted Si–O–Si angles of D3R cage of **3**. In the D4R cage, all Si–O–Si angles are in the range of 146.1–152.8°. The Si–O–Si angles in the trisiloxane and tetrasiloxane rings in **3** are in the range of 130.1–132.0° and 135.9–138.7°, respectively, and they are much smaller than those of the D4R cage. Consequently, it is reasonable for the silanol groups of **3** to form only intermolecular H-bonds, in clear contrast to the D4R siloxanes. Furthermore, the shape of the cage also influenced the crystal structure. Both the D4R siloxane and **3** formed layered structures, but the arrangement of the molecules within the layers was different. The D4R cages were arranged into a tetragonal structure, while the D3R cages of **3** were arranged into a pseudo-hexagonal structure. This difference can be attributed to the different symmetries of the D3R and D4R cages. The absence of pillars in the D3R cage crystals is probably due to the fact that the inclined orientation of the D3R cages in the layer prevented them from forming pillars.

To investigate the possibility of converting the silanol groups in the crystals derived from **3** into siloxane bonds, the crystals^{S6} were reacted with trichlorosilane based on our previous report.⁶ The ²⁹Si MAS NMR spectrum of the product (Figure S11a[†]) showed D², T², and T³ signals with an intensity ratio of 1:0.01:0.2, confirming that the silylation reaction had occurred. However, the intensity ratio of the T and D signals (T/D = 0.20) was smaller than the expected value (0.33–0.50, assuming that each T unit is connected to two or three D units). This fact suggests that the reaction between silanol groups and trichlorosilane did not proceed sufficiently because trichlorosilane could not easily diffuse through unconnected pores. The appearance of a Q⁴ signal at −108.42 ppm in the ²⁹Si MAS NMR spectrum indicated the deterioration of the D3R cage by cleavage and rearrangement of the trisiloxane rings. The intensity ratio of the signals at −99.95 and −108.42 ppm was 1.9:1. The signal at −99.95 ppm could be assigned as either a Q⁴ signal of the D3R cage or a Q³ signal formed by cleavage of the D3R cage. Assuming that this signal corresponded to the Q⁴ unit of the D3R cage, the signal at −108.42 ppm suggests that at least 34% of the three-membered ring was deteriorated. This is probably caused by the attack of the dimethylsilanol groups or silanol groups formed by the cleavage onto Si atoms of the D3R cages. This side reaction is probably catalyzed by hydrogen chloride generated upon partial silylation. The powder XRD pattern of the silylated product showed two broad peaks at 1.11 and 0.93 nm, indicating that the periodicity of the molecules was lost during silylation (Figure S11b[†]). Thus, to successfully convert the silanol groups into siloxane bonds, the presence of open channels in the molecular crystals is favorable to allow chlorosilanes to enter, and protection of the D3R cages by bulky substituents or optimization of the silylation conditions, e.g., low-temperature conditions, is required to avoid side reactions.

Synthesis and crystal structure of the dimethylsilanol-modified T₆ cage (**6**)

The T_6 cage **4** was synthesized from bis(triethoxysilyl)methane (BTESM) according to our previous report.⁸ The ^{29}Si NMR spectrum of **4** shows two T^2 ($\text{CSi}(\text{OSi})_2$; OH or O^-) signals (-54.88 and -57.62 ppm, Figure S12a[†]) corresponding to the two chemically inequivalent Si atoms in the asymmetric cage structure. Dimethylsilylation of **4** was performed by dropping a solution of **4** into chlorodimethylsilane at -78 °C, giving **5** as a colorless liquid. The ^{29}Si NMR spectrum of **5** (Figure S12b[†]) shows two T^3 signals ($\text{CSi}(\text{OSi})_3$; -60.29 and -64.01 ppm) and two M^1 signals ($\text{Me}_2\text{HSi}(\text{OSi})$; -3.54 and -3.92 ppm), indicating that dimethylsilyl groups are attached to the cage corners. The ^1H NMR spectrum (Figure S13a[†]) shows signals assigned to SiH (4.40 – 5.00 ppm), SiCH_2Si , and SiCH_3 (from -0.10 to 0.40 ppm). These results demonstrated the successful synthesis of **5**. Although it has been reported that the introduction of trimethylsilyl, dimethylvinylsilyl, and ethoxydimethylsilyl groups on **4** can be achieved by silylation at room temperature,^{2a, 8} dimethylsilylation of **4** with chlorodimethylsilane at room temperature was unsuccessful, as was the case for **1**. The oxidation of the SiH groups and cleavage of the Si-O-Si bonds in **4** were confirmed by ^{29}Si NMR and MALDI-TOF MS analyses (Figure S14 and S15[†]). The latter side reaction, i.e., cleavage of the strained Si-O-Si bonds in **4**, probably occurred due to the lower steric protection of the attached dimethylsilyl groups against the nucleophilic attack of H_2O and/or OH^- on the cage framework compared to that of the aforementioned silyl groups.

