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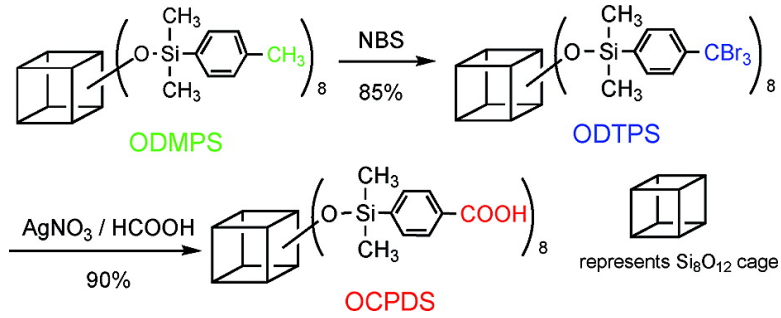

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Synthesis of Octacarboxy Spherosilicate

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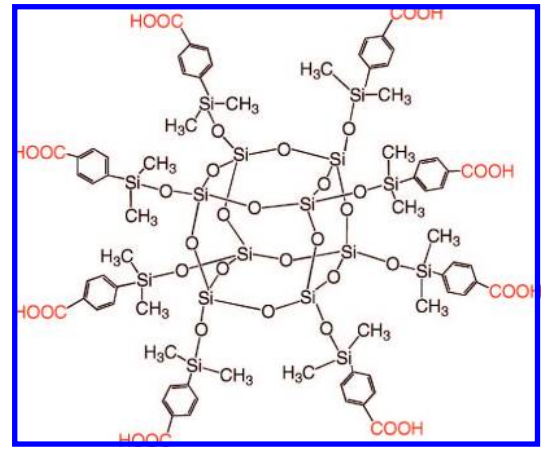
Functionalized cage siloxanes play key intermediate roles in the building of inorganic−organic hybrid molecular composites.[1] Among them, octacarboxy functionalized cages are one of the most promising compounds because of their potential use in supramolecular chemistry and crystal engineering, which is currently being pursued.[2] Cage siloxanes, consisting of polyhedral oligomeric silsesquioxanes (POSS) or spherosilicates, denote inorganic−organic hybrid molecules containing cage-like Si_8O_{12} cores and substituents attached to each vertex of the core.[3−6] They have been widely used as excellent platforms for synthesis of new hybrid materials,[7−10] as homogeneous models for silica supports,[11−13] as supports for organometallic catalysts,[14−16] and even as anion receptors.[17,18] With the discovery of new cages, many new and potentially valuable applications will emerge.

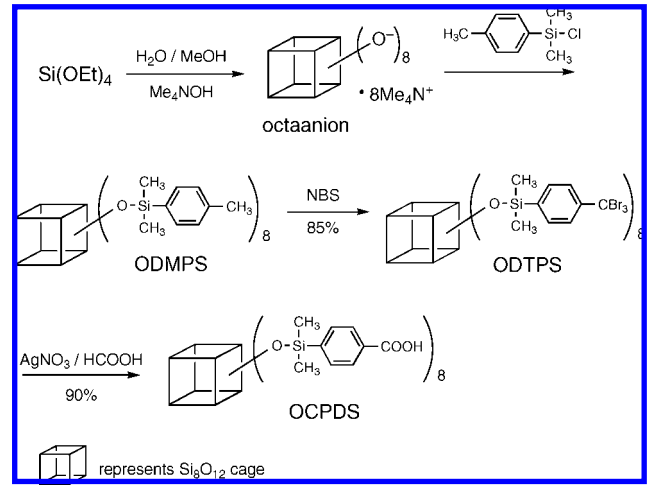
A few octafunctionalized cage siloxanes bearing functional groups such as methacrylates,[19] epoxies,[20] alcohols,[21] and isocyanate[22] can be prepared by hydrosilylation using $(HSiO_{1.5})_8$ or $(HMe_2SiOSiO_{1.5})_8$ as nanoplatforms. In further efforts to improve the versatility of cages, nonhydrosilylation-based techniques to prepare new octafunctionalized cages have been developed.[23−26] To date, however, an octacarboxy functionalized cage has not been reported, which could offer greater versatility through further functionalization to produce other derivatives, for example, acid halides, esters, amides, etc. Morris et al. prepared an octaaldehyde-functionalized POSS by hydrosilylation and tried to obtain the octacarboxyphenyl functionalized POSS by oxidation; unfortunately, they could not separate the target compound from the reaction mixture.[2] Recently, Chujo et al. synthesized a dendrimer with 16 aliphatic carboxy groups using a POSS core.[27]

