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Selective Synthesis of *cis*–*trans*–*cis* Cyclic Tetrasiloxanes and the Formation of Their Two-Dimensional Layered Aggregates

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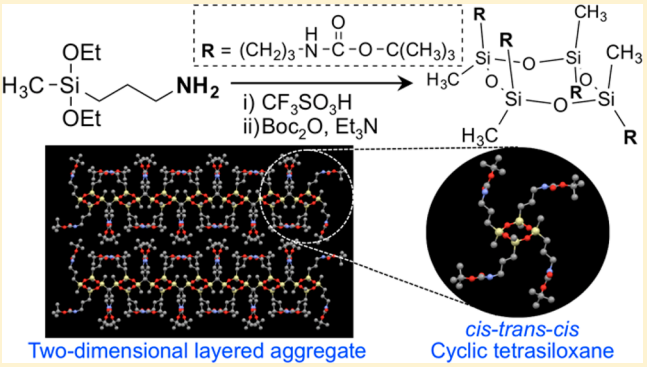
Supporting Information

ABSTRACT: In this study, a single cyclic tetrasiloxane containing propylammonium trifluoromethanesulfonate and methyl side-chain groups (Am-CyTS) was selectively prepared by the hydrolytic condensation of 3-aminopropyldiethoxymethylsilane using aqueous superacid trifluoromethanesulfonic acid. The ^{1}H NMR spectrum of Am-CyTS in D_2O exhibited a single signal assigned to a methyl group, and the ^{29}Si NMR spectrum of Am-CyTS in DMSO-d_6 also exhibited only one signal. In the matrix-assisted laser desorption ionization-time-of-flight mass spectrometry (MALDI-TOF MS) and the electrospray ionization mass spectrometry (ESI MS) analyses, the peaks corresponding to the masses of the cyclic tetrasiloxane were observed. These results indicate that Am-CyTS is a single cyclic tetrasiloxane without isomers. In addition, the result of a single-crystal X-ray structural analysis of its *tert*-butoxycarbonyl (Boc)-protected compound (Boc-CyTS) indicated the formation of a *cis*–*trans*–*cis* cyclic tetrasiloxane forming two-dimensional layered aggregates. Moreover, it was found that two-dimensional layered aggregates could be formed by drop-casting an aqueous solution of Am-CyTS and chloroform solution of Boc-CyTS onto glass substrates, as shown by powder X-ray diffraction measurements.



INTRODUCTION

Cyclic siloxanes are well-known raw materials to prepare silicones, cosmetics, dry-cleaning solvents, skin cleansing agents, emulsifiers, etc. They are generally prepared by the hydrolytic condensation of silane compounds containing two reactive groups and two organic groups. In the case of cyclic tetrasiloxanes obtained from silane compounds containing two different organic groups, they stochastically have four isomers, all-*cis*, all-*trans*, *cis*–*trans*–*cis*, and *cis*–*cis*–*trans* structures. Because it is difficult to selectively synthesize a single cyclic tetrasiloxane among these four isomers, isolation by distillation, recrystallization, and/or chromatography are generally required to obtain such a single cyclic tetrasiloxane.[1]

As a few examples of selectively synthesized single cyclic tetrasiloxanes, all-*cis* cyclic tetrasiloxanetetraols and their derivatives, for example, $[PhSi(OR)O]_4$ (R = H, Na),[2] $[i\text{-}PrSi(OH)O]_4$,[3] $[p\text{-}RC_6H_4Si(OR')O]_4$ (R = Cl, Br, CH=CH_2, CH_2Cl; R′ = Na, $SiMe_3$),[4] and $[RSi(OM)O]\cdot nL$ (R = Me, Et, Pr, CH=CH_2; M = Na, K; L = R′OH, H_2O),[5] can be prepared by single- and multistep reactions from the corresponding silane compounds. Other examples are the syntheses of *cis*–*trans*–*cis* cyclic tetrasiloxane containing isocyanato and methyl groups by the intramolecular cyclization condensation of the linear siloxane tetramer[6] and *cis*–*trans*–*cis* cyclic tetrasiloxanetetraol by isomerization of all-*cis* cyclic tetrasiloxanetetraol potassium salt.[7] Although a few synthetic methods for single cyclic tetrasiloxanes have been reported as mentioned above, the resulting compounds have unstable reactive groups and are then used as precursors for regularly structured oligomeric[8] and polymeric[1c,8e,9] silsesquioxanes. If single stereoregular cyclic tetrasiloxanes containing chemically stable organic groups can be selectively synthesized using a facile hydrolytic condensation method, it may be applied to many academic and industrial studies.