Conversion of the SiH groups of **5** into SiOH groups was achieved without deterioration of the cage structure. After treating **5** with water in the presence of a Pd/C catalyst, the ^1H NMR spectrum showed a broad signal assigned to SiOH in addition to the SiCH_3 and SiCH_2Si signals (Figure S12b[†]), and the signals assigned to SiH disappeared. The ^{29}Si NMR spectrum (Figure S13c[†]) showed two D^1 ($\text{Me}_2(\text{HO})\text{Si}(\text{OSi})$) signals (-11.6 and -11.7 ppm) and a slight shift in the T^3 signals of the cage (-61.30 and -64.95 ppm). These results demonstrated the almost quantitative conversion of **5** to **6** without decomposition of the cage or condensation of the SiOH groups. Crystallization of **6** was induced by cooling the concentrated solution to give rhombic crystals (Figure S16[†]). The crystals were soluble in polar solvents such as THF and acetone.

The Fourier-transform infrared (FT-IR) spectrum of the crystals of **6** showed a broad OH stretching vibration centered at 3300 cm^{-1} , which is characteristic of H-bonded silanol groups (Figure S17[†]). Single crystal X-ray structural analysis of **6** revealed that the cages were crystallized in a monoclinic lattice, in which the three-membered rings of **6** were oriented along the same direction (Figure 2a–c). The O–O distances between the adjacent silanol groups (2.65 Å, 2.63 Å, and 2.66 Å) were close enough to form H-bonds. The crystals of **6** appeared to contain cyclic hexameric H-bonds between the silanol groups of four molecules (dashed lines in Figure 2d and S17[†]). The cyclic hexameric H-bond is composed of two intramolecular H-bonds and four intermolecular H-bonds. It is interesting to note that the intramolecular H-bonds are formed between the two silanol groups that are bridged by Si-O-Si linkages. This was attributed to the longer distance between the silanol groups, which arose

from the larger Si-O-Si angle (146.3°) compared to the $\text{Si-CH}_2\text{-Si}$ angle (117.5°). Specifically, the distance between the oxygen atoms attached directly to the cage was estimated to be 0.48 nm for Si-O-Si bridged oxygens and 0.56 nm for $\text{Si-CH}_2\text{-Si}$ bridged oxygens (Figure S8[†]). The formation of a cyclic hexameric H-bond from four molecules of **6** was similar to the behavior of D4R siloxane with dimethylsilanol groups.⁶ This fact suggests that silanol groups tend to form intramolecular H-bonds because of their proximity, and also tend to form cyclic hexameric H-bonds.

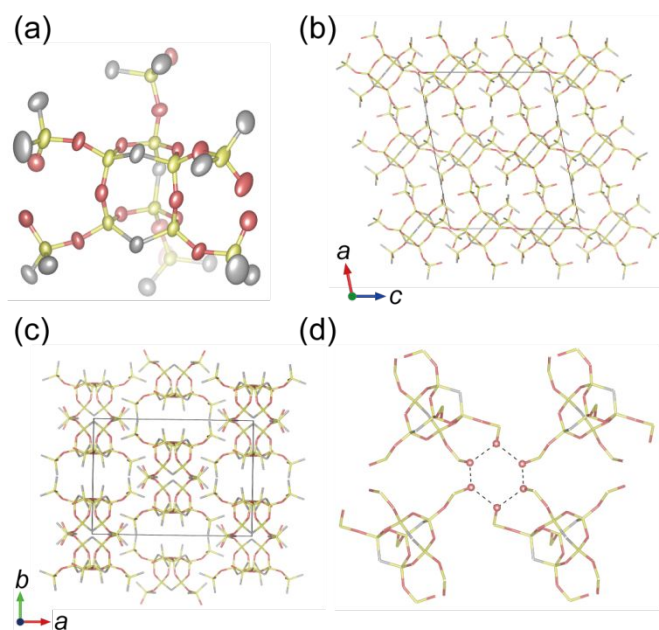


Figure 2 (a) The molecular structure of **6** obtained by single crystal X-ray structural analysis. The ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. (b,c) Crystal structures of **6** viewed along the (b) $[010]$ and (c) $[001]$ directions. Hydrogen atoms are omitted for clarity. (d) The cyclic hydrogen-bonding network formed by the silanol groups of **6**. Dashed lines indicate hydrogen bonds. Methyl groups are omitted for clarity. Atom colors: Yellow: Si, red: O, and gray: C.

