A facile synthesis of octa(carboxyphenyl)silsesquioxane†

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A facile method was reported for a robust octa(carboxyphenyl) functionalized silsesquioxane (OCS), which offers excellent potential as a nanobuilding-block for the preparation of functional materials. OCS was fully characterized by FT-IR, 1H, 13C, 29Si-NMR, Maldi-TOF-MS spectra, and W-XRD analysis.

Polyhedral oligomeric silsesquioxanes (POSS) referred to as the minimum hybrid molecule have attracted intensive interest, owing to their unique molecular architecture, in the fields of OLEDs, catalysts, hybrid composites and biomaterials and continue to receive considerable attention in the preparation of new functional materials. Most of the POSS used in these researches were synthesized from the basic POSS, nearly all of which are available from Hybrid Plastics Inc., via coupling reaction, hydrosilylation reaction, click reaction, and so on. The synthesis of every new basic POSS with functional groups would also bring hundreds of their derivatives, and so many new and potentially valuable applications will emerge.

POSS with carboxyl groups, which could be further functionalized to produce their derivatives such as acid halides, esters, amides, etc., provide a versatile nanoplatform for the preparation of nanohybrid composites and POSS-core dendrimers, and could be potentially applied as a carrier for heterogeneous catalysis, as a building block for the preparation of 3-D materials and as a monomer for the synthesis of POSS-core star-like polymers. At this moment, to the best of our knowledge, there are only two published papers on POSS with carboxyphenyl groups. p-Octacarboxyphenyl spherolicate, which was first synthesized via a four-step reaction by Liu et al., has a well-defined structure, but it easily decomposes in air (T = 180 °C). After that, Wang et al. reported so-called polycarboxy-POSS first via bromination of octaphenyl silsesquioxane, and then lithiation of the polybromo-POSS under lower temperature, and final carboxylation with carbon dioxide; unfortunately, the result showed the desired product was a mixture of compounds with different contents of carboxyl groups. Hence, a new approach to robust POSS, containing carboxyl groups, with good thermal stability and well-defined structures is intensively pursued.

Here, we report a facile synthesis of octa(carboxyphenyl)silsesquioxane (OCS). OCS appears to offer excellent potential as a nanobuilding-block for preparation of materials ranging from hybrid nanocomposites, to precursors to OLEDs, to multi-armed stars, and to templates for high temperature porous materials of use in catalysis, sensing, separations, etc. Prior to the synthesis of OCS, according to the ref. 23 and 24, we have successfully prepared octaphenylsilsesquioxane (OPS) in 96% yield. On the basis of the literature, originally, we have attempted to oxidize octa(acetylylphenyl)silsesquioxane (OAS) using halogen in NaOH-H2O solution (show in Fig. 1) for OCS; unluckily, the Si–O–Si cage collapsed under alkaline condition, judged from 1H-NMR spectrum. Then, we employed more mild oxidizing condition, but the result also showed the Si–O–Si cages collapsed. After exhaust effort, we succeeded in the preparation of OCS in 85% yield via the Friedel-Crafts reaction. This route provided an alternative method for the preparation of silsesquioxane with carboxyphenyl groups, and got the desired product with a well-defined structure by more simple and convenient process than those methods mentioned above. Firstly, under magnetic stirring, 150 mL of dry CH2Cl2-CS2 (v/v = 1 : 1) mixed solvent, 5 mol of OPS and 80 mmol of anhydrous AlCl3 were added to a 250 mL, three-necked, round-bottomed flask. Secondly, A U-style drying tube filled with NaOH and CaCl2, and a 100 mL pressure-equalized addition funnel was attached to the flask. The reaction

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Fig. 1 The synthetic route for OCS.
temperature was maintained at −5 to 0 °C. Finally, 120 mmol of \((\text{COCl})_2\) was slowly added into the flask over 15 min by means of the funnel. It should be noted that the tail gas must be absorbed by NaOH–H₂O solution after passing through the drying tube. After the addition of \((\text{COCl})_2\), it easily was observed that a red complex soon formed in the drying tube, which indicated that the reaction in the flask was occurring. Subsequently, the reaction solution in the flask slowly turned brownish and transparent; after 3 h, red-brown viscous solid slowly precipitated; after 6 h, the transparent reaction solution was transferred into other flask and 40 mL of dry tetrahydrofuran was poured into the three-necked flask for dissolution of the red-brown viscous solid; and then the cold tetrahydrofuran solution was slowly added into a stirred mixture of 300 g of crushed ice and 200 g of hydrochloric acid at a rate to maintain the temperature below 5 °C. The mixture water solution was stirred in a stink cupboard at room temperature for 48 h until the acyl chloride was completely hydrolyzed. A pale pink solid was collected after removal of tetrahydrofuran by rotary evaporator and acid water solution by filtration, respectively; and then the solid (OCS) was washed with distilled water until neutral. The crude OCS was further washed three times with absolute alcohol, and then dissolved in 30 mL of tetrahydrofuran. When the tetrahydrofuran solution was precipitated drop-wise into 800 mL of hexanes, a white powder was collected by filtration and dried at 80 °C in vacuum.

