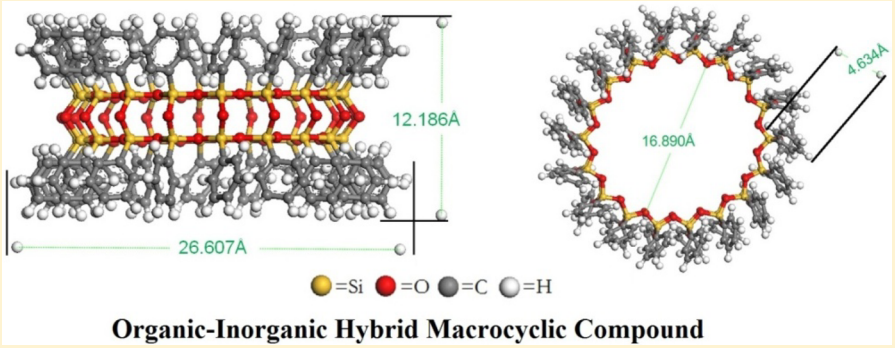
Inorganic Chemistry
Cite This: Inorg. Chem. 2018, 57, 3883−3892
Article
pubs.acs.org/IC

Preparation and Characterization of Organic−Inorganic Hybrid Macrocyclic Compounds: Cyclic Ladder-like Polyphenylsilsesquioxanes

Wenchao Zhang, Xiaoxia Wang, Yiwei Wu, Zhi Qi, and Rongjie Yang*

National Engineering Technology Research Center of Flame Retardant Material, School of Materials, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100081, P. R. China

Supporting Information



ABSTRACT: Organic−inorganic hybrid macrocyclic compounds, cyclic polyphenylsilsesquioxanes (cyc-PSQs), have been synthesized through hydrolysis and condensation reactions of phenyltrichlorosilane. Structural characterization has revealed that cyc-PSQs consist of a closed-ring double-chain siloxane inorganic backbone bearing organic phenyl groups. The cyc-PSQ molecules have been simulated and structurally optimized using the Forcite tool as implemented in Materials Studio. Structurally optimized cyc-PSQs are highly symmetrical and regular with high stereoregularity, consistent with the dimensions of their experimentally derived structures. Thermogravimetric analysis showed that these macrocyclic compounds have excellent thermal stability. In addition to these perfectly structured compounds, macrocyclic compounds with the same ring ladder structure but bearing an additional Si−OH group, cyc-PSQs-OH, have also been synthesized. A possible mechanism for the formation of the closed-ring molecular structures of cyc-PSQs and cyc-PSQs-OH is proposed.

1. INTRODUCTION

In organic chemistry, a macrocyclic compound is defined as any molecule containing a ring of 12 or more atoms, while in coordination chemistry it is more narrowly defined as a cyclic molecule with three or more potential donor atoms. Macrocyclic organic compounds have broad application prospects in the fields of molecular recognition, supramolecular self-assembly, bionic research, and drug carriers because of their unique structural characteristics and physical and chemical properties.[1,2] Therefore, the synthesis and application of macrocyclic organic compounds has been extensively studied. Besides the traditional three generations of macrocyclic compounds shown in Figure 1 (crown ethers,[3] cyclodextrins,[4] and calixarenes[5]), additional macrocyclic organic compounds such as cucurbiturils,[6] porphyrins,[7] phthalocyanines, cyclic peptides, and pillararenes[8] have gradually become established. However, in the present research we introduce novel macrocyclic compounds based on organic−inorganic hybrid molecules, polysilsesquioxanes (PSQs).

PSQs are organic−inorganic hybrid materials with the general formula $(RSiO_{1.5})_n$ that are synthesized from silanes bearing halogen or alkoxy groups through a hydrolysis−condensation process. These materials show a myriad of advantageous properties, including excellent thermal stability, low dielectric constant, good mechanical properties, chemical resistance, and biocompatibility.[9,10] Moreover, metal-containing silsesquioxanes of polyhedral geometry, also called cage-like metallasilsesquioxanes (CLMSs), are an intensively studied class of molecular materials because of their unique ability to form unprecedented molecular architectures and to exhibit high activity in different catalytic applications.[11−14] To date, polysilsesquioxane compounds have been assigned four generally accepted structures, as shown in Figure 1: randomly structured branched sols, partial cage structures,[15] cage-structured polyhedral oligomeric silsesquioxanes (POSS), and linear ladder-structured polysilsesquioxanes (L-PSQs).[10,16,17] POSS generally have a three-dimensional cage structure or a partial cage structure. L-PSQs are generally polymeric analogues with a linear, double-stranded siloxane backbone.[18]

Received: January 4, 2018
Published: March 20, 2018

Downloaded via LBRY FOR NATURAL SCIENCES RAS on August 27, 2018 at 10:29:35 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

© 2018 American Chemical Society

DOI: 10.1021/acs.inorgchem.7b03264
Inorg. Chem. 2018, 57, 3883−3892

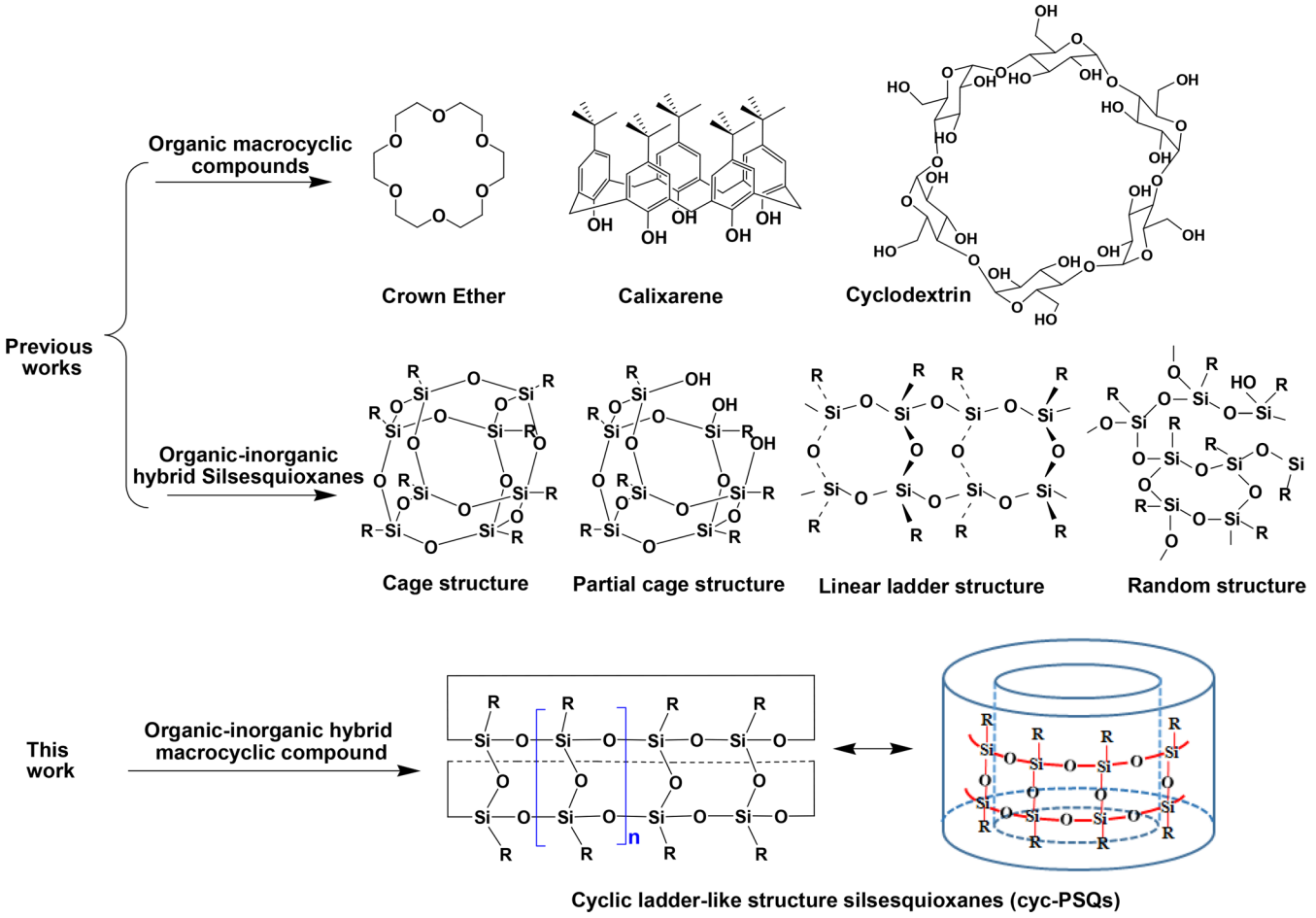
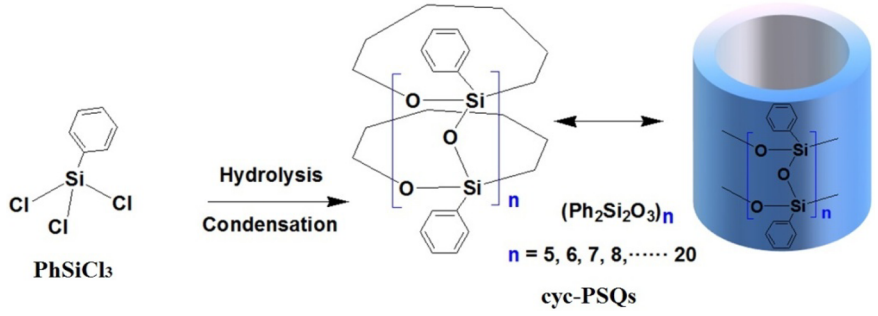