The differences in the crystal structures of **6** and **3** can be attributed to the differences in their molecular structures. While the silanol groups of **6** formed hexameric cyclic H-bond networks, those of **3** formed a linear network. The difference in their H-bond networks can be attributed to the different distances between adjacent silanol groups on the corners of cages **6** and **3**. While the adjacent silanol groups of **6** are close enough to form intramolecular H-bonds, the silanol groups of **3** were estimated to be too far from each other to form intramolecular H-bonds. As discussed above, the distance between the oxygen atoms attached directly to the cage and bridged by Si-O-Si bonds in **6** was estimated to be 0.48 nm, which was shorter than the distance of 0.52 nm estimated for **3** (Figure S9[†]). Consequently, it is favorable for the silanol groups of **3** to form only intermolecular H-bonds, in clear contrast to the structure of **6**.

Conclusion

We have demonstrated the synthesis and crystal structures of D3R siloxanes (Q_6 and T_6 cages) modified with dimethylsilanol groups. We found that low-temperature conditions are quite effective for the silylation of labile silicates. The Q_6 and T_6 cages were found to assemble via different H-bond structures. While the silanol groups of **3** assembled into a linear structure with intermolecular H-bonds because the adjacent silanol groups were too far from one another to form intramolecular H-bonds, the silanol groups of **6** formed a cyclic hexameric ring because some of the adjacent silanol groups were close enough to form intramolecular H-bonds. Comparison of the crystal structures of **3** and **6** demonstrated the influence of the shape of the cage on molecular assembly. The different assembly behavior of **3**, **6**, and silanol-modified D4R siloxane⁶ shows that the presence or absence of an intramolecular H-bond and the possible positions of this type of H-bond can be estimated to some extent from the shape of the cages, which can provide important information about their crystal structures.

Experimental Section

Materials

The following chemicals were used without further purification: acetone (Kanto Chemical Co. Inc., >95.0%), chlorodimethylsilane (Tokyo Chemical Industry Co., Ltd., >95.0%), ethanol (Junsei Chemical Co. Ltd., 99.5%), hexane (Kanto Chemical Co. Ltd., >96.0%), palladium 5% on carbon (Wako Pure Chemical Industries, Ltd.), tetraethylammonium hydroxide (35% aqueous solution, Aldrich), tetrahydrofuran (Wako Pure Chemical Industries, Ltd., ≥99.5%), tetramethylammonium hydroxide pentahydrate (TMAOH 5H₂O, Aldrich, ≥95.0%), toluene (Wako Pure Chemical Industries, Ltd., ≥99.5%), and magnesium sulfate (Junsei Chemical Co. Ltd., ≥99.5%). BTESM was synthesized according to a previously reported method¹⁷ using trichlorosilane (Tokyo Chemical Industry Co., Ltd., ≥98.0%), tri-*n*-butylamine (Kanto Chemical Co. Ltd., >98.0%), acetonitrile (Wako Pure Chemical Industries, Ltd., ≥99.8%), chloroform (Wako Pure Chemical Industries, Ltd., ≥99.0%, dehydrated), and ethanol.

Synthesis of D3R siloxane modified with SiMe₂H groups (2)

To a 35% aqueous solution of tetraethylammonium hydroxide (10 mL, 24.3 mmol, 1 equiv.), tetraethoxysilane (5.42 mL, 24.3 mmol, 1 equiv.) was added, and the mixture was stirred at room temperature for 1 d. After the addition of ethanol (1.11 mL) and acetone (27.4 mL), the solution was added dropwise into chlorodimethylsilane (43.8 mL, 403 mmol, 16.8 equiv.) under a nitrogen atmosphere in an acetone-liquid N₂ bath (−94 °C). After allowing the biphasic mixture to stand at −94 °C for 3 h, the organic phase was separated, and the aqueous phase was extracted with hexane. After the removal of volatile compounds from the combined organic layers under reduced pressure, a small amount of hexane was added, and the insoluble solids thus formed were removed using a syringe

filter (0.22 μm). The solvent was removed to obtain a colorless solid (2.51 g, ca. 81%). Although a small amount of impurity remained as a viscous liquid, the product was used for the subsequent reaction without further purification. ¹H NMR (500 MHz, CDCl₃): δ(ppm) = 0.27 (d, *J* = 2.9 Hz; SiCH₃), 4.75 (m; SiH); ¹³C NMR (125.7 MHz, CDCl₃): δ(ppm) = −0.02; ²⁹Si NMR (99.4 MHz, CDCl₃): δ(ppm) = 0.11, −99.03; HR-MS (ESI) calcd. for Si₁₂O₁₅C₁₂H₄₂Na⁺: 784.9647; found: 784.9640.

