Sol-Gel Processing of Polyhedral Oligomeric Silsesquioxanes – Nanohybrid Materials Incorporating T₈ and T₁₀ cages

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Abstract

Polyhedral oligomeric silsesquioxanes (POSS, T₈ and T₁₀) have been incorporated in hybrid silica materials via hydrolysis-condensation of octa- and deca(triethoxysilylated)-POSS precursors, respectively. The precursors were synthesized via a thiol-ene Click reaction involving the corresponding octastyryl-T₈ or decastyryl-T₁₀ molecules and thiopropyltriethoxysilane. Following addition of water and HCl (as catalyst) to a solution of the precursors, gels were formed within a few minutes. The resulting hybrids were characterized by TEM, FTIR, N₂ physisorption analyses, solid state NMR (²⁹Si and ¹³C) and TGA, which indicated that the T₈ and T₁₀ cages were incorporated and remained intact within the hybrid gel network, with no Si-C cleavage being observed via ²⁹Si NMR. FTIR data indicated that water retained within the gels following drying and aging at ambient temperature exhibited an unusual “connective”, ice-like structure, suggesting that it is initially retained as a key component of the gel network during consolidation and aging at ambient temperature. Following aging, the water was readily removed by evacuation at 100 °C without significantly modifying the network structure, on the basis of the FTIR spectrum of the gel. To the best of our knowledge, this is the first report of the incorporation of T₁₀ cages in such gels.

1. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) are an interesting and widely-studied family of molecular hybrid compounds, which have commanded significant interest within the materials chemistry community since first being identified in the 1940s and 1950s [1,2]. These compounds, which feature a well-defined polyhedral cage ((SiO_{1.5})_n, T_n) covalently bonded to functional organic moieties, can be readily incorporated into nanostructured materials via reactions on the organic group such as polymerization [3-6]. The functionalized cage silsesquioxanes ((R-SiO_{1.5})_n, where n=8, 10, 12, etc), have been of particular interest [7,8], with n=8 being the most widely studied. In addition to porous materials [3,9] in which the porosity can either arise from the voids between the cages or cage's central void (0.3 nm) [3], self-organized systems [10-13], POSS micelles and templated POSS systems leading to mesoporous materials with T₈ cages embedded with the walls [14], and organic polymer-based nanohybrids [15-20] can be obtained by modulating the properties of the functional organic moieties.

Application domains that have been explored for these systems include bio/nanomedicine [21-26], catalysis [27-30], optoelectronics [31], polymer chemistry [15,16,32], optical and sensing applications [16,33-35], etc.

We recently reported the synthesis and characterization of a new family of styryl-functionalized T_n ($n=8, 10$ or 12) compounds, in which a styryl group was linked to all n vertices of the cages via the phenylene group rather than the vinyl group [36]. Such cage silsesquioxanes, with organic moieties that can be further modified via reactions such as hydrosilylation, Heck coupling, thiol-ene Click reactions, metathesis, etc. These are of particular interest, since they do not modify the structure of the T_n cage, thus expanding the range of potential applications described above. A feature of the styryl-functionalized family of compounds is the availability of larger cages than those previously investigated for post-functionalization and incorporation into materials, since the majority of earlier work has focused on the use of T_8 cages.

In this paper, we describe the successful modification of styryl-functionalized T_8 and T_{10} molecules via a thiol-ene Click reaction to graft a propyl triethoxysilyl moiety onto all n vertices of the cages. The modified precursors are then transformed into gels via sol-gel processing, to yield organic-inorganic hybrid material in which the T_8 and T_{10} cages remain intact and covalently linked to the hybrid silica network. There have been only limited prior reports of sol-gel materials incorporating T_8 cages [14,37-41], and to the best of our knowledge, this is the first report of such materials incorporating T_{10} cages. The possibility of extending such processing to include larger cages is also addressed.

2. Experimental

2.1 Chemicals and purification methods

Styryl functionalized cages were synthesized following the procedure previously described by our group. Mercaptopropyltriethoxysilane (MPTEOS) was purchased from Fluorochem and was distilled prior to use. Hydrochloric acid (35 %) and water (HPLC grade) were obtained from VWR. Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich and was recrystallized. All solvents were dried prior to use.

2.2 Synthesis of triethoxysilylated functionalized T_8 from styryl-functionalized precursors

The synthesis of styryl-functionalized T_8 has been previously described [36] and full details are provided in the Supplementary Information. In a flame dried Schlenk flask equipped with a Teflon rotaflo® tap, styryl-functionalized T_8 (84 mg, 68 μ mol, 1 eq) and AIBN (6.3 mg, 38 μ mol, 7 mol% per styryl function) were dissolved in toluene (0.7 mL) under an inert atmosphere. The mixture was heated to 40 °C. MPTEOS (131 μ L, 542 μ mol, 8 eq) was then added dropwise and the temperature was increased to 60 °C. The mixture was stirred at 60 °C overnight and the solvent was then evaporated. The excess of solvent was finally evaporated to yield a yellowish oil.