OCS was characterized by \(^1\text{H}, \, ^{13}\text{C}, \, ^{29}\text{Si}-\text{NMR}, \, \text{FT-IR and Maldi-TOF-MS} \) spectra and W-XRD (see ESI†). In the FT-IR spectrum, absorption peaks at 3200–2800 cm⁻¹ and 1695 cm⁻¹ were assigned to the hydroxyl group and carbonyl group of carboxylic acid, respectively; in the \(^{13}\text{C}\) NMR spectrum, peaks located at 167.2 ppm and 140–125 ppm were identified characteristic peak of the carbon atom of the carboxylic acid group and the aryl group, respectively. This indicated that the sample contained carboxylic acid groups. In the W-XRD pattern, the peaks located at 8.12, 12.08, 13.78, 19.10, 21.86 and 24.38, respectively, indicated OCS was crystalline but the melt point was not detected before 300 °C by differential scanning calorimetry. In the \(^1\text{H}\) NMR spectrum, three single peaks located at 7.5, 8.0 and 8.3 ppm were assigned to aryl-H (the detailed assignment is shown in ESI†), and the peak at about 13 ppm was assigned to the H of aromatic carboxylic acids. The area ratio (aryl-H–COOH) was 4 : 0.9, which matched well with the theoretical value (4 : 1). Consequently, it was inferred that the meta-H of the benzene ring was substituted by a carboxyl group. In the \(^{29}\text{Si}-\text{NMR}\) spectrum, the singlet peak at −78.56 ppm means that all Si atoms had the same chemical environment. As shown in Fig. 2, the mass spectrum provided further evidence that the target compound had a well-defined structure. The two peaks located at 1408.8 and 1424.8 Da were assigned to the result of OCS calculated molecular mass plus Na⁺ and K⁺, respectively, which were probably from either the matrix or the solvent. It was concluded that OCS was octa-(meta-carboxoxyphenyl)silsesquioxane and its cage-like core did not collapse.

From the article,\(^ {17}\) it was easily concluded that what caused a mixture of target polycarboxy-POSS was mainly due to lack of control of the bromination and the carboxylation. In this method, the carbonium ion formed between AlCl₃ and \((\text{COCl})_2\) attacked the benzene ring and replaced one of aryl-H by the electrophilic substitution reaction, and so the benzene ring could not be further substituted by the carbonium ion because of electron-withdrawing characteristics of the substituational.\(^ {31,32}\) This determined that only one of aryl-H in the benzene ring could be substituted. In this manner, all of the benzene ring could be substituted under enough oxalyl chloride. These two aspects contributed to the well-defined carboxylation. It was worth noting that the cage core of OCS collapsed after neutralization using NaOH–H₂O solution, which was ascribed to the break of the Si–O–Si bond under basic conditions.\(^ {33}\)

OCS easily dissolved in 1,4-dioxane, THF, Py, DMSO and DMF, and hardly dissolved in EtOH, AcOEt, CHCl₃ and hexane. In DMSO solution, OCS intensively absorbed wave lengths located at 274 nm (see ESI†), which was higher by 2 nm than benzoic acid, probably due to the 3-D conjugation through the silsesquioxane cores.\(^ {34}\) The thermo-gravimetric analysis of OCS in nitrogen (see ESI†) displayed that it had good thermal stability. The initial thermal decomposition temperature \(T_d\) was defined as the temperature at which 3% mass loss occurred. It is worth noting that OCS exhibits higher \(T_d\) (321 °C) than the compound \((T_d = 180 °C)\) in ref. 22. The initial decomposition of OCS was probably ascribed to decarboxylic reaction by thermal initiation; after about 700 °C, the rate of mass loss suddenly decreased and the char yield (58%) was much higher than the theoretical values (30%). This could be explained by, after the decarboxylic reaction, the degradation products (Si–O–Si fragment) trapping some of the aryl carbons and forming a hybrid material like ceramic; this hybrid then had a higher thermal stability and so needed a higher temperature to further decompose.\(^ {35}\)

In conclusion, a novel, robust octa(carboxyphenyl)silsesquioxane was synthesized by a facile method. The good reactivity of the carboxylic acid groups makes it an attractive synthetic platform for the preparation of star-like polymer, hybrid polymers, and supramolecular materials, etc. Undoubtedly, OCS will serve as an important nanobuilding-block for multiple avenues of research.

![Fig. 2](image) The Maldi-TOF-MS spectrum of OCS, the insert picture was the partial magnification between 1320 and 1560 Da.
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Notes and references