Synthesis of D3R siloxane modified with SiMe₂OH groups (3)

To a mixture of D3R siloxane with SiMe₂H groups (0.92 g, 1.2 mmol, 1 equiv.) and Pd/C (0.093 g) in THF (9.3 mL), water (0.26 mL, 14.5 mmol, 12 equiv.) was added. After stirring at 40 °C for 4 h, magnesium sulfate and hexane (18.6 mL) were added into the mixture to aggregate the Pd/C. After filtration of the mixture over Celite[®] 545, the solvent was removed under reduced pressure at 0 °C. The product was dissolved in THF and recrystallized by layering the solution with a mixture of toluene and hexane and allowing it to stand at −18 °C to obtain colorless crystals. The ratio of the volumes of THF, toluene, and hexane was 4:3:3. ¹H NMR (500 MHz, THF-*d*₈): δ(ppm) = 0.11 (s, 36H; SiCH₃), 5.68 (br, 6H; SiOH); ¹³C NMR (125.7 MHz, THF-*d*₈): δ(ppm) = 0.04; ²⁹Si NMR (99.4 MHz, THF-*d*₈): δ(ppm) = −10.76, −99.94; HR-MS (ESI) calcd. for Si₁₂O₂₁C₁₂H₄₂Na⁺: 880.9342; found: 880.9340.

Synthesis of D3R-structured organosiloxane (4)

The cage compound **1** was synthesized according to our previous report.⁸ A mixture of 3.50 g of BTESM (10.3 mmol), 5.59 g of TMAOH·5H₂O (30.8 mmol), and 0.92 mL of H₂O and ethanol was stirred at room temperature for 6 d. The molar ratio was BTESM:EtOH:H₂O:TMAOH = 1:20:20:3. The reaction mixture containing **1** was used in the following reaction.

Synthesis of D3R-structured organosiloxane modified with SiMe₂H groups (5)

To 37.3 mL of chlorodimethylsilane (34.3 mmol) was added dropwise the as-prepared solution of **4** at ca. −78 °C using a dry ice-acetone bath. The molar ratio of chlorodimethylsilane to **4** was 100, assuming that the yield of **4** was 100%. After being stirred for 3 h at −78 °C, the product was extracted with hexane twice, and volatile compounds were removed in vacuo. Removal of insoluble species by filtration followed by evaporation of the solvent gave a colorless liquid (1.96 g, 75%). ¹H NMR (500 MHz, CDCl₃): δ(ppm) = −0.10–0.40 (m, 44H; SiCH₃ and SiCH₂Si), 4.40–5.00 (m, 6H; SiH); ¹³C NMR (126 MHz, CDCl₃): δ(ppm) = −0.10, −0.06, 0.37; ²⁹Si NMR (99.4 MHz, CDCl₃): δ(ppm) = −3.54, −3.92, −60.29, −64.01; HR-MS (ESI) calcd. for Si₁₂O₁₂C₁₅H₄₈Na⁺: 779.0269; found: 779.0266.

Synthesis of D3R-structured organosiloxane with SiMe₂OH groups (6)

In 10 mL of THF, 1.00 g of **5** (1.17 mmol) and 0.10 g of Pd/C were mixed, followed by the addition of 214 μL of H_2O (11.9 mmol). The mixture was stirred at 40 °C for 4 h and then dried with magnesium sulfate. The solution was filtered to remove Pd/C. After concentration of the solution using a rotary evaporator, the product was cooled at -196 °C. Allowing the product to stand at -18 °C gave colorless rhombic crystals. ^1H NMR (500 MHz, acetone- d_6): $\delta(\text{ppm}) = -0.10$ – 0.40 (m; SiCH_3 and SiCH_2Si), 5.45 (br; SiOH), 5.48 (br; SiOH); ^{13}C NMR (126 MHz, acetone- d_6): $\delta(\text{ppm}) = 0.37$, 0.39, 0.81; ^{29}Si NMR (99.4 MHz, acetone- d_6): $\delta(\text{ppm}) = -11.54$, -11.65 , -61.30 , -64.95 ; HR-MS (ESI): calcd. for $\text{Si}_{12}\text{O}_{18}\text{C}_{15}\text{H}_{48}\text{Na}^+$: 874.9964; found: 875.9959.