Triethoxysilylated functionalized T_8 : Yellowish oil. ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 7.66 (d, CH_{ar} , 16H, $J=7.7$), 7.19 (d, CH_{ar} , 16H, $J=7.7$ Hz), 3.80 (q, Si-O- CH_2 - CH_3 , 48H, $J=7.0$ Hz), 2.87 (m, Ph- CH_2 - CH_2 -S, 16H), 2.73 (m, Ph- CH_2 - CH_2 -S, 16H), 2.58 (m, S- CH_2 - CH_2 - CH_2 -Si) 1.74 (quint, S- CH_2 - CH_2 - CH_2 -Si, 16H, $J=7.4$ Hz), 1.22 (q, Si-O- CH_2 - CH_3 , 72H, $J=$

7.0 Hz) 0.74 (m, Si-O-CH₂-CH₃, 16H). **²⁹Si NMR** (80 MHz, CDCl₃, δ, ppm): -45.80 (Si(OEt)₃), -78.22 (cage).

2.3 Synthesis of triethoxysilylated functionalized T₁₀ from styryl-functionalized precursors

The synthesis of styryl-functionalized T₁₀ has been previously described [36] and full details are provided in the Supplementary Information. In a flame dried Schlenk flask equipped with a Teflon rotaflo® tap, styryl-functionalized T₁₀ (230 mg, 148 μmol, 1 eq) and AIBN (12.2 mg, 74 μmol, 5 mol% per styryl function) were dissolved in toluene (1.2 mL) under an inert atmosphere. The mixture was heated to 40 °C. MPTEOS (355 μL, 1.48 mmol, 10 eq) was then added dropwise and the temperature was increased to 60 °C. The mixture was stirred at 60 °C overnight and the solvent was then evaporated. The excess of solvent was finally evaporated to yield a colorless oil.

Triethoxysilylated functionalized T₁₀: Colorless oil). **¹H NMR** (400 MHz, CDCl₃, δ, ppm): 7.52 (d, CH_{ar}, 20H, J=7.7), 7.10 (d, CH_{ar}, 20H, J=7.7 Hz), 3.84 (q, Si-O-CH₂-CH₃, 60H, J=7.0 Hz), 2.84 (m, Ph-CH₂-CH₂-S, 20H), 2.73 (m, Ph-CH₂-CH₂-S, 20H), 2.58 (m, S-CH₂-CH₂-CH₂-Si) 1.74 (quint, S-CH₂-CH₂-CH₂-Si, 20H, J= 7.4 Hz), 1.25 q, Si-O-CH₂-CH₃, 90H, J= 7.0 Hz), 0.75 (m, Si-O-CH₂-CH₃, 20H). **²⁹Si NMR** (80 MHz, CDCl₃, δ, ppm): -45.80 (Si(OEt)₃), -79.56 (cage).

2.4 Synthesis of T₈ or T₁₀ gels

Equivalent approaches were used to prepare both the T₈ and T₁₀ gels, and hence only the detailed approach used for the T₈ gel synthesis will be given here. In a flame dried Schlenk flask, a solution of the triethoxysilylated T₈ precursor in chloroform (203 mg, 64.4 μmol) was evaporated and then dissolved in dry THF (0.4 mL). Water (18 μL, 1.0 mmol, 2 eq per -Si(OEt)₃) and HCl (0.5 μL, 5.7 μmol, 1.1x10⁻² eq per -Si(OEt)₃) were then successively added under stirring. After 3 min, the agitation was ceased due to the increasing viscosity of the mixture, which gelled in ~ 10 min. After three days of aging, the transparent solid was crushed and washed three times with water and then acetone. The product was dried overnight under vacuum and recovered as a yellowish powder, while the corresponding T₁₀ gel was recovered as a white powder.

T₈ Gel (yellowish powder): **¹³C NMR** (75 MHz, CP-MAS, δ, ppm): 142.3 (C_{ar}), 134.3 (CH_{ar}), 127.5 (CH_{ar}), 57.8 (residual ethoxy), 34.3, 30.7, 29.9, 27.8, 24.4, 18.4 (residual ethoxy), 12.2. **²⁹Si NMR** (60 MHz, CP-MAS, δ, ppm): -48.9 (T¹), -57.1 (T²), -66.0 (T³), -77.0 (T₈ cage). **IR**(ν, cm⁻¹): 1606 (C-C ring), 1048 (Si-O-Si).

T₁₀ Gel (white powder): **¹³C NMR** (75 MHz, CP-MAS, δ, ppm): 143.9 (C_{ar}), 134.4 (CH_{ar}), 128.4 (CH_{ar}), 58.6 (residual ethoxy), 34.7, 30.8, 28.0, 24.2, 18.7 (residual ethoxy), 12.7. **²⁹Si NMR** (60MHz, CP-MAS, δ, ppm): -49.4 (T¹), -57.9 (T²), -67.0 (T³), -78.6 (T₁₀ cage). **IR**(ν, cm⁻¹): 1606 (C-C ring), 1081 (Si-O-Si).

2.5 Characterization methods

FTIR spectra were recorded from 650 to 4000 cm⁻¹ using a PerkinElmer Spectrum 100 equipped with a Gladia-ATR accessory.