To prepare a single stereoregular cyclic tetrasiloxane, we focused on our previous studies on the facile preparation of ammonium group-containing cage-like oligosilsesquioxane (POSS) compounds.[10] Hydrolytic condensation of 3-aminopropyltrimethoxysilane (APTMS),[10a] 3-(2-aminoethylamino)-propyltrimethoxysilane (AEAPTMS),[10b] and a mixture of APTMS and AEAPTMS[10b] using aqueous superacid trifluoromethanesulfonic acid (CF_3SO_3H) resulted in the facile preparation of polyhedral cyclic compounds, that is, POSSs. On the other hand, the use of aqueous strong acids such as a hydrochloric acid (HCl) and a nitric acid (HNO_3) for the hydrolytic condensation of APTMS and AEAPTMS gave the soluble rod- and ladder-like polysilsesquioxanes.[10c,d,11] A plausible formation mechanism of POSS can be expected as follows. The protonation of amino groups of APTMS and

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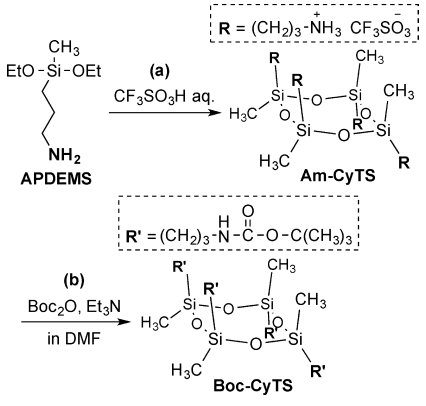
AEAPTMS with a superacid CF_3SO_3H in water easily occurs because of dissociation of proton from the superacid. Charge repulsion then occurred between these ammonium cations during the condensation reaction, resulting in the formation of the compounds containing the structures with long distance between the side-chain groups, which are cage-like (POSS) structures. In the dilute aqueous solutions of strong acids such as HCl and HNO_3, it is also expected that the same behavior occurs. However, in our synthetic method, aqueous acid solutions of APTMS and AEAPTMS were concentrated by heating in an open system for the condensation reaction. It is difficult to completely dissociate protons in high-concentrated aqueous solutions of strong acids. Therefore, the CF_3SO_3H-mediated formation of ammonium cations from APTMS or AEAPTMS is important in facilitating the preparation of these polyhedral cyclic compounds. On the basis of these results, we assumed that the hydrolytic condensation method using a combination of an amino group-containing organoalkoxysilane and a superacid may be applicable for preparing a cyclic tetrasiloxane, as described above.

In this study, when the hydrolytic condensation of 3-aminopropyldiethoxymethylsilane (APDEMS) was performed using aqueous CF_3SO_3H, we found that a *cis*–*trans*–*cis* cyclic tetrasiloxane containing propylammonium trifluoromethanesulfonate and methyl side-chain groups (Am-CyTS) was selectively prepared. In addition, Am-CyTS and its *tert*-butoxycarbonyl (Boc)-protected compound (Boc-CyTS) gave two-dimensional layered aggregates. Such low-dimensional aggregates based on cyclic siloxanes are novel inorganic supramolecules, which are expected to attract much attention in a wide range of research fields.

RESULTS AND DISCUSSION

The hydrolytic condensation of APDEMS was performed by the following procedure: the reagent was stirred in 0.5 mol L^{-1} aqueous CF_3SO_3H (CF_3SO_3H/APDEMS, mol/mol = 1.5) at room temperature for 2 h. CF_3SO_3H was played as both the reagent for the formation of ion pair with APDEMS and the catalyst of hydrolytic condensation. The resulting mixture was then heated at ca. 60 °C in an open system until the solvent completely evaporated (ca. 6 h). Next, the resulting crude product was maintained continuously at 100 °C for ca. 2 h and then washed with acetone–chloroform mixed solvent (1:1 v/v) at room temperature and dried under reduced pressure to obtain Am-CyTS in relatively high yield (ca. 82%) (Scheme 1a). Am-CyTS was soluble in polar solvents such as 2-propanol, 1-propanol, acetone, ethanol, methanol, acetonitrile, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and water.