Figure 1. Structures of organic macrocyclic compounds, organic−inorganic hybrid silsesquioxanes, and organic−inorganic hybrid macrocyclic compounds.

Scheme 1. Synthesis and Formulas of Cyclic Ladder-like Polyphenylsilsesquioxanes (cyc-PSQs)



In 1960, Brown et al.[19] first prepared L-PSQ from phenyltrichlorosilane ($PhSiCl_3$) by hydrolysis and polycondensation. Thereafter, various researchers synthesized L-PSQs through equilibration polymerization. Pavlova[20] obtained L-PSQs of different molecular weights by hydrolysis equilibration of $PhSiCl_3$ under catalysis by KOH in different solvents. Zhang and co-workers[21−23] have carried out a great deal of research on the synthesis and characterization of L-PSQs bearing different organic groups, which modulate their solubility, and proposed a method of stepwise coupling polymerization. Baek and co-workers[18] developed a facile synthesis of structurally controlled L-PSQs through fine-tuning of the reaction conditions for an aqueous base-catalyzed hydrolysis−polycondensation procedure. The obtained L-PSQs were either unsubstituted or bore several different organic groups, such as phenyl, methyl, vinyl, and side chains with amino terminal groups.[21,22,24] However, to the best of our knowledge, all of the hitherto-characterized L-PSQs have been linear with a double-stranded siloxane backbone.

Our previous work has been devoted to the synthesis of functional L-PSQs. In this research, cyclic ladder-like polyphenylsilsesquioxanes (cyc-PSQs) have been synthesized through the hydrolysis and polycondensation of $PhSiCl_3$ under catalysis by tetramethylammonium hydroxide with the assistance of magnesium chloride. In the cyc-PSQ product, the ladder-like double-stranded siloxane backbone clearly has a closed-ring shape, making it very different from the randomly structured, cage-structured, and linear ladder-structured poly-

DOI: 10.1021/acs.inorgchem.7b03264
Inorg. Chem. 2018, 57, 3883−3892

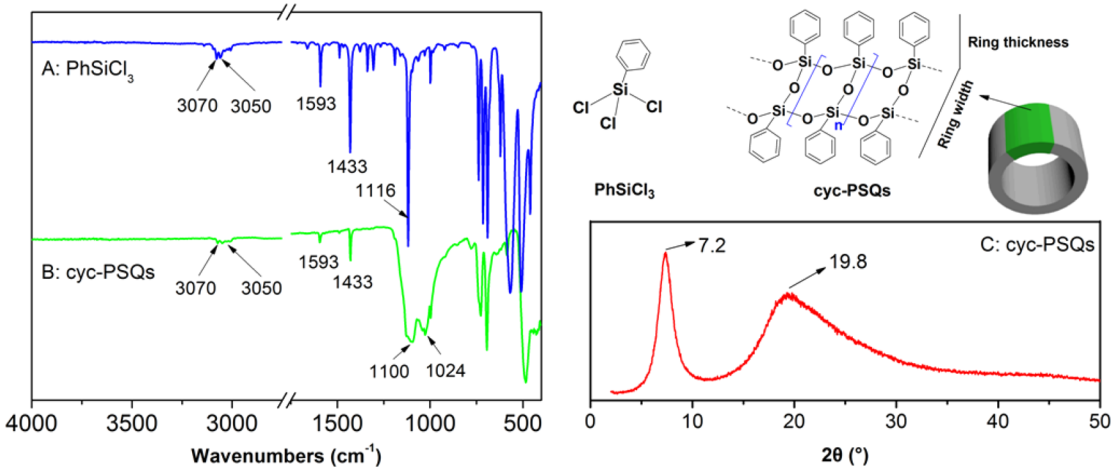


Figure 2. FT-IR spectra of $PhSiCl_3$ (A) and cyc-PSQs (B) and XRD pattern of cyc-PSQs (C).

silsesquioxanes shown in Figure 1. Indeed, cyc-PSQs may be viewed as belonging to a new class of macrocyclic compounds with excellent thermal stability that may find specific applications in supramolecular chemistry.

2. EXPERIMENTAL SECTION

Materials. $PhSiCl_3$ (>99%) was purchased from Yuanyong Organosilicon Factory (Dalian, China). Tetramethylammonium hydroxide ($(CH_3)_4NOH$, 98%) was purchased from Beijing Chaofu Chemical Experimental Factory (Beijing, China). Magnesium chloride ($MgCl_2$) was purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Benzene, methanol, ethanol, and hexane were purchased from Beijing Chemical Reagent Co. and were used without further purification. Methyltrichlorosilane ($(CH_3)SiCl_3$, CP), dimethyldichlorosilane ($(CH_3)_2SiCl_2$, CP), and trimethylchlorosilane ($(CH_3)_3SiCl$, CP) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Synthesis of cyc-PSQs. The synthetic route to cyc-PSQs is shown in Scheme 1. In a 500 mL round-bottom flask, a solution of $PhSiCl_3$ (21.2 g) in benzene (100 mL) was hydrolyzed by the dropwise addition of water (200 mL) at 0 °C. $MgCl_2$ (2.56 g) was dissolved in water (10 mL) to prepare an aqueous solution. The hydrolysate of $PhSiCl_3$, as the organic phase, was separated and mixed with the aqueous solution of $MgCl_2$ by stirring. The mixture was heated to 80 °C, whereupon a 50 wt % solution of $(CH_3)_4NOH$ in methanol was added. The condensation reaction was allowed to proceed for 24 h under vigorous stirring. Thereafter, the mixture was washed with deionized water (3 × 200 mL). CH_3SiCl_3 (2 g) was added to the solution at 50 °C. After 30 min, $(CH_3)_2SiCl_2$ (3 g) was also added. The temperature was held at 50 °C for 6 h. After completion of the reaction, a very small amount of solid byproducts (the cross-linked products formed in the reaction) was separated by filtration. Then a white precipitate was obtained upon addition of ethanol to the filtrate. After filtration, the solvent was removed under vacuum, and the crude product was purified by short column chromatography (hexane/ethyl acetate, 5:2) to afford cyc-PSQs in 32% yield. FT-IR (ATR, cm^{-1}): 3072−3014 (aromatic C−H stretching), 1593 and 1433 (aromatic C−C stretching), 724 (aromatic C−H out-of-plane bending), 691 (phenyl ring C−C out-of-plane deformation). XRD (2θ, deg): 7.2 and 19.8. ^1H NMR ($CDCl_3$, δ, ppm, TMS): 6.40−7.88 (6H, H in phenyl group). ^{13}C NMR ($CDCl_3$, δ, ppm, TMS): 127.55, 130.13, 131.27, 133.96. ^{29}Si CP-MAS NMR (δ, ppm): −78.6. MALDI-TOF MS ($[M + Na]^+$, $(Ph_2Si_2O_3)_n$): 1313.7 (n = 5), 1571.5 (n = 6), 1829.9 (n = 7), 2087.3 (n = 8), 2345.6 (n = 9), 2603.2 (n = 10), 2862.0 (n = 11), 3118.9 (n = 12), 3377.2 (n = 13), 3635.4 (n = 14), 3893.5 (n = 15), 4151.3 (n = 16), 4409.7 (n = 17), 4667.1 (n = 18), 4925.9 (n = 19).