Characterization

Liquid-state ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a JEOL JNM ECZ 500 spectrometer with resonance frequencies of 500.0 MHz, 125.7 MHz, and 99.4 MHz, respectively, at ambient temperature using 5 mm glass tubes. Tetramethylsilane was used as an internal reference at 0 ppm. Acetone- d_6 , CDCl_3 , methanol- d_6 and THF- d_8 were used to obtain lock signals. A small amount of $\text{Cr}(\text{acac})_3$ (acac = acetylacetonate) was also used as a relaxation agent for ^{29}Si nuclei. ^{29}Si NMR spectra were measured using a 45° pulse with a recycle delay of 10 s. Solid-state ^{29}Si MAS NMR spectra were recorded on a JEOL JNM CMX 400 spectrometer at a resonance frequency of 79.42 MHz with 90° pulse and a relaxation delay of 300 s at ambient temperature. The sample was put in a 4 mm zirconia rotor. High-resolution (HR) electrospray ionization mass spectrometry (ESI-MS) analysis was performed with a JEOL JMS-T100 CS instrument. Samples were dissolved in ethanol for analysis. MALDI TOF-MS spectra were recorded using a Bruker Autoflex instrument with dithranol and sodium trifluoroacetate as the matrix and cationization agents, respectively. FT-IR spectra were obtained using a JASCO FT/IR-6100 spectrometer by the KBr method. Single crystal X-ray structural analysis was performed using a Rigaku R-Axis RAPID diffractometer with graphite monochromated $\text{Cu-K}\alpha$ ($\lambda = 1.54187$ Å) radiation. All calculations were performed using the CrystalStructure crystallographic software package. The structure was solved using the charge direct method of SHELXT.¹⁸ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The refinement was performed using SHELXL Version 2014/6.¹⁹ The crystal structures were visualized using the software VESTA.²⁰ Disordered molecules and silyl groups were omitted for clarity.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

§Crystal data for **3**: $\text{C}_{15}\text{H}_{50}\text{O}_{22}\text{Si}_{12}$, $M = 931.58$, monoclinic, $a = 17.2739(5)$, $b = 10.8748(3)$, $c = 23.2168(7)$ Å, $\beta = 90.452(6)^\circ$, $V = 4361.1(2)$ Å³, $T = -150$ °C, space group Cc (#9), $Z = 4$, $D_{\text{calc}} = 1.419$ g/cm³, $F_{000} = 1960.00$, $R1$ ($I > 2.00\sigma(I)$) = 0.0620, $wR2 = 0.1350$, 35301 reflections collected, 7872 unique ($R_{\text{int}} = 0.0882$); equivalent reflections were merged.

§§Most of the peak positions of the powder XRD pattern of the crystal were consistent with those simulated from the crystal structure obtained by the single-crystal X-ray structural analysis of **3** (Figures S10a and b). However, there are some small peaks which were not consistent with the simulated pattern, suggesting the presence of a small amount of another crystalline phase, possibly containing a different solvent such as toluene. We found that recrystallization from a THF-hexane solution suppressed the formation of the undefined phase, although the obtained crystals were too small for single-crystal X-ray structural analysis (Figure S10c).

‡Crystal data for **6**: $\text{C}_{15}\text{H}_{48}\text{O}_{18}\text{Si}_{12}$, $M = 853.56$, monoclinic, $a = 19.8884(4)$, $b = 14.1218(3)$, $c = 16.2519(3)$ Å, $\beta = 101.415(7)^\circ$, $V = 4474.2(2)$ Å³, $T = -150.0$ °C, space group $C2/c$ (#15), $Z = 4$, $D_{\text{calc}} = 1.267$ g/cm³, $F_{000} = 1800.00$, $R1$ ($I > 2.00\sigma(I)$) = 0.0831, $wR2 = 0.2426$, 25058 reflections collected, 4061 unique ($R_{\text{int}} = 0.0746$); equivalent reflections were merged.

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Two types of cage-type oligosiloxanes with double-three ring (D3R) structures are modified with dimethylsilanol groups to form crystalline supramolecular assemblies.