Scheme 1. Preparation of (a) Am-CyTS and (b) Boc-CyTS



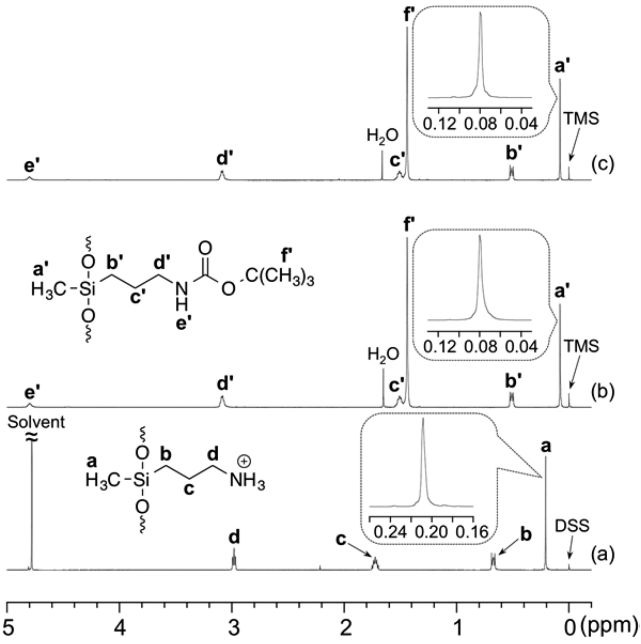


Figure 1. ^{1}H NMR spectra of (a) Am-CyTS in D_2O, (b) Boc-CyTS in $CDCl_3$, and (c) recrystallized Boc-CyTS in $CDCl_3$. Chemical shifts were referenced to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) (δ 0.0) in D_2O and tetramethylsilane (TMS) (δ 0.0) in $CDCl_3$.

The ^{1}H NMR spectrum of Am-CyTS in D_2O showed a single signal **a** assigned to a methyl group at 0.21 ppm (Figure 1a). In addition, the ^{29}Si NMR spectrum of Am-CyTS in DMSO-d_6 also showed only one signal at −19.4 ppm (Figure 2a). These results indicate that Am-CyTS is a single compound

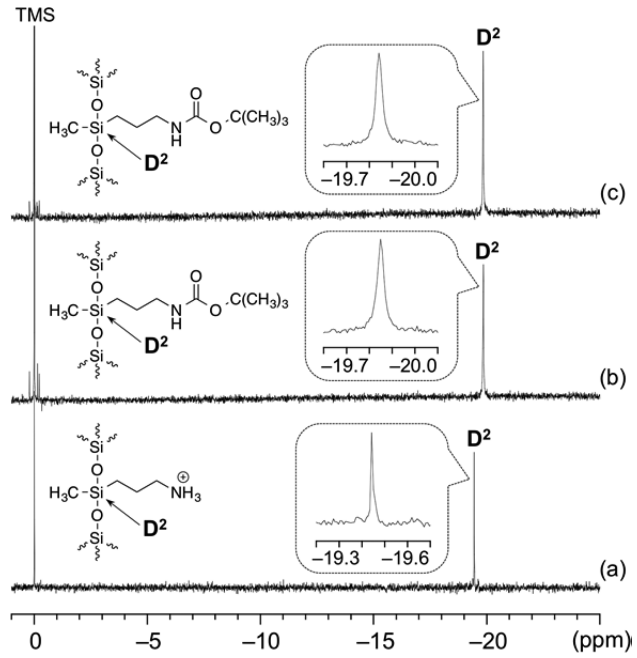


Figure 2. ^{29}Si NMR spectra of (a) Am-CyTS in DMSO-d_6, (b) Boc-CyTS, and (c) recrystallized Boc-CyTS in $CDCl_3$. Chemical shifts were referenced to TMS (δ 0.0).

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without isomers. In the matrix-assisted laser desorption ionization-time-of-flight mass spectrometry (MALDI-TOF MS) analysis of Am-CyTS, several peaks were observed, which corresponded to the mass of cyclic tetrasiloxane (Figure 3a). Furthermore, the electrospray ionization mass spectrometry (ESI MS) analysis supported the mass result from the MALDI-TOF MS.