Thermogravimetric analyses (TGA) were carried out between 25 and 800 °C, on a TA Instruments Q50 apparatus, with a heating rate of 10 °C.min⁻¹ under an air flow of 60 mL.min⁻¹. A Micromeritics ASAP 2020 instrument was used for the determination of nitrogen physisorption isotherms at 77.35 K. The sample were activated at 100 °C for 3 days under secondary vacuum prior to analysis. Transmission electron microscopy (TEM) images were recorded on a JEOL 1400 + microscope operating at 120 kV with a LaB₆ source. Samples were prepared by deposition on Lacey/Carbon 300 Mesh TEM grids (LC325-Cu-25).

²⁹Si and ¹³C solid-state NMR spectra were performed using magic-angle spinning techniques (MAS) or cross-polarization and magic-angle spinning techniques (CP-MAS) on a Varian VNMR 300 MHz spectrometer. Liquid ¹H, ¹³C and ²⁹Si NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in CDCl₃ at room temperature and at concentrations of around 10 mg/mL. ¹³C and ²⁹Si NMR spectra were proton decoupled and all chemical shifts (δ) were calibrated against the signal of tetramethylsilane as internal standard.

3. Results and Discussion

As indicated above, the materials chemistry literature now features a rich diversity of work describing various approaches for covalently incorporating functionalized T_n cages (particularly T₈) in a variety of polymeric materials, with many such systems and corresponding applications summarized in a recent review [16]. However, the covalent functionalization of such cages with hydrolysable silylated moieties, and the direct formation of hybrid organic-inorganic materials incorporating POSS cages via sol-gel processing (as demonstrated in the current work) is much less common. For example, Li's group reported the partial functionalization of the vinyl T₈ POSS with triethoxysilane prior to hydrolysis-condensation in presence of surfactant to obtain a porous gel [42]. Similarly, Seino et al. described the synthesis of a T₈ precursor in which all eight vertices of the cage were linked to a hydrolysable Si(OEt)₃ moiety via an ethylene linker [14], which was used to prepare a low-*k* material in which the POSS cages were embedded in the walls of a PMO. The preparation of a maleimide-T₈-SiO₂/TiO₂ nanohybrid was also reported. In this case, the silicate network was covalently linked to the T₈ cage via all eight vertices of the cage [37], and the resulting material exhibited antimicrobial activity against selected pathogens. Liu et al. described the preparation of T₈-based hybrid materials, in which T₈ cages were covalently linked by a corner into a hybrid silica network, as high-performance materials for electrochromatography [39,40], although the functionalized T₈ cages were post-grafted onto a pre-formed column. Gunji et al. prepared T₈/polysiloxane copolymers, in which T₈ cages were linked via all eight vertices with siloxane linker of varying lengths to produce both films and bulk gels [41], although no hydrolysable -Si(OR)_n sites were incorporated within the copolymers for post sol-gel processing. The production of an aerogel in which vinyl-functionalized T₈ cages were functionalized with thiopropyltriethoxy ligands and subsequently converted into aerogels via sol-gel processing was also reported, although neither the complete functionalization of all eight vertices nor the incorporation of intact cages was demonstrated [43]. However, to the best of our knowledge, no earlier studies have reported the covalent incorporation of a T₁₀ cage silsesquioxane into a material via sol-gel processing.

In the present study, the styryl-functionalized T₈ and T₁₀ precursors reported in our earlier study [36] have been post-functionalized via a thiol-ene Click reaction to incorporate a triethoxysilylated moiety onto each of the n vertices on the T_n cages, prior to their conversion into a gel via sol-gel processing.

3.1 Functionalization of octastyryl-T₈ and decastyryl-T₁₀

The thiol-ene Click reaction used in this work to post-modify the vinyl groups on styryl-functionalized T₈ and T₁₀ with a propyltriethoxysilylated moiety has previously been employed to post-functionalize POSS compounds bearing substituents with C=C bonds [29,44,45], and the approach taken here is illustrated in **Fig. 1**. Briefly, the styryl-functionalized cages were subjected to a thiol-ene Click reaction in dry toluene, using AIBN as the radical initiator in the presence of MPTEOS. A comparison of the ¹H solution NMR spectra of the styryl-functionalized T₈ (reported and fully assigned in an earlier study [36]) and the propyltriethoxysilylated product is shown in **Fig. S1**. The spectra demonstrate the loss of signals arising from the vinylic protons at around 6.7 ppm, together with the emergence of new signals at 2.87 and 2.73 ppm associated with the -S-CH₂-CH₂- moiety, indicating completion of the thiol-ene Click reaction and functionalization of all eight styryl groups. Signals arising from the propylene moiety are observed at 2.58, 1.74 and 0.74 ppm, together with those of the ethoxy groups at 3.80 and 1.22 ppm. It should be noted that a singlet observed at 1.74 ppm, which overlaps the signals associated with the propyl group, arises from AIBN. A slight broadening of the signals is also observed, due presumably to the presence of minor quantities of homopolymerized products. A signal at 1.33 ppm is attributed to -SH species arising from an excess of thiopropyltriethoxysilane resulting from the homopolymerization. The corresponding ¹H solution NMR spectra of the T₁₀ system also demonstrate completion of the thiolene Click reaction on all 10 styryl groups, together with minor quantities of homopolymerization products. The ²⁹Si solution NMR spectra of the products (**Fig. S2**) also exhibit the expected resonances, with sharp signals observed at -78.27 and -79.56 ppm arising from intact T₈ and T₁₀ cages, respectively, in the products [36]. Both products also exhibit a signal at -45.6 ppm arising from the triethoxysilyl groups.

