รายงานวิจัยฉบับสมบูรณ์

โครงการ การสังเคราะห์ และ วิเคราะห์สารประกอบ Octakis(2-(3-propyl)isoindoline-1,3-dione)octasilsesquioxane และ Octakis(5-(3-propyl)-1,1-dioxo-1,2-benzothiazol-3-one)octasilsesquioxane

โดย อ.ดร.วุฒิชัย เอื้อวิทยาศุภร และ คณะ

วันที่ 30 มิถุนายน พ.ศ. 2557

สัญญาเลขที่ MRG5580011

รายงานวิจัยฉบับสมบูรณ์

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ผู้วิจัย สังกัด

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2. ศูนย์ความเป็นเลิศด้านนวัตกรรมทางเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล
3. หน่วยเสริมสร้างศักยภาพทางนาโนศาสตร์ และ นาโนเทคโนโลยี คณะวิทยาศาสตร์ มหาวิทยาลัยมหิดล

สนับสนุนโดยสำนักงานคณะกรรมการการอุดมศึกษา สำนักงานกองทุนสนับสนุนการวิจัย และ มหาวิทยาลัยมหิดล

Abstract

Project Code : MRG5580011

Project Title : Synthesis and Characterization of Octakis(2-(3-propyl)isoindoline-1,3-dione)octasilsesquioxane and Octakis(5-(3-propyl)-1,1-dioxo-1,2-benzothiazol-3-one)octasilsesquioxane

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Project Period : 2 years (July 1, 2012 – June 30, 2014)

Novel synthesis and functionalization of polyhedral oligomeric silsesquioxanes have been investigated. We first studied the reactivity and functionalization *via* nucleophilic substitution reactions on octakis(3-chloropropyl)octasilsesquioxane (T_8) with fine-tunable functions, leading to the formation of novel T_8 compounds (e.g. *o*-sulfobenzimide, phthalimide, bromo, iodo, acrylate, and methacrylate). However, some of them (e.g. phthalimide, acrylate, and methacrylate) have found the formation of deca- and dodecasilsesquioxanes (T_{10} and T_{12}) cages during substitution reactions. Consequently, we found the electronic effect of nucleophiles to promote cage-rearranged silsesquioxanes (T_8, T_{10}, and T_{12}). Moreover, the isolated products of each pure cage were found the chemical structure/ physical property relationship (e.g. states of matter, glass transition temperature, and melting point) of silsesquioxane cages not only is dependent on the symmetry of the inorganic silsesquioxane core at a given temperature but also is dictated by the organic substituent mobility.

Keywords : Cage-rearrangement, Nucleophilic substitution reaction, Polyhedral Oligomeric Silsesquioxane

บทคัดย่อ

รหัสโครงการ : MRG5580011

ชื่อโครงการ : การสังเคราะห์ และ วิเคราะห์สารประกอบ Octakis(2-(3-propyl)isoindoline-1,3-dione)octasilsesquioxane และ Octakis(5-(3-propyl)-1,1-dioxo-1,2-benzothiazol-3-one)octasilsesquioxane

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ระยะเวลาโครงการ : 2 ปี (1 ก.ค. 2555 ถึง 30 มิ.ย. 2557)

การเปลี่ยนแปลงหมู่แทนที่ และ ศึกษาผลของความว่องไวในการเกิดปฏิกิริยาแทนที่ บนสารตั้งต้น octakis(3-chloropropyl)octasilsesquioxane ซึ่งมีลักษณะแบบชนิดลูกบาศก์ หรือ ทรงกรงแปดเหลี่ยม ด้วยหมู่แทนที่ หรือ นิวคลิโอไฟล์ ชนิดต่างๆ เช่น *o*-sulfobenzimide phthalimide bromo iodo acrylate และ methacrylate โดยสามารถให้ผลิตภัณฑ์ที่มีหมู่แทนที่ตามนิวคลิโอไฟล์ที่เลือกใช้ และ ยังคงโครงสร้างรูปทรงกรงแปดเหลี่ยมได้เช่นกัน อย่างไรก็ตามทีมผู้วิจัยยังได้ค้นพบสารผลิตภัณฑ์ข้างเคียงชนิดอื่น ที่มีโครงสร้างสมมาตรทางโมเลกุลที่แตกต่างกันออกไป เช่น แบบรูปทรงกรงสิบเหลี่ยม และ สิบสองเหลี่ยม ซึ่งผลิตภัณฑ์ที่มีรูปทรงสมมาตรที่แตกต่างออกไปนี้ จะถูกพบเมื่อทำการแทนที่ด้วยหมู่แทนที่เฉพาะ phthalimide acrylate และ methacrylate ทั้งนี้หลังจากการแยกสารผลิตภัณฑ์ทั้งหมด โดยใช้เทคนิคพื้นฐานคอลัมภ์โครมาโทรกราฟี ทีมผู้วิจัยยังค้นพบข้อสังเกตถึงความแตกต่างของคุณสมบัติเชิงกายภาพของสสารที่มีความสัมพันธ์เชิงโครงสร้างทางโมเลกุล ถึงแม้ว่าสารประกอบเหล่านี้จะมีหมู่ฟังก์ชันเคมีอินทรีย์หรือหมู่แทนที่แบบเดียวกัน แต่เพราะผลของสมมาตรบางส่วนที่เป็นเคมีอินทรีย์ที่แตกต่างกันย่อมส่งถึงสมบัติทางกายภาพตามไปด้วย ได้แก่ อุณหภูมิหลอมเหลว อุณหภูมิทรานสิชั่นแก้ว

คำหลัก : การเปลี่ยนแปลงของกรง ปฏิกิริยาแทนที่ โพลีฮีดรอลโอลิโกเมอริกซิลเซสคิวออกเซน

Objective : To study the reactivity and functionalization of nucleophilic substitution reaction on octameric T_8 silsesquioxane cage with bromide, iodide, o-sulfobenzimide, phthalimide, acrylate, and methacrylate anions

Introduction :

Silsesquioxanes are class of hybrid organic-inorganic molecules with the general formula of $[RSiO_{3/2}]_n$ (with R as alkyl, aryl, allylene functional groups, or hydrogen atom).[1] They are found in various chemical architectures such as polymeric,[2] cage-like,[3] or ladder structures.[4] Due to their highly discrete nano-scale structures of Si-O inorganic core surrounded by organic functional groups, cage-like structures or polyhedral oligomeric silsesquioxanes are of particular interest. Based on these characteristics, cage-like silsesquioxanes molecules could serve as an excellent nano-building block with fine-tunable properties *via* chemical modifications. Recently, applications for silsesquioxanes-based materials have been found in polymer science,[5] catalysis,[6] biomedicine,[7] nanomaterials,[8] electronic devices,[9] and electrochemistry.[10] In general, organotrihalosilanes or organotrialkoxysilanes readily undergo hydrolytic condensation reactions in the presence of basic or acidic catalysts, leading to the formation of silsesquioxanes adducts.[11] However, the hydrolytic condensation reaction of silsesquioxanes compounds is highly sensitive, and the synthetic conditions crucially affect the selectivity of product's formation. Alternatively, nucleophilic substitution reactions on silsesquioxanes molecules could be developed to achieve high yield of selective products.[12] Based on aforementioned perspective, octakis(3-chloropropyl)octasilsesquioxane (abbreviated as T_8-PrCl, **1**) is considered as a

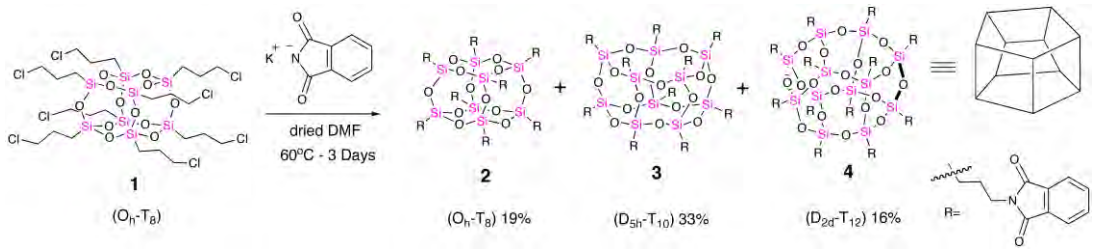
promising precursor for nucleophilic substitution reactions due to its ease of synthesis from commercially available precursor. Thus, novel functionalized-silsesquioxanes could be prepared facilely from this precursor.[13,14]

Project 1

Gabriel method has been known for many decades and customarily used to transform primary alkylhalides to N-alkylated phthalimide precursors *via* a nucleophilic substitution reaction. Traditional Gabriel synthesis consists of two-steps synthesis, which was then followed by acidic hydrolysis or refluxing with hydrazine to produce primary amines. Alternatively, another chemical such as sulfonamides could be used as Gabriel reagents and the subsequent precursors could be readily hydrolyzed to form secondary amines. From this aspect, we strongly believe that the Gabriel method could be utilized as an effective approach to produce N-alkylated phthalimide and sulfobenzimide silsesquioxanes through nucleophilic substitution reactions on T_8-PrCl. However, our products in this study obtained from these dissimilar nitrogen nucleophiles exhibited significant diversity. The reaction with phthalimide anion surprisingly leads to the formation of a mixture (T_8R_8, $T_{10}R_{10}$, and $T_{12}R_{12}$ where $T_n = (SiO_{1.5})_n$) of octakis(3-(1,3-dioxoisoindolin-2-yl)propyl)octasilsesquioxane (**2**), decakis(3-(1,3-dioxoisoindolin-2-yl)propyl)decasilsesquioxane (**3**), anddodecakis(3-(1,3-dioxoisoindolin-2-yl)propyl)dodecasilsesquioxane (**4**), while the reaction with *o*-sulfobenzimide anion, at harsher synthetic condition, yields too nly a single cubic compound of octakis(3-(1,2-benzisothiazole-3-(2H)-one-1,1′-dioxydyl)propyl)octasilsesquioxane (**5**). From these

unexpected results, studying the effect of electronic nature on nitrogen nucleophiles toward a selective formation of silsesquioxanes products should reveal the insightful knowledge about the selectivity in cage-rearrangement or cage-degradation phenomena.

RESULTS AND DISCUSSION:



Scheme 1. Synthetic approach for preparation of cage-rearrangement octa-, deca-, and dodeca-phthalimide functionalized-silsesquioxanes

Preparation and Characterization of Cage-rearrangement silsesquioxanes. To investigate the nucleophilic substitution reactions, ^{1}H NMR spectroscopy was used to monitor the reactions' progress. After heating a mixture of **1** and potassium phthalimide salt in dried DMF solution at 60^{o}C for 3 days (Scheme 1), ^{1}H-NMR spectrum of the crude product revealed a complete disappearance of the 3-chloropropyl's signals and the appearance of five new signals at 0.55, 1.65, 3.53, 7.59, and 7.67 ppm. The first three signals are consistent with protons in propylene linkages, while the multiplet signals within aromatic regions arise from phthalimide moieties. However, the spectrum shows broad signals with clear splitting patterns, possibly indicating cage decomposition products. Surprisingly, the ^{29}Si{^{1}H} NMR spectrum of crude product gives

distinguishably four singlet signals at -67.10, -68.71, -68.94, and -71.43 ppm that can be attributed to the cage-rearrangement products (T_8, T_{10}, and T_{12}) (Figure 1), along with a large peak of glass wall between -80 and -120 ppm. Following the satisfactory chromatographic analysis, their separations to obtain each pure compound were further undertaken. We observed that the crude product (1.00 g) by using only conventional column chromatography in a mixture solvent of ethyl acetate/hexane (4.0:1.0) could be easily separated into T_{10}; **3** (0.33 g; R_f = 0.33) as a major product, while T_8; **2** (0.19 g; R_f = 0.45) and T_{12}; **4** (0.16 g; R_f = 0.23) are obtained as minor products.

According to our previous report, the cage-rearrangement of **1** under the reaction with azide anion in a solution of DMF at elevated temperature also yields to a mixture (T_8, T_{10}, and T_{12}) of azido-functionalized silsesquioxane products. Similarly, the decasilsesquioxane T_{10} cage was reported as a major form. Our hypothesis predicts that a cage-rearrangement mechanism would be reasonable only when the nucleophilicity of nitrogen anions is strong enough to induce the cleavage of silicon-oxygen bonds in the core network to produce particular fragments. Nitrogen-silicon bonds formed during substitution reactions and the subsequent molecular self-assembly of these fragments would allow to the formation of thermodynamically favorable cage-like silsesquioxanes.

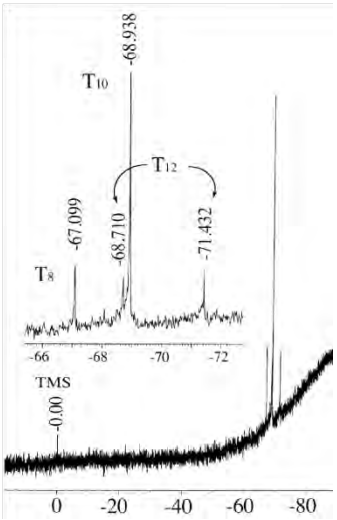


Figure 1. $^{29}Si\{^{1}H\}$ NMR spectrum of phthalimide functionalized-silsesquioxanes crude product

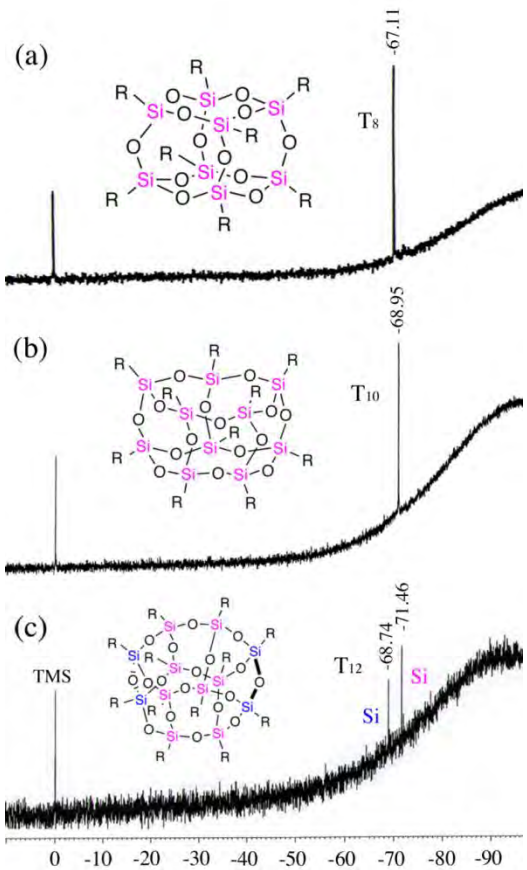
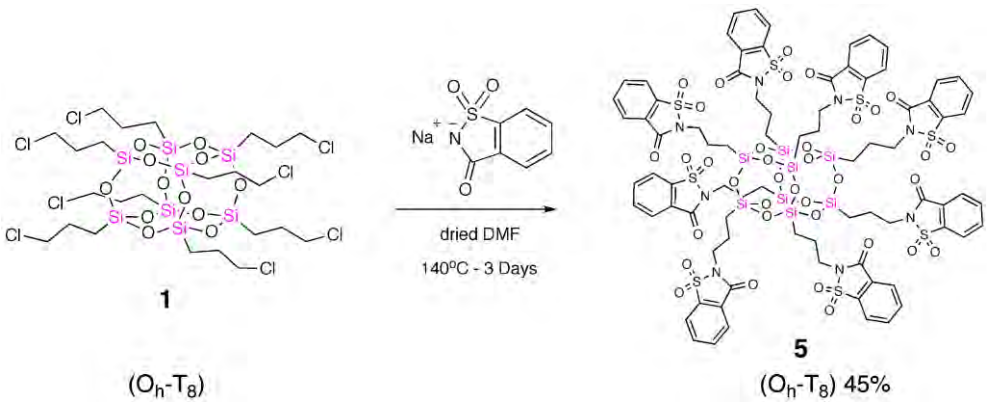


Figure 2. $^{29}Si\{^{1}H\}$ NMR spectra of purified compounds (a) octa- (b) deca- and (c) dodeca-phthalimide-functionalized silsesquioxanes (2, 3, and 4)

Moreover, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of compounds **2**; T_8 and **3**; T_{10} exhibit identical pattern, thus cannot be distinguished. In this study, further characterizations by $^{29}Si\{^{1}H\}$ NMR and mass spectrometry enable the determination of the identity of each compound. $^{29}Si\{^{1}H\}$ NMR spectra for both pure **2** and **3** exhibit only singlet signals at -67.11 and -68.95 ppm (Figure 2a and 2b), respectively. A symmetrical environment for silicon atoms on each structure (T_8 and T_{10}) would be predicted. Nevertheless, $^{29}Si\{^{1}H\}$ NMR spectrum of **4** (T_{12}) produces double singlet signals at -68.74 and -71.46 ppm (Figure 2c), corresponding to the two different types of silicon atoms in a dodecasilsesquioxane cage. Among the twelve silicon atoms in dodeca-structure, eight atoms are presented in the interior within two 10- and one 8-membered fused rings but another four atoms are in two 8- and one 10-membered fused rings. These differences in the chemical shift are attributed to a ring-strain on the silsesquioxane cages (T_8, T_{10}, and T_{12}). This interpretation is consistent with the studies by Marsmann et al and Kawakami *et al*. As a result, the $^{13}C\{^{1}H\}$ NMR spectrum of **4** shows doubly singlet signals for each carbon in propylene linkages, which are the strong evidence in order to confirm the presence of two distinct environments in the dodecasilsesquioxanes cage.



Scheme 2. Synthesis of octa*o*-sulfobenzimide functionalized-silsesquioxane

Preparation and Characterization of cubic octasilsesquioxane. The reaction of *o*-sulfobenzimide salt on **1** was shown in Scheme 2. From the observation, even minuscule amount of water crucially affected the reaction, leading to the decomposition of precursor **1** and yielding various unwanted by-products. Since commercial *o*-sulfobenzimide salt attains a large amount of water, removal of water molecules in the lattice salt is necessary prior to perform the reaction. It is also worth noting that the regioselectivity in the reaction must be taken into account, since *o*-sulfobenzimide anions is an ambident nucleophile with the possibility to be alkylated at both nitrogen and oxygen atoms. Several reports have indicated the effects of solvent, temperature, and catalyst toward regioselectivity of O- and N-alkylations on sulfobenzimide. In dried DMF solution, the thermal transformation of O-alkylated into more stable N-alkylated products proceeds *via* a Chapman-Mumm rearrangement mechanism. Interestingly, our harsh conditions were also capable for both O- and N-alkylations, depending mainly on the synthetic temperature. At 100 ^{o}C, the substitution conversion was found in 87% with the 1:10 ratio of O-alkylated to N-alkylated products. The explanation for the O-/N-alkylated proportion arises from the fact that stronger nucleophile of nitrogen anion reacts more rapidly than weaker nucleophile of oxygen anion (kinetic factors). Nevertheless, after the synthetic temperature was elevated to 140 ^{o}C, ^{1}H NMR spectra of crude product reveals >99% substitution. The O-alkylation was negligibly detected, while the N-alkylation was mainly perceived. We propose that a less stable O-alkylation product transforms reversibly into a more stable N-alkylated product at higher

temperature (thermodynamic factors). From chromatographic analysis of crude product in the solvent mixture of ethyl acetate/hexane (19.0:1.0), three major fractions were identified. The first two fractions at R_f = 0.34 and 0.42 appear as broad stains, which may likely represent a tangible evidence, later confirmed by $^{29}Si\{^{1}H\}$ NMR analysis, of incomplete substitutions and decompositions of oligomeric fragments. By means of conventional column chromatography, pure compound of **5** (R_f= 0.23) was obtained in 45% yield.^{1}H NMR analysis of **5** revealsthree new signals of aliphatic protons on propylene linkages at 0.77, 1.97, and 3.76 ppm, and additionally two multiplet signals of aromatic protons on *o*-sulfobenzimide moieties at 7.75 and 7.95 ppm. In addition, $^{29}Si\{^{1}H\}$ NMR spectrum displays only one singlet at -67.12 ppm, and high-resolution mass analysis detected a molecular ion at *m/z* 2247.1077. According to this analysis, we conclude that, under this synthetic condition, the octasilsesquioxane cage was obtained as a major compound without the occurrence of additional cage-rearrangement products.

To testify the validity of our presumption, we analyzed the mass spectrum of crude product from *o*-sulfobenzimide substitution reaction and found that the highest molecular ion falls into the octasilsesquioxane region. In fact, no other molecular ion of larger cages was clearly observed. We suggest that nucleophilicity of nitrogen atom in *o*-sulfobenzimide anion is significantly suppressed by the presence of more electron-delocalizing groups such as sulfonyl ($-SO_2R$). Likewise, decreased reactivity of the nucleophilic substitution reaction *via* S_N2 is also consistent with this proposition. Consequently, an *o*-sulfobenzimide nucleophile ineffectively interacts with silicon atoms

and unfavorably induces cage-opening at the silsesquioxane core. Thus, the nitrogen atom of *o*-sulfobenzimide anion could not lead to a cage-rearrangement or yield to a mixture of octa-, deca-, and dodecasilsesquioxanes cages which were found in the reactions with azide and phthalimide anions.

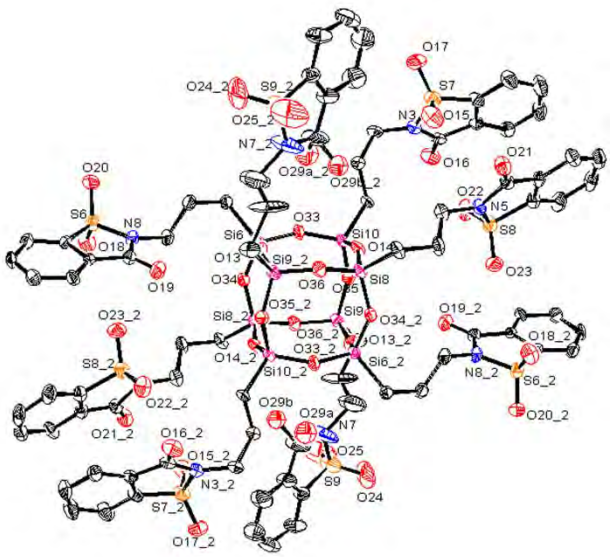


Figure 3. The thermal ellipsoids plot at 30% probability level of **5** and H atoms are omitted for clarity.