Synthesis of the cyc-PSQs/cyc-PSQs-OH Polydisperse Mixture. In a 1 L round-bottom flask, a solution of $PhSiCl_3$ (42.4 g) in benzene (200 mL) was hydrolyzed by the dropwise addition of water (400 mL) at 0 °C. $MgCl_2$ (5.2 g) was dissolved in water (20 mL) to prepare an aqueous solution. The hydrolysate of $PhSiCl_3$, as the organic phase, was separated and mixed with the aqueous solution of $MgCl_2$ by stirring. The mixture was heated to 80 °C, whereupon a 50 wt % solution of $(CH_3)_4NOH$ in methanol was added. The condensation reaction was allowed to proceed for 24 h under vigorous stirring. When the condensation reaction was complete, a very small amount of cross-linked solid byproducts was separated by filtration. The desired products were in the organic-phase filtrate. The filtrate was then poured into a large volume of ethanol, whereupon the polydisperse mixture of products was precipitated as a white solid. After filtration, the products were washed with hexane and dried in a vacuum oven at 100 °C. The mass of the final cyc-PSQs/cyc-PSQs-OH polydisperse mixture was 19.6 g, corresponding to a 76.0% yield. MALDI-TOF MS ($[M + Na]^+$, $(Ph_2Si_2O_3)_n$): 1313.5 (n = 5), 1571.1 (n = 6), 1829.4 (n = 7), 2087.7 (n = 8), 2347.3 (n = 9), 2603.1 (n = 10), 2861.1 (n = 11), 3119.0 (n = 12), 3377.6 (n = 13), 3635.5 (n = 14), 3893.1 (n = 15), 4151.7 (n = 16), 4409.9 (n = 17); ($[M + Na]^+$, $(Ph_2Si_2O_3)_m$O−PhSi−OH): 1449.9 (m = 5), 1707.3 (m = 6), 1965.7 (m = 7), 2223.1 (m = 8), 2481.5 (m = 9), 2739.9 (m = 10), 2998.0 (m = 11), 3256.3 (m = 12), 3514.7 (m = 13), 3772.8 (m = 14), 4031.0 (m = 15), 4289.1 (m = 16), 4546.9 (m = 17).

Method for Derivatizing Si−OH Groups. To identify the number of Si−OH groups, the obtained polydisperse mixed product of cyc-PSQs and cyc-PSQs-OH (1 g) was dissolved in benzene (23 mL). The solution was heated to 50 °C, whereupon $(CH_3)_3SiCl$ (0.08 g) was added along with several drops of triethylamine. The mixture was maintained at 50 °C for 6 h. After completion of the reaction, a white precipitate was obtained upon the addition of ethanol, which was washed with ethanol and then dried in a vacuum oven at 100 °C.

Characterization. Matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF MS) was performed on a Bruker Germany BIFLEX III spectrometer equipped with a pulsed nitrogen laser (λ = 337 nm, pulse width = 3 ns, and average power = 5 mW at 20 Hz). The extraction voltage in the TOF analyzer was 20 kV, and ions were obtained by irradiation at just above the threshold laser power (ca. one-third of the average laser power). The samples were examined in positive-ion mode. Usually, 50 scans were accumulated. α-Cyano-4-hydroxycinnamic acid was used as the matrix, and the salts were a mixture of NaCl and KCl.

Gel-permeation chromatography (GPC) in tetrahydrofuran (THF) was performed using three Waters gel columns (HT3, HT4, and HT5), a Waters 1515 isocratic HPLC pump, and a Waters 2414 refractive index detector. THF was used as the eluent at a flow rate of 1.00 mL/min. Polystyrene standards were used for the calibration.

FT-IR spectra with a resolution of 4 cm^{-1} were recorded on a Nicolet USA 6700 IR spectrometer by accumulating 32 scans.

DOI: 10.1021/acs.inorgchem.7b03264
Inorg. Chem. 2018, 57, 3883−3892

^{29}Si cross-polarization magic-angle spinning (CP-MAS) NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer with a 7.5 mm CP-MAS probe in air at 298 K with a contact time of 4 ms and a spin rate of 10 kHz with an automated spinner.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer operated in Fourier-transform mode. $CDCl_3$ was used as the solvent with tetramethylsilane as an internal reference.

X-ray diffraction (XRD) analysis was carried out over the 2θ range 5−60° with an X'Pert PRO MPD diffractometer system (PANalytical, Tokyo, Japan). Cu Kα_1 radiation (λ = 0.154 nm) was used with a copper target.

Thermogravimetric analysis (TGA) was performed with a 209 F1 thermal analyzer (Netzsch, Selb, Germany) at a heating rate of 10 °C/min under a nitrogen atmosphere over the temperature range from 40 to 850 °C.

RESULTS AND DISCUSSION

Whereas traditional macrocyclic compounds, such as crown ethers,[3] cyclodextrins,[4] and calixarenes,[5] have a single chain forming the ring, cyc-PSQs have a double-stranded siloxane inorganic backbone bearing organic phenyl groups. Compared with L-PSQs, cyc-PSQs have a ring structure of variable pore size, and their structures are also more complete and regular. FT-IR analysis is a powerful tool for evaluating well-defined siloxane structures such as those of POSS and L-PSQs. The FT-IR spectra of $PhSiCl_3$ and cyc-PSQs are shown in Figure 2A,B. The cyc-PSQ structure gives rise to two absorption peaks at 1100 and 1024 cm^{-1}, which can be assigned to asymmetric stretching of the Si−O−Si groups in the horizontal (−Si−O−Si−) and vertical (−Si−O−Si−Ph) directions of the siloxane bond.[25,26] It is reported that the FT-IR spectra of random polysilsesquioxanes and POSS feature only one strong absorbance peak in the 1000−1200 cm^{-1} region, but L-PSQs with a perfect ladder-like structure show two peaks.[27,28] The aforementioned peaks at 1100 and 1024 cm^{-1} support the presence of ladder-like double-stranded siloxane backbones in the obtained cyc-PSQs. Furthermore, there are the characteristic peaks at 3072−3014 cm^{-1} (aromatic C−H stretching), 1593 and 1433 cm^{-1} (aromatic C−C stretching), 724 cm^{-1} (aromatic C−H out-of-plane bending), and 691 cm^{-1} (phenyl ring C−C out-of-plane deformation), as befits the presence of phenyl groups in the cyc-PSQs.[29] However, no absorbance for the Si−OH group in the 3000−3500 cm^{-1} region could be detected, which means that there were no Si−OH groups in cyc-PSQs.

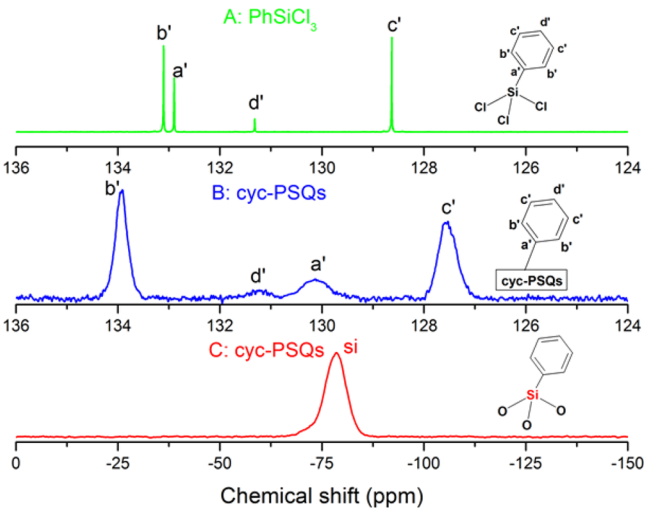


Figure 3. ^{13}C NMR spectra of $PhSiCl_3$ (A) and cyc-PSQs (B) and ^{29}Si CP-MAS NMR spectrum of cyc-PSQs (C).