It would be anticipated that the desired thiol-ene Click reaction would compete with homopolymerization of the styryl-functionalized T₈ and T₁₀ precursors in the presence of a radical initiator such as AIBN, and such direct homopolymerization reactions have also been investigated in the current work. In direct homopolymerization experiments (i.e. with no MPTEOS present), the styryl-functionalized T₈ and T₁₀ precursors yielded solid products within two hours in the presence of AIBN. In contrast, under the same conditions, but in presence of MPTEOS, oils are obtained. This indicates that the Click reaction is favored over homopolymerization. However, as indicated above, the presence of some homopolymer products is evident from the excess of unreacted -SH species identified in the ¹H solution NMR spectra, and it was estimated that around 15 to 20 % of homopolymer is present in the products.

3.2 Formation of gels incorporating intact T₈ and T₁₀ silsesquioxane cages

We next investigated the acid-catalyzed conversion of the triethoxysilylated T₈ and T₁₀ precursors described above into hybrid silica-based networks via sol-gel processing, as illustrated in **Fig. 1**.

Fig. 1 Synthesis of triethoxysilylated (a) T₈ and (b) T₁₀ cages via thiol-ene Click reaction and production of hybrid silica gels. Note that all *n* vertices of the cages were functionalized (for clarity, the functional group is shown on only one vertex of the cages)

Following addition of water and the aqueous HCl catalyst solution to the silane solutions, transparent gels formed within 5 minutes, as shown in **Fig. 2**.

Fig. 2 Products obtained via sol-gel processing of (a) T₈ and (b) T₁₀ triethoxysilylated precursors. The images were recorded around 15 min after addition of the aqueous catalyst solution to the silane precursors

Notably, the T₈ gel was yellow in color, while the T₁₀ material was colorless. The corresponding TEM images obtained from finely-ground gel samples, **Fig. 3**, both exhibited a mixture of irregular fragments and spherical particles with diameters of around 150 nm. No porosity was evident by TEM, which was confirmed by N₂ physisorption measurements (following sample outgassing at 100 °C) that indicated low surface area and porosity in both materials.

Fig. 3 TEM images of T₈ (A, B) and T₁₀ gels (C, D), illustrating the formation of irregular gel fragments and nanoparticles (size bar, 100 nm)

The ²⁹Si solid state NMR spectra of the gels are shown in **Fig. 4**. A key goal of this work was to prepare sol-gel-derived materials in which the T_n cages were retained intact within the hybrid gel networks, and this is evident from the retention of the characteristic T³ resonances at -77.0 and -78.6 ppm for the T₈ and T₁₀ silsesquioxane cages, respectively. These appear at similar chemical shifts to the signals of the corresponding precursors in the solution NMR spectra at -78.27 and -79.56 ppm (see above). The upfield shift in the position of the T₁₀ resonance compared to that of the T₈ sample is consistent with the different ring strains in the cages, with the 4³ silicon environment in the T₈ cage being more strained than the 5¹4² environment in the T₁₀ cages [46]. The signal of the T₈ cage in the hybrid gel is sharper than that of the corresponding T₁₀ resonance, suggesting that minor degradation of the T₁₀ cages may have occurred. An additional broad signal is also evident as a shoulder on the downfield side of the main T₈ and T₁₀ resonances at -76.3 and -74.7 ppm, respectively. These additional signals are most likely due to small quantities of homopolymerization products. No Qⁿ resonances are evident, indicating that the T³ speciation of all silicon sites is preserved.

In addition to the signals arising from the T_n cages, the ²⁹Si NMR spectra also exhibit the expected T¹, T² and T³ resonances arising from the aliphatic R-SiO_{1.5} gel network at -49, -57 to -58 and -66 to -67 ppm, respectively. The relative intensities of the T¹ and T² signals in both materials, which are significantly stronger than the corresponding aliphatic T³ signals, indicate that the gel networks are not fully condensed (as expected for catalysis under acidic conditions), with condensation being more complete in the T₈ system. An additional signal is observed downfield of the main aliphatic T² signal of the T₁₀ gel at -54.8 ppm, which also presumably

arises from aliphatic T² species. Although not as clearly evident in the corresponding T₈ gel, the shape and breadth of the signal centered at -57.1 ppm in that case is consistent with the presence of more than one T² signal in the T₈ gel network. These additional aliphatic T² signals are attributed to either (a) a secondary gel network arising from hydrolysis of the residual MPTEOS due to homopolymerization; or (b) secondary T₈/T₁₀ gel networks incorporating partially cleaved cages. The transparent nature of the gel samples (**Fig. 2**) suggests that the secondary gel networks are well integrated with the primary networks, with any segregation being smaller than 1/10th of the wavelength of visible light (i.e. < 35 nm).

