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Synthesis of Novel Cage Silsesquioxanes from Cyclic Tetrasiloxanetetrol

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Introduction

Polyhedral oligomeric silsesquioxanes (POSS), [$(RSiO_{1.5})_n$; R-T_8, R-T_{10}, R-T_{12} ,where n = 8, 10, 12], are built through stable siloxane bonds and surrounded by organic peripheries, embody both organic-inorganic characteristics and cage-like structures in one small nanoentity. Among POSS, especially Ph-T_8, has been paid much attention as precursors for organic-inorganic nano-hybrid materials [1]. The Ph-T_8 is usually obtained from phenyltrichlorosilane or phenyltrialkoysilane under acidic or basic condition [2]. Silsesquioxane-based compounds can be also used as the starting materials for the formation of cages [3]. Kabe et al. reported the amine-catalyzed formation of the mixture of T_8, T_{10}, T_{12} including vinyl derivative in acetone in moderate yield from various silsesquioxane derivatives. In some cases, Ph-T_8 and *o*-tolyl-T_8 could be selectively obtained by the reaction [3 (a), (b)]. Formation of completely or incompletely condensed POSS is not a simple reaction, but includes many steps of equilibration depending on the reaction conditions. The reaction mechanism in the formation of Ph-T_8 has not been well established.

Meanwhile, tetraphenyltetrasiloxanetetrol (Ph-T_4-tetrol) is another possible interesting starting material for the synthesis of Ph-T_8 cage. Brown originally reported the formation of all-*cis*-Ph-T_4-tetrol from phenyltrichlorosilane, and commented on the possibility of the compound being an intermediate for Ph-T_8 [4]. We reported the formation and isolation of all stereo-isomers of Ph-T_4-tetrol [5]. Shchegolikhina et al. reported the formation of the all-*cis*-Ph-T_4-tetrol from phenyltributoxysilane [6]. It should be noticed that all-*cis* cyclic tetrasiloxanetetrol, namely all-*cis* T_4-tetrol, or its alkali metal salt is actually often selectively formed under similar reaction condition to obtain T_8 cages. Since, all-*cis*-Ph-T_4-tetrol might be a possible key intermediate for the formation of various Ph-T_8 derivatives, and stereochemistry of the formed Ph-T_4-tetrol can be controlled by the reaction condition, elucidation of stereochemistry of the T_8, possibly formed from the cyclic tetramer, will give some information about the reaction mechanism. The first purpose of this research is to confirm the reaction mechanism in the formation of T_8 from the condensate of alkoxysilane.

To widen the applicability of POSS derivatives, functionalization of phenyl group directly attached to the core silicon atom has been desired. To synthesize cage T_8 with functional group, functionalized T_4-tetraol is needed. However, selective synthesis and isolation of functionalized Ph-T_4-tetrol is not an easy task. Functionalized T_4-tetrol can be sometimes isolated as alkaline salt, but treatment of the salt with acid to isolate free silanol gives further condensed products. This fact has limited the possible synthesis of functionalized Ph-T_8 from Ph-T_4-tetrol. Meanwhile, direct synthesis of functionalized Ph-T_8, or introduction of functional groups to the phenyl moiety, in which functional group can act as the scaffold to build nano-hybrid materials, has not been well established, either. To solve the problem, formation of pure 4-bromo-substituted phenyl-T_8 as a new building block from the condensed products was investigated. Synthesis of novel cage silsesquioxane with C_{4v}-symmetry structure (Figure 1) and functional transformation of T_4-tetrol were also investigated.

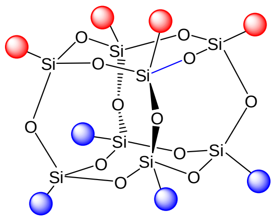
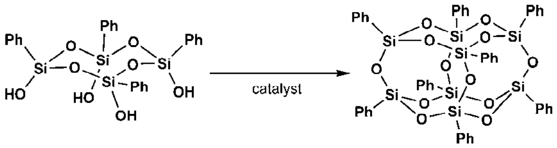


Figure 1. Structure of C_{4v}-symmetry T_8 Cage.

Results and discussion

When all-*cis*-Ph-T_4-tetrol was treated with benzyltrimethylammonium hydroxide (BzTMAH), Ph-T_8 cage was obtained and confirmed by NMR and TOF-MS, and shown in Scheme 1. Another effective catalyst was tetrabutylammonium fluoride (TBAF). It is interesting to comment that benzene is the best choice as the solvent to produce T_8 from T_4-tetraol as is the same with direct synthesis of T_8 from phenyltri(ethoxy)silane in the presence of BzTMAH (24.0 mol %). Under such condition, kinetic rate of the formation and further scrambling and decomposition seems competetive. Solubility of the products in the



Scheme 1. Synthesis of T_8 cage from all-*cis*-Ph-T_4-tetrol

solvent is another important factor to determine the products.

To study the reaction mechanism, mixture of Ph-T_4-tetrol and Ph-d_5-T_4-tetrol was treated under the same reaction condition. The MS of the product shown in Figure 2 clearly indicates the random distribution of each component in the produced T_8. Both Ph and Ph-d_5 units are distributed statistically in T_8 cage. Decomposition of T_4-tetrol and reassembling T_8 are simultaneously occuring in the reaction system.

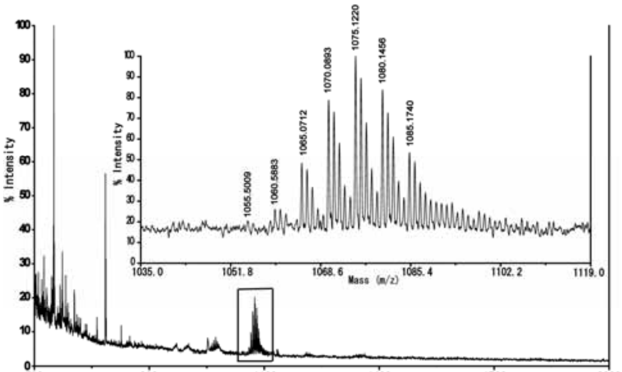
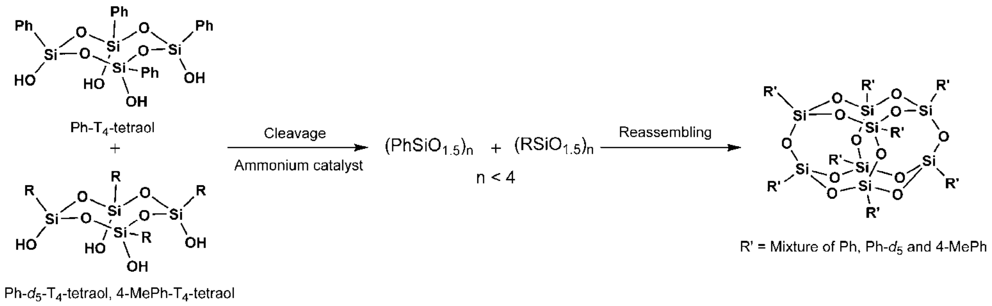


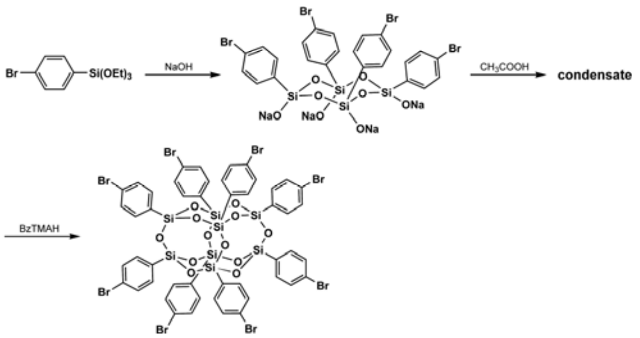
Figure 2. Mass spectrum of the product cages from the mixture of Ph- and Ph-d_5-T_4-tetrol.

When p-Tol-T_4-tetraol and Ph-T_4-tetrol were treated with BzTMAH in benzene for 24h, a mixture of crystalline products was obtained in 30% yield. This product has the arrays of mass ranging from 1069 [peak of $(p\text{-Tol})_1(\text{Ph})_7$-$T_8$ with Na^+] to 1125 [peak of $(p\text{-Tol})_5(\text{Ph})_3$-$T_8$ with Na^+) indicating the cage products composed of mixed substituents of p-Tol and Ph. By proton NMR, the ratio was determined to be 4 : 1. Relatively low yield of mixed cages (30% compared to >90% from Ph-T_8 itself) and absence of p-Tol-T_8 cage may indicate that scrambling of substituents had occurred, and at least 5 to 6 phenyl substituents are needed to make the cage crystalline to precipitate from the reaction mixture. Besed on these facts, reaction mechanism was considered. If the formation of T_8 is a simple dimerization reaction of T_4-tetrol, cage T_8 should be consist of the three types of T_8; p-Tol-T_8, Ph-T_8 and $(p\text{-Tol})_4(\text{Ph})_4$-$T_8$, but this is not the case. Random distribution of substituents in the products in the co-condensation reaction of p-Tol-T_4-tetrol and Ph-T_4-tetrol provides strong evidence that the reaction is a reshuffling process, by which the tetrol decomposed into smaller fragments, and then reassembled to form T_8 structure (Scheme 2). This process provides opportunities for the preparation of variety of new functionalized POSS from T_4-tetrol.



Scheme 2. Reaction mechanism in the formation of T_8 from T_4-tetrol using ammonium catalysts

Direct synthesis of functionalized Ph-T_8, or introduction of functional groups to the phenyl moiety, in which functional group can act as the scaffold to build nano-hybrid materials, has not been well established, either. Laine reported the bromination and nitration of Ph-T_8, but the number and position of the functional groups were not well-controlled [7]. However, we found that when the condensed product of 4-bromophenyl-T_4-tetrol was treated with BzTMAH, corresponding 4-bromophenyl-T_8 was obtained as the pure crystalline material in reasonable yield (58%) (Scheme 3). The compound shows a pair of doublet at δ 7.55 and 7.58 assigned to meta and ortho protons of 1,4-bromo and silyl substituted benzene. The molar mass (1687.4) by MALDI-TOF MS well coincides with the calculated value (1686.4). This is the first report on the direct synthesis of pure 4-bromophenyl-T_8. The brominated T_8 can be used in the synthesis of new POSS systems.



Scheme 3. Synthesis of octa(4-bromophenyl)octasilsesquioxane

It was found that the formation of Ph-T_8 from Ph-T_4-tetrol by using ammonium catalyst proceed through reshuffling process evidenced by scrambling of the substituents as shown in scheme 2. Because all of the silsesquioxane units in T_4-tetarol were cleavaged by the catalyst in the reaction, C_{4v}-symmetry T_8 with two different types of substituents in each side of the molecule could not be obtained. Therefore, the synthesis of T_8 cage from T_4-tetrol by another catalyst was assessed as a strategy.

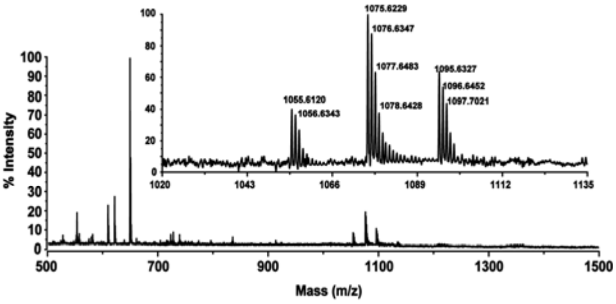
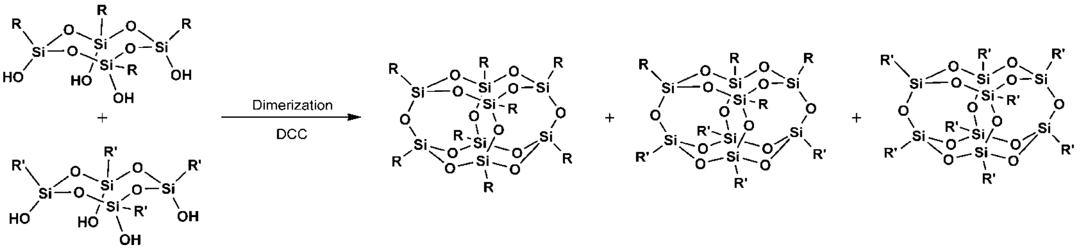


Figure 3. Mass spectrum of the product T_8 cages from the mixture of Ph- and Ph-d_5-T_4-tetrol.

Condensation reaction of T_4-tetrol with *N,N'*-dicyclohexylcarbodiimide (DCC) was investigated to synthesize C_{4v}-symmetry T_8. Ph-T_8 was obtained by the reaction of Ph-T_4-tetrol with DCC in THF. Purity of the product was enough for further analysis. of Ph-T_4-tetrol by ammonium catalyst was carried out, not only Ph-T_8 but also a little amount of Ph-T_7 was formed. As a result, it was found that DCC is a good catalyst for the formation of T_8 from T_4-tetrol without the formation of by-products such as T_7 or unidentified oligomers. In order to investigate the mechanism of this kind of reaction, co-condensation of Ph-T_4-tetrol with Ph-d_5-T_4-tetrol was carried out. MALDI TOF MS of the product is shown in Figure 3. As shown in Figure 3, three kinds of molar mass (1055.61, 1075.62, 1095.63 $[M+Na]^+$) were observed and assigned to Ph-T_8, $Ph_4(Ph\text{-}d_5)_4$-T_8 and (Ph-d_5)-T_8, respectively. The molar ratio of Ph-T_8, $Ph_4(Ph\text{-}d_5)_4$-T_8, (Ph-d_5)-T_8, according to relative intensity of MALDI TOF MS, was 1:2:1.3 which coincided theoretical value of 1:2:1. The formation of three kinds of the T_8 products in the reaction of Ph-T_4-tetrol and Ph-d_5-T_4-tetrol using DCC catalyst provide strong evidence for the reaction of T_4-tetrol as a dimerization reaction (Scheme 4). C_{4v}-symmetry T_8 which has phenyl group and phenyl-d_5 group in the molecule was successfully synthesized.



Scheme 4. Synthesis of T_8 cages from co-condensation of Ph-T_4-tetrol and Ph-d_5-T_4-tetrol by DCC

In case of dimerization reaction from two kinds of T_4-tetrol using DCC, the yield of the obtained C_{4v}-symmetry T_8 cage was low. This reason could be due to produce not only C_{4v}-symmetry T_8, but also homo condensed T_8 cages such as Ph-T_8 or Ph-d_5-T_8. To solve the problem, some new synthetic strategies which were achieved by cross-coupling reaction from methoxy group with hydrosilyl group to avoid homo condensation reaction of T_4-tetrol were suggested. The functional transformation of Ph-T_4-tetrol with tetramethoxysilane was investigated. The formation of Ph-T_4-OMe was confirmed by ^{29}Si-NMR and HMBC.

These compounds will be used as a scaffold to build new POSS compounds, and contribute to develop new materials to be applied in electro industry, for instance, high performance insulating materials.

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Contents of doctoral dissertation

Publications

1. Seiji Tateyama, Yuriko Kakihana and Yusuke Kawakami. Cage Octaphenylsilsesquioxane from Cyclic Tetrasiloxanetetraol and Its Sodium Salt, *J. Organomet. Chem.* In Press.

2. Yusuke Kawakami, Yuriko Kakihana, Akio Miyazato, Seiji Tateyama and Md. Asadul Hoque, Polyhedral Oligomeric Silsesquioxanes with Controlled Structure: Formation and Application in New Si-based Polymer Systems, *Adv. Polym. Sci.* Submitted.