XRD is another important tool for evaluating well-defined siloxane structures. Figure 2C presents the XRD pattern of the synthesized cyc-PSQs, in which two characteristic diffraction peaks are apparent. The first sharp peak at about 7.2° (12.4 Å) and the second peak at about 19.8° (4.6 Å) are used to assign the structures of cyc-PSQs. According to previous studies, there are two opinions on the origin of the first peak. The first opinion is that the diffraction peak at 7.2° can be assigned to the chain-to-chain distance.[18,30] The second opinion is that this diffraction peak may be attributed to the ladder width of the superstructure.[25,27] In this research, the first diffraction peak at about 7.2° (12.4 Å) seemingly corresponds to the average ring width in the cyclic ladder-like superstructure. For the second diffraction peak at 19.8° (4.6 Å), assignments in the literature are very consistent and indicate that it may be considered as the average ring thickness of the cyc-PSQs.[18,25] The XRD results are also comparable with the patterns presented in previous L-PSQ studies and imply that the ladder-like backbones in the synthesized cyc-PSQs are highly complete and ordered.

The ^{13}C NMR spectra of $PhSiCl_3$ and cyc-PSQs are shown in Figure 3A,B. Compared with the ^{13}C NMR spectrum of $PhSiCl_3$, the chemical shifts of C atoms a′, b′, and c′ of cyc-PSQs show obvious changes. In particular, the signal of the C

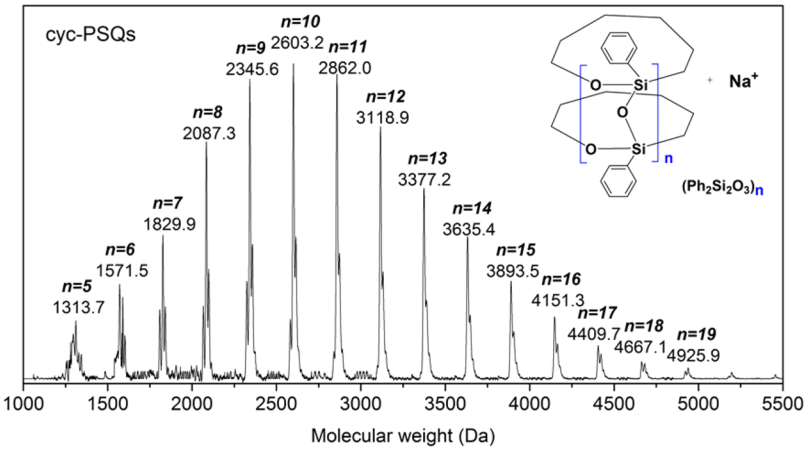


Figure 4. MALDI-TOF mass spectrum of cyc-PSQs.

DOI: 10.1021/acs.inorgchem.7b03264
Inorg. Chem. 2018, 57, 3883−3892

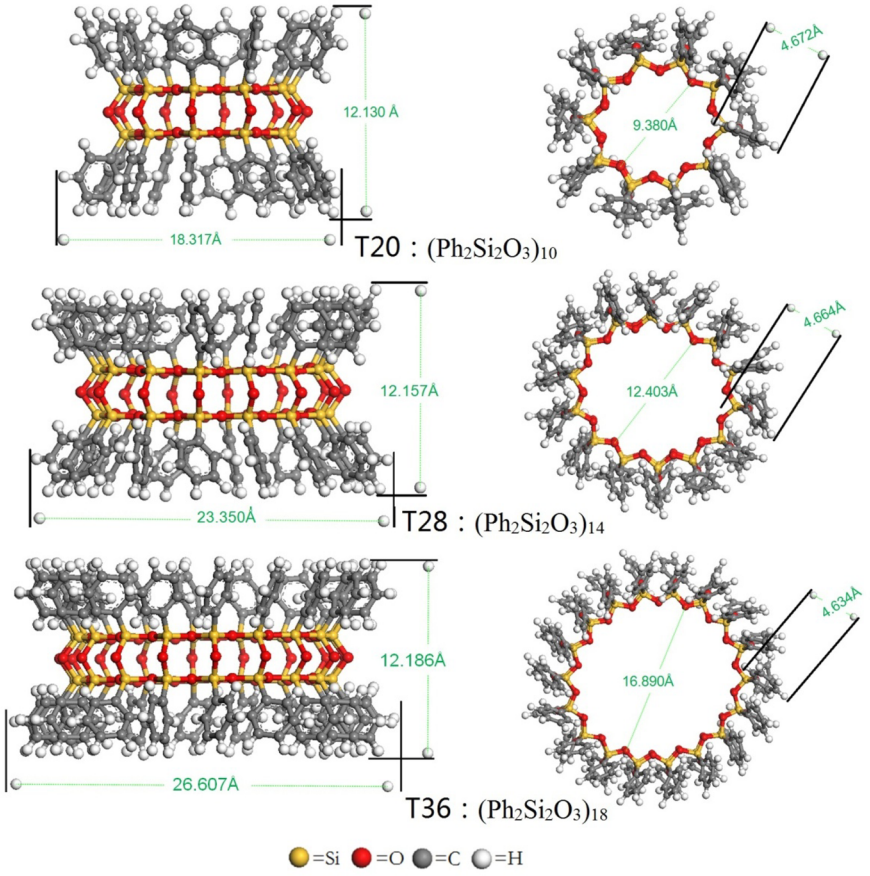


Figure 5. Theoretically optimized structures of T20, $(Ph_2Si_2O_3)_{10}$; T28, $(Ph_2Si_2O_3)_{14}$; and T36, $(Ph_2Si_2O_3)_{18}$.

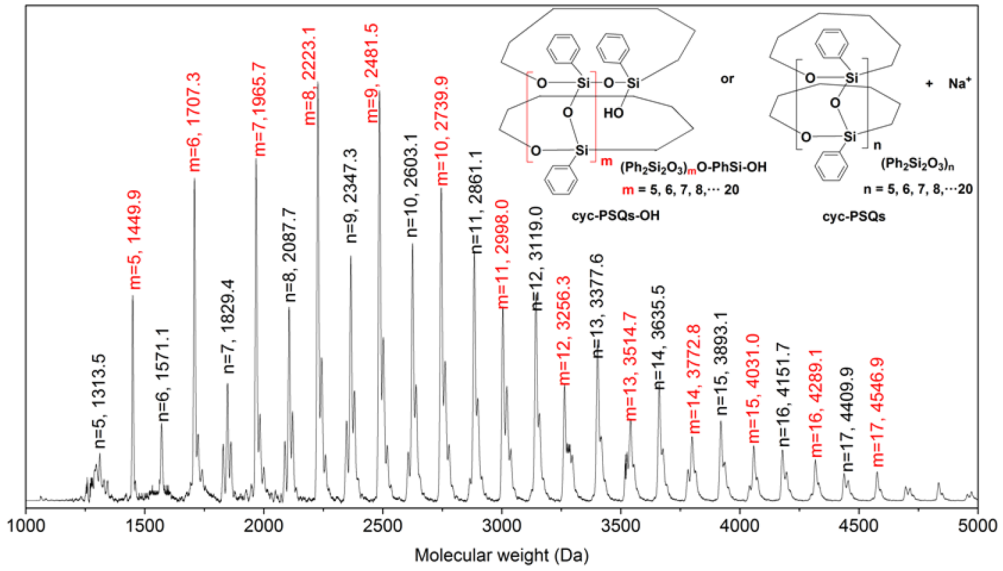


Figure 6. MALDI-TOF mass spectrum of the cyc-PSQs/cyc-PSQs-OH polydisperse mixture.

atom labeled a′ in the C−$SiCl_3$ group is shifted from 132.89 to 130.12 ppm. Feher and Budzichowski[31] suggested that the cage offers electron-withdrawing character equivalent to that of a CF_3 group. Thus, the largest downfield shift of the C atom labeled a′ can be attributed to the electron-withdrawing character of the cyc-PSQ ring. The broad peaks assigned to carbon atoms a′, b′, c′, and d′ suggest that cyc-PSQs have variable molecular weights with a wide distribution. This is also implied by the broad peaks in the ^{1}H NMR spectrum of cyc-PSQs in SI Figure 1.