Fig. 4 ²⁹Si solid state NMR spectra of T₈ (blue line) and T₁₀ gels (orange line)

The FTIR spectra of the T₈ and T₁₀ gels are compared in **Fig. 5** from 600 to 4000 cm⁻¹. The spectra were normalized against the intensity of the phenyl ring stretching band at 1606 cm⁻¹, since this moiety is retained within the structure and not transformed during the sol-gel process. The broad profile observed in the spectra of both gels from 3100 to 3700 cm⁻¹ (**Fig. 5**) is attributed to ν_{O-H} modes of water and silanol species. The corresponding H-O-H deformation mode for water in sol-gel silica and in zeolite cages is typically observed at 1630 to 1650 cm⁻¹ [47-51], comparable to that observed for bulk water. In contrast, this mode is observed at ~1700 cm⁻¹ for both the T₈ and T₁₀ gels, indicating that the speciation of the water in the latter gels is significantly different to that normally observed in sol-gel silicas. Falk reported a comprehensive investigation of the positions of the stretching and bending modes of water in a variety of systems, and demonstrated that increasing H-bond strength in water led to a decrease in the wavenumber of the stretching mode and an increase in that of the bending mode [52]. Subsequent computational and experimental studies reached similar conclusions [53]. Crupi et al. assigned a peak observed at 1678 cm⁻¹ in zeolite NaA to “connective”, ice-like water within the zeolite cage, with properties significantly different to those of bulk water [54]. On the basis of these assignments, the mode observed at ~1700 cm⁻¹ in the present study is attributed to “structural” water that is strongly H-bonded to the gel network, analogous to the “connective” water identified by Crupi et al [54]. This suggests that the water is initially retained as a key component of the gel network during consolidation and aging at ambient temperature.

Fig. 5 ATR-FTIR spectra of the T₈ (blue) and T₁₀ gels (orange) (absorbances corrected for ATR refractive index effects). Note that the region from 2000 to 2500 cm⁻¹ (not shown) is impacted by the absorbance of the ATR crystal and is not shown here. The inset shows the region from 1200 to 1800 cm⁻¹ for the T₈ gel

As indicated above, outgassing of the T₈ and T₁₀ gel samples at 100 °C under vacuum yielded a material with low surface area and porosity. The infrared spectra of the gel samples recovered after outgassing, compared to that of the as-prepared gel in **Fig. 6**, indicated that the “structural” water was removed by outgassing with the associated loss of the band at ~1702 cm⁻¹ in both systems (note that only the T₈ system is illustrated in **Fig. 6**). The structure of the organosilica framework remains essentially intact after outgassing, as indicated by the similar shapes of the peaks associated with the Si-O-Si network at 900 to 1200 cm⁻¹. The broad profile above 3200 cm⁻¹ is retained, although with shifts in the band maxima, consistent with the retention of silanol species in the outgassed gels and a modified H-bonding network following removal of the water.

Fig. 6 ATR-FTIR spectra of the as-prepared (blue) and outgassed (100 °C) T₈ gel (red, dashed). Note that the region from 2000 to 2500 cm⁻¹ is impacted by the absorbance of the ATR crystal and is not shown here. Inset: Expanded view of the region from 1300 to 1800 cm⁻¹

Thermogravimetric analyses of the gel samples, **Fig. 7**, revealed several well-defined weight loss events during heating of the gels to 800 °C in air. The samples exhibit almost identical TGA and dTGA profiles up to 400 °C, although they diverge at higher temperatures. The weight losses at temperatures below 200 °C (3.2 and 3.4 % for the T₈ and T₁₀ gels, respectively) are assigned to loss of the “structural” water identified by FTIR spectroscopy. Subsequent weight loss up to 400 °C gives rise to a well-defined peak in the dTGA data at around 345 °C, and the associated weight loss is attributed to partial decomposition of the organic species in the gel. A second major weight loss event, which commences at around 550 °C and is complete by 700 °C, is typically observed for simple organo-functionalized POSS compounds [55-57] and is associated with the combustion of organic species, although additional contributions from the loss of silanol species are also expected in our system. The data indicate that the weight loss from 400 to 700 °C is greater for the T₁₀ sample than the T₈ gel, consistent with the ²⁹Si solid state NMR data that indicated a lower degree of condensation in the former case. This presumably arises from the geometrical constraints imposed by the T₁₀ cages, which each immobilize one end of 10 aliphatic chains to a single fixed point within the gel matrix, thus limiting the mobility of the hydrolysable/condensable triethoxysilyl moieties. In contrast, fewer chains (i.e. eight) are anchored to each cage in the T₈ system, leading to a relative increase in the mobility of the aliphatic chains and to a corresponding increase in the ability of the system to interpenetrate and form T² and T³ species. Hence, the impact of cage size on the extent of condensation within the gel provides a means for modulating the abundance of free, unreacted hydroxyl species within the gel matrices.