We report here a simple route to an octacarboxyphenyl functionalized cage, octakis[(*p*-carboxyphenyl)dimethylsilyl]silicate (OCPDS, Scheme 1). Before the synthesis of OCPDS, we successfully prepared another new spherosilicate monomer − octakis[dimethyl(*p*-methylphenyl)silyl]silicate (ODMPS), the structure of which was confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR and FT-IR spectra and elemental analysis (see Supporting Information). It was expected that ODMPS could be further functionalized to produce new spherosilicates. Initially, we attempted to oxidize ODMPS using $KMnO_4$ in a pyridine/water mixture; however, the peripheral arms of ODMPS were cleaved from the cage core and combined together to form 1,3-bis(*p*-carboxyphenyl)-1,1,3,3-tetramethyldisiloxane.[28,29] Therefore, we sought a milder way to synthesize OCPDS without breaking the spherosilicate cage structure. After many trials, we succeeded in synthesizing OCPDS.[30] First, ODMPS was brominated by NBS to produce octakis[dimethyl(4-tribromomethylphenyl)silyl]silicate (ODTPS) in 85% yield. Then, ODTPS was hydrolyzed

Scheme 1



Scheme 2. The Synthetic Route to OCPDS



in the presence of $AgNO_3$ and formic acid to give OCPDS in 90% yield (Scheme 2).

The formation of ODTPS was confirmed by the ^{1}H, ^{13}C, ^{29}Si NMR and FT-IR spectra (see Supporting Information). The ^{1}H NMR spectrum showed the disappearance of the singlet of aryl-CH_3 groups of ODMPS at $\delta = 2.3$ ppm and the appearance of aryl peaks of ODTPS at $\delta = 7.57$ and 7.91 ppm, respectively. In the ^{13}C NMR spectrum, the CBr_3 peak was observed at $\delta = 36.3$ ppm. The ^{29}Si NMR spectrum displayed two singlets at 6.9 and −104.6 ppm, assigned to the M- and Q-type silicons of the spherosilicate, respectively. The presence of only two singlets in the ^{29}Si NMR spectrum demonstrates that bromination proceeds without decomposition of the spherosilicate cage. The carboxyphenyl derivative OCPDS was fully characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and

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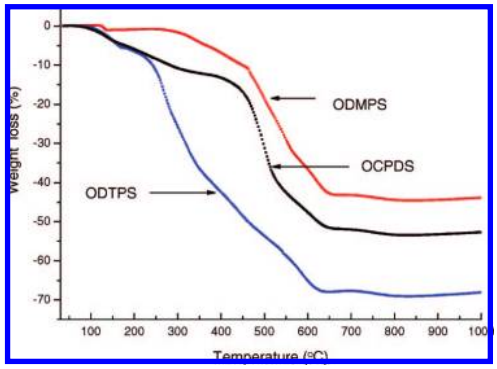

Figure 1. TGA curves of the three spherosilicates.

FT-IR spectra, ESI-MS, and elemental analysis (see Supporting Information). In the ^{13}C NMR spectrum, the characteristic C═O signal was observed at 167.2 ppm. The ^{29}Si NMR analysis also showed two peaks at 3.4 and −108.7 ppm, corresponding to the M- and Q-type silicons of the spherosilicate, respectively. This result implies that the spherosilicate cage structure remains intact during the hydrolysis of ODTPS. In the FT-IR spectrum, the characteristic absorption peaks appeared at 2300−3300 (O−H stretching), 1697 (C═O stretching), and 1100 (−Si−O−Si− stretching) cm^{-1}. The result of ESI-MS provides further evidence that the target compound was formed (m/z = 988.1, corresponding to $[M - 2H]^{2-}$; 898.8, corresponding to $[M - 2H - R]^{2-}$; 809.4, corresponding to $[M - 2H - 2R]^{2-}$; 719.8, corresponding to $[M - 2H - 3R]^{2-}$, respectively; R = $SiMe_2C_6H_4COOH$). More importantly, C, H analyses agree with the calculated values.

Figure 1 shows the thermogravimetric analysis of the three spherosilicates in air (10 °C/min). The three spherosilicates display different mass loss curves, ascribed to different decomposition mechanisms. Two mass losses are observed. The first mass loss is attributed to cleavage of the peripheral arms; whereas, the second mass loss can be due to decomposition of the Si−O−Si structure of the cage.[22] The initial thermal decomposition temperature (T_d) is defined as the temperature at which 5% mass loss occurs. It is worth noting that OCPDS exhibits lower T_d (180 °C) than ODMPS (370 °C), which may be ascribed to easier decomposition of the carboxyphenyl groups than the tolyl groups. As for ODTPS (T_d = 164 °C), the increased mass loss rate should be explained by quick removal of the tribromomethylphenyl groups under heating conditions. The TGA ceramic yields for the three spherosilicates agree with the theoretical values, respectively (see Supporting Information).

In conclusion, we have synthesized a novel octacarboxyphenyl functionalized spherosilicate monomer—OCPDS. The reactivity of the carboxyphenyl groups makes it an attractive synthetic platform for derivatives of spherosilicate molecules, new monomers and new dendrimers, metal−organic framework (MOF) type of materials, hybrid polymers, and supramolecular materials, etc. Undoubtedly, OCPDS will play an important role in providing an important starting point for multiple avenues of research. The authors believe that much research will be performed arising from OCPDS.

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Supporting Information Available: Details of experimental procedure, spectra of all compounds, and data for crystallographic analysis for 1,3-bis(*p*-carboxyphenyl)-1,1,3,3-tetramethyldisiloxane (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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