^{29}Si CP-MAS NMR spectroscopy can provide insight into the regularity of PSQ chains. The chemical shifts of the silicon atoms in PSQ are denoted using the traditional terminology "T*n*", where "*n*" indicates the number of oxygen bridges to other silicon atoms.[28,32,33] Figure 3C show the solid-state ^{29}Si CP-MAS NMR spectrum of cyc-PSQs, which features a single

DOI: 10.1021/acs.inorgchem.7b03264
Inorg. Chem. 2018, 57, 3883−3892

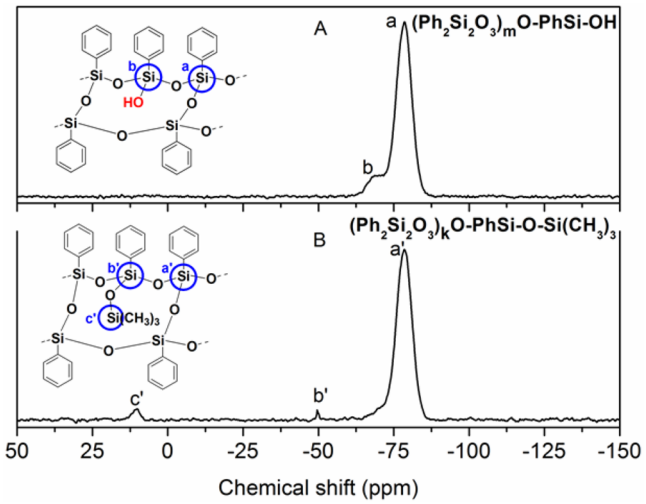


Figure 7. ^{29}Si CP-MAS NMR spectra of $(Ph_2Si_2O_3)_m$O−PhSi−OH (A) and $(Ph_2Si_2O_3)_k$O−PhSi−O−Si$(CH_3)_3$ (B).

peak at −78.7 ppm due to T3 units [PhSi(O−)$_3$].[25] This single broad peak due to T3 units showed an exceedingly high similarity of the chemical environments of the silicon atoms, which can generally only be seen in well-defined POSS. However, the broad peak shape can be ascribed to its high molecular weight and wide molecular weight distribution.[28,30]

MALDI-TOF MS analysis yields the molecular ion peaks of cyc-PSQs, providing further structural information.[34,35] From the regularity of the molecular structure of cyc-PSQs in Figure 4, it is readily apparent that the difference in molecular weights between peaks n and n + 1 is about 258, corresponding to the structural unit "$Ph_2Si_2O_3$". In Figure 4, the possible molecular formulas were calculated, and each molecular ion peak was assigned. The molecular formulas of cyc-PSQs correspond to the series $(Ph_2Si_2O_3)_n$ (n = 5, 6, ···, 20), that is, integral multiples of the cyclic ladder structure. Furthermore, GPC results for cyc-PSQs are presented in SI Figure 2, which shows a unimodal peak with M_n = 2730 and M_w/M_n = 1.33. These GPC results are consistent with the results of the MALDI-TOF MS analysis above.

Furthermore, the molecular formulas $(Ph_2Si_2O_3)_n$ (n = 5, 6, ···, 20) were simulated and structurally optimized using the Forcite tool as implemented in Materials Studio. For n = 10, 14, and 18, the structurally optimized cyc-PSQs are highly symmetrical and regular with high stereoregularity (Figure 5). The widths of the ladder-like structures of $(Ph_2Si_2O_3)_{10}$, $(Ph_2Si_2O_3)_{14}$, and $(Ph_2Si_2O_3)_{18}$ are similar at around 12.1 Å, and their thicknesses are similar at around 4.6 Å (Figure 5). The widths and thicknesses of the structurally optimized cyc-PSQs are very similar to those calculated from XRD analysis (average width = 12.4 Å; average thickness = 4.6 Å). Furthermore, the internal diameters (d) of $(Ph_2Si_2O_3)_{10}$, $(Ph_2Si_2O_3)_{14}$, and $(Ph_2Si_2O_3)_{18}$ are 9.380, 12.403, and 16.890 Å, respectively, and their external diameters are 18.317, 23.350, and 26.607 Å, respectively (Figure 5). The dimensions of the experimentally determined structures are consistent with those of the theoretically optimized structures, which further proves the closed-ring ladder structure of cyc-PSQs.

The thermal stability of cyc-PSQs was analyzed by TGA in nitrogen, and the 1% and 5% weight loss temperatures of cyc-PSQs were determined as 458 and 533 °C, respectively (SI Figure 3).The temperature of maximum mass loss rate, T_{max}, is about 558 °C, and the residue from cyc-PSQs at 850 °C is 76.9%. These results show that these macrocyclic products have superior thermal stability, which is obviously higher than those of known macrocyclic compounds such as cyclodextrins, crown ethers, and calixarenes.

In addition to these perfectly structured products, a series of macrocyclic products with the same ring ladder structure but bearing an additional Si−OH group [$(Ph_2Si_2O_3)_m$O−PhSi−OH, cyc-PSQs-OH] were also synthesized alongside the cyc-PSQs, as shown in SI Scheme 1. The hydroxyl groups can be used to tune the macrocyclic chemical environment of the pores, or further reactions can be carried out to diversify the functionality of the macrocyclic products.

Because of the regularity of the molecular structure of the macrocyclic products, it is readily apparent that the difference in molecular weight between the n and n + 1 peaks (and also the m and m + 1 peaks) is again 258, corresponding to a step of the ladder-like structure (Figure 6). Each molecular ion peak in Figure 6 was identified, and its possible molecular formula was calculated (SI Table 1). Surprisingly, there are only two series of formulas (Figure 6). The first series corresponds to cyc-PSQs [$(Ph_2Si_2O_3)_n$, n = 5, 6, ···, 20] as above, which could be separated and characterized in detail. The second series of molecular formulas corresponds to cyc-PSQs-OH [$(Ph_2Si_2O_3)_m$O−PhSi−OH, m = 5, 6, ···, 20].

To confirm the structure of $(Ph_2Si_2O_3)_m$O−PhSi−OH, a substitution reaction was used to convert the Si−OH groups

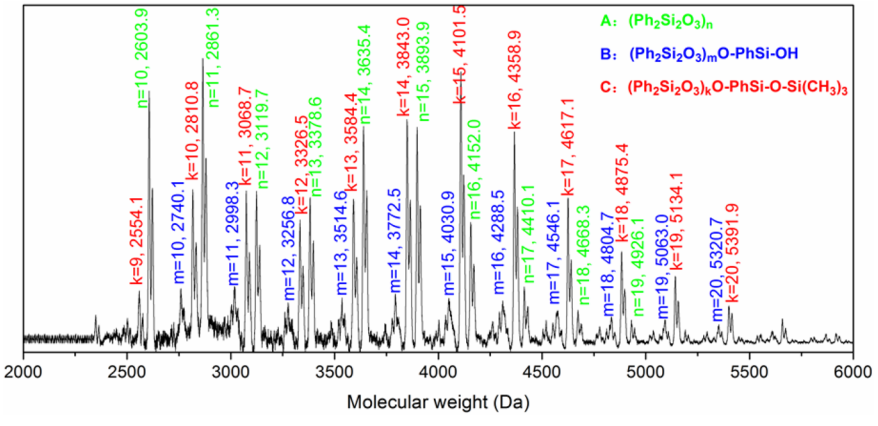


Figure 8. MALDI-TOF mass spectrum of the $(Ph_2Si_2O_3)_n$, $(Ph_2Si_2O_3)_m$O−PhSi−OH, and $(Ph_2Si_2O_3)_k$O−PhSi−O−Si$(CH_3)_3$ polydisperse mixture.

DOI: 10.1021/acs.inorgchem.7b03264
Inorg. Chem. 2018, 57, 3883−3892

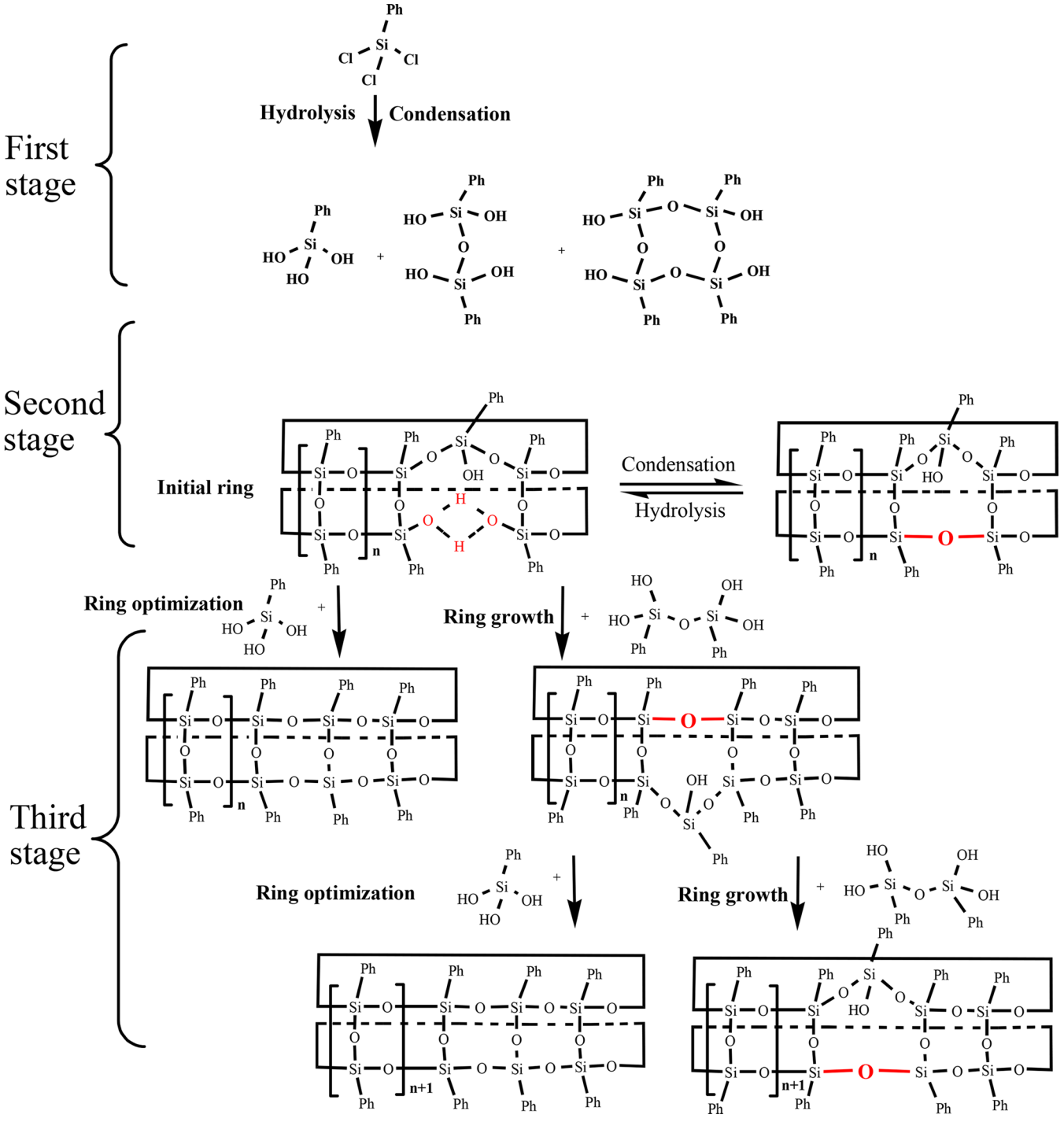


Figure 9. Proposed formation mechanism for the macrocyclic compounds cyc-PSQs and cyc-PSQs-OH.

into Si−O−Si$(CH_3)_3$ groups, as shown in SI Scheme 2. ^{29}Si CP-MAS NMR spectra before and after this substitution reaction are shown in Figure 7A,B, respectively. Figure 7A shows the main peak at −78.7 ppm due to T3 units [PhSi(O−)$_3$] and a very small shoulder peak at −69.1 ppm due to T2 units with one Si−OH group [PhSi(O−)$_2$OH].[25,36] After the substitution reaction between cyc-PSQs-OH and $(CH_3)_3$SiCl (Figure 7B), the peak of the T3 units at −78.7 ppm remained unchanged, the minor peak at −69.1 ppm was almost lost, and two new minor peaks appeared at −49.6 and 10.2 ppm.[37,38] This result confirmed that all of the Si−OH groups in cyc-PSQs-OH had been converted into Si−O−Si$(CH_3)_3$ groups by the substitution reaction.

The MALDI-TOF mass spectrum of the products after the substitution reaction is shown in Figure 8, and the calculated possible molecular formulas are summarized in SI Table 2. The results show that the molecular formula $(Ph_2Si_2O_3)_n$ had not changed. The peaks due to $(Ph_2Si_2O_3)_m$O−PhSiOH became very weak, and a series of new peaks due to $(Ph_2Si_2O_3)_k$O−PhSi−O−Si$(CH_3)_3$ clearly appeared. No other new molecular peaks appeared after the substitution reaction. The increment in the molecular weight in going from $(Ph_2Si_2O_3)_m$O−PhSi−OH to $(Ph_2Si_2O_3)_k$O−PhSi−O−Si$(CH_3)_3$ indicates that there

DOI: 10.1021/acs.inorgchem.7b03264
Inorg. Chem. 2018, 57, 3883−3892

was only one Si−OH group in each $(Ph_2Si_2O_3)_mO-PhSi-OH$ molecule. These results confirm that the polydisperse mixture comprised only two kinds of molecular formula, cyc-PSQs $[(Ph_2Si_2O_3)_n]$ and cyc-PSQs-OH $[(Ph_2Si_2O_3)_mO-PhSi-OH]$.

As regards the mechanism of formation of L-PSQ compounds, Zhang and co-workers proposed a supramolecular template strategy termed "supramolecular-architecture-directed stepwise coupling/polymerization" by which a series of ordered L-PSQs were prepared.[39,40] Another mechanism, termed "monomer self-organization lyophilization surface-confined polycondensation", has been proposed for the formation of well-defined L-PSQs.[25] Furthermore, Brook,[41] Frye,[42] Kovář,[43] and Andrianov[44] have also proposed their own mechanisms for the synthesis of L-PSQs. However, their mechanisms apply only to the assembly of linear ladder-like polysilsesquioxanes, which clearly do not apply for the formation of circular PSQs.

According to the foregoing results, after removal of the insoluble cross-linked products during the post-treatment stage, the synthesized polydisperse mixture contained only two series of molecular structures, the closed-ring double-chained structure [cyc-PSQs, $(Ph_2Si_2O_3)_n$] and the similar closed-ring structure with one Si−OH group on a longer chain [cyc-PSQs-OH, $(Ph_2Si_2O_3)_mO-PhSi-OH$]. Furthermore, both cyc-PSQs and cyc-PSQs-OH show a continuous series of molecular weights, with "*n*" and "*m*" values increasing incrementally. Therefore, we surmise that the closed-ring structure was formed at the beginning of the condensation and could be incrementally enlarged under appropriate conditions in only two ways.

A possible mechanism is outlined in Figure 9. The first stage is the hydrolysis of $PhSiCl_3$. For the formation of L-PSQ, the hydrolysate from the first stage contains the T0 structure of $PhSi(OH)_3$, the dimer $[Ph(OH)_2-Si-O-Si-(OH)_2Ph]$, and the T4 tetraol (called a half-cage). In the second stage, the initial ring is formed under conditions of $MgCl_2$-catalyzed polycondensation. When $n = 1$, the structure is a classic T7 cage structure. The last stage is ring growth. Because of the presence of the additional Si−OH on one chain, the adjacent Si−O−Si bond (Figure 9, red-colored part) is relatively weak and is susceptible to form an intermediate state to react with $PhSi(OH)_3$ or the dimer $[Ph(OH)_2-Si-O-Si-(OH)_2Ph]$. When the intermediate state reacts with $PhSi(OH)_3$, it forms a complete ring with double chains. When the intermediate state reacts with the dimer $[Ph(OH)_2-Si-O-Si-(OH)_2Ph]$, the ring of cyc-PSQs-OH forms a larger ring with one chain bearing an Si−OH group. This can form another complete ring or new larger rings (Figure 9). Furthermore, in addition to the cyclic products, a very small amount of cross-linked solid byproducts is also formed during the reaction.

CONCLUSIONS

Organic−inorganic hybrid macrocyclic compounds, cyclic polyphenylsilsesquioxanes (cyc-PSQs), have been synthesized through the hydrolysis of phenyltrichlorosilane at 0−5 °C and condensation at 80 °C with magnesium chloride as an assisting catalyst. This method produces both complete and incomplete organic−inorganic hybrid macrocyclic compounds. FT-IR, XRD, and ^{29}Si CP-MAS NMR analyses have shown that cyc-PSQs have a closed-ring double-chain siloxane inorganic backbone bearing organic phenyl groups. MALDI-TOF MS analysis has indicated that cyc-PSQs comprise ideal cyclic ladder-like chains $(Ph_2Si_2O_3)_n$. Structurally optimized cyc-PSQs are highly symmetrical and regular with high stereoregularity, consistent with the dimensions of the experimentally derived structures. TGA results have shown that cyc-PSQs are among the most thermally stable macrocyclic compounds, with a 5% weight loss temperature of 533 °C. In addition to these perfectly structured compounds, a series of macrocyclic compounds with the same ring ladder structure but bearing an additional Si−OH group (cyc-PSQs-OH) have also been synthesized. The hydroxyl groups can be used to tune the macrocyclic chemical environment of the pores, or its further reactions can diversify the functionality of the macrocyclic compounds. A ring growth mechanism has been proposed to rationalize the formation of cyc-PSQs with a continuous incremental series of molecular weights as well as the formation of only two kinds of closed-ring molecular structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b03264.

^1H NMR spectra of (A) $PhSiCl_3$ and (B) cyc-PSQs (SI Figure 1); GPC curve of cyc-PSQs (SI Figure 2); TGA curve of cyc-PSQs (SI Figure 3); synthesis and formulas for the cyc-PSQs/cyc-PSQs-OH polydisperse mixture (SI Scheme 1); synthesis of $(Ph_2Si_2O_3)_kO-PhSi-O-Si(CH_3)_3$ from $(Ph_2Si_2O_3)_mO-PhSi-OH$ by a substitution reaction (SI Scheme 2); formulas of the recorded molecular ions for the cyc-PSQs/cyc-PSQs-OH polydisperse mixture (SI Table 1); formulas of the recorded molecular ions for the $(Ph_2Si_2O_3)_n/(Ph_2Si_2O_3)_mO-PhSi-OH/(Ph_2Si_2O_3)_kO-PhSi-O-Si(CH_3)_3$ polydisperse mixture (SI Table 2) (PDF)

AUTHOR INFORMATION

Corresponding Author

*Telephone: +86-10-6891-2927. E-mail: yrj@bit.edu.cn.

ORCID

Yiwei Wu: 0000-0003-0581-4356

Rongjie Yang: 0000-0002-7499-0073

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project was funded by the National Program on Key Research Project (2016YFB0302101), the National Natural Science Foundation of China (51603011), and the International Science and Technology Cooperation Program of China (S2014ZR0465).

REFERENCES

(1) Prochowicz, D.; Kornowicz, A.; Lewiński, J. Interactions of Native Cyclodextrins with Metal Ions and Inorganic Nanoparticles: Fertile Landscape for Chemistry and Materials Science. *Chem. Rev.* **2017**, *117* (22), 13461−13501.

(2) Bishop, M. M.; Lee, A. H. W.; Lindoy, L. F.; Turner, P.; Skelton, B. W.; White, A. H. Self-assembly of Hydrogen-bonded Supramolecular Structures Based on the Neutral Pseudo-macrocyclic Complex Bis(dimethylglyoximato)copper(II). *Supramol. Chem.* **2005**, *17* (1−2), 37−45.

(3) Yu, L.; Li, F.-z.; Wu, J.-y.; Xie, J.-q.; Li, S. Development of the aza-crown ether metal complexes as artificial hydrolase. *J. Inorg. Biochem.* **2016**, *154*, 89−102.

DOI: 10.1021/acs.inorgchem.7b03264
Inorg. Chem. 2018, 57, 3883−3892

(4) Zhu, G.; Yi, Y.; Chen, J. Recent advances for cyclodextrin-based materials in electrochemical sensing. *TrAC, Trends Anal. Chem.* **2016**, *80*, 232−241.
(5) Zhang, F.; Sun, Y.; Tian, D.; Shin, W. S.; Kim, J. S.; Li, H. Selective molecular recognition on calixarene-functionalized 3D surfaces. *Chem. Commun.* **2016**, *52* (86), 12685−12693.
(6) Lee, J. W.; Samal, S.; Selvapalam, N.; Kim, H.-J.; Kim, K. Cucurbituril Homologues and Derivatives: New Opportunities in Supramolecular Chemistry. *Acc. Chem. Res.* **2003**, *36* (8), 621−630.
(7) Sessler, J. L.; Gross, Z.; Furuta, H. Introduction: Expanded, Contracted, and Isomeric Porphyrins. *Chem. Rev.* **2017**, *117* (4), 2201−2202.
(8) Xue, M.; Yang, Y.; Chi, X.; Zhang, Z.; Huang, F. Pillararenes, A New Class of Macrocycles for Supramolecular Chemistry. *Acc. Chem. Res.* **2012**, *45* (8), 1294−1308.
(9) Li, G.; Wang, L.; Ni, H.; Pittman, C. U., Jr. Polyhedral oligomeric silsesquioxane (POSS) polymers and copolymers: a review. *J. Inorg. Organomet. Polym.* **2001**, *11* (3), 123−154.
(10) Laine, R. M.; Roll, M. F. Polyhedral phenylsilsesquioxanes. *Macromolecules* **2011**, *44* (5), 1073−1109.
(11) Cordes, D. B.; Lickiss, P. D. Preparation and Characterization of Polyhedral Oligosilsesquioxanes. In *Applications of Polyhedral Oligomeric Silsesquioxanes*; Hartmann-Thompson, C., Ed.; Springer: Dordrecht, The Netherlands, 2011; pp 47−133.
(12) Bilyachenko, A. N.; Kulakova, A. N.; Levitsky, M. M.; Petrov, A. A.; Korlyukov, A. A.; Shul'pina, L. S.; Khrustalev, V. N.; Dorovatovskii, P. V.; Vologzhanina, A. V.; Tsareva, U. S.; Golub, I. E.; Gulyaeva, E. S.; Shubina, E. S.; Shul'pin, G. B. Unusual Tri-, Hexa-, and Nonanuclear Cu(II) Cage Methylsilsesquioxanes: Synthesis, Structures, and Catalytic Activity in Oxidations with Peroxides. *Inorg. Chem.* **2017**, *56* (7), 4093−4103.
(13) Bilyachenko, A. N.; Yalymov, A. I.; Korlyukov, A. A.; Long, J.; Larionova, J.; Guari, Y.; Vologzhanina, A. V.; Es'kova, M. A.; Shubina, E. S.; Levitsky, M. M. Unusual penta- and hexanuclear Ni(ii)-based silsesquioxane polynuclear complexes. *Dalton Trans.* **2016**, *45* (17), 7320−7327.
(14) Bilyachenko, A. N.; Yalymov, A. I.; Levitsky, M. M.; Korlyukov, A. A.; Es'kova, M. A.; Long, J.; Larionova, J.; Guari, Y.; Shul'pina, L. S.; Ikonnikov, N. S.; Trigub, A. L.; Zubavichus, Y. V.; Golub, I. E.; Shubina, E. S.; Shul'pin, G. B. First cage-like pentanuclear Co(II)-silsesquioxane. *Dalton Trans.* **2016**, *45* (35), 13663−13666.
(15) Pielichowski, K.; Njuguna, J.; Janowski, B.; Pielichowski, J. Polyhedral Oligomeric Silsesquioxanes (POSS)-Containing Nanohybrid Polymers. *Adv. Polym. Sci.* **2006**, *201*, 225−296.
(16) Kuo, S.-W.; Chang, F.-C. POSS related polymer nanocomposites. *Prog. Polym. Sci.* **2011**, *36* (12), 1649−1696.
(17) Feher, F. J.; Phillips, S. H.; Ziller, J. W. Synthesis and structural characterization of a remarkably stable, anionic, incompletely condensed silsesquioxane framework. *Chem. Commun.* **1997**, *9*, 829−830.
(18) Choi, S.-S.; Lee, A. S.; Hwang, S. S.; Baek, K.-Y. Structural Control of Fully Condensed Polysilsesquioxanes: Ladderlike vs Cage Structured Polyphenylsilsesquioxanes. *Macromolecules* **2015**, *48* (17), 6063−6070.
(19) Brown, J. F.; Vogt, L. H.; Katchman, A.; Eustance, J. W.; Kiser, K. M.; Krantz, K. W. Double Chain Polymers of Phenylsilsesquioxane. *J. Am. Chem. Soc.* **1960**, *82* (23), 6194−6195.
(20) Pavlova, S. A.; Pakhomov, V. I.; Tverdokhlebova, I. I. The structure of polyphenylsiloxane and the properties of its solutions. *Polym. Sci. U.S.S.R.* **1964**, *6* (7), 1415−1420.
(21) Duan, Q.; Yong, Z.; Jiang, J.; Deng, K.; Zhang, T.; Xie, P.; Zhang, R.; Fu, P. Synthesis and characterization of ethoxy-terminated ladder-like polymethylsilsesquioxane oligomer. *Polym. Int.* **2004**, *53* (1), 113−120.
(22) Liu, C.; Liu, Y.; Xie, P.; Zhang, R.; He, C.; Chung, N. T. Synthesis and characterization of a novel alcohol-soluble ladderlike polysilsesquioxane containing side-chain with amino terminal groups. *React. Funct. Polym.* **2000**, *46* (2), 175−184.
(23) Li, Z.; Cao, X.; Xu, H.; Xie, P.; Cao, M.; Zhang, R. Synthesis and characterization of reactive ladderlike polyallylsilsesquioxane and polyvinylsilsesquioxane. *React. Funct. Polym.* **1999**, *39* (1), 1−7.
(24) Gu, H. W.; Xie, P.; Shen, D. Y.; Fu, P. F.; Zhang, J. M.; Shen, Z. R.; Tang, Y. X.; Cui, L.; Kong, B.; Wei, X. F.; Wu, Q.; Bai, F.-L.; Zhang, R.-B. Photo-Induced Orientation of a Film of Ladderlike Polysiloxane Bearing Dual Photoreactive Side Groups. *Adv. Mater.* **2003**, *15* (16), 1355−1358.
(25) Zhang, Z. X.; Hao, J.; Xie, P.; Zhang, X.; Han, C. C.; Zhang, R. A Well-Defined Ladder Polyphenylsilsesquioxane (Ph-LPSQ) Synthesized via a New Three-Step Approach: Monomer Self-Organization−Lyophilization—Surface-Confined Polycondensation. *Chem. Mater.* **2008**, *20* (4), 1322−1330.
(26) Ma, J.; Shi, L. H.; Zhang, J. M.; Li, B. Y.; Shen, D. Y.; Xu, J. Study on Pyrolysis of Polyphenylsilsesquioxane. *Chin. J. Polym. Sci.* **2002**, *20* (6), 573−577.
(27) Zhang, X.; Chen, S.; Shi, L. Studies on Regularity of Polyphenylsilsesquioxane Chains. *Chin. J. Polym. Sci.* **1987**, *5* (2), 162−168.
(28) Unno, M.; Matsumoto, T.; Matsumoto, H. Synthesis of laddersiloxanes by novel stereocontrolled approach. *J. Organomet. Chem.* **2007**, *692* (1−3), 307−312.
(29) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. CHAPTER 15 − Organosilicon Compounds. In *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: San Diego, CA, 1991; pp 251−261.
(30) Choi, S.-S.; Lee, H. S.; Hwang, S. S.; Choi, D. H.; Baek, K.-Y. High photo- and electroluminescence efficiencies of ladder-like structured polysilsesquioxane with carbazole groups. *J. Mater. Chem.* **2010**, *20* (44), 9852−9854.
(31) Feher, F. J.; Budzichowski, T. A. Syntheses of highly-functionalized polyhedral oligosilsesquioxanes. *J. Organomet. Chem.* **1989**, *379* (1), 33−40.
(32) Sankaraiah, S.; Lee, J. M.; Kim, J. H.; Choi, S. W. Preparation and Characterization of Surface-Functionalized Polysilsesquioxane Hard Spheres in Aqueous Medium. *Macromolecules* **2008**, *41* (16), 6195−6204.
(33) Unno, M. New Chemistry Created by Silanols: From Supramolecular Aggregates to Next-Generation Materials with Highly Regulated Structures. *Yuki Gosei Kagaku Kyokaishi* **2011**, *69* (4), 413−425.
(34) Ren, Z.; Sun, D.; Li, H.; Fu, Q.; Ma, D.; Zhang, J.; Yan, S. Synthesis of Dibenzothiophene-Containing Ladder Polysilsesquioxane as a Blue Phosphorescent Host Material. *Chem. - Eur. J.* **2012**, *18* (13), 4115−4123.
(35) He, J.; Yue, K.; Liu, Y.; Yu, X.; Ni, P.; Cavicchi, K. A.; Quirk, R. P.; Chen, E. Q.; Cheng, S. Z. D.; Zhang, W. B. Fluorinated polyhedral oligomeric silsesquioxane-based shape amphiphiles: molecular design, topological variation, and facile synthesis. *Polym. Chem.* **2012**, *3* (8), 2112−2120.
(36) Yamamoto, S.; Yasuda, N.; Ueyama, A.; Adachi, H.; Ishikawa, M. Mechanism for the Formation of Poly(phenylsilsesquioxane). *Macromolecules* **2004**, *37* (8), 2775−2778.
(37) Li, J.; Cao, J.; Huo, L.; He, X. One-step synthesis of hydrophobic silica aerogel via in situ surface modification. *Mater. Lett.* **2012**, *87*, 146−149.
(38) Hara, K.; Akahane, S.; Wiench, J. W.; Burgin, B. R.; Ishito, N.; Lin, V. S. Y.; Fukuoka, A.; Pruski, M. Selective and Efficient Silylation of Mesoporous Silica: A Quantitative Assessment of Synthetic Strategies by Solid-State NMR. *J. Phys. Chem. C* **2012**, *116* (12), 7083−7090.
(39) Zhang, R.; Dai, D.; Cui, L.; Xu, H.; Liu, C.; Xie, P. A glance at the relation of stepwise coupling polymerization to supramolecular chemistry. *Mater. Sci. Eng., C* **1999**, *10* (1−2), 13−18.
(40) Zhang, T.; Deng, K.; Zhang, P.; Xie, P.; Zhang, R. Supramolecular Template-Directed Synthesis of Perfect Phenelenediimino-Bridged Ladderlike Polyphenylsiloxanes. *Chem. - Eur. J.* **2006**, *12* (13), 3630−3635.

DOI: 10.1021/acs.inorgchem.7b03264
Inorg. Chem. 2018, 57, 3883−3892

(41) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley-Interscience: New York, 2000; pp 309−331.
(42) Frye, C. L.; Klosowski, J. M. So-called "ladder structure" of equilibrated phenylsilsesquioxane. *J. Am. Chem. Soc.* **1971**, *93* (18), 4599−4601.
(43) Kovář, J.; Mrkvičková-Vaculová, L.; Bohdanecký, M. A study of branching in polyphenylsilasesquioxane chains by hydrodynamic and light-scattering methods. *Makromol. Chem.* **1975**, *176* (6), 1829−1847.
(44) Tsvetkov, V. N.; Andrianov, K. A.; Ryumtsev, Y. N.; Shtennikova, I. N.; Vitovskaya, M. G.; Makarova, N. N.; Kurasheva, N. A. Molecular conformations, hydrodynamics and optics of ladder polymers. *Polym. Sci. U.S.S.R.* **1973**, *15* (2), 455−471.

DOI: 10.1021/acs.inorgchem.7b03264
Inorg. Chem. 2018, 57, 3883−3892