Fig. 7 TGA (solid lines) and dTGA (dashed lines) of T₈ (blue) and T₁₀ gels (orange)

Finally, as indicated above we note that, to the best of our knowledge, this is the first report of a material successfully incorporating a relatively large T₁₀ cage within the gel matrix, where all 10 vertices of the cage are covalently linked to the gel network. We also attempted to incorporate the styryl-functionalized T₁₂ cage that we reported [36] into a gel via sol-gel processing, following the same procedure as that outlined above for the styryl-functionalized T₈ and T₁₀ precursors. However, in the case of the T₁₂ compound, the competition between the thiol-ene Click reaction and homopolymerization favored the latter reaction, thus hindering the formation of the triethoxysilylated product in the T₁₂ system. It is not immediately obvious why styryl groups in the T₁₂ system should be more susceptible to homopolymerization than those

in the corresponding T₈ and T₁₀ systems, although it is evident that there are more vinyl bonds available for polymerization on the periphery of the T₁₂ compound compared to the T₈ and T₁₀. The sizes of the T₈, T₁₀ and T₁₂ styryl-functionalized molecules are similar, with equivalent spherical diameters varying from 19 to 21 Å, and hence, the projected surface areas at the peripheries of the clusters would be comparable. This suggests that the higher rate of homopolymerization in the case of the T₁₂ cluster might be related to the greater number of vinyl groups per unit area at the periphery of the cluster which are available for homopolymerization, prior to addition of the MPTEOS to the reaction mixture. The competition between homopolymerization and functionalization via a thiol-ene Click reaction in the case of larger cages will be investigated in a future paper.

4. Conclusion

In summary, two styryl-POSS cages (T₈ and T₁₀) were successfully functionalised with peripheral triethoxysilyl groups via a thiol-ene Click reaction with 3-thiopropyltriethoxysilane, and subsequently converted to gels via sol-gel processing under acid-catalyzed conditions. To the best of our knowledge, this is the first report of a T₁₀ cage covalently incorporated within a hybrid silica matrix. Although some homopolymerization of the two styryl-POSS “monomers” was observed, the thiol-ene Click reaction leading to the silylated product was favored in the case of the T₈ and T₁₀ systems. In contrast, in the case of larger cages such as T₁₂, it was found that homopolymerization at the styryl site dominated the thiol-ene Click reaction, with only the homopolymerization reaction being observed in the latter case.

Gels subsequently prepared via sol-gel processing of the silylated precursors under acid-catalyzed conditions yielded materials in which intact POSS cages were covalently incorporated within the gel network, with the organic bridge covalently bound to the cage and peripheral silicon atoms. Only Tⁿ silicon species were observed in the gel networks, with the absence of Qⁿ species demonstrating that no cleavage of the Si-C bonds occurred during the reaction. Water retained within the aged gels exhibited an unusual “connective”, ice-like structure, suggesting that it was initially retained as an intrinsic component of the gel network during consolidation at ambient temperature. The extent of hydrolysis and condensation of the triethoxysilyl species was lower in the case of the T₁₀ gel system. This was attributed to geometrical constraints imposed by the T₁₀ cages, which each immobilize one end of 10 aliphatic chains to a single fixed point within the gel matrix, thus limiting the mobility of the hydrolysable/condensable triethoxysilyl moieties. In contrast, fewer chains (i.e. eight) are anchored to each cage in the T₈ system, leading to a relative increase in the mobility of the aliphatic chains and to a corresponding increase in the ability of the system to form T² and T³ species. Hence, the impact of cage size on the extent of condensation within the gel would enable the abundance of free, unreacted hydroxyl species within the gel matrices to be modulated.

The approach outlined in this study opens up new possibilities for producing functional materials that incorporate geometrically well-defined, functionalized POSS cages of varying sizes, with potential applications in such areas as low-*k* materials. We are currently developing a range of such silylation reactions to produce a family of new precursors for sol-gel processing; this work will be reported in future studies.

