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An Efficient Approach to Monophenyl-Functionalized Octasilsesquioxanes

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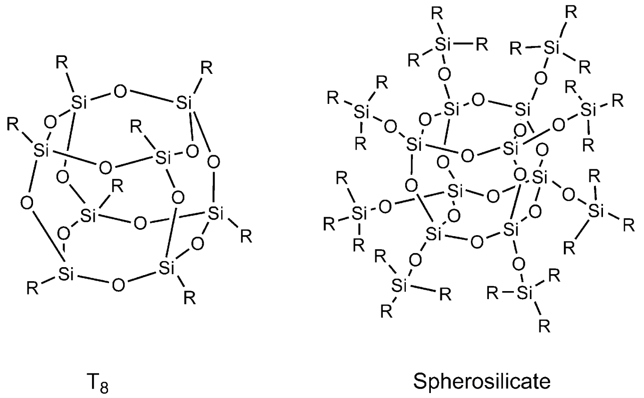
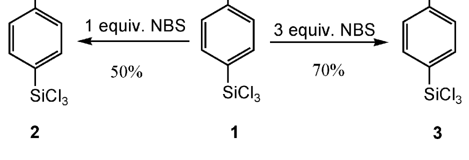
By controlling the ratio of *N*-bromosuccinimide (NBS) to trichloro(*p*-tolyl)silane, [4-(bromomethyl)phenyl]trichlorosilane and trichloro[4-(tribromomethyl)phenyl]silane were selectively prepared for the first time. Then, by treating the above two trichlorosilanes with incompletely condensed silsesquioxane, $R_7Si_7O_9(OH)_3$, a (monobromomethyl)phenyl-tethered octasilsesquioxane and (tribromomethyl)phenyl-tethered octasilsesquioxane were easily obtained. Finally, the resulting two compounds were further hydrolyzed to form a (monohydroxymethyl)phenyl- and monocarboxyphenyl-functionalized octasilsesquioxane, respectively.

Introduction

Recently, polyhedral oligomeric silsesquioxanes (POSS) of the general formula $(RSiO_{3/2})_n$, as well as spherosilicates (especially silyl-substituted ones), $(R_3SiO)_8Si_8O_{12}$ (Q_8^M) (Scheme 1), have received great interest because they can be widely used as excellent platforms for new hybrid materials,[1–6] homogeneous models for silica supports,[7,8] supports for organometallic catalysts,[9–11] biocompatible drug carriers,[12] and also as anion receptors.[13,14] The incorporation of cages into polymers produces nanocomposites with improved properties such as glass transition temperature, mechanical strength, thermal and chemical stability, and ease of processing.[15–18] Early in the development of silsesquioxane chemistry, Feher and co-workers discovered that incompletely condensed cages with the formula $R_7Si_7O_9(OH)_3$ (R = *i*Bu, Ph, Me, *c*Hex, cyclopentyl, etc.) could be isolated and then capped with an organosilane ($R'SiX_3$) reagent to produce a wide variety of octasilsesquioxanes (**T$_8$**) with one uniquely modified apex.[19–21] The *i*Bu substituent was chosen in this paper. In order to take advantage of this class of compounds further, effective approaches to specific trichlorosilanes appear very important in the course of preparation of monofunctionalized **T$_8$**. Especially when hydrosilylation, the typical method to introduce functional groups to the **T$_8$** cage, is not effective, exploring new chlorosilanes appears necessary.[22–24] Although some monofunctionalized **T$_8$** compounds are now available, to the best of our knowledge, monocarboxyphenyl-functionalized **T$_8$** has not been reported. The carboxylate substituents render it a unique and novel nanosized building block (NBB) for hybrid materials, because they provide new linkage options for the synthesis of such materials. As a model compound, it will play a different, but also very important role in basic and applied research, comparable to that of an octacarboxyl cage.[25] We report here the first preparation of monocarboxyphenyl-functionalized



Scheme 1. The structures of POSS (typically, **T$_8$**) and spherosilicate.



Scheme 2. Synthesis of **2** and **3**.

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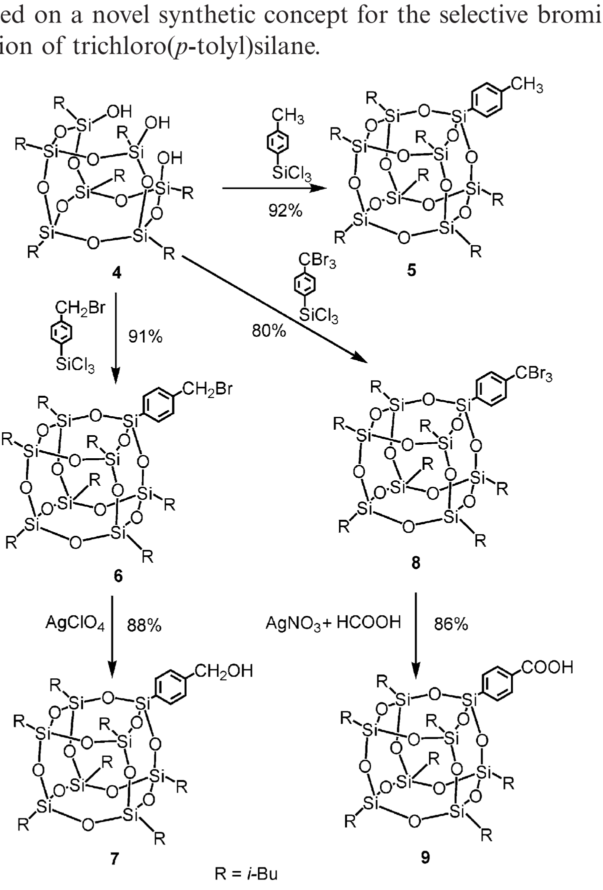
$\mathbf{T_8}$ and some other $\mathbf{T_8}$ compounds (Scheme 2 and Scheme 3) based on a novel synthetic concept for the selective bromination of trichloro(*p*-tolyl)silane.



Scheme 3. Synthetic routes to functionalized $\mathbf{T_8}$.

Results and Discussion

The starting point of our investigation was monotolyl-tethered $\mathbf{T_8}$ **5**, which was expected to produce monocarboxy-functionalized $\mathbf{T_8}$ and other derivatives.[26] Although an octacarboxyl spherosilicate was successfully prepared through complete bromination of an octatolyl-tethered spherosilicate following hydrolysis,[25] all attempts to prepare monocarboxy-functionalized $\mathbf{T_8}$ via **5** by following a similar method failed. This failure was due to the production of a mixture of monobromo, dibromo, and tribromo derivatives and the inability to purify the crude product, which should be ascribed to the low reactivity of the tolyl group in **5** due to steric hindrance of the large cage core. That is to say, the tolyl group in **5** is directly linked to the $\mathbf{T_8}$ cage, and it is difficult to obtain the complete tribromo derivative. In contrast, tolyl groups in spherosilicate are not linked to the cage directly, appearing more reactive and easy to be brominated completely. Thus, it also represents a challenge to synthesize such a compound. Therefore, we need to seek a new synthetic strategy. Just as described above, specific trichlorosilanes would help resolve this problem.

Previously, the preparation of trichloro[4-(chloromethyl)-phenyl]silane and trichloro[4-(trichloromethyl)phenyl]silane by halogenation of trichloro(*p*-tolyl)silane with Cl_2 was reported.[27,28] However, this method is problematic in industrial use, as Cl_2 is toxic and its handling is potentially hazardous. Here, we report a milder and more convenient way to halogenate trichloro(*p*-tolyl)silane with *N*-bromosuccinimide (NBS). NBS is a useful reagent for the bromination of carbons at allylic and benzylic positions. The bromination of tolyl derivatives produced (bromo-, dibromo-, and tribromomethyl)phenyl derivatives, depending on the amount of NBS used.[29,30] Presently, however, no research deals with the preparation of brominated chloro(tolyl)-silanes by reaction with NBS. We found trichloro(*p*-tolyl)-silane could be brominated by NBS to form [4-(bromomethyl)phenyl]trichlorosilane and trichloro[4-(tribromomethyl)phenyl]silane (Scheme 2). The control of the ratio of NBS to trichloro(*p*-tolyl)silane is the key factor for the selective synthesis of these brominated compounds. It should be pointed out that even the use of one equivalent or less NBS produced trichloro[4-(dibromomethyl)phenyl]-silane and **3**, along with the main product **2**. The addition of excess NBS was required to prepare **3**. However, trichloro[4-(dibromomethyl)phenyl]silane always remains in the final product, even after a prolonged reaction. By optimizing the reaction condition and separation, we obtained **2** and **3** in satisfactory yields. The isolation of trichloro[4-(dibromomethyl)phenyl]silane by the reaction of **1** with two equivalents of NBS did not work, because it is difficult to separate it from the reaction mixture.

This method is general, milder, and could be widely applied to the bromination of other chlorosilanes [for example, chlorodimethyl(tolyl)silane]. These brominated chlorosilanes will play an important role in preparing new molecules and materials.

We used the above two chlorosilanes (**2** and **3**) to react with **4**[20,31] and succeeded in obtaining the desired compounds (**6** and **8**) in high yields (Scheme 3). The resulting two compounds could be further hydrolyzed to form (monohydroxymethyl)phenyl- and monocarboxyphenyl-functionalized $\mathbf{T_8}$ (**7** and **9**). At first, we attempted to obtain **7** by hydrolysis of **6** with $AgNO_3$; however, the ^{1}H NMR spectrum showed that only a mixture of alcohol and nitrate ester was obtained. It was efficient to use $AgClO_4$ for the hydrolysis of **6** to yield **7** (Figure 1). The effectiveness of this reaction should be ascribed to the greater nucleophilicity of NO_3^- than that of ClO_4^-.[32] Target compound **9** could be easily prepared by hydrolysis of **8** in the presence of $AgNO_3$ and formic acid (Figure 2). These new $\mathbf{T_8}$ enrich the pool of silsesquioxanes. The versatility and reactivity of these three derivatives (**6**, **7**, and **9**) make them very useful precursors for the preparation of new compounds. They are also very useful in polymer preparation. For example, 4-(bromomethyl)phenyl-functionalized $\mathbf{T_8}$ **6** will act as an initiator in atom transfer radical polymerization (ATRP),[33,34] and (monohydroxymethyl)phenyl-functionalized $\mathbf{T_8}$ **7** will initiate ring opening metathesis polymerization (ROMP).[35] As for monocarboxyphenyl-functionalized $\mathbf{T_8}$ **9**, it can form hybrid polyesters or polyamides by condensation polymerization; in addition, this compound will produce other derivatives, which further react to form polymers.

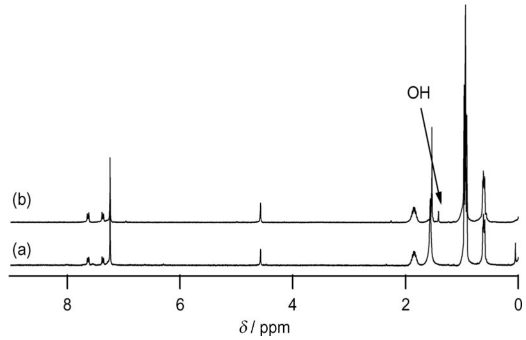


Figure 1. The ^{1}H NMR spectra of compound **6** (a) and **7** (b).

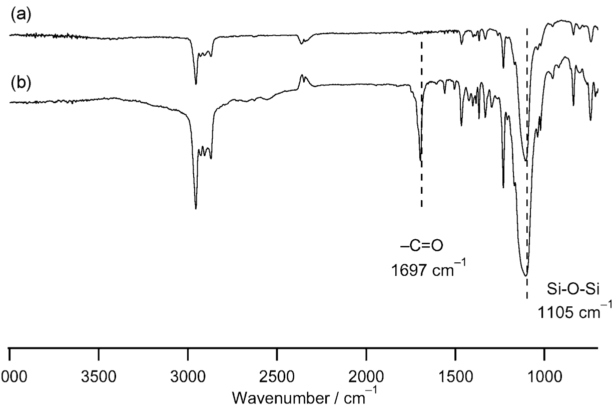


Figure 2. The FTIR spectra of compound **8** (a) and **9** (b).

Conclusions

In summary, we developed a new and practical synthesis of two organofunctional trichlorosilanes, i.e. [4-(bromomethyl)phenyl]trichlorosilane and trichloro[4-(tribromomethyl)phenyl]silane, through selective bromination of trichloro(*p*-tolyl)silane by NBS. By utilizing the above two chlorosilanes, several monophenyl-functionalized octasilsesquioxane monomers are easily accessible in high yields.

Supporting Information (see footnote on the first page of this article): Experimental details, NMR and FTIR spectra for compounds **5**–**9**.

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