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COMMUNICATION

Synthesis of Aromatic Functionalized Cage-Rearranged Silsesquioxanes (T_8 , T_{10} , and T_{12}) via Nucleophilic Substitution Reactions

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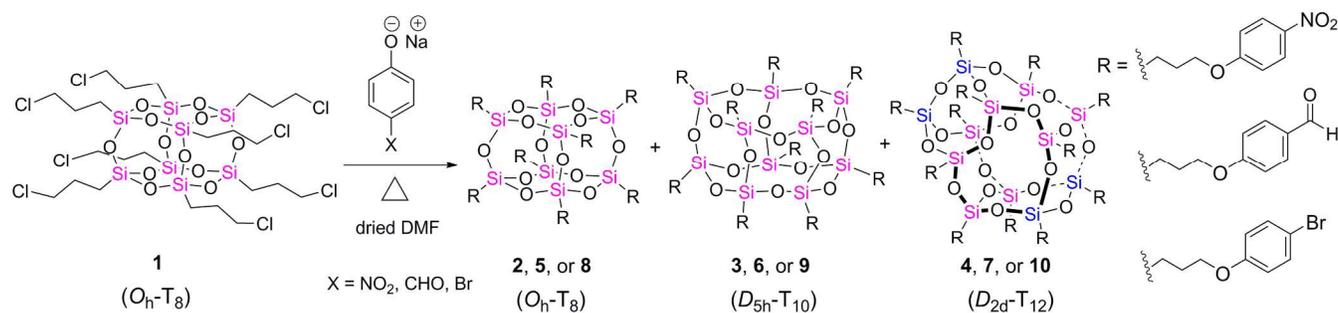
Organic-inorganic hybrid nano-building blocks of aromatic nitro-, aldehyde-, and bromo-functionalized polyhedral oligomeric silsesquioxanes were easily prepared through nucleophilic substitutions, starting from the reactions between octakis(3-chloropropyl)octasilsesquioxane and phenoxide derivatives. These phenoxide anions not only supplies the substitution functions to a silsesquioxane cage, but can also induce a cage-rearrangement leading to the formation of octa-, deca-, and dodecahedral silsesquioxane cages.

Aromatic compounds play important roles as intermediates in organic synthesis, as the reactive functional groups (e.g. nitro,¹ aldehyde,² bromo³) on aromatic rings have been widely utilized for a century as key chemicals for the synthesis of explosives,⁴ dyes,⁵ pharmaceuticals,⁶ and polymers.⁷ Meanwhile, polyhedral oligomeric silsesquioxanes have been well recognized as useful nanosized building blocks in the synthesis of organic-inorganic hybrid materials due to their versatile structure consisting of an inorganic Si-O-Si core and peripheral organic functional groups.⁸ Recently, a cage-like silsesquioxane with three-dimensional symmetry with combined organic and inorganic properties, has been used for advanced applications such as in the formation of porous materials,⁹ polymer nanocomposites,¹⁰ OLEDs,¹¹ and in catalysis.¹²

For example, silsesquioxane-based nitro functions are promising precursors in many synthetic reactions because of their ability to introduce nitrogen atoms bound to carbons. The first preparation of silsesquioxane-based nitro aromatics, a silsesquioxane cage featuring nitrophenyl substituents, was reported by Laine and co-workers in which nitration of octaphenylsilsesquioxane (Ph- T_8) was performed by fuming nitric acid.¹³ However, this method suffered from uncontrolled regioselectivity and multiple substitutions of nitro groups on the benzene ring.¹⁴ Subsequent reduction of the nitro groups to yield silsesquioxane-based amino functions, in

particular, is highly desirable as the amino derivatives could lead to a wide range of applications.¹⁵ Meantime, it has been well known that phenyl-silicon bonds are capable of electrophilic cleavage. For example, Deans and Eaborn successfully treated 1,3-bis(trimethylsilyl)benzene by fuming nitric acid led to the regioselective formation of monosubstituted trimethylsilyl-para-nitrobenzene.^{16a} Along this line, 4-nitrophenyl- T_8 , T_{10} , and T_{12} was successfully prepared by Kawakami and co-workers through nitration of the reactive precursors: 4-trimethylsilylphenyl- T_8 , T_{10} , and T_{12} (4-TMSPH- T_8 , T_{10} , and T_{12}) at ipso-position.^{16b} However, this synthetic approach still possesses several complicated steps (linear synthesis), as the starting precursors of 4-TMSPH- T_8 , T_{10} , and T_{12} must be initially prepared through hydrolytic-condensation of the non-commercially available (4-TMSPH)triethoxysilane. Thus, both methods are not synthetically practical since they involve either electrophilic aromatic substitution, which must be carried out under vigorous conditions with concentrated acid.