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References

1. Scott DW (1946) Thermal Rearrangement of Branched-Chain Methylpolysiloxanes. *J Am Chem Soc* 68 (3):356-358. doi:10.1021/ja01207a003
2. Barry AJ, Daudt WH, Domicone JJ, Gilkey JW (1955) Crystalline Organosilsesquioxanes. *J Am Chem Soc* 77 (16):4248-4252. doi:10.1021/ja01621a025
3. Zhang C, Babonneau F, Bonhomme C, Laine RM, Soles CL, Hristov HA, Yee AF (1998) Highly porous polyhedral silsesquioxane polymers. Synthesis and characterization. *J Am Chem Soc* 120 (33):8380-8391. doi:10.1021/ja9808853
4. Hoebbel D, Endres K, Reinert T, Pitsch I (1994) Inorganic-organic polymers derived from functional silicic acid derivatives by additive reaction. *J Non Cryst Solids* 176 (2-3):179-188. doi:10.1016/0022-3093(94)90076-0
5. Morrison JJ, Love CJ, Manson BW, Shannon IJ, Morris RE (2002) Synthesis of functionalised porous network silsesquioxane polymers. *J Mater Chem* 12 (11):3208-3212. doi:10.1039/b204240a
6. Sangtrirutnugul P, Chaiprasert T, Hunsiri W, Jitjaroendee T, Songkhum P, Laohhasurayotin K, Osotchan T, Ervithayasuporn V (2017) Tunable Porosity of Cross-Linked-Polyhedral Oligomeric Silsesquioxane Supports for Palladium-Catalyzed Aerobic Alcohol Oxidation in Water. *ACS Appl Mater Interfaces* 9 (14):12812-12822. doi:10.1021/acsami.7b03910
7. Cordes DB, Lickiss PD, Rataboul F (2010) Recent developments in the chemistry of cubic polyhedral oligosilsesquioxanes. *Chem Rev* 110 (4):2081-2173. doi:10.1021/cr900201r
8. Laine RM (2005) Nanobuilding blocks based on the $[\text{OSiO}_{1.5}]_x$ ($x = 6, 8, 10$) octasilsesquioxanes. *J Mater Chem* 15 (35-36):3725-3744. doi:10.1039/b506815k
9. Harrison PG, Kannengiesser R (1996) Porous materials derived from trigonal-prismatic $\{\text{Si}_6\text{O}_9\}$ and cubane $\{\text{Si}_8\text{O}_{12}\}$ cage monomers. *Chem Commun* (3):415-416. doi:10.1039/cc9960000415
10. Akbari A, Arsalani N, Amini M, Jabbari E (2016) Cube-octameric silsesquioxane-mediated cargo copper Schiff base for efficient click reaction in aqueous media. *J Mol Catal A Chem* 414:47-54. doi:10.1016/j.molcata.2015.12.022
11. Köytepe S, Demirel MH, Gültek A, Seçkin T (2014) Metallo-supramolecular materials based on terpyridine-functionalized polyhedral silsesquioxane. *Polym Int* 63 (4):778-787. doi:10.1002/pi.4596
12. Kowalewska A (2017) Self-assembling polyhedral silsesquioxanes - Structure and properties. *Curr Org Chem* 21 (14):1243-1264. doi:10.2174/1385272821666170303103747
13. Heeley E, El Aziz Y, Ellingford C, Jetybayeva A, Wan C, Crabb E, Taylor PG, Bassindale A (2019) Self-assembly of fluoride-encapsulated polyhedral oligomeric silsesquioxane (POSS) nanocrystals. *Crystengcomm* 21 (4):710-723. doi:10.1039/C8CE01750F
14. Seino M, Wang W, Lofgreen JE, Puzzo DP, Manabe T, Ozin GA (2011) Low-k periodic mesoporous organosilica with air walls: POSS-PMO. *J Am Chem Soc* 133 (45):18082-18085. doi:10.1021/ja2080136

15. Kausar A (2017) State-of-the-Art Overview on Polymer/POSS Nanocomposite. *Polym-Plast Technol Eng* 56 (13):1401-1420. doi:10.1080/03602559.2016.1276592
16. Zhou H, Ye Q, Xu J (2017) Polyhedral oligomeric silsesquioxane-based hybrid materials and their applications. *Mater Chem Front* 1 (2):212-230. doi:10.1039/c6qm00062b
17. Chiacchio MA, Borrello L, Di Pasquale G, Pollicino A, Bottino FA, Rescifina A (2005) Synthesis of functionalized polyhedral oligomeric silsesquioxane (POSS) macromers by microwave assisted 1,3-dipolar cycloaddition. *Tetrahedron* 61 (33):7986-7993. doi:10.1016/j.tet.2005.06.006
18. Haddad TS, Viers BD, Phillips SH (2001) Polyhedral oligomeric silsesquioxane (POSS)-styrene macromers. *J Inorg Organomet Polym* 11 (3):155-164
19. Phillips SH, Haddad TS, Tomczak SJ (2004) Developments in nanoscience: Polyhedral oligomeric silsesquioxane (POSS)-polymers. *Curr Opin Solid State Mater Sci* 8 (1):21-29. doi:10.1016/j.cossms.2004.03.002
20. Romo-Uribe A, Mather PT, Haddad TS, Lichtenhan JD (1998) Viscoelastic and morphological behavior of hybrid styryl-based polyhedral oligomeric silsesquioxane (POSS) copolymers. *J Polym Sci Part B* 36 (11):1857-1872. doi:10.1002/(SICI)1099-0488(199808)36:11<1857::AID-POLB7>3.0.CO;2-N
21. Kannan RY, Salacinski HJ, Butler PE, Seifalian AM (2005) Polyhedral oligomeric silsesquioxane nanocomposites: The next generation material for biomedical applications. *Acc Chem Res* 38 (11):879-884. doi:10.1021/ar050055b
22. Ghanbari H, Cousins BG, Seifalian AM (2011) A nanocage for nanomedicine: Polyhedral oligomeric silsesquioxane (POSS). *Macromol Rapid Commun* 32 (14):1032-1046. doi:10.1002/marc.201100126
23. Solouk A, Cousins BG, Mirahmadi F, Mirzadeh H, Nadoushan MRJ, Shokrgozar MA, Seifalian AM (2015) Biomimetic modified clinical-grade POSS-PCU nanocomposite polymer for bypass graft applications: A preliminary assessment of endothelial cell adhesion and haemocompatibility. *Mater Sci Eng C* 46:400-408. doi:10.1016/j.msec.2014.10.065
24. Nayyer L, Birchall M, Seifalian AM, Jell G (2014) Design and development of nanocomposite scaffolds for auricular reconstruction. *Nanomed Nanotechnol Biol Med* 10 (1):235-246. doi:10.1016/j.nano.2013.06.006
25. Kannan RY, Salacinski HJ, De Groot J, Clatworthy I, Bozec L, Horton M, Butler PE, Seifalian AM (2006) The antithrombogenic potential of a polyhedral oligomeric silsesquioxane (POSS) nanocomposite. *Biomacromolecules* 7 (1):215-223. doi:10.1021/bm050590z
26. Kannan RY, Salacinski HJ, Odlyha M, Butler PE, Seifalian AM (2006) The degradative resistance of polyhedral oligomeric silsesquioxane nanocore integrated polyurethanes: An in vitro study. *Biomaterials* 27 (9):1971-1979. doi:10.1016/j.biomaterials.2005.10.006
27. Quadrelli EA, Basset JM (2010) On silsesquioxanes' accuracy as molecular models for silica-grafted complexes in heterogeneous catalysis. *Coord Chem Rev* 254 (5-6):707-728. doi:10.1016/j.ccr.2009.09.031
28. Giacalone F, Gruttadauria M (2016) Covalently Supported Ionic Liquid Phases: An Advanced Class of Recyclable Catalytic Systems. *ChemCatChem* 8 (4):664-684. doi:10.1002/cctc.201501086
29. Bivona LA, Giacalone F, Carbonell E, Gruttadauria M, Aprile C (2016) Proximity Effect using a Nanocage Structure: Polyhedral Oligomeric Silsesquioxane-Imidazolium Tetrachloro- palladate Salt as a Precatalyst for the Suzuki-Miyaura Reaction in Water. *ChemCatChem* 8 (9):1685-1691. doi:10.1002/cctc.201600155
30. Zhou Y, Yang G, Lu C, Nie J, Chen Z, Ren J (2016) POSS supported C2-symmetric bisprolinamide as a recyclable chiral catalyst for asymmetric Aldol reaction. *Catal Commun* 75:23-27. doi:10.1016/j.catcom.2015.11.017
31. Li Z, Kong J, Wang F, He C (2017) Polyhedral oligomeric silsesquioxanes (POSSs): An important building block for organic optoelectronic materials. *J Mater Chem C* 5 (22):5283-5298. doi:10.1039/c7tc01327b
32. Gnanasekaran D, Madhavpan K, Reddy RSR (2009) Developments of polyhedral oligomeric silsesquioxanes (POSS), POSS nanocomposites and their applications: A review. *J Sci Ind Res* 68 (6):437-464