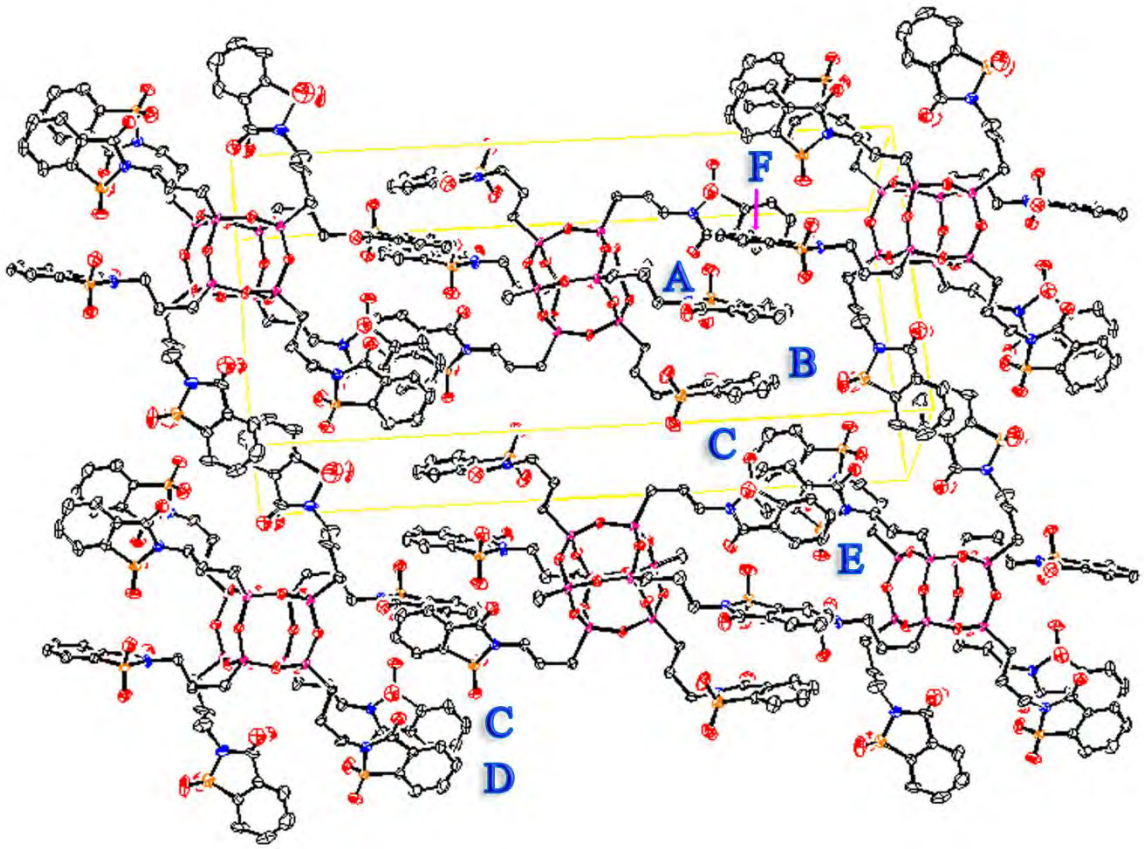


Figure 4. Packing diagram of **5** is presented by intra- and intermolecular π-π interactions.

Crystal Structure. In order to prove our assumption above, the crystallized product **5** was also analyzed by the single-crystal X-ray diffraction analysis. In figure 3, the final refinement of structure reveals unambiguously that this compound is actually cubic T_8octasilsesquioxane cage (Figure 3). This evidence could strongly support our previous characterizations by $^{29}Si\{^{1}H\}$ NMR and mass spectrometry. The packing diagram of **5** in Figure 4 and Supporting Information also shows the extended molecular structure by shorter distances of intermolecular π-π stacking interactions between neighboring molecules of sulfobenzimide A (S1, N9, C1, C2, C3, C8, C9, C10, C11)

and F (S6, N8, C34, C35, C36, C41, C42, C43, C44) rings and between C (S8, N5, C60, C61, C62, C63, C64, C65, C66) and E (S5, N1, C16, C17, C18, C19, C20, C21, C22) rings. The centroid-to-plane distances between A-F and C-E benzene rings are 1.410 Å and 1.379 Å, respectively, and the dihedral angles between these ring planes are 6.13° and 6.19°. In addition, it should be noted that there are two intramolecularly symmetry-unrelated weak slipping face to face π-π stacking interactions between benzene rings on sulfobenzimide groups: A and B (S3, N10, C27, C28, C29, C30, C31, C32, C33)rings, C and D (S10, N3, C45, C46, C47, C48, C49, C50, C51)rings. The centroid-to-plane distances between A-B and C-D benzene rings are 1.640(3) Å and 1.665(3) Å, respectively. Thus, the dihedral angles between these ring planes are 12.767° and 13.069°.

Influence of nitrogen nucleophiles toward the selectivity of cage-rearrangement phenomena. According to the experimental results, nitrogen atom in phthalimide anion leads to the formation of cage-rearrangement products, while sulfobenzimide anion does not, even at harsher conditions. We hypothesize that the electronic nature of nitrogen anions is the major factor in promoting cage-rearrangement reaction. The silicon-structures of products (T_8, T_{10}, and T_{12}) obtained from the reaction of **1** with phthalimide anion are the same as azide anion in our previous report. Since the cleavage of Si-O bond, and subsequent formation of nitrogen-silicon bonds occur within the core of cage-structure, azide and phthalimide anions must be able to get through to the inorganic core structure of silsesquioxane, sulfobenzimide anion yet could not. In this model, the electron density of nitrogen atoms

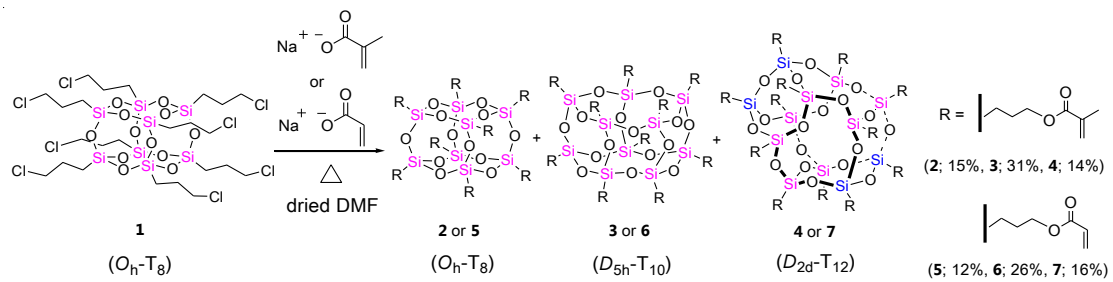
among these three nucleophiles is consistent with the degree of nucleophilicity in substitution reaction. We conclude that the experimental rate of nucleophilicity-induced cage-rearrangement would be azide > phthalimide > sulfobenzimide anions.

CONCLUSION

Four highly functionalized T_n silsesquioxanes (n = 8, 10, and 12) have been successfully synthesized as novel precursors for Gabriel synthesis. Despite the dissimilar nitrogen nucleophiles, substitution reaction with the phthalimide anion surprisingly yields toa mixture of octa-, deca-, and dodecasilsesquioxanes cages, whereas reaction with sulfobenzimide anion produces only the octasilsesquioxane cage. Thus, the influence of the electronic nature of nitrogen anions induced cage-rearrangement silsesquioxane was experimentally reported for the first time. The theoretically mechanistic study of these reactions is currently under investigation. Authors believe that these cage-liked silsesquioxanes are promising materials for further functionalization and preparation of other reactive nitrogen-based silsesquioxanes, especially for future generation of unreported amino-functionalized deca- and dodecasilsesquioxanes.

Project 2

In order to broaden the applications of polyhedral oligomeric silesquioxane chemistry, it is necessary to develop new types of reactions. In this study, we report on the design, synthesis and characterization of multi-methacrylate and acrylate organic functions for silsesquioxane cage-like structures (T_8, T_{10}, and T_{12}). Here, we performed characterization with the clean and purified forms of these compounds for the first time, in contrast to previous reports which have only relied on crude mixtures of freshly prepared and commercially available products without further purification. Moreover, several important aspects regarding the optimal reaction conditions were not taken into consideration in those studies. We report several relationships between the chemical structures of each pure silsesquioxane cage and its physical properties. For example, octakis(3-propyl methacrylate)octasilsesquioxane (**2**) is a colorless, crystalline solid which makes it unique among othersilsesquioxanes which are in the liquid state at room temperature.



Scheme 1. Cage-rearrangement T_8 cage of compound **1** upon full introduction of methacrylate and acrylate functions leading to (a) compounds **2**, **3**, and **4**; 70^{o}C-2 days,

0.048 mol L^{-1}, 1.4 eq. sodium methacrylate/$RSiO_{3/2}$; (b) compounds **5**, **6**, and **7**; 100^{o}C-1 day, 0.098 mol L^{-1}, 1.4 eq. sodium acrylate/$RSiO_{3/2}$.

RESULTS AND DISCUSSION

Preparation and Characterization of Methacrylate-Functionalized Cage-Rearrangement Silsesquioxanes. We first prepared octakis(3-propyl methacrylate)octasilsesquioxane (**2**), decakis(3-propyl methacrylate)decasilsesquioxane (**3**), and dodecakis(3-propyl methacrylate)dodecasilsesquioxane (**4**) through nucleophilic substitution reactions. Upon treatment octakis(3-chloropropyl)octasilsesquioxane (**1**) with sodium methacrylate in anhydrous DMF at 70^{o}C (Scheme 1a), an almost complete substitution conversion (~98%) of crude product could be observed within 48 hours, as monitored by the shift in the ^{1}H NMR peaks from 3.53, 1.82, and 0.75 (3-chloropropyl groups) to 4.09, 1.74, and 0.68 (3-methacryloxypropyl groups) ppm, respectively.

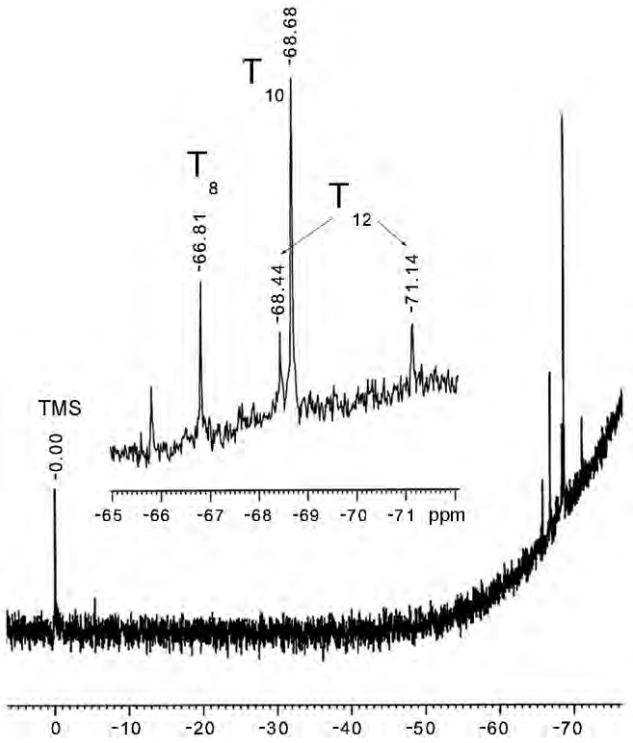


Figure 1. $^{29}Si\{^{1}H\}$ NMR spectrum of the crude product of methacrylate-functionalized polyhedral oligomeric silsesquioxanes.

Meanwhile, we observed extensive cage-rearrangement (T_8 cage) of **1,** through the presence of four very distinguishable singlet signals in the $^{29}Si\{^{1}H\}$ NMR spectrum of the crude product (Figure 1) at -66.81, -68.44, -68.68, and -71.14 ppm. Unambiguously, this crude product consists of a cage mixture of T_8 (**2**; -66.81 ppm), T_{10} (**3**; -68.68 ppm), and T_{12} (**4**; -68.44 and -71.14 ppm). In addition to undergoing substitution reactions, it is likely that methacrylate anions further attack, cleave, fragment, and reassemble the Si–O–Si bonds of the inorganic core, leading to the formation of a thermodynamically stable mixture of cage-rearrangement products (T_8, T_{10}, and T_{12}). This phenomenon is possible due to the direct effects of the electron withdrawing groups present and the low steric hindrance of the 3-substituted propyl

chains on the silsesquioxane cage under these harsher reaction conditions in which there are stronger nucleophiles present. According to the satisfactory chromatographic analysis on TLC plates; silica gel, their isolations to obtain each pure product were carefully examined.

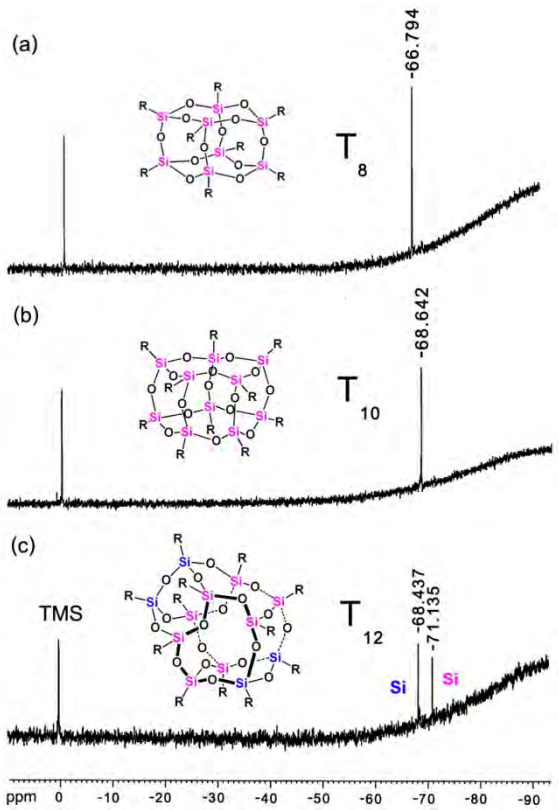


Figure 2. $^{29}Si\{^{1}H\}$ NMR spectra of purified compounds (a) octa-, (b) deca-, and (c) dodecameric-methacrylate-functionalized silsesquioxanes (**2**, **3**, and **4**).

In figure 2, we found that only by using conventional silica gel column chromatography in a solvent mixture of ethyl acetate/n-hexane (3:7), the crude product (0.80 g) could be easily separated into **3** (T_{10}; 0.25 g; R_f = 0.40) as a major product, while **2** (T_8; 0.12 g; R_f = 0.45) and **4** (T_{12}; 0.11 g; R_f = 0.35) are present as minor products. It is noteworthy to mention that purification was necessary, as we also

observed an intense baseline on TLC separation under UV light. This indicates that during substitution reactions side reactions likely occur, yielding unwanted by-products or polar components of polysilsesquioxanes. Apparently, compound **2** in T_8 cage is a crystalline solid with a melting point of 66.7-67.2^{o}C, while the other cages (**3**; T_{10} and **4**; T_{12}) are in the liquid phase (viscous fluid-like substances) at room temperature. These specific physical properties also support our recent observation on the states of matter of cage-rearrangement phthalimide-functionalized polyhedral oligomeric silsesquioxanes. Although, the colorless crystal of the T_8 cage (m.p.247-248^{o}C), the amorphous-like white-fluffy formation of the T_{10}cage (T_g~65^{o}C) and the thin film of the T_{12} cage are all solids at room temperature, the symmetry could be a key to determining the relative lattice energies, as higher symmetry allows for better packing and higher phase transition temperatures in the solid state. In polyhedral geometry, the higher degree of symmetrical faces in a cage is typically thought to allow neighboring molecules to get very close in three-dimensional space.

All faces in a T_8 cube (O_h) mainly consist of six symmetrical 8-membered rings of an inorganic Si-O-Si core, in contrast to lower symmetrical cages like T_{10} (D_{5h}; five 8-membered and two 10-membered rings) and T_{12} (D_{2d}; four 8- and four 10-membered rings). Therefore, close-packed and crystallized states are usually observed in T_8 cage. In addition, the flexible Si-O-Si bond makes the larger cages change shape easily, also contributing to the low crystallinity of these compounds. We suggest that the tendency to form such a condensed matter for these compounds would be $T_8 > T_{10} > T_{12}$.

Preparation and Characterization of Acrylate-Functionalized Cage-Rearrangement Silsesquioxanes. In order to prepare octakis(3-propyl acrylate)octasilsesquioxane (**5**), decakis(3-propyl acrylate)decasilsesquioxane (**6**), and dodecakis(3-propyl acrylate)dodecasilsesquioxane (**7**), the reaction condition between **1** and acrylate anion was also studied. As expected, the substitution rate on **1** at 70^{o}C with acrylate anion was slower than methacrylate anions and the substitution conversion after 2 days reached only 55%. We suggest that the difference in the relative nucleophilicity between methacrylate and acrylate anions is due to the differences in the electron density on the nucleophilic oxygen. In fact, acrylic acid has a higher K_a value, and thus the acrylate anion could be considered to be more stable or less reactive than that methacrylate anion. As the temperature increases up to 100^{o}C, the substitution reaction with acrylate anion was found to be almost complete (~96%) within 24 hours (Scheme 1b). Similarly, the pattern of the ^{29}Si{^{1}H} spectrum of crude product also reveals the existence of cage mixture of T_8 (**5**; -66.81 ppm), T_{10} (**6**; -68.69 ppm), and T_{12} (**7**; -68.47 and -71.18 ppm). We hypothesize that acrylate anion plays the same role as methacrylate anion in the induction of cage-rearrangement of the silsesquioxane. After 0.90 gram of crude mixture was passed through silica column chromatography (ethyl acetate/*n*-hexane: 2:3), compounds **5** (T_8; 0.11 g; R_f = 0.40), **6** (T_{10}; 0.23 g; R_f = 0.35), and **7** (T_{12}; 0.14 g; R_f = 0.25) were successfully isolated in their pure forms. However, all three cages found in viscous liquids are similar to the case of cage-rearrangement azido-functionalized polyhedral oligomeric silsesquioxanes.

To understand the effects of relative organic substituents on some physical properties, it was known that poly(methyl acrylate) is a soft rubber, but poly(methyl methacrylate) is a strong, hard, and clear plastic at room temperature. Thus, only a small methyl group is able to have a significant impact on the physical properties and behavior of the material. As it turns out, how soft or hard a silsesquioxane cage is not only dependent on the identity of the inorganic core at a given temperature, but is also determined by organic substituent mobility, or how easily the substituents move and pass around each other. If the organic substituents between molecules can glide smoothly over each other, the overall whole mass of molecules will be able to flow more easily. Thus, a silsesquioxane cage, which has lower substituent mobility, will be more rigid, and have lower flexibility, whereas one which has higher substituent mobility will be softer and more pliable.

CONCLUSION

Octa-, deca-, and dodecameric-methacrylate and acrylate-functionalized silsesquioxanes were successfully synthesized and readily isolated in their pure forms through conventional column chromatography. Organic-inorganic silsesquioxane domain-based features allow us to understand the chemical structure-physical property relationships. Rather than using a mixture, the authors believe that using such an application for each pure silsesquioxane monomer could diversely obtain the specific properties of a material.

Project 3

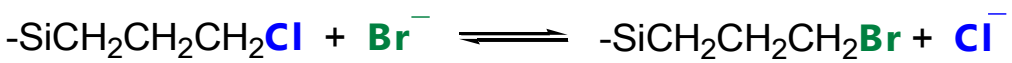
However, functionalizations on octakis(3-chloropropyl)octasilsesquioxane (**1**) usually require such a strong reaction (e.g. high temperatures, strong nucleophiles) leading to decrease the product yield, since its attachments of poorer leaving groups of chlorine atoms have been already known. This together with highly sensitive nature of inorganic silsesquioxane cage by the electronic influence of chlorine atoms and thermal decomposition could even lead to cage-rearrangement products (T_8, T_{10}, and T_{12}) during substitution reactions. Only a few study against cage-decomposition on **1** has been reported under mild condition during functionalization. In addition, organic alkylhalides particularly possessing either bromo or iodo atoms have been already proved to be more reactive precursors than chlorides in the nucleophilic substitution reaction because of favorable leaving ability.

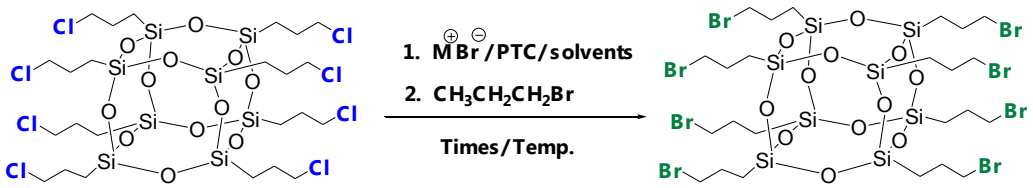
Likely, octakis(3-bromopropyl)octasilsesquioxane (**2**) and octakis(3-iodopropyl)octasilsesquioxane (**3**) could be served as better candidates to solve any problems above. For example, Fabritz *et al* reported the substitution reaction under strongly nucleophilic agent such as azide anions on either **2** or **3** at room temperature could give the desired product in very good yield and that mild synthesis conditions could not affect the inorganic silsesquioxane core of octameric T_8 structure. Nevertheless, the preparation of compounds **2** and **3** through halogen exchange or Finkelstein reaction has been reported to be impractical, if only **1** was alone with metal

halides. In this study, we found the most efficient method to prepare **2** and **3** with a complete halogen exchange under “one pot” reaction.

RESULTS AND DISCUSSION

Compound **2** was firstly synthesized *via* $FeCl_3$-catalyzed hydrolytic polycondensation starting from 3-bromopropyl trichlorosilane, but only 3% yield was obtained. Alternative approach to prepare **2** was also applicable when starting from **1** in the presence of lithium bromide (LiBr), however Fabritz *et al* also encountered at least five cycles of the procedure described to ensure complete substitution. Moreover, we further examined a variety of factors (Scheme 1) such as solvents (Table 1: Entries A1-A2), equivalences of reagent (Entries B1-B4), and reaction times (Entries C1-C3), however the complete substitution like Fabritz’s procedure in the first cycle can never be achieved. The most substitution at 72% was found in the reaction of **1** under refluxing THF either with 8 eq. LiBr for a day or with 5 eq. LiBr for 5 days (Entries B3 and C3, respectively). We suggest that the similar nucleophilicity and leaving ability between chloride and bromide anions play an important role to preclude the completion of substitution. The attacking and displaced groups would compete in equilibrium:





1 2

Scheme 1 General approach to synthesize Octakis(3-bromopropyl)octasilsesquioxane (**2**) in "one-pot" method.

In order to drive the equilibrium forward, excessive amount of bromide anions are needed, nonetheless the incomplete substitutions can still be observed (Entry B4). It seems unlikely that the complete substitution could be accomplished in the homogeneous fashion. We designed an alternative method toward successful synthesis of **2** in one-pot method. In this report, we further study the halogen exchange reaction under the heterogeneous system using sodium bromide (NaBr), if it were successful. Unlike highly soluble LiBr in polar aprotic solvents, NaBr could not be dissolved well in such solvents. Generally, substitution reactions, without any catalytic agents such as crown ethers or other phase-transfer catalysts (PTC) like tetrabutyl ammonium bromide (TBAB), were considered to be less effective (Entries D1-D2), because the nucleophile and reactant remain in separated phases.

Marsmann *et al* firstly introduced 18-crown-6 to enhance the solubility of nucleophilic agents from inorganic salts in order to functionalize silsesquioxanes. We suggest that either18-crown-6 or TBAB could act as a good candidate which solvates positively charged metal ions or induces electrostatic interaction, respectively, to ferry them into the homogeneous system. These processes then promote the solubility and

freedom of the corresponding anion in polar aprotic solvents. Interestingly, after optimization of catalyst types (Entries E1-E2), equivalences of NaBr (Entries F1-F3), and reaction times (Entries G1-G3 andH1-H3), the reaction of **1** with 3 eq. NaBr in refluxing acetone solvent for a day with the presence of 18-crown-6 gives the highest rate of halogen exchange reaction. Acetone and tetrahydrofuran (THF) are both polar aprotic solvent with the medium donor strength, however the dissociating power of acetone is greater compared to the THF (dielectric constant: $\varepsilon_{acetone}$= 21.36 and ε_{THF}= 7.47) According to the report, for most alkali metal salts, the predominant species in acetone solution are solvent-separated ion pairs in which the cationic and anionic groups are freely separated by the solvent, while those in THF solution are contact ion pairs, in which the cationic and anionic groups tend to form an aggregation. Furthermore, the solubility of sodium chloride (NaCl) by-product in acetone is far less than that of THF. Therefore, substitution reaction using alkali metal salt as a nucleophilic agent is more favourable in acetone solvent.

Unfortunately, both chloride-to-bromide exchange reaction in the presence of 18-crown-6 and TBAB were found to be incomplete, and substitution conversions were maximized at 79% and 78%, respectively. Once again, the existence of leaving chloride anions in reaction phase results in equilibrium and precludes the complete substitution. Attempting to minimize the amount of chloride ions, we introduced 3-bromopropane as an alkylating reagent *in situ* to accomplish the halogen exchange reaction. The reaction between 3-bromopropane and undesired chloride ions, yielding to the lower boiling point compound of 3-chloropropane, lessens the amount of chloride anions, while

supplements bromide anions. Thus, the equilibrium will be driven toward the desired compound **2**, leading to the complete substitution. From our experimental results, the addition of alkylating agent could significantly improve the substitution portion in all reaction conditions. For example, the percent substitution in Fabritz's method with the addition of 3-bromopropane was improved from 69% to 82%. It is also worth noting that 3-bromopropane must be introduced after the reaction mixtures exist at equilibrium, otherwise incomplete substitution reaction can be still observed (Entry O1).

Interestingly, we found that only TBAB could accomplish >99% substitution conversion (Entry M2 and N2), while 18-crown-6 could maximize at only 98% conversion (Entry K1-K7). In this case, a strong coordination ability of 18-crown-6 is responsible for the incomplete substitution. We suggest that a TBAB weakly bond with a solid lattice of NaCl, while 18-crown-6 firmly coordinates with sodium in the lattice and returns both sodium and chloride ions back into the reaction solution. Although, NaCl by-product could not be dissolved in acetone the same as NaBr, it will subsequently precipitate after its formation. The increasing concentration of chloride ions, competing with the decreasing by 3-bromopropane alkylating agent, will drive back the equilibrium. The maximum substitution conversion at 98%, even at a very long reaction time, well supports our explanation. The reaction progress was examined by means of ^{1}H NMR spectroscopy. As the results (Entry M2), the disappearance of 3-chloropropyl signals at δ 3.53, 1.82, 0.75 ppm and the appearance of new 3-bromopropyl signals at δ 0.81, 1.95, 3.42 ppm suggest a completion of halogen exchange reaction in 5 days to give the high yield. Its ^{29}Si{^{1}H} NMR of isolated product also shows a singlet signal at δ -

67.30 ppm. Hence, this result confirms the successful synthesis with the retention of T_8 silsesquioxanes cage. However, the ESI-MS result of **2** shows a strong signal at1352.4810 m/z. Alkylhalides, specifically said alkyl bromide, are known to have low thermal and chemical stability. The mass spectrum of **2** was obtained by using low ionization method, this compound yet readily undergoes decomposition and fragmentation, yielding to a variety of silsesquioxanes' fragments and isomers, for example ·R, ·RSi, ·RSiO, and ·$RSiO_2$. In addition, the replacement of terminal halide with hydroxide group is also noticeable in some studies. Therefore, we hypothesize that a peak at 1352.4810 m/z is consistent with $[C_{24}H_{49}Br_7NaO_{13}Si_8]^+$, in which it is produced when one bromo-substituent is replaced by hydroxide ion from water molecule.

However, it should be mentioned that using dry THF instead of acetone at the same conditions as Entries M2 and N2 with either TBAB (Entries P1-P2) or 18-crown-6 (Entries Q1-Q2) catalysts, none of the experiments satisfies the complete substitution reaction. Their crude products (Entries P1-P2) were obtained in a gummy form after working up and their ^1H NMR spectra also indicate the mixture of incomplete substitution products and other impurities. Moreover, ^1H NMR spectra of crude products (Entries Q1-Q2) clearly substantiate with the lowest efficiency of halogen exchange reaction, even the alkylating agent like 3-bromopropane was presented. These results strongly confirm that acetone is likely to give more sufficient and cleaner reaction than that of THF.

Table 1 Optimized conditions to prepare Octakis(3-bromopropyl)silsesquioxane (**2**) in “one pot” reaction

General procedure: All reactions were performed using 0.05 M of **1** in either acetone or THF solvent under reflux condition (70^{o}C at the oil bath temperature) with specific reagent’s equivalence and reaction time for each entry. If any phase transfer catalysts (PTC) was needed, either 30% w/w of 18-crown-6 or 37% w/w of TBAB were used in all reactions. An alkylating agent (37% v/v of *n*-propyl bromide, *n*-PrBr), if was presented, was added in situ and the resulting mixture was additionally refluxed in a certain time.

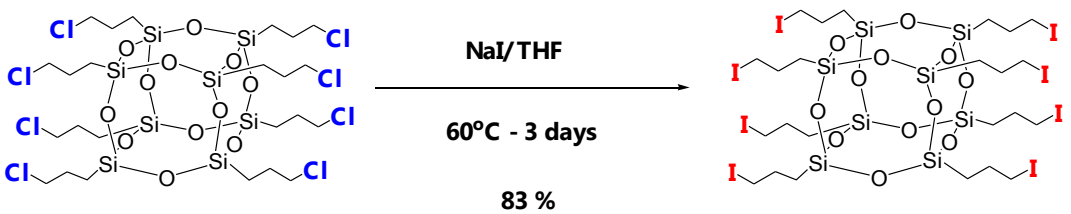
Entries	$M^{+}Br^{-}$ (eq)[a]	Solvents	PTC[b]	T (^{o}C)	Times (days)	Times (days) after addition of *n*-PrBr[c]	% sub[n]	% yield[d]
A1	LiBr (3eq)	Acetone	-	Reflux	1	-	54	N/A
A2	LiBr (3eq)	THF	-	Reflux	1	-	58	N/A
B1	LiBr (2eq)	THF	-	Reflux	1	-	47	N/A
B2	LiBr (5eq)	THF	-	Reflux	1	-	69	N/A
B3	LiBr (8eq)	THF	-	Reflux	1	-	72	N/A
B4	LiBr (10eq)	THF	-	Reflux	1	-	83	N/A

C1	LiBr (5eq)	THF	-	Reflux	2	-	68	N/A
C2	LiBr (5eq)	THF	-	Reflux	3	-	71	N/A
C3	LiBr (5eq)	THF	-	Reflux	5	-	72	N/A
D1	NaBr (3eq)	Acetone	-	Reflux	1	-	7	N/A
D2	NaBr (3eq)	THF	-	Reflux	1	-	0	N/A
E1	NaBr (3eq)	Acetone	CE	Reflux	1	-	79	N/A
E2	NaBr (3eq)	Acetone	TBAB	Reflux	1	-	71	N/A
F1	NaBr (2eq)	Acetone	CE	Reflux	1	-	72	N/A
F2	NaBr (3eq)	Acetone	CE	Reflux	1	-	79	N/A
F3	NaBr (5eq)	Acetone	CE	Reflux	1	-	79	N/A
G1	NaBr (3eq)	Acetone	CE	Reflux	2	-	79	N/A
G2	NaBr (3eq)	Acetone	CE	Reflux	3	-	78	N/A
G3	NaBr (3eq)	Acetone	CE	Reflux	5	-	78	N/A
H1	NaBr (3eq)	Acetone	TBAB	Reflux	2	-	79	N/A
H1	NaBr (3eq)	Acetone	TBAB	Reflux	3	-	78	N/A
H2	NaBr (3eq)	Acetone	TBAB	Reflux	5	-	79	N/A
I1	LiBr (5eq)	THF	-	Reflux	1	1	82	N/A
I2	LiBr (5eq)	THF	-	Reflux	1	3	93	N/A
I3	LiBr (5eq)	THF	-	Reflux	1	5	96	N/A
I4	LiBr (5eq)	THF	-	Reflux	1	7	94	N/A

J1	LiBr (10eq)	THF	-	Reflux	1	1	93	N/A
J2	LiBr (10eq)	THF	-	Reflux	1	3	95	N/A
J3	LiBr (10eq)	THF	-	Reflux	1	5	96	N/A
J4	LiBr (10eq)	THF	-	Reflux	1	7	95	N/A
K1	NaBr (3eq)	Acetone	CE	Reflux	1	1	86	N/A
K2	NaBr (3eq)	Acetone	CE	Reflux	1	2	90	N/A
K3	NaBr (3eq)	Acetone	CE	Reflux	1	3	93	N/A
K4	NaBr (3eq)	Acetone	CE	Reflux	1	5	95	N/A
K5	NaBr (3eq)	Acetone	CE	Reflux	1	7	98	89
K6	NaBr (3eq)	Acetone	CE	Reflux	2	3	97	N/A
K7	NaBr (3eq)	Acetone	CE	Reflux	3	2	96	N/A
L1	NaBr (3eq)	Acetone	TBAB	Reflux	1	2	90	N/A
L2	NaBr (3eq)	Acetone	TBAB	Reflux	1	3	94	N/A
L3	NaBr (3eq)	Acetone	TBAB	Reflux	1	4	95	N/A
M1	NaBr (3eq)	Acetone	TBAB	Reflux	2	2	96	N/A
M2	NaBr (3eq)	Acetone	TBAB	Reflux	2	3	>99	94
N1	NaBr (3eq)	Acetone	TBAB	Reflux	3	1	93	N/A
N2	NaBr (3eq)	Acetone	TBAB	Reflux	3	2	>99	85
O1	NaBr (3eq)	Acetone	TBAB	Reflux		5[e]	92	N/A
P1	NaBr (3eq)	THF	TBAB	Reflux	2	3	97	N/A
P2	NaBr (3eq)	THF	TBAB	Reflux	3	2	95	N/A

Q1	NaBr (3eq)	THF	CE	Reflux	2	3	75	N/A
Q2	NaBr (3eq)	THF	CE	Reflux	3	2	77	N/A

[a]equivalence per $RSiO_{3/2}$ unit. [b]CE = 18-crown-6, TBAB = tetrabutyl ammonium bromide. [c]In case of presented alkylating agent, after the halogen exchange reaction was reached in a certain time, 37%v/v of *n*-propyl bromide (*n*-PrBr) was subsequently added in situ. [d]N/A = not applicable. In all entries, only more than 98% substitution must be obtained prior the calculation of yield, otherwise the data would be invalid. [e]In O1 entry, all reagents including 3-bromopropane were added together at the beginning of the reaction.



1 **3**

Scheme 2 Synthesis of Octakis(3-iodopropyl)octasilsesquioxane (**3**) in "one-pot" method.

To prepare compound **3**, Marsmann *et al* firstly reported the halogen exchange reaction on **1** by using the excess of NaI under refluxing acetone solvent, however the complete reaction could not be accomplished until the introduction of countless regenerating cycles was introduced. We suggest that every chlorine atoms on **1** were unlike to be perfectly substituted under this particular condition. Later, Heyl, D. *et al* has

successfully improved the synthesis of **3** for the one-pot system. However, there was a report by the addition of catalytic agents: tetrabutyl ammonium iodide and 3-iodopropane under 2-butanone solvent and reflux condition. This would allow us to confirm its excessive reagents, although the homogeneous reaction was performed.

In this study, we found the catalytic-free system for NaI by standing alone in THF solvent. Under this particular condition, the complete halogen exchange reaction could be easily achieved without any addition of catalytic agents (Scheme 2). We suggest that only the stronger solvation around Na^+ by oxygen atoms in ether bonds of higher polarity of aprotic THF solvent would be enough to enhance the ion-pair dissociation between Na^+ and I^-. Consequently, the nucleophilicity of some carbanions would be extended as suggested by Chabanel *et al*. ^{1}H NMR spectroscopy was also used to monitor the reaction progress by the disappearance of signals of 3-chloropropyls, giving the appearance of new signals at δ 0.78, 1.91, and 3.23 (3-iodopropyl). Complete halogen exchange reaction (>99% substitution) was easily observed in 3 days at 60^{o}C to give the high yield (83%). Its ^{29}Si{^{1}H} NMR of isolated product also shows a singlet signal at δ -67.86 ppm, indicating that the cage-decomposition could not be occurred under such a condition. The formation of NaCl precipitation as an insoluble by-product, indicating the faster progression of reaction, should be easily noticed. Thus, it should be noted that if no elevated temperature was needed, the complete substitution reaction by iodine atoms could be even observed in an extended reaction time as a mild condition.

In Fig. 1, X-ray quality crystals of **3** were easily grown from THF : hexane (1:1)

as refined crystal structure is presented. Single-crystal X-ray diffraction analysis reveals that **3** was crystallized in the triclinic space group $P\bar{1}$ with the cubic silsesquioxane cage and the six faces of eight-membered ring of T_8 core.

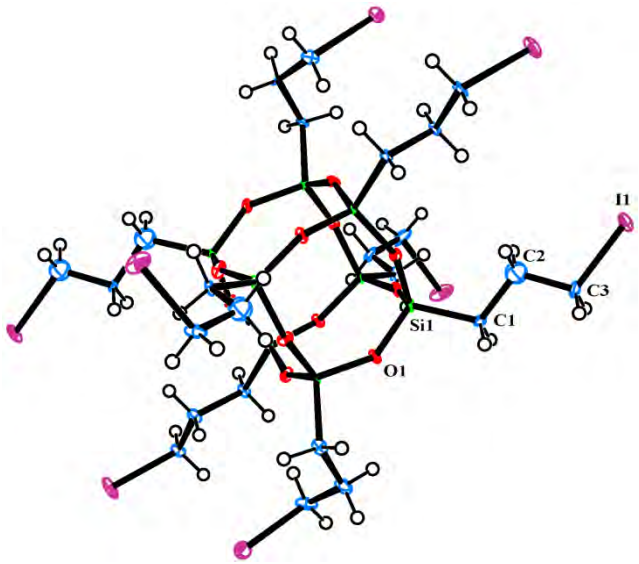


Fig. 1 ORTEP drawing of the asymmetric unit of **3** at 50% probability ellipsoids with some atomic labels**.**

It should be noted that a decomposition of colourless crystalline **3** was observed upon the X-ray explosionat 296 K yielding a yellow opaque solid. However, the quality of crystal could be sustained by decreasing the measurement temperature (100 K). It is commonly observed for compounds with highly containing iodine atoms under prolong or intense irradiation of X-ray.

CONCLUSION

This part describes the improvement in synthetic procedures as the most efficient method to obtain two cage-like T_8 silsesquioxanes: octakis(3-bromopropyl)octasilsesquioxane (**2**) and octakis(3-iodopropyl)octasilsesquioxane (**3**) under one-pot system with >99% substitution and excellent yield. The interesting results of how factors like reaction times, solvent effects, catalysts, and alkylating agents affect the S_N2 reaction on silsesquioxanes' moieties are profoundly discussed in this part.

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Output จากโครงการวิจัยที่ได้รับทุนจาก สกอ. และ สกว.

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

1.1 Jaroentomeechai, T.; Yingsukkamol, P.; Phurat, C.; Somsook, E.; Osotchan, T.; **Ervithayasuporn, V.***, "Synthesis and Reactivity of Nitrogen Nucleophiles-Induced Cage-Rearrangement Silsesquioxanes" *Inorg. Chem*. **2012**, *51*, 12266–12272. (Impact factor 2011 = 4.61)

1.2 **Ervithayasuporn, V.***,Chimjarn, S.“Synthesis and Isolation of Methacrylate and Acrylate-functionalized Polyhedral OligomericSilsesquioxanes (T_8, T_{10}, and T_{12}) and Characterization of the Relationship between Their Chemical Structures and Physical Properties" *Inorg. Chem.* **2013**, 52, 13108-13112. (Impact factor 2012 = 4.593)

1.3 **Ervithayasuporn, V.***; Pornsamutsin, N.; Prangyoo, P.; Sammawutthichai, K.; Jaroentomeechai, T.; Phurat, C.; Teerawatananond, T. “One-pot synthesis of Halogen exchange silsesquioxanes: Octakis(3-bromopropyl)octasilsesquioxane and Octakis(3-iodopropyl)octasilsesquioxane” *Dalton Trans.* **2013**, 42, 13747-13753. (Impact factor 2012 = 3.806)

1.4 **Ervithayasuporn, V.***; Sodkhomkhum, R.; Teerawatananond, T.; Phurat, C.; Phinyocheep, P.; Somsook, E.; Osotchan, T. "Unprecedented formation of cis- and trans-di[(3-chloropropyl)-isopropoxysilyl]-bridged Double-decker Octaphenylsilsesquioxanes" *Eur. J. Inorg. Chem.* **2013**, 3292-3296. (Impact factor 2012 = 3.12)

2. การนำผลงานวิจัยไปใช้ประโยชน์

- เชิงวิชาการ

ทีมผู้วิจัยประสบความสำเร็จในการ การสังเคราะห์ และการแยกของสารประกอบกลุ่ม Silsesquioxane ที่มีหมู่ฟังก์ชันเป็น o-Sulfobenzimide Phthalimide Iodo Bromo Acrylate และ Methacrylate ได้สำเร็จ โดยใช้เทคนิคการแยกแบบพื้นฐานเพียงคอลัมภ์โครมาโทรกราฟี หรือ การตกผลึก ซึ่งสามารถทำให้เกิดการนำไปประยุกต์ใช้การสังเคราะห์ ในระบบอุตสาหกรรมที่มีขนาดใหญ่ต่อไป ทั้งนี้ทีมผู้วิจัยยังได้ตั้งข้อสังเกตถึงคุณสมบัติเชิงกายภาพที่แตกต่างกัน อันเนื่องมาจากผลของโครงสร้างของผลิตภัณฑ์แต่ละชนิดที่แยกได้ ถึงแม้ว่าสารประกอบเหล่านี้จะมีหมู่ฟังก์ชันเคมีอินทรีย์แบบเดียวกัน แต่เนื่องจากเพราะผลของสมมาตรทางโมเลกุลของโครงสร้างบางส่วนที่เป็นเคมีอินทรีย์ที่แตกต่างกัน ย่อมส่งถึงสมบัติทางกายภาพตามไปด้วย ยกตัวอย่างเช่น สารประกอบ octakis(3-propyl methacrylate)octasilsesquioxane ในงานวิจัยนี้ มีโครงสร้างเป็นกรง T_8 คล้ายรูปทรงลูกบาศก์ มีลักษณะเป็นของแข็ง ผลึกใส ในขณะโครงสร้างกรงในรูปแบบชนิดอื่นๆ (T_{10} และ T_{12}) กลับพบมีลักษณะเป็นของเหลวหนืดใส โดยสารผลิตภัณฑ์ที่สังเคราะห์และแยกได้นั้น มักถูกใช้เป็นสารตั้งต้นพื้นฐานในการผลิตพอลิเมอร์ต่อไป

3. การเสนอผลงานในที่ประชุมวิชาการ

3.1 "Synthesis, Reactivity, and Functionalization of Polyhedral Oligomeric Silsesquioxanes (T_8, T_{10}, and T_{12})" , **V. Ervithayasuporn**, *Thailand-SKKU Nanotechnology Workshop*, Pathumthani (Thailand), January **2014**. (Invited speaker)

3.2 "Synthesis of Cage-rearrangement silsesquioxanes (T_8, T_{10}, and T_{12})" **V. Ervithayasuporn**, *Preprints of the 3rd International Symposium on Element Innovation Project*, Gunma (Japan), September **2013**. (Plenary speaker)

Inorganic Chemistry

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Synthesis and Reactivity of Nitrogen Nucleophiles-Induced Cage-Rearrangement Silsesquioxanes

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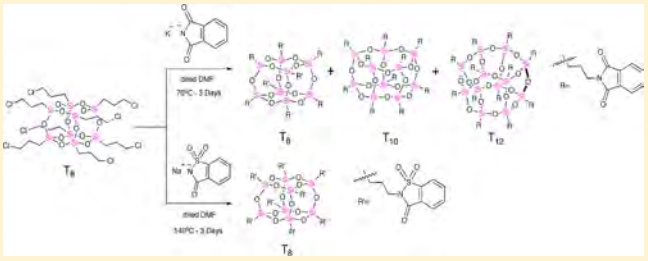
Supporting Information

ABSTRACT: Novel phthalimide and *o*-sulfobenzimide-functionalized silsesquioxanes were successfully synthesized via nucleophilic substitution reactions from octakis(3-chloropropyl)octasilsesquioxane. Surprisingly, the formation of deca- and dodecasilsesquioxanes cages was discovered during substitution with phthalimide, but only octasilsesquioxane maintained a cage in the *o*-sulfobenzimide substitution reaction. Moreover, we report the electronic effect of nitrogen nucleophiles to promote cage-rearrangement of inorganic silsesquioxane core for the first time. Structures of products were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, ESI−MS analysis, and single-crystal X-ray diffraction.



INTRODUCTION

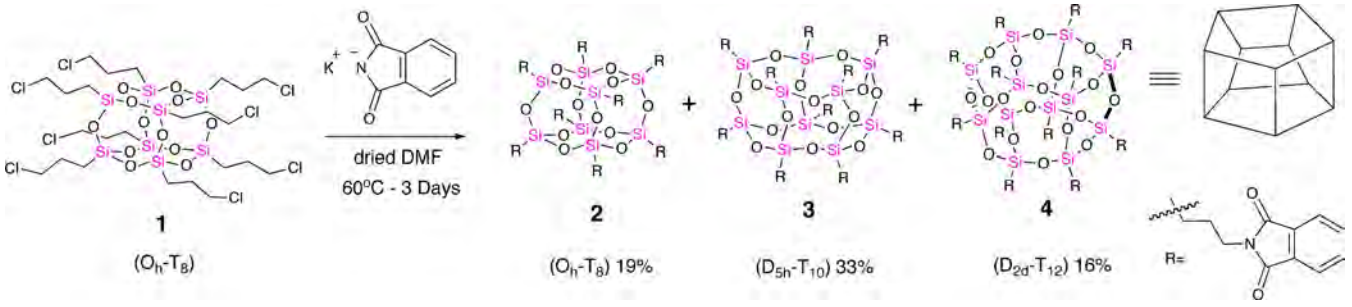
Silsesquioxanes are a class of hybrid organic−inorganic molecules with the general formula of $[RSiO_{3/2}]_n$ (with R as alkyl, aryl, allylene functional groups, or hydrogen atom).[1] They are found in various chemical architectures such as polymeric,[2] cage-like,[3] and ladder structures.[4] Because of their highly discrete nanoscale structures of Si−O inorganic core surrounded by organic functional groups, cage-like structures or polyhedral oligomeric silsesquioxanes are of particular interest. On the basis of these characteristics, cage-like silsesquioxanes molecules could serve as an excellent nanobuilding block with fine-tunable properties via chemical modifications. Recently, applications for silsesquioxanes-based materials have been found in polymer science,[5] catalysis,[6] biomedicine,[7] nanomaterials,[8] electronic devices,[9] and electrochemistry.[10] In general, organotrihalosilanes or organotrialkoxysilanes readily undergo hydrolytic condensation reactions in the presence of basic or acidic catalysts, leading to the formation of silsesquioxanes adducts.[11] However, the hydrolytic condensation reaction of silsesquioxanes compounds is highly sensitive, and the synthetic conditions crucially affect the selectivity of product's formation. Alternatively, nucleophilic substitution reactions on silsesquioxanes molecules could be developed to achieve high yield of selective products.[12] On the basis of the aforementioned perspective, octakis(3-chloropropyl)octasilsesquioxane (abbreviated as T_8-PrCl, **1**) is considered as a promising precursor for nucleophilic substitution reactions due to its ease of synthesis from commercially available precursor. Thus, novel functionalized silsesquioxanes could be prepared facilely from this precursor.[13,14]

The Gabriel method has been known for many decades and customarily used to transform primary alkylhalides to N-alkylated phthalimide precursors via a nucleophilic substitution reaction.[15] Traditional Gabriel synthesis consists of a two-step synthesis, which was then followed by acidic hydrolysis or refluxing with hydrazine to produce primary amines. Alternatively, another chemical such as sulfonamides could be used as Gabriel reagent,[16,17] and the subsequent precursors could be readily hydrolyzed to form secondary amines. From this aspect, we strongly believe that the Gabriel method could be utilized as an effective approach to produce N-alkylated phthalimide and sulfobenzimide silsesquioxanes through nucleophilic substitution reactions on T_8-PrCl. However, our products in this study obtained from these dissimilar nitrogen nucleophiles exhibited significant diversity. The reaction with phthalimide anion surprisingly leads to the formation of a mixture (T_8R_8, $T_{10}R_{10}$, and $T_{12}R_{12}$ where T_n = $(SiO_{1.5})_n$) of octakis(3-(1,3-dioxoisoindolin-2-yl)propyl)octasilsesquioxane (**2**), decakis(3-(1,3-dioxoisoindolin-2-yl)propyl)decasilsesquioxane (**3**), and dodecakis(3-(1,3-dioxoisoindolin-2-yl)propyl)-dodecasilsesquioxane (**4**), while the reaction with *o*-sulfobenzimide anion, at harsher synthetic condition, yields only a single cubic compound of octakis(3-(1,2-benzisothiazole-3-(2*H*)-one-1,1′-dioxydyl)propyl)octasilsesquioxane (**5**). From these unexpected results, studying the effect of electronic nature on

Received: July 12, 2012
Published: November 7, 2012

   dx.doi.org/10.1021/ic3015145 | *Inorg. Chem.* 2012, 51, 12266−12272

Scheme 1. Synthetic Approach for Preparation of Cage-Rearrangement Octa-, Deca-, and Dodeca-phthalimide-Functionalized Silsesquioxanes



nitrogen nucleophiles toward a selective formation of silsesquioxanes products should reveal the insightful knowledge about the selectivity in cage-rearrangement or cage-degradation phenomena.

RESULTS AND DISCUSSION

Preparation and Characterization of Cage-Rearrangement Silsesquioxanes. To investigate the nucleophilic substitution reactions, ^{1}H NMR spectroscopy was used to monitor the reaction's progress. After a mixture of **1** and potassium phthalimide salt was heated in dried DMF solution at 60 °C for 3 days (Scheme 1), the ^{1}H NMR spectrum of the crude product revealed a complete disappearance of the 3-chloropropyl's signals and the appearance of five new signals at 0.55, 1.65, 3.53, 7.59, and 7.67 ppm. The first three signals are consistent with protons in propylene linkages, while the multiplet signals within aromatic regions arise from phthalimide moieties. However, the spectrum shows broad signals with clear splitting patterns, possibly indicating cage decomposition products. Surprisingly, the ^{29}Si{^{1}H} NMR spectrum of crude product gives distinguishably four singlet signals at −67.10, −68.71, −68.94, and −71.43 ppm that can be attributed to the cage-rearrangement products[19] (T_8, T_{10}, and T_{12}; Figure 1), along with a large peak of glass wall between −80 and −120 ppm. Following the satisfactory chromatographic analysis, their separations to obtain each pure compound were further undertaken. We observed that the crude product (1.00 g) by using only conventional column chromatography in a mixture solvent of ethyl acetate/hexane (4.0:1.0) could be easily separated into T_{10}, **3** (0.33 g; R_f = 0.33) as a major product, while T_8, **2** (0.19 g; R_f = 0.45) and T_{12}, **4** (0.16 g; R_f = 0.23) are obtained as minor products.

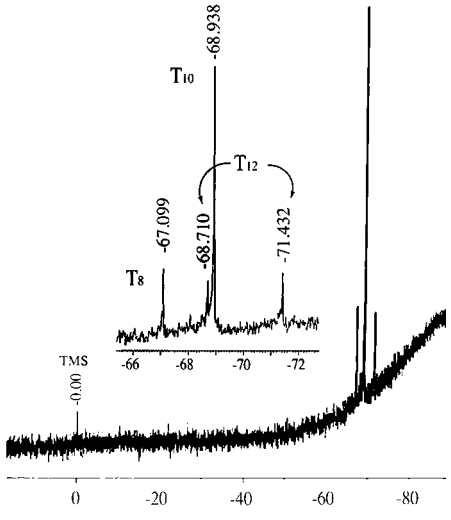


Figure 1. ^{29}Si{^{1}H} NMR spectrum of phthalimide-functionalized silsesquioxanes crude product.

According to our previous report,[18] the cage-rearrangement of **1** under the reaction with azide anion in a solution of DMF at elevated temperature also yields a mixture (T_8, T_{10}, and T_{12}) of azido-functionalized silsesquioxane products. Similarly, the decasilsesquioxane T_{10} cage was reported as a major form. Our hypothesis predicts that a cage-rearrangement mechanism would be reasonable only when the nucleophilicity of nitrogen anions is strong enough to induce the cleavage of silicon−oxygen bonds in the core network to produce particular fragments. Nitrogen−silicon bonds formed during substitution reactions and the subsequent molecular self-assembly of these fragments would allow the formation of thermodynamically favorable cage-like silsesquioxanes.

Moreover, ^{1}H and ^{13}C{^{1}H} NMR spectra of compounds **2**, T_8 and **3**, T_{10} exhibit identical patterns, and thus cannot be distinguished. In this study, further characterizations by ^{29}Si{^{1}H} NMR and mass spectrometry enable the determination of the identity of each compound. ^{29}Si{^{1}H} NMR spectra for both pure **2** and **3** exhibit only singlet signals at −67.11 and −68.95 ppm (Figure 2a and 2b), respectively. A symmetrical environment for silicon atoms on each structure (T_8 and T_{10}) would be predicted. Nevertheless, the ^{29}Si{^{1}H} NMR spectrum of **4** (T_{12}) produces double singlet signals at −68.74 and −71.46 ppm (Figure 2c), corresponding to the two different types of silicon atoms in a dodecasilsesquioxane cage. Among the twelve silicon atoms in dodeca-structure, eight atoms are present in the interior within two 10- and one 8-membered fused rings, but another four atoms are in two 8- and one 10-membered fused rings. These differences in the chemical shift are attributed to a ring-strain on the silsesquioxane cages (T_8, T_{10}, and T_{12}). This interpretation is consistent with the studies by Marsmann and Kawakami et al.,[18,19] as well as Rikowski[19a] proposed the electron withdrawing group (chlorine atom) on octakis(3-chloropropyl)-octasilsesquioxane effects to the cage-rearrangement reaction under basic conditions. As a result, the ^{13}C{^{1}H} NMR spectrum of **4** shows doubly singlet signals for each carbon in propylene linkages, which are strong evidence to confirm the presence of two distinct environments in the dodecasilsesquioxanes cage.

Preparation and Characterization of Cubic Octasilsesquioxane. The reaction of *o*-sulfobenzimide salt on **1** was shown in Scheme 2. From the observation, even a minuscule amount of water crucially affected the reaction, leading to the

dx.doi.org/10.1021/ic3015145 | Inorg. Chem. 2012, 51, 12266−12272

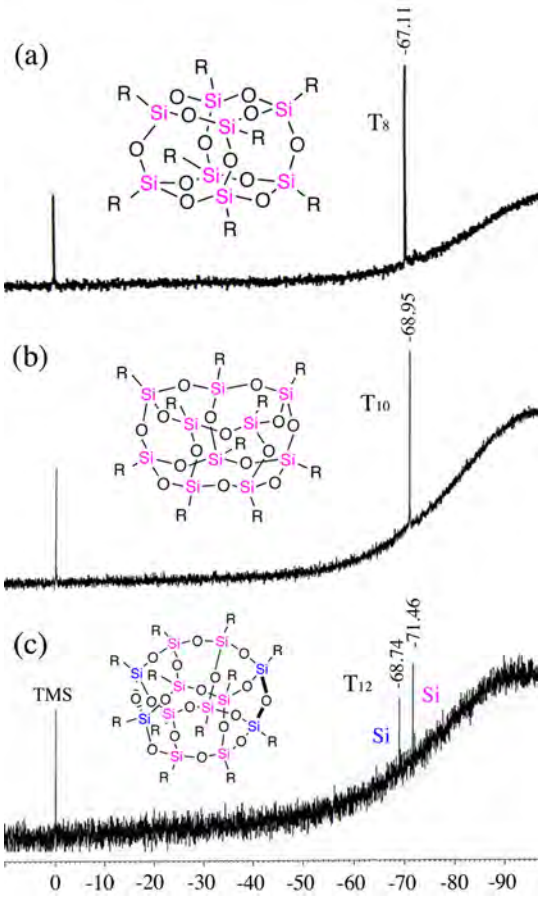
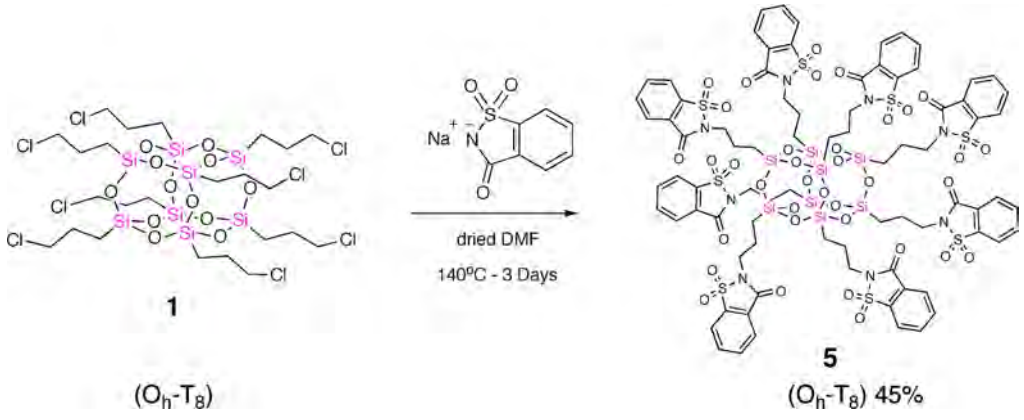


Figure 2. $^{29}Si\{^{1}H\}$ NMR spectra of purified compounds (a) octa-, (b) deca-, and (c) dodeca-phthalimide-functionalized silsesquioxanes (**2**, **3**, and **4**).

decomposition of precursor **1** and yielding various unwanted by-products. Because commercial *o*-sulfobenzimide salt attains a large amount of water, removal of water molecules in the lattice salt is necessary prior to performing the reaction. It is also worth noting that the regioselectivity in the reaction must be taken into account, because *o*-sulfobenzimide anion is an ambident nucleophile with the possibility to be alkylated at both nitrogen and oxygen atoms.[20] Several reports have indicated the effects of solvent, temperature, and catalyst toward regioselectivity of O- and N-alkylations on sulfobenzimide.[21] In dried DMF solution, the thermal transformation of O-alkylated into more stable N-alkylated products proceeds via a Chapman–Mumm rearrangement mechanism.[22] Interestingly, our harsh conditions were also capable for both O- and N-alkylations, depending mainly on the synthetic temperature. At 100 °C, the substitution conversion was found in 87% with the 1:10 ratio of O-alkylated to N-alkylated products. The explanation for the O-/N-alkylated proportion arises from the fact that stronger nucleophile of nitrogen anion reacts more rapidly than weaker nucleophile of oxygen anion (kinetic factors). Nevertheless, after the synthetic temperature was elevated to 140 °C, ^{1}H NMR spectrum of crude product reveal >99% substitution. The O-alkylation was negligibly detected, while the N-alkylation was mainly perceived. We propose that a less stable O-alkylation product transforms reversibly into a more stable N-alkylated product at higher temperature (thermodynamic factors). From chromatographic analysis of crude product in the solvent mixture of ethyl acetate/hexane (19.0:1.0), three major fractions were identified. The first two fractions at R_f = 0.34 and 0.42 appear as broad stains, which may likely represent a tangible evidence, later confirmed by $^{29}Si\{^{1}H\}$ NMR analysis, of incomplete substitutions and decompositions of oligomeric fragments. By means of conventional column chromatography, pure compound of **5** (R_f = 0.23) was obtained in 45% yield. ^{1}H NMR analysis of **5** reveals three new signals of aliphatic protons on propylene linkages at 0.77, 1.97, and 3.76 ppm, and additional two multiplet signals of aromatic protons on *o*-sulfobenzimide moieties at 7.75 and 7.95 ppm. In addition, the $^{29}Si\{^{1}H\}$ NMR spectrum displays only one singlet at −67.12 ppm, and high-resolution mass analysis detects a molecular ion at m/z 2247.1077. According to this analysis, we conclude that, under this synthetic condition, the octasilsesquioxane cage was obtained as a major compound without the occurrence of additional cage-rearrangement products.

To testify the validity of our presumption, we analyzed the mass spectrum of crude product from *o*-sulfobenzimide substitution reaction and found that the highest molecular ion falls into the octasilsesquioxane region. In fact, no other molecular ion of larger cages was clearly observed. We suggest that nucleophilicity of nitrogen atom in *o*-sulfobenzimide anion is significantly suppressed by the presence of more electron-delocalizing groups such as sulfonyl ($-SO_2R$). Likewise, decreased reactivity of the nucleophilic substitution reaction via S_N2 is also consistent with this proposition. Consequently,

Scheme 2. Synthesis of Octa *o*-Sulfobenzimide-Functionalized Silsesquioxane



dx.doi.org/10.1021/ic3015145 | *Inorg. Chem.* 2012, 51, 12266–12272

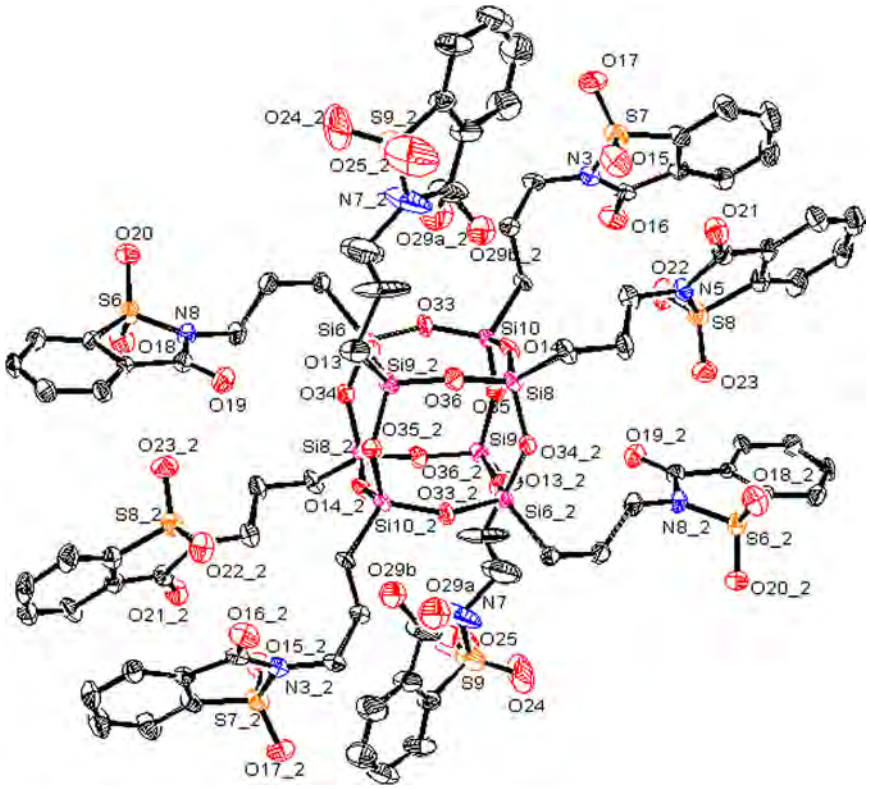


Figure 3. Thermal ellipsoids plot at 30% probability level of **5**; H atoms are omitted for clarity.

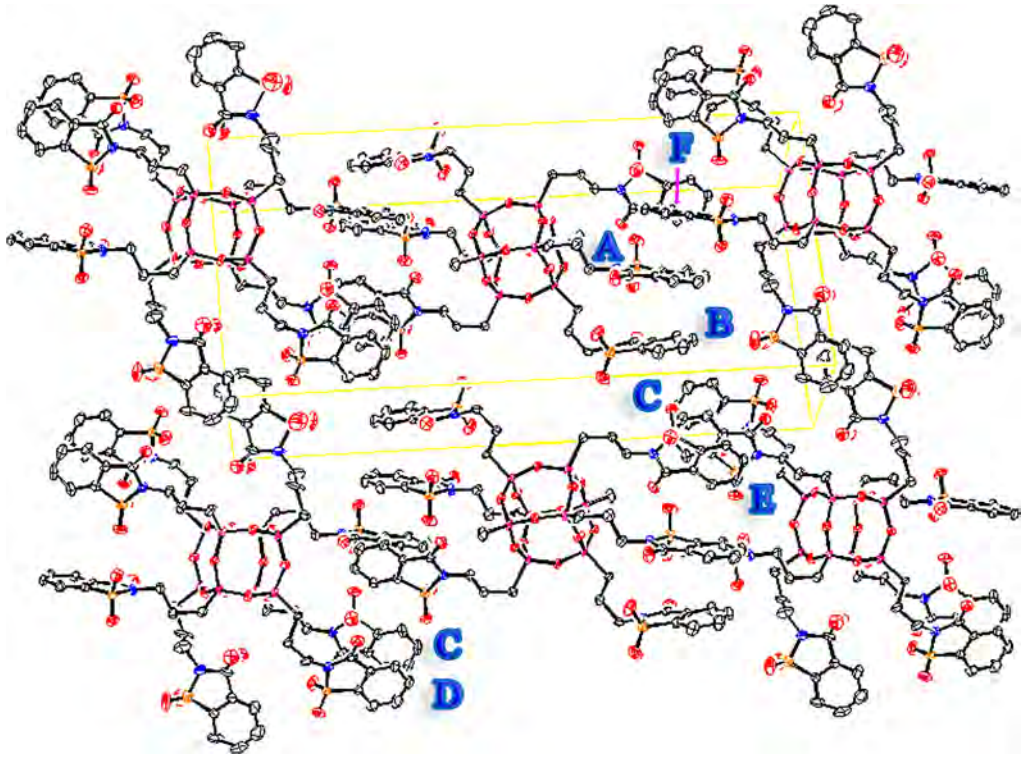


Figure 4. Packing diagram of **5** is presented by intra- and intermolecular $\pi-\pi$ interactions.

an *o*-sulfobenzimide nucleophile ineffectively interacts with silicon atoms and unfavorably induces cage-opening at the silsesquioxane core. Thus, the nitrogen atom of *o*-sulfobenzimide anion could not lead to a cage-rearrangement or yield a mixture of octa-, deca-, and dodecasilsesquioxanes cages, which were found in the reactions with azide and phthalimide anions.

Crystal Structure. To prove our assumption above, the crystallized product **5** was also analyzed by the single-crystal X-ray diffraction analysis. In Figure 3, the final refinement of

dx.doi.org/10.1021/ic3015145 | *Inorg. Chem.* 2012, 51, 12266−12272

structure reveals unambiguously that this compound is actually cubic T_8 octasilsesquioxane cage (Figure 3). This evidence could strongly support our previous characterizations by $^{29}Si\{^1H\}$ NMR and mass spectrometry. The packing diagram of **5** in Figure 4 and the Supporting Information also shows the extended molecular structure by shorter distances of intermolecular $\pi-\pi$ stacking interactions between neighboring molecules of sulfobenzimide A (S1, N9, C1, C2, C3, C8, C9, C10, C11) and F (S6, N8, C34, C35, C36, C41, C42, C43, C44) rings and between C (S8, N5, C60, C61, C62, C63, C64, C65, C66) and E (S5, N1, C16, C17, C18, C19, C20, C21, C22) rings. The centroid-to-plane distances between A−F and C−E benzene rings are 1.410 and 1.379 Å, respectively, and the dihedral angles between these ring planes are 6.13° and 6.19°. In addition, it should be noted that there are two intramolecularly symmetry-unrelated weak slipping face to face $\pi-\pi$ stacking interactions between benzene rings on sulfobenzimide groups: A and B (S3, N10, C27, C28, C29, C30, C31, C32, C33) rings, and C and D (S10, N3, C45, C46, C47, C48, C49, C50, C51) rings. The centroid-to-plane distances between A−B and C−D benzene rings are 1.640(3) and 1.665(3) Å, respectively. Thus, the dihedral angles between these ring planes are 12.767° and 13.069°.

Influence of Nitrogen Nucleophiles toward the Selectivity of Cage-Rearrangement Phenomena. According to the experimental results, nitrogen atom in phthalimide anion leads to the formation of cage-rearrangement products, while sulfobenzimide anion does not, even at harsher conditions. We hypothesize that the electronic nature of nitrogen anions is the major factor in promoting cage-rearrangement reaction. The silicon structures of products (T_8, T_{10}, and T_{12}) obtained from the reaction of **1** with phthalimide anion are the same as azide anion in our previous report.[18] Because the cleavage of Si−O bond, and subsequent formation of nitrogen−silicon bonds occur within the core of cage-structure, azide and phthalimide anions must be able to get through to the inorganic core structure of silsesquioxane, sulfobenzimide anion, yet could not. In this model, the electron density of nitrogen atoms among these three nucleophiles is consistent with the degree of nucleophilicity in the substitution reaction. We conclude that the experimental rate of nucleophilicity-induced cage-rearrangement would be azide > phthalimide > sulfobenzimide anions.

CONCLUSION

Four highly functionalized T_n silsesquioxanes (n = 8, 10, and 12) have been successfully synthesized as novel precursors for Gabriel synthesis. Despite the dissimilar nitrogen nucleophiles, substitution reaction with the phthalimide anion surprisingly yields a mixture of octa-, deca-, and dodecasilsesquioxanes cages, whereas reaction with sulfobenzimide anion produces only the octasilsesquioxane cage. Thus, the influence of the electronic nature of nitrogen anions induced cage-rearrangement silsesquioxane was experimentally reported for the first time. The theoretically mechanistic study of these reactions is currently under investigation. We believe that these cage-liked silsesquioxanes are promising materials for further functionalization and preparation of other reactive nitrogen-based silsesquioxanes, especially for future generation of unreported amino-functionalized deca- and dodecasilsesquioxanes.

EXPERIMENTAL SECTION

Materials. 3-Chloropropyltrimethoxysilane (purity; >95.0%), potassium phthalimide (purity; >98.0%), and sodium saccharin (purity; >98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. and used without additional purification. Anhydrous *N*,*N*-dimethylformamide was purchased from Sigma Aldrich, while the commercial grade of ethyl acetate, methylene chloride, and hexane was further distilled. Precoated silica gel 60 F_{254} plates and silica gel (no. 60) used for chromatography were purchased from Merck & Co., Inc.

Physical Measurement and Instrumentation. Fourier transform nuclear magnetic resonance spectra were obtained by using a Bruker-DPX 300 high-resolution nuclear magnetic resonance spectrometer for ^1H nuclei (300 and 500 MHz) and a Bruker-AV 500 high-resolution magnetic resonance spectrometer for $^{13}C\{^1H\}$ (125 MHz) and $^{29}Si\{^1H\}$ (99 MHz) nuclei. Chemical shifts were reported in δ units (parts per million) relative to tetramethylsilane, and residual solvents peaks were used as a reference. High-resolution mass spectrometry was performed with a VQ-TOF 2 Micromass spectrometer.

Synthesis of Cage-Rearrangement Silsesquioxanes. *Octakis(3-(1,3-dioxoisoindolin-2-yl)propyl)octasilsesquioxane (**2**), Decakis(3-(1,3-dioxoisoindolin-2-yl)propyl)decasilsesquioxane (**3**), and Dodecakis(3-(1,3-dioxoisoindolin-2-yl)propyl)dodecasilsesquioxane (**4**).* Octakis(3-chloropropyl) octasilsesquioxanes (**1**) was prepared following established procedures.[23] A mixture of **1** (0.80 g, 0.77 mmol) and potassium phthalimide (1.94 g, 10.47 mmol) was added into a dried two-necked flask. The solid mixture was further dried over vacuum at room temperature for an additional hour. Anhydrous DMF (20.00 mL) was added into the flask via a transfer syringe, and the solution mixture was connected to the condenser under dried nitrogen. After being heated at 60 °C for 3 days, the reaction solution was cooled and worked up by pouring into a slurry of deionized-water/ice. A white precipitate containing the crude product (1.56 g) was immediately formed, filtered, and dried in air. The composition of the crude product was further analyzed by TLC method with a solvent mixture of ethyl acetate:hexane (4.0:1.0) to obtain three major fractions at R_f values at 0.45, 0.33, and 0.23, identified as octakis(3-(1,3-dioxoisoindolin-2-yl)propyl)octasilsesquioxane (**2**), decakis(3-(1,3-dioxoisoindolin-2-yl)propyl)decasilsesquioxane (**3**), and dodecakis(3-(1,3-dioxoisoindolin-2-yl)propyl)dodecasilsesquioxane (**4**), respectively. Subsequently, 1.00 g of crude product was separated by silica gel column chromatography to give **2** (0.19 g, 0.098 mmol, 18.84% as a white powder solid), to give **3** (0.33 g, 0.14 mmol, 33.64% as a white powder solid), and to give **4** (0.16 g, 0.055 mmol, 15.86% as a transparent film). **2**, ^1H NMR ($CDCl_3$): δ 0.64 (t, 16H, $^3J_{H-H}$ = 8.10 Hz), 1.74 (quintet, 16H, $^3J_{H-H}$ = 7.80 Hz), 3.58 (t, 16H, $^3J_{H-H}$ = 6.0 Hz), 7.59 (multiplet, 16H), 7.66 (multiplet, 16H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.48, 21.81, 40.11, 122.94, 132.19, 133.43, 168.14 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ −67.11 ppm. HRMS (ESI): $[M + Na]^+$ calcd for $[C_{88}H_{80}N_8NaO_{28}Si_8]^+$, m/z 1943.3128; found, m/z 1943.3844. **3**, ^1H NMR ($CDCl_3$): δ 0.63 (t, 20H, $^3J_{H-H}$ = 8.15 Hz), 1.73 (quintet, 20H), 3.61 (t, 20H, $^3J_{H-H}$ = 7.47 Hz), 7.58 (multiplet, 20H), and 7.65 (multiplet, 20H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.54, 21.97, 40.22, 122.96, 132.26, 133.41, 168.14 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −68.95 ppm. HRMS (ESI): $[M + Na]^+$ calcd for $[C_{110}H_{100}N_{10}NaO_{35}Si_{10}]^+$, m/z 2425.4010; found, m/z 2425.4967. **4**, ^1H NMR ($CDCl_3$): δ 0.55 (t, 24H, $^3J_{H-H}$ = 8.01 Hz), 1.64 (quintet, 24H), 3.53 (t, 24H, $^3J_{H-H}$ = 7.30 Hz), 7.50 (multiplet, 24H), and 7.58 (multiplet, 24H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.55, 10.11, 22.01, 22.08, 40.12, 40.31, 122.92, 132.27, 133.33, 168.06, 168.07 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$) δ −68.74, −71.46 ppm. HRMS (ESI): $[M + Na]^+$ calcd for $[C_{132}H_{120}N_{12}NaO_{42}Si_{12}]^+$, m/z 2905.4819; found, m/z 2905.5907.

Synthesis of Cubic Octasilsesquioxane. *Octakis(3-(1,2-benzisothiazole-3-(2H)-one-1,1′-dioxydyl)propyl)octasilsesquioxane (**5**).* Initially, *o*-sulfobenzimide sodium salt dihydrate (4.85 g, 23.64 mmol) was dried over a vacuum at 60 °C for 6 h in a dried two-necked flask. After being cooled to room temperature, **1** (1.03 g, 0.99 mmol) was added into the reaction portion, and the solid mixture was further dried over vacuum at room temperature for an additional hour.

dx.doi.org/10.1021/ic3015145 | *Inorg. Chem.* 2012, 51, 12266−12272

Anhydrous DMF (20.00 mL) was added into the flask via a transfer syringe, and the solution mixture was connected to the condenser under dried nitrogen. After being heated at 140 °C for 3 days, the reaction solution was cooled and worked up by pouring into slurry of deionized-water/ice. A white precipitate containing the crude product (3.19 g) was immediately formed, filtrated, and then dried over air. The composition of the crude product was further analyzed by TLC method with a solvent mixture of ethyl acetate:hexane (19.0:1.0) to reveal one major fraction at R_f value = 0.23, corresponding to octakis(3-(1,2-benzisothiazole-3-(2*H*)-one-1,1′-dioxydyl)propyl)-octasilsesquioxane (**5**), while other fractions were assigned to byproducts. Subsequently, 1.00 g of crude product was separated by silica gel column chromatography to obtain **5** (0.42 g). Recrystallization in CH_2Cl_2/hexane mixed-solvent yielded a colorless needle-like crystal (0.31 g, 0.14 mmol, 45% yield). Note that repeated recrystallization may be required to obtain purified compound. ^{1}H NMR ($CDCl_3$): δ 0.77 (t, 16H, $^3J_{H-H}$ = 8.10 Hz), 1.97 (quintet, 16H, $^3J_{H-H}$ = 7.50 Hz), 3.76 (t, 16H, $^3J_{H-H}$ = 6.00, 7.50 Hz), 7.75 (multiplet, 24H), and 7.95 (d, 8H, $^3J_{H-H}$ = 3.30 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 8.86, 21.93, 41.37, 102.69, 125.00, 127.56, 133.87, 134.22, 137.72, and 158.72 ppm. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ −67.12 ppm. HRMS (ESI): $[M + K]^+$ calcd for $[C_{80}H_{80}KN_8O_{36}S_8Si_8]^+$, m/z 2247.0232; found, m/z 2247.1077.

X-ray Structural Determination. Crystalline **5** suitable for X-ray structural analysis was obtained by recrystallization in CH_2Cl_2/hexane. X-ray data were collected by Bruker SMART APEX II CCD area-detector diffractometer, with Mo Kα radiation source (λ = 0.7107 Å) at 296 K. The crystal structures were solved by the directed method with SHELXS-97.[24] The full matrix least-squares procedures using SHELXL-97 on F^2 anisotropic for all non-hydrogen atom was used to refine the crystal structures. Hydrogen atoms were placed in their calculated positions and refined following the riding model. The crystal data and structural refinement parameters are summarized in Table 1 (Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C, ^{29}Si NMR, and ESI−MS spectra giving characterization data for new compounds **2**−**5** and crystallographic data in a CIF file of **5** (CCDC 891141). 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.

■ ACKNOWLEDGMENTS

This research is financially supported by the Thailand Research Fund (MRG5580011), the Office of the Higher Education Commission, Center of Excellence for Innovation in Chemistry (PERCH-CIC), and NANOTEC Center of Excellence at Mahidol University, National Nanotechnology Center, Thailand. Moreover, we are very grateful to Assoc. Prof. Nongnuj Muangsin and Mr. Thapong Teerawatananond for a discussion in single-crystal X-ray analysis.

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Synthesis and Isolation of Methacrylate- and Acrylate-Functionalized Polyhedral Oligomeric Silsesquioxanes (T_8, T_{10}, and T_{12}) and Characterization of the Relationship between Their Chemical Structures and Physical Properties

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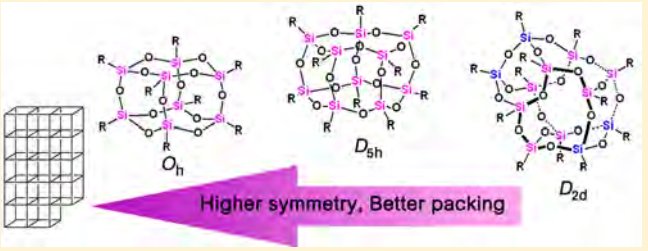
Supporting Information

ABSTRACT: Novel organic−inorganic hybrid nanobuilding blocks of methacrylate- and acrylate-functionalized polyhedral oligomeric silsesquioxanes were easily prepared via nucleophilic substitution on octakis(3-chloropropyl)-octasilsesquioxane, using sodium methacrylate and sodium acrylate, respectively. From a practical standpoint, these cage-rearranged silsesquioxanes (T_8, T_{10}, and T_{12}) could be readily isolated in their pure form with conventional silica gel column chromatography. Octakis(3-propyl methacrylate)-octasilsesquioxane (T_8) is a colorless, crystalline solid with a melting point of 66.7−67.2 °C, while other cage products are colorless viscous liquids at room temperature. Moreover, we report that the chemical structure/physical property relationship of silsesquioxane cages not only is dependent on the symmetry of the inorganic silsesquioxane core at a given temperature but also is dictated by the organic substituent mobility. Structures of the products were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and high resolution electrospray ionization mass spectrometry analysis.



INTRODUCTION

Acrylate and methacrylate esters are reactive unsaturated monomers that form polymers that have numerous applications as adhesives, coatings, photopolymer printing plates, and contact lenses.[1] These monomers can also be utilized for organic synthesis in Michael additions with enolates,[2] amines,[3] and thiols.[4] More recently, significant attention has been placed on organic−inorganic hybrid materials, particularly the polyhedral oligomeric silsesquioxanes. These hybrid molecules generally consist of an inorganic core made up of a Si−O framework, which is covalently surrounded by organic groups, giving them a dendritic-like structure.[5] For example, octakis(3-chloropropyl)octasilsesquioxane, T_8 (**1**),[6] bearing 1° alkyl chlorides, can be readily modified to contain various functional groups (e.g., azide,[7] thioester,[8] cyano,[9] phthalimide,[10] bromo, and iodo[11]) via nucleophilic substitution reactions. Nevertheless, some studies have found that inorganic phase transformation of the T_8 cage into cage-rearranged products (T_8, T_{10}, and T_{12}) is promoted by strong nucleophiles during substitution reactions.[7,10] Recently, polyhedral oligomeric silsesquioxanes have found a use in materials science as nanocomposites,[12] in optoelectronics,[13] and in biotechnology[14] and as catalysts.[15]

In order to broaden the applications of polyhedral oligomeric silesquioxane chemistry, it is necessary to develop new types of reactions. In this study, we report on the design, synthesis and characterization of multimethacrylate and acrylate organic functions for silsesquioxane cage-like structures (T_8, T_{10}, and T_{12}). Here, we performed characterization with the clean and purified forms of these compounds for the first time, in contrast to previous reports, which have only relied on crude mixtures of freshly prepared[16] and commercially available products[17] without further purification. Moreover, several important aspects regarding the optimal reaction conditions were not taken into consideration in those studies. We report several relationships between the chemical structures of each pure silsesquioxane cage and its physical properties. For example, octakis(3-propyl methacrylate)octasilsesquioxane (**2**) is a colorless, crystalline solid, which makes it unique among other silsesquioxanes, which are in the liquid state at room temperature.

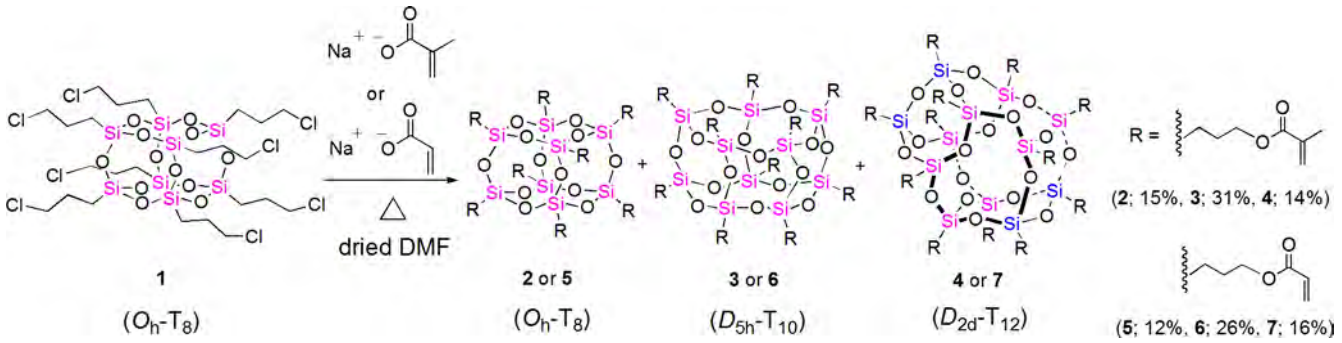
RESULTS AND DISCUSSION

Preparation and Characterization of Methacrylate-Functionalized Cage-Rearranged Silsesquioxanes. We first prepared **2**, decakis(3-propyl methacrylate)-decasilsesquioxane (**3**), and dodecakis(3-propyl methacrylate)-dodecasilsesquioxane (**4**) through nucleophilic substitution reactions. Upon treatment of **1** with sodium methacrylate in

Received: August 2, 2013
Published: October 31, 2013

   dx.doi.org/10.1021/ic401994m | Inorg. Chem. 2013, 52, 13108−13112

Scheme 1. Cage-Rearranged T_8 of Compound 1 upon Full Introduction of Methacrylate and Acrylate Functions, Leading to (a) Compounds 2−4 (70 °C, 2 days, 0.048 mol L^{-1}, 1.4 equiv of Sodium Methacrylate/$RSiO_{3/2}$) and (b) Compounds 5−7 (100 °C, 1 day, 0.098 mol L^{-1}, 1.4 equiv of Sodium Acrylate/$RSiO_{3/2}$)



anhydrous *N*,*N*-dimethylformamide (DMF) at 70 °C (Scheme 1a), an almost complete substitution conversion (~98%) of the crude product could be observed within 48 h, as monitored by the shift in the ^{1}H NMR peaks from 3.53, 1.82, and 0.75 (3-chloropropyl groups) to 4.09, 1.74, and 0.68 (3-methacryloxypropyl groups) ppm, respectively.

Meanwhile, we observed extensive cage rearrangement (T_8 cage) of **1** through the presence of four very distinguishable singlet signals in the ^{29}Si{^{1}H} NMR spectrum of the crude product (Figure 1) at −66.81, −68.44, −68.68, and −71.14

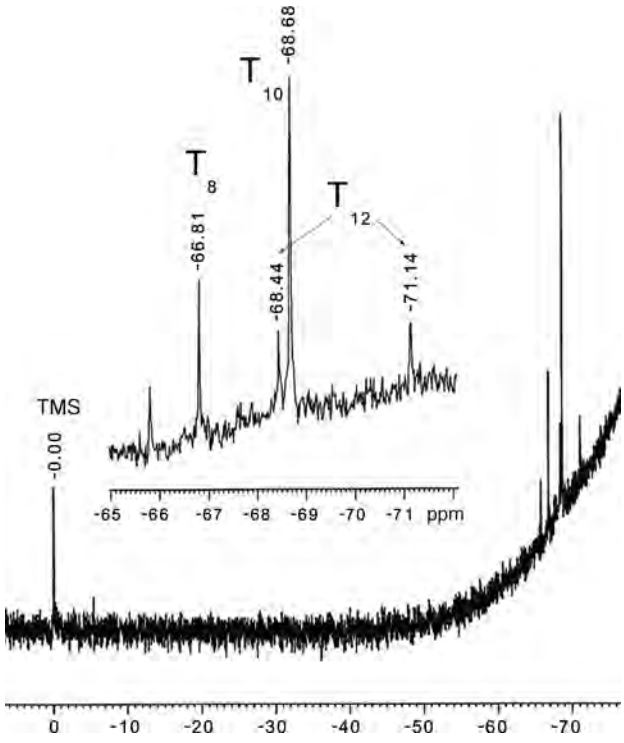


Figure 1. ^{29}Si{^{1}H} NMR spectrum of the crude product of methacrylate-functionalized polyhedral oligomeric silsesquioxanes.

ppm. Unambiguously, this crude product consists of a cage mixture of T_8 (**2**; −66.81 ppm), T_{10} (**3**; −68.68 ppm), and T_{12} (**4**; −68.44 and −71.14 ppm). In addition to undergoing substitution reactions, it is likely that methacrylate anions further attack, cleave, fragment, and reassemble the Si−O−Si bonds of the inorganic core, leading to the formation of a thermodynamically stable mixture of cage-rearranged products (T_8, T_{10}, and T_{12}). This phenomenon is possible due to the direct effects of the electron-withdrawing groups present and the low steric hindrance of the 3-substituted propyl chains on the silsesquioxane cage under these harsher reaction conditions in which there are stronger nucleophiles present.[7a,10,18] According to satisfactory chromatographic analysis on thin-layer chromatography (TLC) plates with silica gel, their isolation to obtain each pure product was carefully examined.

In Figure 2, we found that only by using conventional silica gel column chromatography in a solvent mixture of ethyl acetate/*n*-hexane (3:7), the crude product (0.80 g) could be easily separated into **3** (T_{10}; 0.25 g; R_f = 0.40) as a major product, while **2** (T_8; 0.12 g; R_f = 0.45) and **4** (T_{12}; 0.11 g; R_f = 0.35) are present as minor products. It is worth noting that purification was necessary because we also observed an intense baseline upon TLC separation under UV light. This indicates that during substitution reactions side reactions likely occur, yielding unwanted by-products or polar components of polysilsesquioxanes. Apparently, compound **2** in the T_8 cage is a crystalline solid with a melting point of 66.7−67.2 °C, while the other cages (**3**, T_{10}; **4**, T_{12}) are in the liquid phase (viscous fluidlike substances) at room temperature. These specific physical properties also support our recent observation on the states of matter of cage-rearranged phthalimide-functionalized polyhedral oligomeric silsesquioxanes. Although the colorless crystal of the T_8 cage (mp 247−248 °C), the amorphous-like white-fluffy formation of the T_{10} cage (T_g ~ 65 °C), and the thin film of the T_{12} cage are all solids at room temperature, the symmetry could be a key to determining the relative lattice energies because higher symmetry allows for better packing and higher phase-transition temperatures in the solid state.[10] In polyhedral geometry, the higher degree of symmetrical faces in a cage is typically thought to allow neighboring molecules to get very close in three-dimensional space.

All faces in a T_8 cube (O_h) mainly consist of six symmetrical 8-membered rings of an inorganic Si−O−Si core, in contrast to lower-symmetrical cages like T_{10} (D_{5h}; five 8-membered and two 10-membered rings) and T_{12} (D_{2d}; four 8-membered and four 10-membered rings). Therefore, close-packed and crystallized states are usually observed in the T_8 cage.[8,10,11] In addition, the flexible Si−O−Si bond makes the larger cages change shape easily, also contributing to the low crystallinity of these compounds. We suggest that the tendency to form such a condensed matter for these compounds would be T_8 > T_{10} > T_{12}.

dx.doi.org/10.1021/ic401994m | *Inorg. Chem.* 2013, 52, 13108−13112

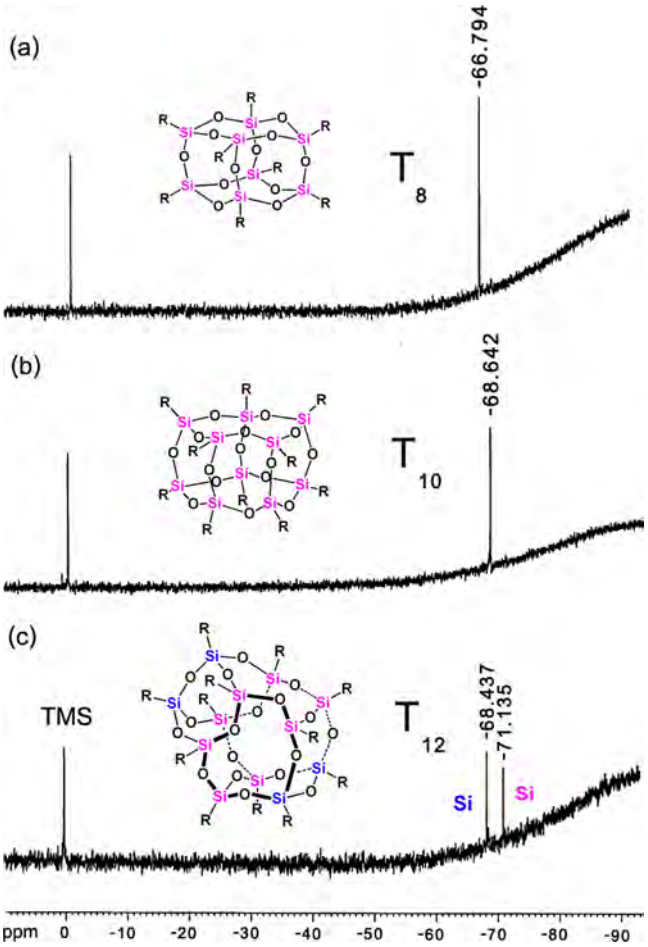


Figure 2. $^{29}Si\{^{1}H\}$ NMR spectra of purified compounds (a) octa-, (b) deca-, and (c) dodecameric methacrylate-functionalized silsesquioxanes (**2**–**4**).

Preparation and Characterization of Acrylate-Functionalized Cage-Rearranged Silsesquioxanes. In order to prepare octakis(3-propyl acrylate)octasilsesquioxane (**5**), decakis(3-propyl acrylate)decasilsesquioxane (**6**), and dodecakis(3-propyl acrylate)dodecasilsesquioxane (**7**), the reaction conditions between **1** and acrylate anion were also studied. As expected, the substitution rate on **1** at 70 °C with an acrylate anion was slower than that with methacrylate anions, and the substitution conversion after 2 days reached only 55%. We suggest that the difference in the relative nucleophilicity between methacrylate and acrylate anions is due to the differences in the electron density on the nucleophilic oxygen. In fact, acrylic acid has a higher K_a value, and thus the acrylate anion could be considered to be more stable or less reactive than the methacrylate anion.[19] As the temperature increased up to 100 °C, the substitution reaction with an acrylate anion was found to be almost complete (~96%) within 24 h (Scheme 1b). Similarly, the pattern of the $^{29}Si\{^{1}H\}$ NMR spectrum of the crude product also reveals the existence of a cage mixture of T_8 (**5**; −66.81 ppm), T_{10} (**6**; −68.69 ppm), and T_{12} (**7**; −68.47 and −71.18 ppm). We hypothesize that the acrylate anion plays the same role as the methacrylate anion in the induction of cage rearrangement of the silsesquioxane. After 0.90 g of crude mixture was passed through a silica column chromatography (ethyl acetate/*n*-hexane: 2:3), compounds **5** (T_8; 0.11 g; R_f = 0.40), **6** (T_{10}; 0.23 g; R_f = 0.35), and **7** (T_{12}; 0.14 g; R_f = 0.25) were successfully isolated in their pure forms. However, all three cages found in viscous liquids are similar to the case of cage-rearranged azido-functionalized polyhedral oligomeric silsesquioxanes.[7a]

To understand the effects of relative organic substituents on some physical properties, it was known that poly(methyl acrylate) is a soft rubber but poly(methyl methacrylate) is a strong, hard, and clear plastic at room temperature.[1] Thus, only a small methyl group is able to have a significant impact on the physical properties and behavior of the material. As it turns out, how soft or hard a silsesquioxane cage is not only is dependent on the identity of the inorganic core at a given temperature but also is determined by organic substituent mobility, or how easily the substituents move and pass around each other. If the organic substituents between molecules can glide smoothly over each other, the overall whole mass of molecules will be able to flow more easily. Thus, a silsesquioxane cage, which has lower substituent mobility, will be more rigid and have lower flexibility, whereas one that has higher substituent mobility will be softer and more pliable.

CONCLUSION

Octa-, deca-, and dodecameric methacrylate- and acrylate-functionalized silsesquioxanes were successfully synthesized and readily isolated in their pure forms through conventional column chromatography. Organic−inorganic silsesquioxane domain-based features allow us to understand the chemical structure−physical property relationships. Rather than using a mixture, the authors believe that using such an application for each pure silsesquioxane monomer could diversely obtain the specific properties of a material.

EXPERIMENTAL SECTION

Materials. (3-Chloropropyl)trimethoxysilane (purity >95.0%) was purchased from Tokyo Chemical Industry Co., Ltd., and used without additional purification. Sodium methacrylate (purity >99.0%), sodium acrylate (purity >97.0%), and anhydrous *N*,*N*-dimethylformamide (DMF) were purchased from Sigma Aldrich, while commercial-grade ethyl acetate and methylene chloride were further distilled. Precoated silica gel 60 F_{254} plates and silica gel (No. 60) used for chromatography were purchased from Merck & Co., Inc.

Physical Measurement and Instrumentation. Fourier transform NMR spectra were obtained using a Bruker-DPX 300 high-resolution NMR spectrometer for ^{1}H nuclei (300 MHz), a Bruker's Ascend 400 high-resolution magnetic resonance spectrometer for ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (100 MHz), and $^{29}Si\{^{1}H\}$ (79 MHz) nuclei, and a Bruker-AV 500 high-resolution magnetic resonance spectrometer for ^{1}H (500 MHz), $^{13}C\{^{1}H\}$ (125 MHz), and $^{29}Si\{^{1}H\}$ (99 MHz) nuclei. Chemical shifts were reported in δ units (parts per million) relative to tetramethylsilane (TMS), and residual solvent peaks were used as a reference. High-resolution mass spectrometry (HRMS) was performed with a VQ-TOF 2 Micromass spectrometer. Melting points were obtained using a Gallenkamp Sanyo melting detector.

Synthesis of Methacrylate-Functionalized Cage-Rearranged Silsesquioxanes. *Octakis(3-propyl methacrylate)-octasilsesquioxane (**2**), Decakis(3-propyl methacrylate)-decasilsesquioxane (**3**), and Dodecakis(3-propyl methacrylate)-dodecasilsesquioxane (**4**).* The starting material consisting of octakis(3-chloropropyl)octasilsesquioxane (**1**) (0.9995 g, 0.964 mmol) freshly prepared according to a previously published procedure[6] and sodium methacrylate (1.1146 g, 10.31 mmol) were added into a two-neck, round-bottomed flask equipped with a condenser and a magnetic stirbar. The mixture was dried under vacuum for 1 h before anhydrous DMF (20 mL) was added. After that, the reaction mixture was heated to 70 °C for 2 days under dry nitrogen. For the workup, deionized ice−water was added into the

dx.doi.org/10.1021/ic401994m | *Inorg. Chem.* 2013, 52, 13108−13112

reaction mixture to remove the NaCl byproduct. The solution mixture was then extracted using CH_2Cl_2 (60 mL × 3). The organic phase was collected and extracted further using H_2O (200 mL × 3). The purified organic phase was then dried using anhydrous sodium sulfate, and evaporation of the solvent resulted in a pale-yellow viscous liquid (1.16 g) as the crude product. Subsequently, 0.80 g of the crude product was separated by silica gel column chromatography in a solvent mixture of ethyl acetate/*n*-hexane (3:7) to give compound **2** (0.12 g, 0.084 mmol, 15% yield as a colorless crystal): R_f = 0.45; mp 66.7−67.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 0.70 (t, ^3J(H,H) = 8.30 Hz, 16H), 1.78 (quintet, ^3J(H,H) = 7.49 Hz, 16H), 1.92 (s, 24H), 4.09 (t, ^3J(H,H) = 6.71 Hz, 16H), 5.53 (s, 8H), 6.08 (s, 8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.06, 18.30, 22.15, 66.30, 125.28, 136.39, 167.35 ppm; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −66.79. HRMS (ESI). Calcd for $C_{56}H_{88}O_{28}Si_8$ + Na^+: *m*/*z* 1456.95 [M + Na^+]. Found: *m*/*z* 1456.3872. Compound **3** (0.25 g, 0.14 mmol, 31% yield as a colorless viscous liquid): R_f = 0.40; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.68 (t, ^3J(H,H) = 8.24 Hz, 20H), 1.74 (quintet, ^3J(H,H) = 7.38 Hz, 20H), 1.92 (s, 30H), 4.08 (t, ^3J(H,H) = 6.60 Hz, 20H), 5.53 (s, 10H), 6.07 (s, 10H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ 8.45, 18.07, 22.14, 66.09, 125.02, 136.23, 167.06; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −68.64. HRMS (ESI). Calcd for $C_{70}H_{110}O_{35}Si_{10}$ + Na^+: *m*/*z* 1813.44 [M + Na^+]. Found: *m*/*z* 1813.5090. Compound **4** (0.11 g, 0.051 mmol, 14% yield as colorless liquid): R_f = 0.35; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.68 (m, 24H), 1.75 (m, 24H), 1.92 (s, 36H), 4.09 (m, 24H), 5.53 (s, 12H), 6.08 (s, 12H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.67, 9.21, 18.30, 22.37, 22.48, 66.38, 125.31, 136.38, 167.29; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −68.44, −71.14. HRMS (ESI). Calcd for $C_{84}H_{132}O_{42}Si_{12}$ + Na^+: *m*/*z* 2173.94 [M + Na^+]. Found: *m*/*z* 2173.6221. Note that repeated chromatography may be required in order to obtain more purified compounds.

Synthesis of Acrylate-Functionalized Cage-Rearranged Silsesquioxanes. *Octakis(3-propyl acrylate)octasilsesquioxane (**5**), Decakis(3-propyl acrylate)decasilsesquioxane (**6**), and Dodecakis(3-propyl acrylate)dodecasilsesquioxane (**7**).* Starting material **1** (1.0205 g, 0.98 mmol) and sodium acrylate (1.0397 g, 11.06 mmol) were added into a two-neck, round-bottomed flask equipped with a condenser and a magnetic stirbar. The mixture was dried under vacuum for 1 h before anhydrous DMF (10 mL) was added. The reaction mixture was then heated to 100 °C for 1 day under dry nitrogen. The workup procedure was the same as that for the synthesis of compounds **2**−**4** and yielded the crude product, a yellow viscous liquid (1.20 g). Subsequently, 0.90 g of the crude product was separated by silica gel column chromatography in a solvent mixture of ethyl acetate/*n*-hexane (2:3) to give compound **5** (0.11 g, 0.083 mmol, 12% yield as a colorless viscous liquid): R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.69 (t, ^3J(H,H) = 8.40 Hz, 16H), 1.75 (quintet, ^3J(H,H) = 7.60 Hz, 16H), 4.11 (t, ^3J(H,H) = 6.8 Hz, 16H), 5.80 (d, ^3J(H,H) = 10.4 Hz, 8H), 6.11 (dd, ^3J(H,H) = 10.4 and 17.2 Hz, 8H), 6.39 (d, ^3J(H,H) = 17.2 Hz, 8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.04, 22.14, 66.14, 128.52, 130.55, 166.13; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −66.81. HRMS (ESI). Calcd for $C_{48}H_{72}O_{28}Si_8$ + Na^+: *m*/*z* 1343.23 [M + Na^+]. Found: *m*/*z* 1343.2836. Compound **6** (0.23 g, 0.13 mmol, 26% yield as colorless viscous liquid): R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.67 (t, ^3J(H,H) = 8.4 Hz, 20H), 1.73 (quintet, ^3J(H,H) = 7.40 Hz, 20H), 4.10 (t, ^3J(H,H) = 6.80 Hz, 20H), 5.79 (d, ^3J(H,H) = 10.4 Hz, 10H), 6.10 (dd, ^3J(H,H) = 10.40 and 17.40 Hz, 10H), 6.38 (d, ^3J(H,H) = 17.40 Hz, 10H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.57, 22.27, 66.15, 128.45, 130.63, 166.10; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −68.695. HRMS (ESI). Calcd for $C_{61}H_{92}O_{35}Si_{10}$ + Na^+: *m*/*z* 1675.18 [M + Na^+]. Found: *m*/*z* 1675.3585. Compound **7** (0.14 g, 0.07 mmol, 16% as colorless viscous liquid): R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.67 (m, 24H), 1.73 (m, 24H), 4.10 (m, 24H), 5.80 (d, ^3J(H,H) = 10.30 Hz, 12H), 6.10 (dd, ^3J(H,H) = 10.71 and 17.3 Hz, 12H), 6.39 (d, ^3J(H,H) = 17.32 Hz, 12H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.60, 9.14, 22.33, 22.45, 66.22, 128.46, 130.62, 166.08; ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C, TMS) δ −68.47, −71.18. HRMS (ESI). Calcd for $C_{72}H_{108}O_{42}Si_{12}$ + Na^+: *m*/*z* 2005.62 [M + Na^+]. Found: *m*/*z* 2005.4373. Note that repeated chromatography may be required in order to obtain more purified compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C, ^{29}Si NMR and ESI-MS spectra giving characterization data for new compounds **2**−**7**. 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.

■ ACKNOWLEDGMENTS

This research was financially supported by the Thailand Research Fund (Grant MRG5580011), the Office of the Higher Education Commission, Center of Excellence for Innovation in Chemistry (PERCH-CIC), and the Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through its program of Center of Excellence Network.

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Dalton Transactions

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PAPER

One-pot synthesis of halogen exchanged silsesquioxanes: octakis(3-bromopropyl)-octasilsesquioxane and octakis(3-iodopropyl)-octasilsesquioxane†

Cite this: *Dalton Trans.*, 2013, **42**, 13747

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Received 28th May 2013,
Accepted 31st May 2013

DOI: 10.1039/c3dt51373d

www.rsc.org/dalton

Metal halides, solvent effects, phase transfer catalysts, alkylating agent and reaction times were found to have important roles to complete halogen exchange reactions in "one pot" synthesis, starting from octakis(3-chloropropyl)octasilsesquioxane to obtain more reactive halide compounds: octakis(3-bromopropyl)octasilsesquioxane and octakis(3-iodopropyl)octasilsesquioxane. To confirm the complete halogen exchange, the desired products were characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy, ESI-MS, elemental analysis and single-crystal X-ray diffraction analysis.

Introduction

In the past decade, polyhedral oligomeric silsesquioxanes have been considered to be promising nano-building blocks because of their characteristic nano-sizes in hybrid skeletons by the combination of inorganic Si–O core and various organic groups.[1] Numerous applications of these materials have recently focused on nanocomposites,[2] biomedicine,[3] catalysis,[4] and optical devices.[5] Octakis(3-chloropropyl)octasilsesquioxane (**1**) as a T_8 structure is one of the most promising molecules to modify organic functions *via* nucleophilic substitution reaction because of the reactive 1° chloroalkyl groups.[6] In addition, Marciniec *et al.* recently introduced a facile method in preparing **1** *via* a hydrolytic–polycondensation reaction with the aid of tin-catalyst, which would allow large-scale synthesis.[7] However, functionalizations on **1** usually require vigorous reaction conditions (*e.g.* high temperatures, strong nucleophiles) leading to a decrease in the product yield, since chlorine atom has been known to be a poor leaving group.[6,8]

This together with the highly sensitive nature of inorganic silsesquioxane cage by the electronic influence of chlorine atoms and thermal decomposition even leads to cage-rearrangement products (T_8, T_{10} and T_{12}) during substitution reactions.[8] Only a few studies against cage-decomposition on **1** have been reported under mild conditions during functionalization.[9] In addition, organic alkyl halides particularly possessing either bromo or iodo atoms have been already proved to be more reactive precursors than chlorides in nucleophilic substitution reactions because of favorable leaving ability.[10]

Likely, octakis(3-bromopropyl)octasilsesquioxane (**2**) and octakis(3-iodopropyl)octasilsesquioxane (**3**) could serve as better candidates to solve any problems above. For example, Fabritz *et al.* reported the substitution reaction with strongly nucleophilic agent such as azide anions on either **2** or **3** at room temperature could give the desired products in very good yield and that mild synthesis conditions could not affect the inorganic silsesquioxane core of the octameric T_8 structure.[11] Nevertheless, the preparation of compounds **2** and **3** through halogen exchange or Finkelstein reaction has been reported to be impractical, by use of only **1** with metal halides. In this study, we found the most efficient method to prepare **2** and **3** with a complete halogen exchange under a "one-pot" reaction.

Materials and characterizations

3-Chloropropyltrimethoxysilane (purity; >95.0%), 18-crown-6 (purity; >98.0%) and tetrabutylammonium bromide (purity; >98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. Sodium bromide (purity; >99.5%) and sodium iodide

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†Electronic supplementary information (ESI) available. CCDC 910950. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51373d

(purity; >99.5%) were obtained from Ajax Finechem Pty Ltd. Potassium bromide (purity; >99.5%), and potassium iodide (purity; >99.5%) were purchased from QReC, while lithium bromide (purity; >99%) was purchased from Riedel-de Haën. All chemicals were used without additional purification. Tetrahydrofuran was purchased from Honeywell International Inc, while commercial grade acetone, methylene chloride and hexane were further distilled prior to use.

Fourier transform nuclear magnetic resonance spectra were obtained by using a Bruker-DPX 300 high-resolution nuclear magnetic resonance spectrometer for ^{1}H nuclei (300 MHz) and a Bruker-AV 500 high-resolution magnetic resonance spectrometer for ^{1}H nuclei (500 MHz), $^{13}C\{^{1}H\}$ (125 MHz) and $^{29}Si\{^{1}H\}$ (99 MHz) nuclei. Chemical shifts were reported in δ units (parts per million) relative to tetramethylsilane, and residual solvents peaks were used as a reference. High-resolution mass spectrometry was performed with a VQ-TOF 2 Micromass spectrometer and elemental analysis was carried out by using an elemental analyzer (EA) (CHNS/O Analyzer) Perkin Elmer, PE2400 Series II.

Experimental

General procedure

All reactions were performed using 0.05 M of **1** in either acetone or THF solvent under reflux condition (70 °C at the oil-bath temperature) with specific reagent equivalents and reaction times for each entry. As phase transfer catalysts (PTC), either 30% w/w of 18-crown-6 or 37% w/w of TBAB were used in all reactions. An alkylating agent (37% v/v of *n*-propyl bromide, *n*-PrBr), if utilized, was added *in situ* and the resulting mixture was additionally refluxed for a certain time.

Octakis(3-bromopropyl)octasilsesquioxane (2)

The starting material **1** was prepared by following the literature method.[7] In entry M2, compound **1** (0.100 g, 0.096 mmol), sodium bromide (0.247 g, 2.40 mmol) and tetrabutylammonium bromide (0.037 g, 0.115 mmol) were transferred to the thick-walled reaction vessel[24] under nitrogen atmosphere within a glove box. Then distilled acetone (2.0 mL) was added *via* transfer syringe into the reaction mixture and the vessel was then purged with dried nitrogen before it was sealed. After heating at 70 °C for 2 days, the reaction solution was cooled to room temperature and the alkylating agent 1-bromopropane (0.75 mL, 8.23 mmol) was added into the reaction. The mixture was placed at 70 °C for another 3 days. Acetone was then evaporated out to obtain a white-yellowish precipitate. Two-phase liquid extraction of CH_2Cl_2–H_2O was used to isolate the product. The CH_2Cl_2 fraction was kept and dried with sodium sulfate. The CH_2Cl_2 solvent was evaporated out to obtain a white precipitate product. Recrystallization from THF–hexane (1 : 1 v/v ratio) mixed solvent yielded colorless crystals of **2** (0.127 g, 0.090 mmol, 94%); ^{1}H NMR ($CDCl_3$) δ 0.78–0.84 (t, 16H, $^{3}J_{H-H}$ = 2.53, 5.64 Hz), 1.90–2.00 (quin, 16H, $^{3}J_{H-H}$ = 2.38, 5.76, 6.77 Hz), and 3.34–3.44 (t, 16H, $^{3}J_{H-H}$ = 6.75 Hz) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 10.78, 26.43 and 36.05 ppm; $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$) δ −67.30 ppm; HRMS (ESI): $[M + Na]^+$; calc. for $[C_{24}H_{48}Br_8NaO_{12}Si_8]^+$: *m*/*z* 1415.5365; found: *m*/*z* 1415.3887; elemental analysis: calc. for $C_{24}H_{48}Br_8O_{12}Si_8$: %C = 20.70, %H = 3.47; found: %C = 20.74, %H = 3.47.

Octakis(3-iodopropyl)octasilsesquioxane (3)

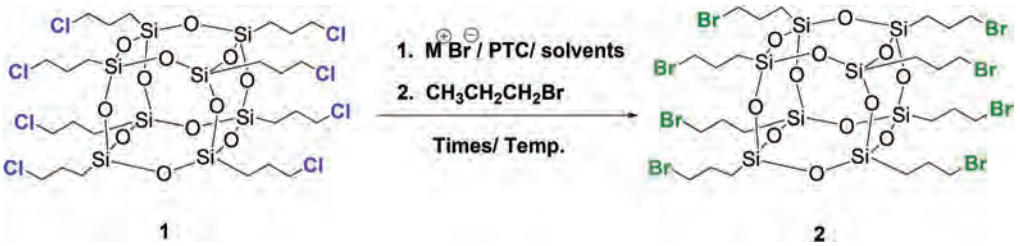
Compound **1** (0.100 g, 0.096 mmol) and sodium iodide (0.576 g, 3.84 mmol) were transferred to a thick-wall reaction vessel within a glove box. Then anhydrous THF (2.0 mL) was added *via* transfer syringe into the reaction mixture and the vessel was then purged with dried nitrogen before it was sealed. After heating at 60 °C in the dark for 3 days, the reaction solution was cooled to room temperature and THF solvent was evaporated out to obtain a yellowish precipitate. After separation with CH_2Cl_2–H_2O two-phase extraction, the dichloromethane fraction was kept and dried with sodium sulfate. The mild reducing agent granular sodium bisulfite was added heterogeneously *in situ* to remove excess iodine. This process can be easily monitored when the pale-yellow solution turned into a colorless liquid. After filtering out the solid sodium sulfate and sodium bisulfite, CH_2Cl_2 solvent was evaporated out to obtain the product as a white precipitate. Recrystallization from THF–hexane (1 : 1 v/v ratio) mixed solvent yielded colorless crystals of **3** (0.141 g, 0.080 mmol, 83%); ^{1}H NMR ($CDCl_3$) δ 0.77–0.80 (t, 16H, $^{3}J_{H-H}$ = 2.71, 5.42 Hz), 1.90–1.96 (quin, 16H, $^{3}J_{H-H}$ = 2.56, 5.47, 7.02 Hz) and 3.21–3.24 (t, 16H, $^{3}J_{H-H}$ = 6.92 Hz) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 9.97, 13.39 and 27.30 ppm; $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$) δ −67.86 ppm; HRMS (ESI): $[M + Na]^+$; calc. for $[C_{24}H_{48}I_8NaO_{12}Si_8]^+$: *m*/*z* 1790.3555; found: *m*/*z* 1790.3837; Elemental analysis: calc. for $C_{24}H_{48}I_8O_{12}Si_8$: %C = 16.30, %H = 2.74; found: %C = 16.30, %H = 2.73.

X-Ray structural determination

Crystalline **3** suitable for X-ray structural analysis was obtained by recrystallization in THF–hexane and crystallographic data has been deposited as CCDC 910950. X-Ray data were collected on a Bruker SMART APEX II CCD area-detector diffractometer, with an Mo-Kα radiation source (λ = 0.7107 Å) at 100 K. The crystal structures were solved by the direct method with SHELXS-97.[25] Full-matrix least-squares procedures using SHELXL-97 on F^2 anisotropic for all non-hydrogen atom was used to refine the crystal structures. Hydrogen atoms were placed in their calculated positions and refined following the riding model.

Results and discussion

Compound **2** was first synthesized *via* $FeCl_3$-catalyzed hydrolytic polycondensation starting from 3-bromopropyl trichlorosilane,[12] but only 3% yield was obtained. An alternative approach to prepare **2** was also applicable when starting from **1** in the presence of lithium bromide (LiBr), however Fabritz *et al.* also encountered at least five cycles of the procedure described to ensure complete substitution.[11] Moreover, we further examined a variety of factors (Scheme 1) such as solvent (Table 1: entries A1–A2), equivalents of reagent (entries



Scheme 1 General approach to synthesize octakis(3-bromopropyl)octasilsesquioxane (**2**) in "one-pot" method.

Table 1 Optimized conditions to prepare octakis(3-bromopropyl)silsesquioxane (**2**) in "one pot" reaction in refluxing solvent

Entry	M^+Br^- (eq.)[a]	Solvent	PTC[b]	*t*/d	*t*′/d[c]	Substitution (%)	Yield[d] (%)
A1	LiBr (3 eq.)	Acetone	—	1	—	54	N/A
A2	LiBr (3 eq.)	THF	—	1	—	58	N/A
B1	LiBr (2 eq.)	THF	—	1		47	N/A
B2	LiBr (5 eq.)	THF	—	1	—	69	N/A
B3	LiBr (8 eq.)	THF	—	1	—	72	N/A
B4	LiBr (10 eq.)	THF	—	1	—	83	N/A
C1	LiBr (5 eq.)	THF	—	2	—	68	N/A
C2	LiBr (5 eq.)	THF	—	3	—	71	N/A
C3	LiBr (5 eq.)	THF	—	5	—	72	N/A
D1	NaBr (3 eq.)	Acetone	—	1	—	7	N/A
D2	NaBr (3 eq.)	THF	—	1	—	0	N/A
E1	NaBr (3 eq.)	Acetone	CE	1	—	79	N/A
E2	NaBr (3 eq.)	Acetone	TBAB	1	—	71	N/A
F1	NaBr (2 eq.)	Acetone	CE	1	—	72	N/A
F2	NaBr (3 eq.)	Acetone	CE	1	—	79	N/A
F3	NaBr (5 eq.)	Acetone	CE	1	—	79	N/A
G1	NaBr (3 eq.)	Acetone	CE	2	—	79	N/A
G2	NaBr (3 eq.)	Acetone	CE	3	—	78	N/A
G3	NaBr (3 eq.)	Acetone	CE	5	—	78	N/A
H1	NaBr (3 eq.)	Acetone	TBAB	2	—	79	N/A
H1	NaBr (3 eq.)	Acetone	TBAB	3	—	78	N/A
H2	NaBr (3 eq.)	Acetone	TBAB	5	—	79	N/A
I1	LiBr (5 eq.)	THF	—	1	1	82	N/A
I2	LiBr (5 eq.)	THF	—	1	3	93	N/A
I3	LiBr (5 eq.)	THF	—	1	5	96	N/A
I4	LiBr (5 eq.)	THF	—	1	7	94	N/A
J1	LiBr (10 eq.)	THF	—	1	1	93	N/A
J2	LiBr (10 eq.)	THF	—	1	3	95	N/A
J3	LiBr (10 eq.)	THF	—	1	5	96	N/A
J4	LiBr (10 eq.)	THF	—	1	7	95	N/A
K1	NaBr (3 eq.)	Acetone	CE	1	1	86	N/A
K2	NaBr (3 eq.)	Acetone	CE	1	2	90	N/A
K3	NaBr (3 eq.)	Acetone	CE	1	3	93	N/A
K4	NaBr (3 eq.)	Acetone	CE	1	5	95	N/A
K5	NaBr (3 eq.)	Acetone	CE	1	7	98	89
K6	NaBr (3 eq.)	Acetone	CE	2	3	97	N/A
K7	NaBr (3 eq.)	Acetone	CE	3	2	96	N/A
L1	NaBr (3 eq.)	Acetone	TBAB	1	2	90	N/A
L2	NaBr (3 eq.)	Acetone	TBAB	1	3	94	N/A
L3	NaBr (3 eq.)	Acetone	TBAB	1	4	95	N/A
M1	NaBr (3 eq.)	Acetone	TBAB	2	2	96	N/A
M2	NaBr (3 eq.)	Acetone	TBAB	2	3	>99	94
N1	NaBr (3 eq.)	Acetone	TBAB	3	1	93	N/A
N2	NaBr (3 eq.)	Acetone	TBAB	3	2	>99	85
O1	NaBr (3 eq.)	Acetone	TBAB	5[e]		92	N/A
P1	NaBr (3 eq.)	THF	TBAB	2	3	97	N/A
P2	NaBr (3 eq.)	THF	TBAB	3	2	95	N/A
Q1	NaBr (3 eq.)	THF	CE	2	3	75	N/A
Q2	NaBr (3 eq.)	THF	CE	3	2	77	N/A

[a] Equivalents per $RSiO_{3/2}$ unit. [b] CE = 18-crown-6, TBAB = tetrabutylammonium bromide. [c] After the halogen exchange reaction was conducted for a certain time *t*, 37% v/v of *n*-propyl bromide (*n*-PrBr) was subsequently added *in situ* for a time *t*′. [d] N/A = not applicable. In all entries, >98% substitution is set for calculation of yield. [e] All reagents including 3-bromopropane were added together at the beginning of the reaction.

B1–B4), and reaction times (entries C1–C3), however the complete substitution, as in Fabritz's procedure in the first cycle can never be achieved. The highest substitution level at 72% was found in the reaction of **1** under refluxing THF either with 8 eq. LiBr for a day or with 5 eq. LiBr for 5 days (entries B3 and C3, respectively). We suggest that the similar nucleophilicity and leaving ability between chloride and bromide anions play an important role to preclude the completion of substitution. The attacking and displaced groups would compete in equilibrium:

$$-SiCH_2CH_2CH_2\mathbf{Cl} + \mathbf{Br}^- \rightleftharpoons -SiCH_2CH_2CH_2\mathbf{Br} + \mathbf{Cl}^-$$

In order to drive the equilibrium forward, an excess amount of bromide anions are needed, nonetheless incomplete substitutions is still observed (entry B4). It seems unlikely that complete substitution could be accomplished in homogeneous fashion. We designed an alternative method toward successful synthesis of **2** in a one-pot method. In this report, we further study the halogen exchange reaction under a heterogeneous system using sodium bromide (NaBr). Unlike highly soluble LiBr in polar aprotic solvents, NaBr could not be dissolved well in such solvents. Generally, substitution reactions, without any catalytic agents such as crown ethers[13] or other phase-transfer catalysts (PTC)[14] such as tetrabutylammonium bromide (TBAB), were considered to be less effective (entries D1–D2), because the nucleophile and reactant remain in separated phases.

Marsmann *et al.* first introduced 18-crown-6 to enhance the solubility of nucleophilic agents from inorganic salts in order to functionalize silsesquioxanes.[6a,8a] We suggest that either 18-crown-6 or TBAB could act as a good candidate which solvates positively charged metal ions or induces electrostatic interaction, respectively, to ferry them into the homogeneous system. These processes then promote the solubility and freedom of the corresponding anion in polar aprotic solvents. Interestingly, after optimization of catalyst types (entries E1–E2), equivalents of NaBr (entries F1–F3), and reaction times (entries G1–G3 and H1–H3), the reaction of **1** with 3 eq. NaBr in refluxing acetone solvent for a day in the presence of 18-crown-6 gives the highest rate of halogen exchange reaction. Acetone and tetrahydrofuran (THF) are both polar aprotic solvents with medium donor strength,[15] however the dissociating power of acetone is greater relative to THF (dielectric constant: $\varepsilon_{acetone}$ = 21.36 and ε_{THF} = 7.47).[16] According to a report,[17] for most alkali metal salts, the predominant species in acetone solution are solvent-separated ion pairs in which the cationic and anionic groups are freely separated by the solvent, while those in THF solution are contact ion pairs, in which the cationic and anionic groups tend to form aggregates. Furthermore, the solubility of sodium chloride (NaCl) by-product in acetone is far less than that of THF.[18] Therefore, substitution reaction using alkali metal salt as a nucleophilic agent is more favourable in acetone solvent.

Unfortunately, both chloride-to-bromide exchange reaction in the presence of 18-crown-6 and TBAB were found to be incomplete, and substitution conversions were maximized at 79 and 78%, respectively. Once again, the presence of leaving chloride anions in the reaction phase results in equilibrium and precludes the complete substitution. Attempting to minimize the amount of chloride ions, we introduced 3-bromopropane as an alkylating reagent *in situ* to accomplish the halogen exchange reaction. The reaction between 3-bromopropane and undesired chloride ions, yielding the lower boiling point compound 3-chloropropane, lessens the amount of chloride anions, while supplementing bromide anions. Thus, the equilibrium will be driven toward the desired compound **2**, leading to complete substitution. From our experimental results, the addition of alkylating agent could significantly improve the substitution portion in all reaction conditions. For example, the percentage substitution in Fabritz's method with the addition of 3-bromopropane was improved from 69 to 82%. It is also worth noting that 3-bromopropane must be introduced after the reaction mixtures reach equilibrium, otherwise incomplete substitution reaction is still observed (entry O1).

Interestingly, we found that only TBAB could accomplish >99% substitution conversion (entries M2 and N2), while 18-crown-6 could maximize at only 98% conversion (entries K1–K7). In this case, a strong coordination ability of 18-crown-6 is responsible for the incomplete substitution. We suggest that TBAB weakly bonds with a solid lattice of NaCl, while 18-crown-6 firmly coordinates with sodium in the lattice and returns both sodium and chloride ions back into the reaction solution.[19] Although, NaCl by-product could not be dissolved in acetone as for NaBr, it will subsequently precipitate after its formation. The increasing concentration of chloride ions, competing with the decreasing by 3-bromopropane alkylating agent, will drive back the equilibrium. The maximum substitution conversion at 98%, even at a very long reaction time, well supports our explanation. The reaction progress was examined by means of ^{1}H NMR spectroscopy. From entry M2, the disappearance of 3-chloropropyl signals at δ 3.53, 1.82, 0.75 ppm and the appearance of new 3-bromopropyl signals at δ 0.81, 1.95, 3.42 ppm suggest a completion of halogen exchange reaction in 5 days to give the high yield. ^{29}Si{^{1}H} NMR of the isolated product also shows a singlet signal at δ −67.30 ppm. Hence, this result confirms the successful synthesis with retention of the T_8 silsesquioxanes cage.

However, the ESI-MS result of **2** (see ESI†) shows a strong signal at 1352.4810 *m*/*z*. Alkyl halides, specifically alkyl bromides, are known to have low thermal and chemical stability. The mass spectrum of **2** was obtained by using low ionization method, yet this compound still readily undergoes decomposition and fragmentation, yielding a variety of silsesquioxane fragments and isomers, for example $^{\cdot}$R, $^{\cdot}$RSi, $^{\cdot}$RSiO, and $^{\cdot}RSiO_2$. In addition, the replacement of terminal halide with hydroxide group is also noticeable in some studies.[20] Therefore, we hypothesize that the peak at 1352.4810 *m*/*z* is consistent with $[C_{24}H_{49}Br_7NaO_{13}Si_8]^+$, in which a bromo-substituent is replaced by hydroxide ion from a water molecule.

However, it should be mentioned that using dry THF instead of acetone at the same conditions as entries M2 and N2 with either TBAB (entries P1–P2) or 18-crown-6 (entries Q1–

Q2) catalysts, that complete substitution reaction was not observed. The crude products (entries P1–P2) were obtained in a gummy form after working up and their ^{1}H NMR spectra also indicate the mixture of incomplete substitution products and other impurities. Moreover, ^{1}H NMR spectra of crude products (entries Q1–Q2) clearly substantiate the low efficiency of the halogen exchange reaction, even for an alkylating agent such as 3-bromopropane. These results strongly confirm that acetone is likely to give more complete and cleaner reaction than that of THF.

To prepare compound **3**, Marsmann *et al.* firstly reported the halogen exchange reaction on **1** by using an excess of NaI under refluxing acetone solvent, however complete reaction could not be accomplished except by a large number of cycles.[6a] Later, Heyl, *et al.* successfully improved the synthesis of **3** for the one-pot system.[21] Although the homogeneous reaction was successful, the previous report was performed with the excessive addition of catalytic agents: tetrabutylammonium iodide and 3-iodopropane in 2-butanone solvent under reflux condition.

In this study, we investigated the catalytic-free system for NaI by standing alone in THF solvent. Under this particular condition, the complete halogen exchange reaction could be easily achieved without any addition of catalytic agents (Scheme 2). We suggest that the stronger solvation around Na^+ by oxygen atoms in ether bonds of higher polarity of aprotic THF solvent would be enough to enhance the ion-pair dissociation between Na^+ and I^-. Consequently, the nucleophilicity of some carbanions would be extended as suggested by Chabanel *et al.*[22] ^{1}H NMR spectroscopy was also used to monitor the reaction progress by the disappearance of signals of 3-chloropropyls, giving the appearance of new signals at δ 0.78, 1.91 and 3.23 (3-iodopropyl). Complete halogen exchange reaction (>99% substitution) was easily observed in 3 days at 60 °C to give high yield (83%). ^{29}Si{^{1}H} NMR of the isolated product also shows a singlet signal at δ −67.86 ppm, indicating that the cage-decomposition does not occur under such a condition. The formation of NaCl precipitation as an insoluble by-product is observed indicating the fast progress of reaction. The complete substitution reaction by iodine atoms could also even be observed at room temperature upon extended reaction times.

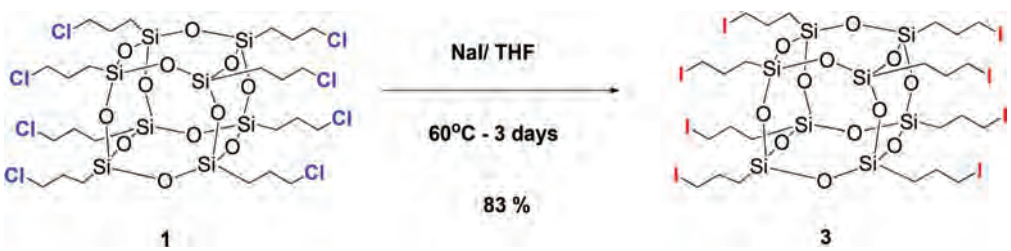
X-Ray quality crystals of **3** were readily grown from THF–hexane (1 : 1) and the refined crystal structure is presented in Fig. 1.[26] Single-crystal X-ray diffraction analysis reveals that **3** was crystallized in the triclinic space group $P\bar{1}$ with the cubic silsesquioxane cage and the six faces of the eight-membered ring of the T_8 core.

It should be noted that a decomposition of colourless crystalline **3** was observed upon the X-ray exposure at 296 K yielding a yellow opaque solid. However, the quality of crystal could be sustained by decreasing the measurement temperature (100 K). Such room-temperature instability is commonly observed for iodine-rich compounds under prolonged or intense X-ray irradiation.[23]

Conclusions

In conclusion, this report describes the improvement in synthetic procedures as the most efficient method to obtain two cage-like T_8 silsesquioxanes: octakis(3-bromopropyl)octasilsesquioxane (**2**) and octakis(3-iodopropyl)octasilsesquioxane (**3**) under a one-pot system with >99% substitution and excellent yield. The interesting results of how factors such as reaction times, solvent effects, catalysts and alkylating agents affect the S_N2 reaction on silsesquioxane moieties are fully discussed in this paper.

Fig. 1 ORTEP drawing of the asymmetric unit of **3** with 50% probability ellipsoids.



Scheme 2 Synthesis of octakis(3-iodopropyl)octasilsesquioxane (**3**) in a "one-pot" method.

Acknowledgements

This research is financially supported by the Thailand Research Fund (MRG5580011), the Office of the Higher Education Commission, Center of Excellence for Innovation in Chemistry (PERCH-CIC), and the Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through its program of Center of Excellence Network.

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EurJIC European Journal of Inorganic Chemistry

ChemPubSoc Europe

SHORT COMMUNICATION

DOI:10.1002/ejic.201300283

Unprecedented Formation of *cis*- and *trans*-Di[(3-chloropropyl)isopropoxysilyl]-Bridged Double-Decker Octaphenylsilsesquioxanes

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Dedicated to Professor Dr. James W. Pavlik and Professor Dr. Yusuke Kawakami on the occasion of their retirement

Keywords: Organic–inorganic hybrid composites / Main group elements / Silanes / Silsesquioxanes

Silsesquioxane formation competing with the deprotonation of alcohol solvents in the presence of a strong base to form alkoxides is reported for the first time. Evidently, sodium isopropoxide is formed during the synthesis of the sodium salt of a double-decker octaphenylsilsesquioxane tetrasilanolate in 2-propanol as the solvent, which leads to the formation of unexpected *cis*- and *trans*-di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxanes after in situ coupling with 3-chloropropyltrichlorosilane. The desired products were characterized by ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectroscopy; ESI-MS; and single-crystal X-ray diffraction.

Introduction

The sodium salt of double-decker octaphenylsilsesquioxane tetrasilanolate (**2**) is classified as one of the promising precursors of polyhedral oligomeric silsesquioxanes.[1] They have recently been coupled with dialkyldichlorosilanes[2] and alkyltrichlorosilanes[3] and later transformed into a new type of condensed polyhedral structures. Nowadays, these promising double-decker silsesquioxane monomers are considered to be novel types of carbosilane and siloxane materials that provide several specific properties such as heat resistance,[3] and they have been used in optoelectronic[4] and hybrid nanoassemblies.[5] So far, the number of available reactive double-decker silsesquioxane monomers has been limited, because isolated precursor **2** is most likely to exist in a mixture of sodium salts.[1i,2a] Therefore, the reaction progress during the formation of the sodium salt of double-decker silsesquioxanes must be investigated.

In this report, we explore the use of sodium isopropoxide (**3**) during the synthesis of **2**. After coupling **2** with 3-chloropropyltrichlorosilane, we found that **3** plays a crucial role in the formation of an isomeric mixture of unexpected products *cis*- and *trans*-di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxane (**5**). For future aspects, it is noteworthy that these novel double-decker monomers could be further functionalized through nucleophilic substitution, as a method has already been proved to be efficient to obtain new silsesquioxane materials in high yield.[6]

Results and Discussion

The synthesis of **2** was first proposed by Yoshida et al. through hydrolytic condensation of phenyltrimethoxysilane in alkaline solution.[1a] Later, Woo, and Kawakami studied the conversion of the sodium salt of heptaphenylsilsesquioxane trisilanolate (**1**) into **2**.[2a] In fact, compounds **1**

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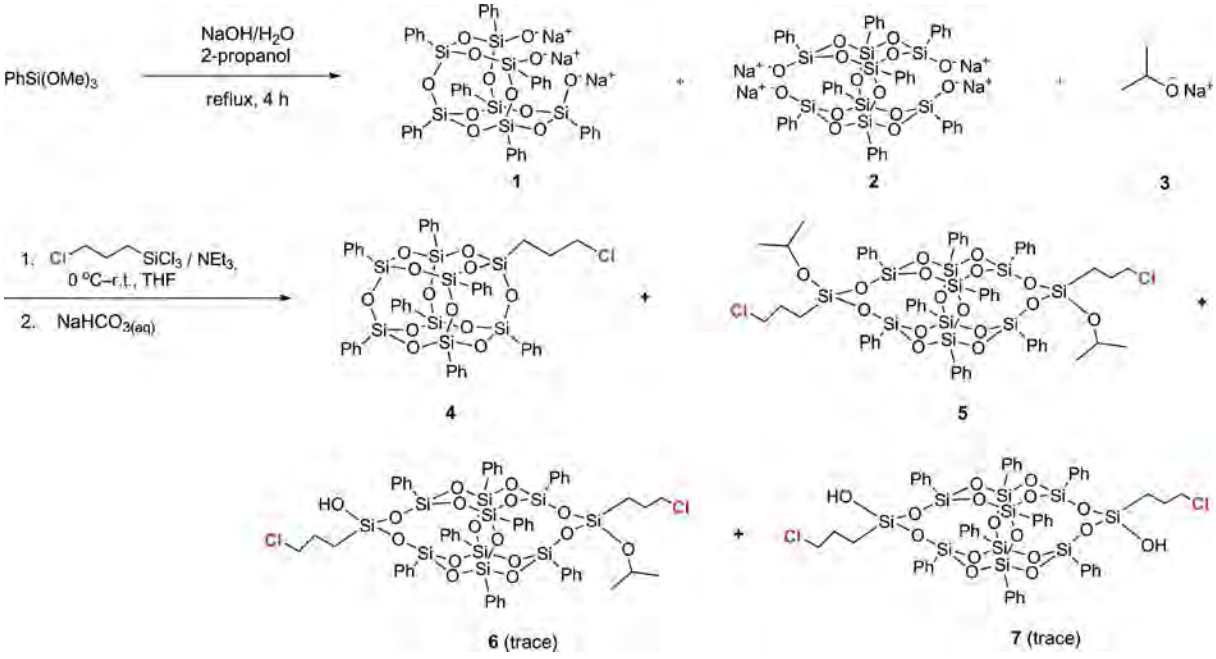
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201300283.

and **2** shown in Scheme 1 are likely found in an equilibrium mixture, which was isolated as coprecipitated sodium salts.[1i,2a] Thus, there is no direct evidence of characterization of these materials, because of their poor solubility in organic solvents. However, the original structures could only be determined qualitatively after treatment with organosilanes to obtain more-soluble materials.[2,4a] Kawakami et al. first attempted the coupling of isobutyltrichlorosilane to these precipitated mixtures of sodium salts; however, the only products found were hydrolyzable *cis*- and *trans*-di[(isobutyl)silanol]-bridged double-decker octaphenylsilsesquioxanes. The separation of the desired materials could be easily achieved by precipitation from a toluene solution, but no further analysis of the soluble products in the mother liquid was performed.[4a] In contrast, in our experiments involving the coupling of **2** with 3-chloropropyltrichlorosilane in a similar manner (Scheme 1), only 3-chloropropyl heptaphenylsilsesquioxane (**4**) could be detected and identified among the insoluble products. This result strongly confirms that not only double-decker sodium salt **2** was formed but also that T_7 sodium salt **1** exists in the precipitated mixture during double-decker formation. In addition, we further analyzed the other soluble products in the toluene solution, and our results obtained by thin-layer chromatography (CH_2Cl_2/hexane = 1:4 v/v) analysis of the mother liquid revealed the existence of three major compounds (R_f = 0.35, 0.15, 0). After purification by column chromatography to separate each pure compound, we found that the least polar (R_f = 0.35) compound was the octameric T_8 silsesquioxane of **4**, which was first isolated in 9% yield in a pure form.

Second, the major product consisted of an isomeric mixture of *cis*-**5**/*trans*-**5** in equal ratios. These compounds have an identical R_f value of 0.15. The mixture was isolated in 14% yield, and its structure was confirmed by its distinguishable $^{29}Si\{^1H\}$ NMR spectrum (Figure S7, Supporting Information). The signals at δ = –61.26, –79.08, –79.13, and –79.57 ppm are assigned to the *cis* isomer, whereas the signals at δ = –61.26, –79.08, and –79.35 ppm are assigned to the *trans* isomer. This result is also consistent with our previous report on the existence of isomeric mixtures of *cis*- and *trans*-di[(3-chloropropyl)methyl]-bridged double-decker octaphenylsilsesquioxane.[2b] Interestingly, its ^1H NMR spectrum exhibits unknown signals at δ = 4.35 and 1.09 ppm, whereas the integrated intensity of the other signals confirms the protons on eight aromatic rings and dibridging 3-chloropropyl side chains in a double-decker structure. To draw a molecular picture, mass spectrometry (ESI-MS) may give useful evidence associated with the appearance of the molecular ion at *m*/*z* = 1417.0561 (Figure S8, Supporting Information). This result strongly suggests that the double-decker backbone must be covalently attached to unexpected dibridging isopropoxysilyl substituents. Consequently, we hypothesize that this unexpected formation of **5** could actually support the presence of **3** among precipitated mixtures of **1** and **2** and could involve isopropoxide–chloride exchange during the coupling reaction with 3-chloropropyltrichlorosilane to form completely condensed double-decker silsesquioxane. Thus, such an intermediate was not suggested elsewhere, after the synthesis of **2** was known. Herein, we suggest that under strongly basic conditions, the deprotonation of any alcohol solvent to



Scheme 1. Synthetic approach to the formation of *cis*- and *trans*-di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxane (**5**).

form alkoxides competes with the formation of silsesquioxane materials, and researchers should be aware of this fact.

Further attempts to separate each pure isomer from the *cis*-**5**/*trans*-**5** mixture by recrystallization in THF/hexane (1:1) successfully provided colorless crystals of pure *trans*-**5**. In Figure 1, the perspective view of *trans*-**5** obtained by single-crystal X-ray diffraction analysis is displayed, and its crystalline data and structural refinement parameters are summarized in Tables S1 and S2 (Supporting Information).

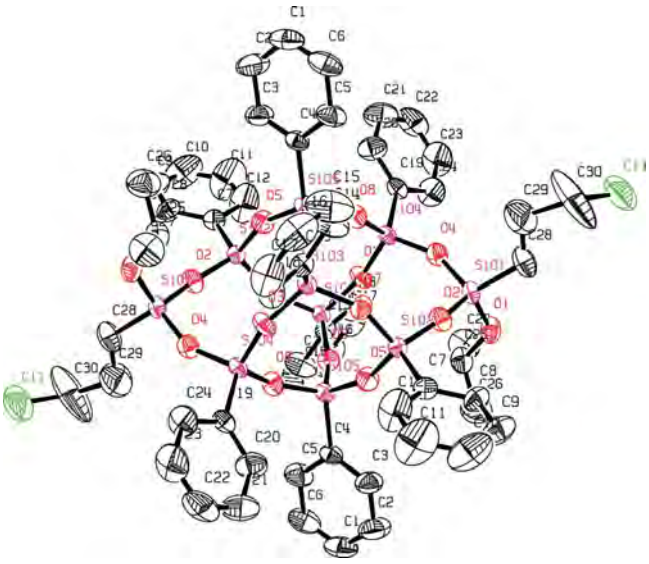


Figure 1. Thermal ellipsoid plot of *trans*-**5** at the 30% probability level; hydrogen atoms are omitted for clarity.

Other double-decker products were obtained in trace amounts (<5% yield) from fractions obtained at a later stage during purification by column chromatography. Partially hydrolyzed di(3-chloropropyl)[(isopropoxysilyl)silanol]-bridged double-decker octaphenylsilsesquioxane (**6**) could be isolated by gradient elution [R_f = 0.31, CH_2Cl_2/hexane (2:3)]. Its NMR spectra (Figures S17–S19, Supporting Information) also confirm that one side of the bridging double-decker is already hydrolyzed to a silanol group, whereas the other still remains alkylated. Moreover, completely hydrolyzed di[(3-chloropropyl)silanol]-bridged double-decker octaphenylsilsesquioxane (**7**) was also collected in a trace amount (R_f = 0.50, CH_2Cl_2). In fact, this isolated fraction was found to be insoluble in chloroform, dichloromethane, and THF but showed good solubility in DMSO. However, the majority of the peaks in the $^{29}Si\{^1H\}$ NMR spectrum (Figure S23, Supporting Information) in [D_6]DMSO can be attributed to the *trans* isomer. We suggest that most of *cis*-**7**/*trans*-**7** is possibly excluded as an insoluble material as a result of its poor solubility in common organic solvents. Unlikely, hydrolyzable *cis*- and *trans*-di[(isobutyl)silanol]-bridged double-decker octaphenylsilsesquioxanes could be considered to be more soluble in organic solvents because of the hydrophobic incorporation of the isobutyl groups into the double-decker structure.[4a] These hydrolytic products can be possibly formed after quenching with an aqueous solution under acid–base conditions.

Conclusions

The discovery of sodium isopropoxide (**3**) during the formation of the sodium salt of double-decker octaphenylsilsesquioxane (**1**) by coincidence of the deprotonation of 2-propanol as the solvent under strongly basic conditions has been reported for the first time. Thus, **3** plays a crucial role in an isopropoxide–chloride exchange reaction during the coupling of **1** with slightly sterically hindered 3-chloropropyltrichlorosilane, which directly leads to the formation of unexpected *cis*- and *trans*-di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxane (**5**). Finally, the authors believe that the use of these novel monomers in polymerization and functionalization through nucleophilic substitution reactions to obtain various functional materials should be considered in the near future.

Experimental Sections

Materials and Methods: Phenyltrimethoxysilane and 3-chloropropyltrichlorosilane were obtained from Tokyo Chemical Industry Co., Ltd., and used without additional purification. 2-Propanol and THF were purchased from B&J Company. THF was further dried with sodium metal and distilled under anhydrous conditions. Fourier-transform NMR spectra were obtained by using Bruker-AV 300 for ^1H (300 MHz) and Bruker-AV 500 high-resolution NMR spectrometers for ^1H (500 MHz), $^{13}C\{^1H\}$ (125 MHz), and $^{29}Si\{^1H\}$ (99 MHz). The chemical shifts are reported in δ units (parts per million) relative to $SiMe_4$ (TMS), and the residual solvents peaks ($CHCl_3$) were used for reference. High-resolution mass spectrometry was performed by using a Micromass VQ-TOF 2.

X-ray Structural Determination: Crystalline *trans*-**5** suitable for X-ray structural analysis was obtained by recrystallization in THF/hexane. X-ray data were collected with a Bruker SMART APEX II CCD area-detector diffractometer with a Mo-K_α radiation source (λ = 0.7107 Å) at 296 K. The crystal structures were solved by direct methods with SHELXS-97.[7] The full-matrix least-squares procedures by using SHELXL-97 on F^2 anisotropic for all non-hydrogen atoms was used to refine the crystal structures. Hydrogen atoms were placed in their calculated positions and refined following the riding model.

CCDC-912558 (for *trans*-**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of the Sodium Salt of Heptaphenylsilsesquioxane Trisilanolate (1), the Tetrasodium Salt of Double-Decker Octaphenylsilsesquioxane (2), and Sodium Isopropoxide (3): Phenyltrimethoxysilane (50 mL, 47.6 g, 0.27 mol) was added dropwise to a solution 2-propanol (260 mL), deionized water (5.5 mL, 0.31 mol), and sodium hydroxide (7.12 g, 0.18 mol) at room temperature for 15 min. The reaction mixture was heated at reflux for 4 h to obtain a milky-white precipitate. The suspension solution was cooled down at room temperature and left overnight. It was subsequently filtered and washed with 2-propanol and dried at 60 °C for 5 h under vacuum to obtain a completely dry white powder mixture of sodium salts **1**, **2**, and **3** (22.15 g).

Synthesis of *cis*- and *trans*-Di[(3-chloropropyl)isopropoxysilyl]-Bridged Double-Decker Octaphenylsilsesquioxane (5): Under a dry argon atmosphere, a mixture of anhydrous THF (260 mL), sodium

salts **1**, **2**, and **3** (25.81 g), and triethylamine (9.29 mL, 66.81 mmol) was cooled down to 0 °C in an ice bath. 3-Chloropropyltrichlorosilane (14.16 g, 10.49 mL, 66.81 mmol) was added dropwise over 10 min. After warming to room temperature overnight (12 h), the mixture was then cooled down to 0 °C again before the addition of a saturated $NaHCO_3$ solution (60 mL) to neutralize and dissolve any inorganic materials. CH_2Cl_2 (3 × 50 mL) was added to extract the desired products. The combined organic layer was separated, washed repeatedly with water until it became neutral, washed with brine, and dried with anhydrous sodium sulfate. Evaporation of the solvent gave a crude product, which was further dissolved in toluene (200 mL) to form a suspension. To fully precipitate the insoluble materials, the solution mixture was left in a refrigerator overnight, at which point it separated into two phases: insoluble white solid (A) and mother liquid solution (A). The insoluble solid (A, 4.41 g) was collected by filtration and further dissolved in THF to yield a solution containing some insoluble materials, which were further removed by filtration. An equivalent volume of ethyl acetate was added to the remaining clear solution, which was then placed at room temperature until the complete formation of cubic-like T_8 crystal **4** (0.40 g, 0.39 mmol, 9%). Evaporation of the mother liquid solution (A) yielded a white solid (24.06 g), which was then analyzed by thin-layer chromatography (CH_2Cl_2/hexane = 1:4 v/v). The analysis clearly showed three separate spots at R_f = 0.35 and 0.15 along with a broad baseline (R_f = 0.10–0). Crude product (7.13 g) was purified by conventional column chromatography (gradient system CH_2Cl_2/hexane = 1:4, 1:3, 3:7, 2:3, 1:1, and pure CH_2Cl_2) to give an additional product of pure **4** (R_f = 0.35; 0.66 g, 0.64 mmol, 9%) and an isomeric mixture of *cis*-**5**/*trans*-**5** (R_f = 0.15; 1.00 g, 0.72 mmol, 14%). Further recrystallization of *cis*-**5**/*trans*-**5** in THF/hexane (1:1 v/v) yielded colorless crystals of only pure *trans*-**5**, and evaporation of the remaining solution gave a majority of *cis*-**5**. Thus, **6** [R_f = 0.30, CH_2Cl_2/hexane (2:3)] and *trans*-**7** (R_f = 0.50, CH_2Cl_2) were isolated in only trace amounts (<5% yield). Data for **4**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.72 (m, 14 H), 7.50–7.34 (m, 21 H), 3.52 (t, J = 6.6 Hz, 2 H), 1.98 (quint., J = 6.6 Hz, 2 H), 0.99 (t, J = 8.2 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, TMS): δ = 134.18, 134.13, 130.84, 130.79, 130.21, 130.12, 127.92, 127.87, 47.11, 26.25, 9.48 ppm. ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, TMS): δ = –65.61, –78.23, –78.56 ppm. HRMS (ESI): calcd. for $C_{45}H_{41}ClO_{12}Si_8$ [M + K]$^+$ 1071.0100; found 1070.9490. Data for *cis*-**5**/*trans*-**5** (1:1): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53–7.11 (m, 40 H), 4.35 (oct., J = 6.2 Hz, 2 H), 3.37 (t, J = 6.8 Hz, 4 H), 1.86 (quint., J = 8.1 Hz, 4 H), 1.09 (d, J = 6.3 Hz, 12 H), 0.82 (m, 4 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, TMS): δ = 134.19, 134.15, 134.01, 133.98, 133.94, 131.41, 130.61, 130.56, 130.49, 127.90, 127.76, 127.69, 127.62, 65.73, 47.18, 26.52, 25.43, 10.35 ppm. ^{29}Si{^{1}H} NMR [99 MHz, $CDCl_3$, TMS, Cr(acac)$_3$]: δ = –61.26, –79.08, –79.13, –79.57 (*cis*-**5**; relative intensity ratio 1:2:1:1), –61.26, –79.08, –79.35 (*trans*-**5**; relative intensity ratio 1:2:2) ppm. HRMS (ESI): calcd. for $C_{60}H_{66}Cl_2O_{16}Si_{10}$ [M + Na]$^+$ 1417.1300; found 1417.0561. Data for *trans*-**5**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57–7.18 (m, 40 H), 4.40 (oct., J = 6.1 Hz, 2 H), 3.41 (t, J = 6.8 Hz, 4 H), 1.90 (m, 4 H), 1.12 (d, J = 6.1 Hz, 12 H), 0.85 (m, 4 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, TMS): δ = 134.03, 133.99, 131.49, 130.69, 130.57, 130.50, 127.91, 127.71, 65.76, 47.16, 26.58, 25.46, 10.41 ppm. ^{29}Si{^{1}H} NMR [99 MHz, $CDCl_3$, TMS, Cr(acac)$_3$]: δ = –61.28, –79.11, –79.37 ppm. HRMS (ESI): calcd. for $C_{60}H_{66}Cl_2O_{16}Si_{10}$ [M + Na]$^+$ 1417.1300; found 1417.1489. Data for *cis*-**5**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56–7.18 (m, 40 H), 4.39 (oct., J = 6.1 Hz, 2 H), 3.41 (t, J = 6.8 Hz, 4 H), 1.90 (m, 4 H), 1.12 (d, J = 6.2 Hz, 12 H), 0.85 (m, 4 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, TMS): δ = 134.91, 134.83, 132.30, 131.45, 128.78, 128.66, 128.51, 66.61, 48.09, 27.41, 26.32, 11.24 ppm. ^{29}Si{^{1}H} NMR [99 MHz, $CDCl_3$, TMS, Cr(acac)$_3$]: δ = –61.28, –79.08, –79.34, –79.57 ppm. HRMS (ESI): calcd. for $C_{60}H_{66}Cl_2O_{16}Si_{10}$ [M + Na]$^+$ 1417.1300; found 1417.1271. Data for **6**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58–7.20 (m, 40 H), 4.40 (oct., J = 6.1 Hz, 1 H), 3.42 (m, 4 H), 1.89 (m, 4 H), 1.13 (d, J = 8.7 Hz, 6 H), 0.94 (m, 2 H), 0.86 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, TMS): δ = 134.01, 133.96, 133.89, 131.32, 131.11, 130.64, 130.56, 130.43, 127.91, 127.89, 127.73, 127.69, 65.71, 47.18, 26.48, 26.35, 25.40, 10.30 ppm. ^{29}Si{^{1}H} NMR [99 MHz, $CDCl_3$, TMS, Cr(acac)$_3$]: δ = –56.49, –61.20, –78.62, –79.00, –79.10, –79.31 ppm. HRMS (ESI): calcd. for $C_{57}H_{60}Cl_2O_{16}Si_{10}$ [M + Na]$^+$ 1375.0800; found 1375.0634. Data for *trans*-**7**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.18 (m, 40 H), 3.40 (t, J = 6.5 Hz, 4 H), 2.74 (br., 2 H), 1.90 (m, 4 H), 0.93 (t, J = 8.5 Hz, 4 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, TMS): δ = 134.01, 133.89, 131.08, 130.59, 130.36, 127.91, 127.74, 47.17, 26.34, 10.29 ppm. ^{29}Si{^{1}H} NMR [99 MHz, [D$_6$]DMSO, TMS, Cr(acac)$_3$]: δ = –58.11, –78.96, –79.25 ppm. HRMS (ESI): calcd. for $C_{54}H_{54}Cl_2O_{16}Si_{10}$ [M + Na]$^+$ 1332.04; found 1331.9689.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{29}Si{^{1}H} NMR spectra; HRMS (ESI) spectra; characterization data for **4**–**7** including crystallographic data for *trans*-**5**.

Acknowledgments

This research was financially supported by the Thailand Research Fund (MRG5580011), the Office of the Higher Education Commission, Center of Excellence for Innovation in Chemistry (PERCH-CIC), and the Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand through its program of Center of Excellence Network. The authors are very thankful to Assoc. Prof. Dr. Nongnuj Muangsin for a discussion of the single-crystal X-ray analysis.

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Received: February 28, 2013
Published Online: May 29, 2013