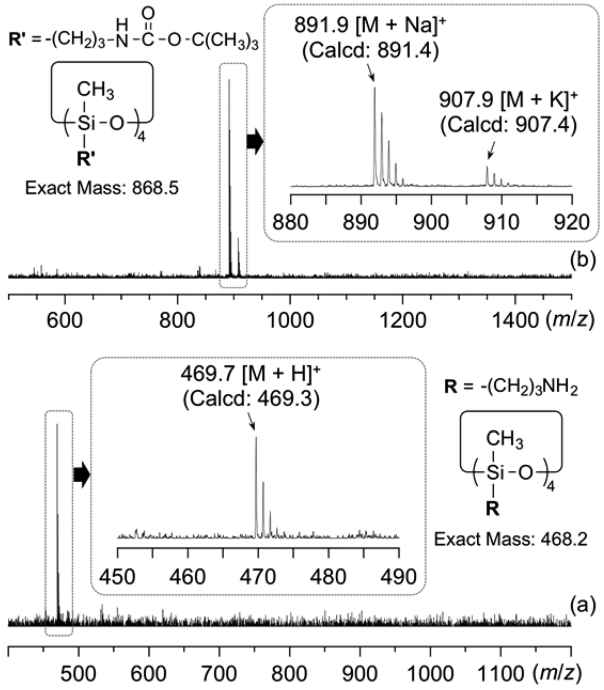

Figure 3. MALDI-TOF MS analyses of (a) Am-CyTS and (b) Boc-CyTS. The matrix was 2,5-dihydroxybenzoic acid (DHB).

Because it was difficult to prepare a single crystal of Am-CyTS for single-crystal X-ray structural analysis, the Boc-protected compound, Boc-CyTS, was prepared by the reaction of Am-CyTS with di-*tert*-butyl dicarbonate (Boc_2O) in DMF in the presence of triethylamine. Boc-CyTS was soluble in chloroform, ethyl acetate, dichloromethane, 1-butanol, 2-propanol, 1-propanol, acetone, ethanol, methanol, DMF, and DMSO. The ^{1}H NMR (Figure 1b) and ^{29}Si NMR (Figure 2b) spectra of Boc-CyTS in $CDCl_3$ also showed only single signals assigned to methyl protons **a**′ at 0.08 ppm, and the silicon atom at −19.8 ppm, indicating that the geometrical structure of the product must be maintained even after protection with Boc groups. Moreover, in the MALDI-TOF MS (Figure 3b) and ESI MS analyses of Boc-CyTS, the peaks corresponding to the masses of the cyclic tetrasiloxane were also observed.

The X-ray structural analysis of Boc-CyTS was performed. Single crystals suitable for analysis were crystallized from hexane/ethyl acetate solution of Boc-CyTS. X-ray diffraction (XRD) data were collected at −100 °C. The Boc-CyTS crystallized in the monoclinic space group $P2_1/c$. The R1 factor was 8.34%, and the structure was sufficiently refined. Crystallographic data are compiled in Table 1. Perspective drawings are shown in Figure 4.[12] The result of X-ray structural analysis of Boc-CyTS indicated the formation of a *cis*−*trans*−*cis* cyclic tetrasiloxane (Figure 4a). Figure 4b−d shows the crystal packing of Boc-CyTS. From the top view, it was found that the molecules were hexagonally arranged to form two-dimensional sheet-like aggregates by intermolecular hydrogen bonding

Table 1. Crystal Data, Data Collection, and Structure Refinement

	Boc-CyTS
chemical formula	$C_{36}H_{76}N_4O_{12}Si_4$
formula weight	869.36
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
a (Å)	17.2620(4)
b (Å)	14.7551(4)
c (Å)	10.0083(2)
β (deg)	92.0691(7)
V (Å^3)	2547.46(11)
D_{calc} (g cm^{-3})	1.133
Z	2
F(000)	944
μ(Mo Kα) (cm^{-1})	1.701
T (°C)	−100.0
no. of measured reflections	40 384
no. of unique reflections	5810
R_{int}	0.0771
R1[a] (wR2[b])	0.0834 (0.2491)

[a]$R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b]$wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$.