33. Chanmungkalakul S, Ervithayasuporn V, Boonkitti P, Phuekphong A, Prigyai N, Kladsomboon S, Kiatkamjornwong S (2018) Anion identification using silsesquioxane cages. *Chem Sci* 9 (40):7753-7765. doi:10.1039/c8sc02959h
34. Chanmungkalakul S, Ervithayasuporn V, Hanprasit S, Masik M, Prigyai N, Kiatkamjornwong S (2017) Silsesquioxane cages as fluoride sensors. *Chem Commun* 53 (89):12108-12111. doi:10.1039/c7cc06647c
35. Liu H, Liu H (2017) Selective dye adsorption and metal ion detection using multifunctional silsesquioxane-based tetraphenylethene-linked nanoporous polymers. *J Mater Chem A* 5 (19):9156-9162. doi:10.1039/c7ta01255a
36. Laird M, Van der Lee A, Dumitrescu D, Carcel C, Ouali A, Bartlett JR, Unno M, Wong Chi Man M (2020) New Functionalized cage silsesquioxanes as nanoblocks for 3-D assembly. *Organometallics* Under Revision
37. Ramesh S, Kim HS, Sivasamy A, Kim J-H (2018) Synthesis of Octa(maleimidophenyl) silsesquioxane-SiO₂/TiO₂ Hybrid Nanocomposites: Adsorption Behavior for the Removal of an Organic Methylene Blue Dye and Antimicrobial Activity against Pathogens. *Polym-Plast Technol Eng* 57 (3):185-195. doi:10.1080/03602559.2017.1320716
38. Ramesh S, Kim J, Kim J-H (2015) Characteristic of hybrid cellulose-amino functionalized POSS-silica nanocomposite and antimicrobial activity. *J Nanomater*:1-10. doi:10.1155/2015/936590
39. Liu Y, Chen Y, Yang H, Nie L, Yao S (2013) Cage-like silica nanoparticles-functionalized silica hybrid monolith for high performance capillary electrochromatography via "one-pot" process. *J Chromatogr A* 1283:132-139. doi:10.1016/j.chroma.2013.01.112
40. Zajickova Z (2017) Advances in the development and applications of organic-silica hybrid monoliths. *J Sep Sci* 40 (1):25-48. doi:10.1002/jssc.201600774
41. Gunji T, Shioda T, Tsuchihira K, Seki H, Kajiwarra T, Abe Y (2010) Preparation and properties of polyhedral oligomeric silsesquioxane-polysiloxane copolymers. *Appl Organomet Chem* 24 (8):545-550. doi:10.1002/aoc.1562
42. Zhang L, Abbenhuis HCL, Yang Q, Wang YM, Magusin PCMM, