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Development of Synthetic Methods for New Functional Polyhedral Oligomeric Silsesquioxane Derivatives

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[Introduction]

Polyhedral oligomeric silsesquioxanes (POSS) have nanometer-size cubic structure with wide surface area and controlled porosity, and can be functionalized with a wide variety of organic groups in the design of nanocomposite materials and hybrid polymer systems. Hydrolysis of trichloro- or trialkoxysilane gives polysilsesquioxane with formal structure $[\text{RSiO}_{1.5}]_n$, but the actual product is often a mixture of insoluble gel, crystalline compounds, or oil. The product distribution depends on reaction conditions, such as solvent, concentration, catalyst, temperature, and organic group.

Well-established methods of the synthesis of these compounds were introduced by Feher's group,^{1,2} Lichtenhan's group^{3,4} and Laine's group.^{5,6} Until now, researches on octasilsesquioxane were mostly focused and limited to the systems with hydrido- ($\text{H}_8\text{-T}_8$), cycloalkyl- ($\text{Cy}_8\text{-T}_8$) and alkyl- ($\text{R}_8\text{-T}_8$). Although the molecular weights of these compounds fall in only 420-2000 Da. region, they still showed high thermal stability. They have been used in numerous areas, such as composite material with typical plastics to enhance the thermal property.^{7,8} However, the yield of the synthesis was considerably low, and long reaction time was required. This bottleneck has made the research and development of octasilsesquioxane as the new material difficult.

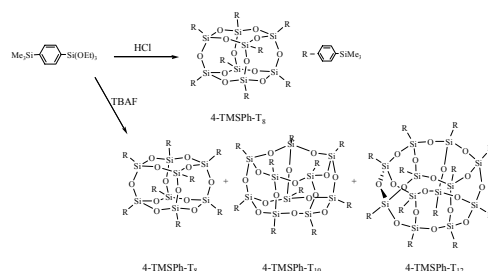
On the other hand, increasing need has been noticed for the introduction of functional groups to POSS, such as cage to be used as the building blocks to construct variety of nano-hybrid materials with precise structure.⁹⁻²² Phenyl derivatives, to which functional groups can be introduced by variety reactions, are the most convenient for the purpose. However, it is normally very difficult to directly synthesize functionalized phenyl-substituted cages, and thus functionalization of phenyl group attached to the cage silicon atom has been long desired.

Amino group is one of the versatile functional groups to construct new structure by condensation or addition reactions, and introduction of nitro group is the key to introduce amino group to the aromatic group. Laine and Olson reported the nitration of octa(phenyl)octasilsesquioxane by fuming nitric acid and further reduction and application of the product.²³ However, the multi-, but incomplete functionalization of phenyl ring often made it unclear to correlate the property of the system with the structure.

In this paper, firstly, synthesis and separation of novel 4-trimethylsilyl-phenyl-POSS cages were described. Next, regioselective nitration of octa(4-tolyl)octasilsesquioxane and octa, deca, dodeca(4-trimethylsilyl-phenyl)- T_8 , -T_{10} , and -T_{12} . Finally, we have developed new cage-type silsesquioxane and their derivatives.

[Results and discussion]

A 4-Tolyl(4-MPh)- T_8 , 4-isopropylphenyl(4-PPh)- T_8 and 4-trimethylsilylphenyl(4-TMSPH)- T_8 were obtained in moderate yield by direct acidic hydrolysis of (4-MPh)triethoxysilane, (4-PPh)triethoxysilane, and (4-TMSPH)triethoxysilane in the presence of hydrochloric acid (HCl). Simple washing with ethanol gave 4-MPh- T_8 and 4-PPh- T_8 . Passage through short silica gel column with hexane as an eluent gave pure 4-TMSPH- T_8 . Hydrolysis of 4-substituted-phenyltriethoxysilane in the presence of tetrabutylammonium fluoride gave a mixture of T_8 , T_{10} , and T_{12} cages having T_{10} as the major fraction. 4-MPh- T_{10} was obtained from the mixture by recrystallization using acetonitrile-THF (1 : 1). Treatment of the mixture of 4-TMSPH cages firstly with hexane removed 4-TMSPH- T_8 (11%) as a crystalline material. Following crystallization using ethanol-hexane (1 : 4) gave 4-TMSPH- T_{12} as crystal in 7% yield. Final crystallization using acetonitrile-THF (1 : 3)



Scheme 1. Synthesis of 4-TMSPH- T_8 , -T_{10} and -T_{12} .

gave 4-TMSPh-T₁₀ as crystal in 30% yield. Each fraction was purified by further recrystallization.