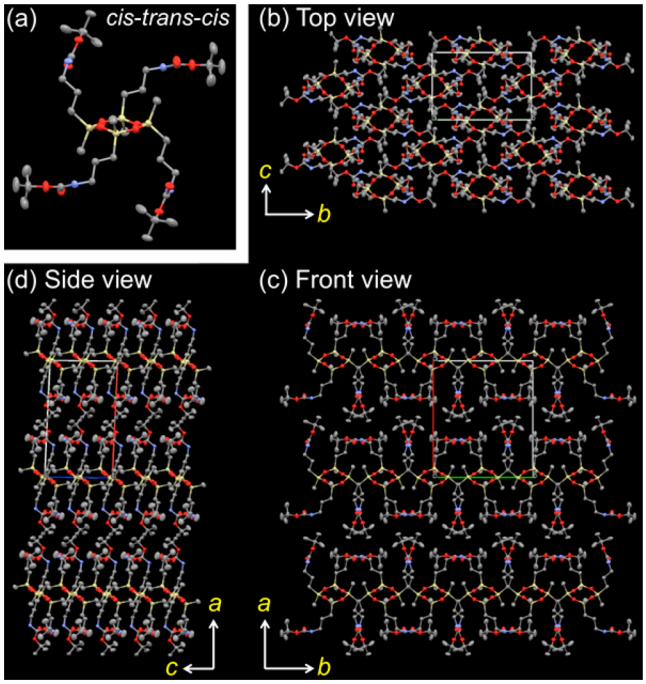

Figure 4. (a) Perspective drawings of Boc-CyTS. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. (b) Top view, (c) front view, and (d) side view of the packing diagram of Boc-CyTS.

between the urethane linkages (Figure 4b). In addition, the front and side views show a layered structure forms by stacking of two-dimensional sheet-like aggregates (Figure 4c and d). On the basis of these results, we conclude that a *cis*−*trans*−*cis* cyclic tetrasiloxane was successfully prepared and a two-dimensional layered aggregate can be formed from this cyclic tetrasiloxane.

The signal assigned to the methyl group at 0.08 ppm in the ^{1}H NMR spectrum (Figure 1c) and the signal at −19.8 ppm in the ^{29}Si NMR spectrum (Figure 2c) of recrystallized Boc-CyTS were exactly the same as those of Boc-CyTS before

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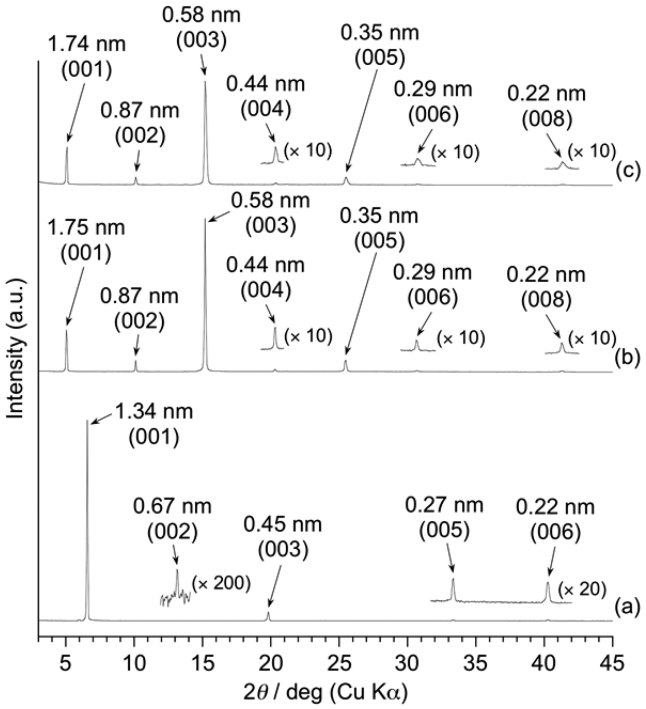

Figure 5. Powder XRD patterns of the films prepared by drop-casting of (a) aqueous solution of Am-CyTS, (b) chloroform solution of Boc-CyTS, and (c) chloroform solution of recrystallized Boc-CyTS. The amount of each product on the glass was ca. 1.0 mg cm^{-2}.

recrystallization (Figures 1b and 2b, respectively). These results indicated that a single (*cis*−*trans*−*cis*) cyclic tetrasiloxane was obtained even before recrystallization.

It was found that two-dimensional layered aggregates could be formed by drop-casting chloroform solutions of Boc-CyTS samples before and after recrystallization onto glass substrates. The powder XRD patterns of the resulting cast films exhibited diffraction peaks assigned to a lamellar phase satisfying Bragg's law, indicating the formation of a two-dimensional layered structure (Figure 5b and c). In addition, the XRD pattern of the film prepared by drop-casting aqueous solution of Am-CyTS onto a glass substrate also showed diffraction peaks assigned to a lamellar phase (Figure 5a). These results suggested that Am-CyTS also formed a two-dimensional layered aggregate, although the detailed packing structure of Am-CyTS was not determined because single crystals could not be obtained. On the basis of these results, we found that Am-CyTS and Boc-CyTS gave two-dimensional layered aggregates even by the simple process of drop-casting.

For comparison, we investigated the hydrolytic condensation of APDEMS using aqueous strong acid such as HCl in place of aqueous CF_3SO_3H. Consequently, the cyclic tetrasiloxane was not obtained; however, polymeric siloxane (Am-PS) was generated. The weight-average molecular weight and molecular weight distribution of its Boc-protected compound (Boc-PS) were estimated by gel permeation chromatography (GPC) to be 38.4k and 2.07, respectively, indicating that use of aqueous superacid CF_3SO_3H is essential to prepare a single cyclic tetrasiloxane as described above.

As is the case with ammonium group-containing POSSs as we previously reported,[10] the protonation of amino group of APDEMS with a superacid CF_3SO_3H occurs easily in water. Consequently, charge repulsion occurred between these ammonium cations during the condensation reaction, resulting in the formation of the compound containing the structure with long distance between the side-chain groups, which is a *cis*−*trans*−*cis* cyclic tetrasiloxane. In the present study, aqueous acid solutions of APDEMS were concentrated by heating in an open system for the condensation reaction. It is difficult to completely dissociate protons in high-concentrated aqueous solutions of strong acids such as HCl. Therefore, a combination of APDEMS with the superacid is important to obtain a cyclic tetrasiloxane.

■ CONCLUSION

A single cyclic tetrasiloxane containing propylammonium trifluoromethanesulfonate and methyl side-chain groups, Am-CyTS, was selectively prepared by the hydrolytic condensation of APDEMS using aqueous superacid CF_3SO_3H. The analysis results of ^1H NMR, ^{29}Si NMR, MALDI-TOF MS, and ESI MS of Am-CyTS indicated the preparation of a single cyclic tetrasiloxane without isomers. In addition, the result of single-crystal X-ray structural analysis of its Boc-protected compound, Boc-CyTS, indicated the formation of a *cis*−*trans*−*cis* cyclic tetrasiloxane affording two-dimensional layered aggregates. Moreover, it was found that two-dimensional layered aggregates could be formed by drop-casting an aqueous solution of Am-CyTS and chloroform solution of Boc-CyTS onto glass substrates, which were evaluated by powder XRD measurements. The present cyclic tetrasiloxanes can be expected in many applications, for example, efficient ion or proton conductors, due to the presence of ionic side-chain groups with two-dimensional regular arrays.

■ EXPERIMENTAL SECTION

Materials. All reagents and solvents were commercially available and used without further purification.

Preparation of Am-CyTS. Aqueous CF_3SO_3H (0.5 mol L^{-1}, 25.0 mL, 12.5 mmol) was added to APDEMS (purity: 97%, 1.644 g, 8.3 mmol) with stirring at room temperature. The resulting solution was further stirred at room temperature for 2 h and then heated at ca. 60 °C in an open system until the solvent completely evaporated (ca. 6 h). Subsequently, the crude product was maintained at 100 °C for ca. 2 h, and then an acetone−chloroform mixed solvent (1:1 v/v, ca. 100 mL) was added at room temperature. The insoluble part was isolated by filtration, washed with this mixed solvent, and then dried under reduced pressure at room temperature to yield 1.820 g of a white-powdered Am-CyTS (yield: ca. 82%; the ideal chemical formula of the repeating unit of this product $[SiO(CH_3)(CH_2)_3NH_3^+ \cdot CF_3SO_3^-$, FW = 267.3] was used for the calculation). ^1H NMR (600 MHz, D_2O): δ 2.98 (t, J = 7.80 Hz, 2H, NH_3CH_2-), δ 1.73 (m, 2H, $NH_3CH_2CH_2CH_2Si-$), δ 0.67 (t, J = 8.70 Hz, 2H, $-CH_2Si-$), δ 0.21 (s, 3H, CH_3Si-). ^{29}Si NMR (120 MHz, DMSO-d_6): δ −19.4 (D^2). MALDI-TOF MS: calcd for $[C_{16}H_{44}N_4O_4Si_4]$ 468.2; found m/z 469.7 $[M + H]^+$. ESI MS: calcd for $[C_{16}H_{44}N_4O_4Si_4]$ 468.2; found m/z 469.3 $[M + H]^+$. Anal. Calcd for $C_{20}H_{48}N_4O_{16}F_{12}Si_4S_4$: C, 22.47; H, 4.53; N, 5.24. Found: C, 22.34; H, 4.67; N, 5.12. Melting temperature (T_m) 309.5 °C.

Preparation of Boc-CyTS. Triethylamine (purity: 99%, 0.920 g, 9.0 mmol) and Boc_2O (purity: 97%, 2.025 g, 9.0 mmol) were successively added to dehydrated DMF solution (6.0 mL) of Am-CyTS (0.802 g, 3.0 mmol unit) under vigorous stirring at room temperature. After the mixture was stirred further for 10 min, the solvent was removed using a rotary evaporator. Acetonitrile (20 mL) was added to the resulting solid product, and the insoluble part was isolated by filtration. The product then was washed with acetonitrile (ca. 20 mL × 2) and dried under reduced pressure at room temperature to yield 0.557 g of a white powder Boc-CyTS (yield: ca. 85%; the ideal chemical formula of the repeating unit of this product

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$[SiO(CH_3)(CH_2)_3NHC(=O)OC(CH_3)_3$, FW = 217.3] was used for the calculation). ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.80 (s, 1H, −NH−), δ 3.08 (br, 2H, $-NHCH_2-$), δ 1.51 (br, 2H, $-NHCH_2CH_2CH_2Si-$), δ 1.44 (s, 9H, $-OC(CH_3)_3$), δ 0.51 (t, J = 8.40 Hz, 2H, $-CH_2Si-$), δ 0.08 (s, 3H, CH_3Si-). ^{29}Si NMR (120 MHz, $CDCl_3$): δ −19.8 (D^2). MALDI-TOF MS: calcd for $[C_{36}H_{76}N_4O_{12}Si_4]$ 868.5; found m/z 891.9 $[M + Na]^+$ and m/z 907.9 $[M + K]^+$. ESI MS: calcd for $[C_{36}H_{76}N_4O_{12}Si_4]$ 868.5; found m/z 891.4 $[M + Na]^+$. Anal. Calcd for $C_{36}H_{76}N_4O_{12}Si_4$: C, 49.74; H, 8.81; N, 6.44. Found: C, 49.56; H, 8.88; N, 6.36. T_m 162.1 °C.

Preparation of Single Crystals of Boc-CyTS. Boc-CyTS (0.100 g) was suspended in *n*-hexane (3.0 mL), and this suspension was stirred at ca. 50 °C. Ethyl acetate (ca. 5.120 g) was added to the suspension until Boc-CyTS dissolved in this mixed solvent. The clear solution then was allowed to stand at room temperature for 1−2 days. Several single crystals suitable for X-ray structural analysis were taken out from the obtained sea urchin-like polycrystal.

Measurements. The ^{1}H and ^{29}Si NMR spectra were recorded using a JEOL ECA-600 spectrometer. The MALDI-TOF MS measurements were performed using a Shimadzu Voyager Biospectrometry Workstation Ver. 5.1 with DHB as the matrix using the positive ion mode. The ESI MS measurements were performed using a Shimadzu LCMS-IT-TOF under positive ion mode. The single-crystal X-ray structural analysis was performed using a Rigaku RAXIS RAPID II imaging-plate diffractometer with graphite-monochromated Mo Kα radiation and the ω scan mode. The powder XRD measurements were performed at a scanning speed of 2θ = 3.0° min^{-1} using an X'Pert Pro diffractometer (PANalytical) with Ni-filtered Cu Kα radiation (λ = 0.15418 nm). Average molecular weights were determined using GPC with polystyrene standards. These GPC analyses were performed using a HITACHI pump L-2130 and a HITACHI RI detector L-2490 on Shodex GPC KF-805L (bead size, 10 μm; measurable molecular weight range, 10^2 to 4×10^6) and KF-803L columns (bead size, 6 μm; measurable molecular weight range, 10^2 to 7×10^4). Chloroform was used as the eluent and pumped through the system at a flow rate of 1.0 mL min^{-1} at 40 °C. The CHN elemental analyses were performed using a CE Instruments EA1110 CHN elemental analyzer. The differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-601 plus at a heating rate of 10 °C min^{-1} under an atmosphere of flowing nitrogen (100 mL min^{-1}). The T_m values were determined from the temperatures of the endotherm peaks in the DSC curves.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallography data for Boc-CyTS in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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