Meantime, only few reports found the preparation of silsesquioxane-based aldehyde^{17a} and bromo functional groups.^{17b} Moreover, all of them only paid attention to octameric T_8 cage, but not found in a larger-cage size. In this study, octakis(3-chloropropyl)octasilsesquioxane (**1**; Cl- T_8),¹⁸ prepared by hydrolytic-polycondensation of the commercially available (3-chloropropyl)trimethoxysilane, has been considered as a promising starting material because of its easy accessibility and facile conversion into other functional groups through nucleophilic substitution reactions.^{8f,19-24} Herein, the independent report of cage rearranged T_8 structure (**1**) under one-pot synthesis toward the multi aryl nitro-, aldehyde-, and bromo-functionalized T_8 , T_{10} , and T_{12} polyhedral oligomeric silsesquioxanes is presented for the first time. Thus, reactive functional groups could be tolerant under such a condition. In addition, this method is also applicable to gram-scale synthesis and the desired products are easily isolated in their clean and pure forms by practical column chromatography.



Scheme 1. Cage-rearranged T_8 cage of compound **1** upon introduction of 4-nitrobenzene, 4-oxybenzaldehyde, and 4-bromobenzene functions produced (a) Compounds **2-4**; 70°C , 3 days, $0.15 \text{ mol}\cdot\text{L}^{-1}$, 1.7 eq. of dried sodium 4-nitrophenoxide/ $\text{RSiO}_3/2$; (b) Compounds **5-7**; 70°C , 1 day, $0.06 \text{ mol}\cdot\text{L}^{-1}$, 2.0 eq of dried sodium 4-oxybenzaldehyde salt/ $\text{RSiO}_3/2$ and (c) Compounds **8-10**; 55°C , 12 hours, $0.13 \text{ mol}\cdot\text{L}^{-1}$, 1.5 eq. of dried sodium 4-bromophenoxide salt/ $\text{RSiO}_3/2$.

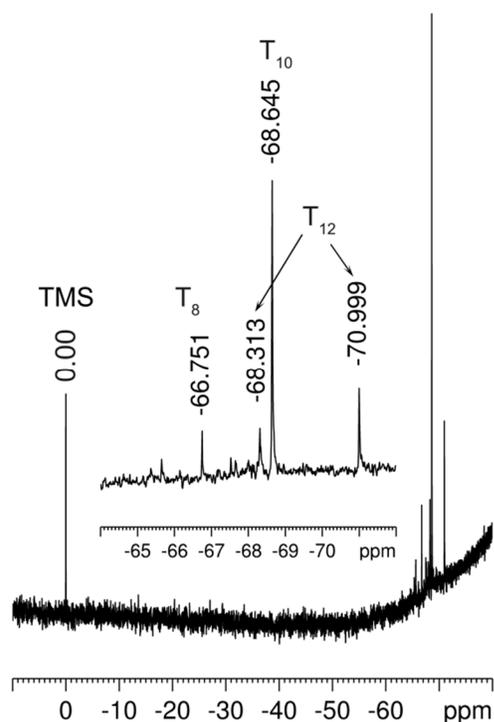


Figure 1. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of crude product in CD_2Cl_2 of *para*-nitrobenzene-functionalized-polyhedral oligomeric silsesquioxanes.