The reaction scheme is shown for 4-TMSPh POSS cages in Scheme 1, and the results of the synthesis of 4-substituted-phenyl-cages are shown in Table 1.

Table 1. Synthesis of 4-substituted-phenyl-POSS cages

Triethoxysilane	Catalyst	Solvent	T ₈ (Yield, %)	T ₁₀ (Yield, %)	T ₁₂ (Yield, %)
4-TMSPh	HCl	EtOH	21	b	b
4-TMSPh	TBAF	CH ₂ Cl ₂	11	30	7
4-MePh	HCl	EtOH	21	b	b
4-MePh	TBAF	CH ₂ Cl ₂	10	41	a
4-PPh	HCl	EtOH	9	b	b

a: Not isolated, b: Not detected by NMR.

Formation of T₁₀ and T₁₂ cages should be the result of the decomposition of the T₈ cage and re-assembling to thermodynamically stabler cages, which are commonly observed under various reaction conditions.

Nitration of 4-TMSPh-POSS cages was examined. For comparison, nitration of (4-tolyl)- and (4-isopropylphenyl)-T₈ were also carried out. Nitration of 4-tolyl-T₈ by fuming nitric acid (added at -30°C), or by copper (II) nitrate trihydrate (copper (II) nitrate/octasilsesquioxane = 1.2 / 0.125 mol/mol) at room temperature gave clean 3-nitration. When starting material's peak in ¹H-NMR has disappeared, three aromatic protons at δ = 8.32, 7.88 and 7.45 and one CH₃Ph at 2.64 ppm have appeared, which strongly indicated the formation of 4-methyl-3-nitrophenyl group. There were no symmetrical doublet pair of protons assignable to 3- and 2-protons of 4-nitrophenyl derivatives, which might be produced by *ipso* substitution. Accurate position of nitration was confirmed by the help of NOE of the product in NMR. Irradiation on methyl protons, only one peak at δ = 7.88 ppm assigned to 2-proton appeared as a positive signal. Other correlation was also consistent with the 3-nitration.

Thus, the NOE analysis of product confirmed the 3-nitration of 4-tolyl-T₈. The ²⁹Si NMR showed only one peak at δ = -79.2 ppm assignable to T³ structure. MALDI-TOF MS showed interesting phenomenon. The highest mass of 1528 Da could be octa(4-methyl-3-nitrophenyl)octasilsesquioxane with one 3-nitro group on each phenyl group of the T₈ cage [(CH₃NO₂PhSiO_{1.5})₈-Na⁺], and the MS spectrum showed arrays of peak differing 15 in molar mass.

Considering the result of NMR, these peaks seemed to appear under ionization condition of the compound by eliminating methyl group, and not by *ipso* substitution.

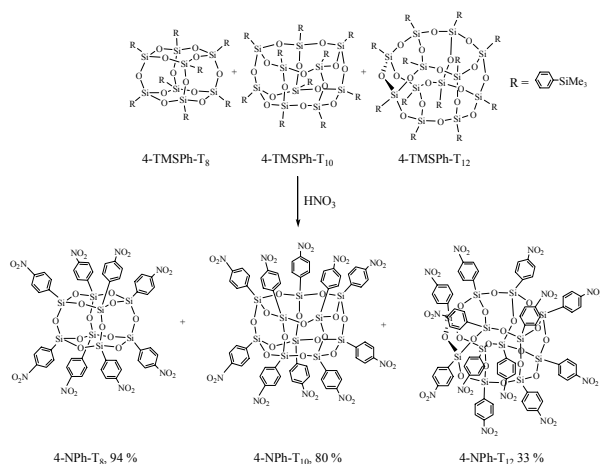
Although some decomposed products were formed when fuming nitric acid was added to 4-TMSPh-T₈ at room temperature, almost pure completely nitrated products were obtained from 4-TMSPh-T₈, -T₁₀, and T₁₂, if the addition of the acid was carried out at -30 °C followed by the reaction at room temperature in 10h as shown in Scheme 2. The ¹H, ¹³C, ²⁹Si-NMR and IR data also support the formation of 4-nitrated product. The IR spectra showed two strong peaks at 1345, 1515 (4-NPh-T₈), 1349, 1520 (4-NPh-T₁₀) and 1348, 1518 cm⁻¹ (4-NPh-T₁₂) assignable to symmetric and antisymmetric stretching of N=O band. ²⁹Si-NMR showed the disappearance of the singlet of trimethylsilyl group of 4-TMSPh-T₈, T₁₀ and T₁₂ at δ = -3.83, -3.98 and -4.06, -4.13 ppm, and the appearance of about 1-2 ppm shifted cage peaks of 4-NPh-T₈, T₁₀, and T₁₂ at δ = -79.2 (NPh-T₈), -80.9 (NPh-T₁₀), and δ = -80.3, -82.2 ppm, respectively.

This is the first report on the effective formation of 4-nitrophenyl cage POSS derivatives. These pure nitro compounds, 4-NPh-T₈, 4-NPh-T₁₀, and 4-NPh-T₁₂ will find applications in designing new nano-hybrid material with precise structure.

Nextly, we have development of new cage-type phenylsilsesquioxane derivatives.

Hydrolysis of phenyltrichlorosilane in the acidic condition gave a new cage type phenylsilsesquioxanes.

The purification of condensation products was also tried with precipitation and preparative SEC. Obtained



Scheme 2. Synthesis of 4-nitrophenyl-T₈, T₁₀, and T₁₂

phenylsilsesquioxane shows relatively narrow molecular distribution and their molecular weight for main peaks are 1212 from MALDI-TOF MS measurement.

On the other hand, hydrolysis of phenyltriethoxysilane in the presence of tetrabutylammonium fluoride (TBAF) gave a DDT₈OH and T₉(OH)₃.

The Obtained product shows relatively narrow molecular distribution and their molecular weight for main peaks are 1352, 1212 and 1092 from MALDI-TOF MS measurement.

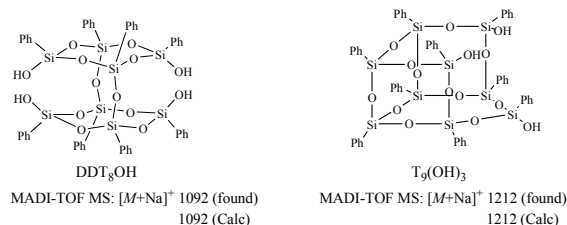


Figure 1. Structure of phenylsilsesquioxane in the presence of tetrabutylammonium fluoride.

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[Contents of doctoral dissertation]

Chapter 1: Introduction	2-26
Chapter 2: Synthesis of Incompletely Condensed-Phenyl Silsesquioxanes	27-38
Chapter 3: Synthesis and Separation of 4-Substituted-Phenyl Silsesquioxane Cages	39-64
Chapter 4: Nitration of 4-Substituted-Phenyl Silsesquioxane Cages	65-87
Chapter 5: Summary	88-89
Publication	90
Contribution to Conferences and Meetings	90
Acknowledgement	91-92
Abstract of Subsidiary Research	93

[Publications]

1. Y. Kawakami, D. W. Lee, C. Pakjamsai, M. Seino, A. Takano, A. Miyazato, I. Imae, "Formation and Functionalization of Aryl-substituted Silsesquioxanes" , *ACS Symp. Ser.* **2006**, 889, 460.
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