To study the reactivity of nucleophilic substitution reactions, ^1H NMR spectroscopy was used as an analytical tool to monitor the reaction progress. For example, the *N,N*-dimethylformamide (DMF) solution of a mixture of dried sodium 4-nitrophenoxide and **1** at 70°C (Scheme 1a) afforded a completed reaction (>99% substitution) within 3 days. Interestingly, under similar conditions with the higher reaction temperature of 100°C , the substitution reaction remained incomplete (~96% substitution) after 3 days. We suggest that at higher temperatures, the nucleophilicity and leaving ability of chloride anions as a by-product may participate to inhibit a complete substitution. More specifically, the substituent displacement reaches an equilibrium at higher temperatures.²²

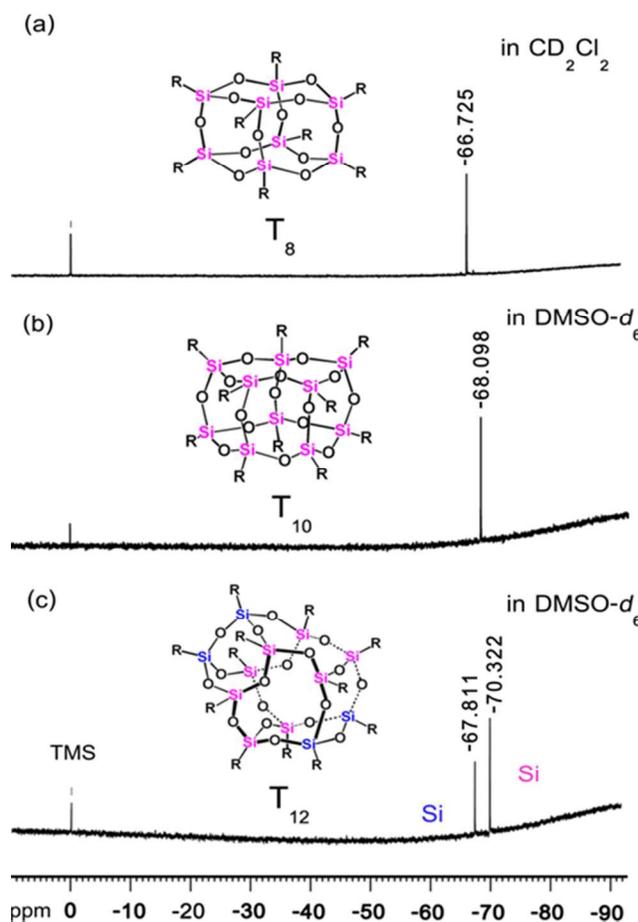


Figure 2. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of purified compounds (a) octa- (b) deca- and (c) dodeca(*para*-nitrobenzene)-functionalized-polyhedral oligomeric silsesquioxanes (**2**, **3**, and **4**).

In order to evaluate the completion of substitution reactions, the ^1H NMR spectrum of the crude product indicates that the proton signals (3.53, 1.82 and 0.75 ppm) of 3-chloropropyl groups are all shifted to 3.98, 1.91 and 0.79 ppm, corresponding to 3-substituted propyl groups, while an additional appearance of signals at 6.91 and 8.05 ppm confirms the regioselective *para*-substitution on the aromatic rings. However, we speculate that broad ^1H NMR signals of the crude product are possibly a result of cage-decomposition.

The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of crude product shown in Fig. 1 in fact confirms formation of the cage-rearranged products (T_8 , T_{10} , and T_{12}). Thin-layer chromatography analysis also reveals three distinct spots at $R_f = 0.45$, 0.30 , and 0.18 along with a broad baseline ($R_f = 0-0.15$) in a mixed solvent of 1.5% ethyl acetate in CH_2Cl_2 . Purification by column chromatography of the crude product (2.74 g) afforded an analytically pure decakis(3-propoxy-4-nitrobenzene)decasilsesquioxane (**3**; 0.81 g, $R_f = 0.30$, 18% yield) as a major product. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **3** contains a singlet resonance at -68.1 ppm (Figure 2b), which is characteristic of the decahedral T_{10} cage. On the other hand, the octakis(3-propoxy-4-nitrobenzene)octasilsesquioxane (**2**; 0.49 g, $R_f = 0.45$, 11% yield) and dodecakis(3-propoxy-4-nitrobenzene)dodecasilsesquioxane (**4**; 0.41 g, $R_f = 0.18$, 9% yield) were isolated as minor products. Their $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of T_8 and T_{12} cages (Figure 2a and 2c) show a singlet at -66.7 ppm and two singlet signals at -67.8 and -70.3 ppm (1:2 ratio), respectively.

Similarly, *para*-oxybenzaldehyde (T_8 ; **5**, T_{10} ; **6**, and T_{12} ; **7**) and *para*-bromobenzene (T_8 ; **8**, T_{10} ; **9**, and T_{12} ; **10**) functionalized-polyhedral oligomeric silsesquioxanes were prepared *via* nucleophilic substitution reactions of freshly prepared sodium 4-oxybenzaldehyde and 4-bromophenoxide salts with **1** (Scheme 1b and 1c). These results are also consistent with the synthesis of silsesquioxanes-based *para*-nitrobenzene, in which the cage-rearrangement phenomenon of the T_8 cage was promoted under basic reaction conditions²² with strong nucleophiles including oxygen (e.g. acrylate and methacrylate)²⁴ and nitrogen (e.g. azide and phthalimide)^{20,21} anions in polar aprotic solvents (e.g. DMF and acetone) at high temperatures. In contrast, soft nucleophiles (e.g. sulfur, bromine, iodide) appear to leave the T_8 cage completely unperturbed.^{19,22} It has also been suggested that this phenomenon could be due to the electronic effect or the electron density of nucleophiles.²⁰ In this study, we further propose that *para*-nitrophenoxide, *para*-oxybenzaldehyde, and *para*-bromophenoxide anions must play the same role as the anions mentioned above. More specifically, the nucleophilicity on the oxygen atom of phenoxide anion is strong enough to induce the breakage of the inorganic Si-O bonds of the T_8 cage, yielding various fragments. During the substitution reaction, these fragments can self-assemble to form thermodynamically stable cage-like silsesquioxanes (T_8 , T_{10} , and T_{12}). Moreover, we found that substitution and cage-rearranged reactions at higher moisture contents resulted in more unwanted and degraded fragments from cage decomposition. These led to higher amounts of undesired by-products or unidentified polysilsesquioxanes (T_n), as evidenced by broader ^1H NMR signals and longer baseline on TLC plate.

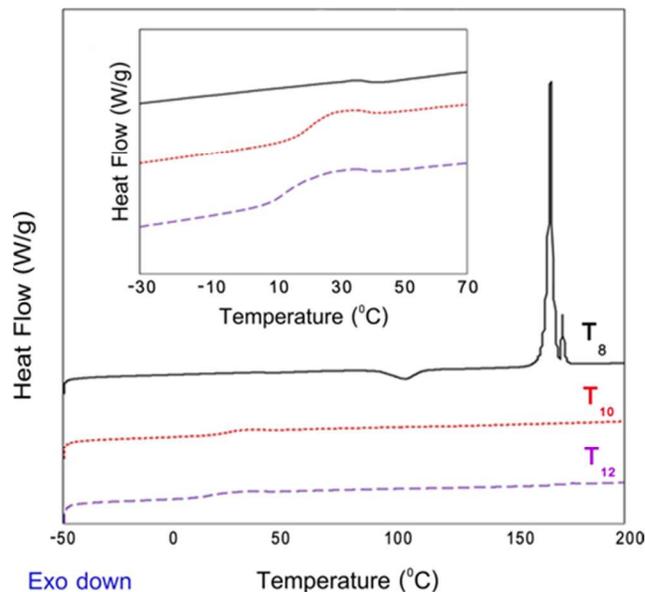


Figure 3. DSC thermograms of purified octa, deca and dodeca(*para*-nitrobenzene)-functionalized-polyhedral oligomeric silsesquioxanes (**2**, **3**, and **4**) over the temperature range from -50 to 200°C , at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

Recently, we reported that the physical state of each silsesquioxane cage was determined by the degree of symmetry at the molecular level.²⁴ For example, the highly symmetrical T_8 cage (O_h) is crystalline,^{18-20,22,24,25} while the less symmetrical T_{10} (D_{5h}) and T_{12} (D_{2d}) cages tend to have a loosely packed structure.^{18,22} Regarding preliminary observations, compound **2** (T_8) is a white powder solid with a melting point (m.p.) of $164.3-165.5^\circ\text{C}$, as determined by a melting detector, while compounds **3** (T_{10}) and **4** (T_{12}) appear as fluffy solids at room temperature. In order to better understand the phase-transition of each pure silsesquioxane cage, differential scanning calorimetry (DSC) analyses were performed over temperatures ranging from -50 to 200°C . As shown in Figure 3, the cubic T_8 cage (**2**) shows a melting temperature (T_m) at around 166°C , comparable to what was observed with the melting detector. During the cooling process, there is an exothermic signal at 139°C (see Supplementary Information (SI); Fig. S5), which corresponds to the crystallization temperature (T_c), always found at lower temperatures compared to the T_m value of the crystalline blocks. In other words, at T_c , the temperature is low enough to slow down the freedom of movement of the otherwise highly mobile and flexible organic chains of the cubic T_8 cage. As a result, the T_8 cages spontaneously align themselves into a more close-packed system. On the other hand, compounds **3** (T_{10}) and **4** (T_{12}) appear to only have the glass transition temperatures (T_g) at 24.5°C and 22.5°C , respectively. This evidence, again, strongly suggests that both deca- and dodecameric silsesquioxanes have a loose-packed structure or behave like a “polymeric or amorphous” material. Noted that higher crystallinity of T_8 may explain why only some of T_8 cubes (and not T_{10} and T_{12}) could readily precipitate out of the reaction solutions.^{18,25} X-ray powder diffraction analysis of **2**, **3**, and **4** (see SI; Fig. S16) further reveals that the T_8 compound **2** is highly

crystalline, whereas compounds **3** (T₁₀) and **4** (T₁₂) are amorphous. Despite these observations, it should be mentioned that highly crystalline T₁₀ and T₁₂ cages have previously been observed in the presence of rigid phenyl substituents, most likely as a result of better molecular packing from aromatic-aromatic interactions (π-π stacking).²⁶

Conclusions

A complete set of novel polyhedral oligomeric silsesquioxanes; T_n (n = 8, 10, and 12) based aromatic nitro-, aldehyde-, and bromo-functional groups were easily prepared *via* nucleophilic substitution reactions. Cage-rearranged silsesquioxanes (T₈, T₁₀, T₁₂) were simply separated in their pure forms by practical column chromatography. Moreover, physical and thermal properties of the pure silsesquioxane products confirm that the octahedral T₈ cage is highly crystalline, while decahedral T₁₀ and dodecahedral T₁₂ cages behave like “polymeric or amorphous” materials. We believe that this study serves as a highly useful prototype method for preparation of other reactive aromatic-based silsesquioxanes.

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Notes and references

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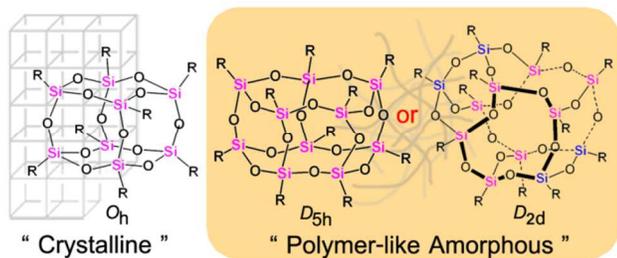
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† Electronic Supplementary Information (ESI) available: Experimental details, ¹H, ¹³C{¹H}, ²⁹Si{¹H} NMR, HR ESI-MS, and MALDI-TOF MS spectra of the new compounds **2–10**. See DOI: 10.1039/c000000x/

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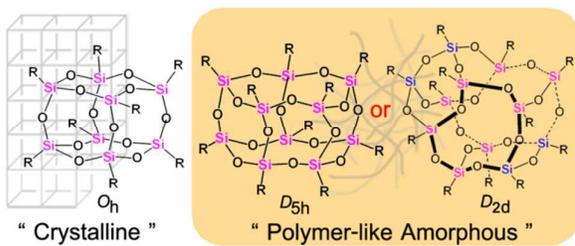
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Graphical Abstract



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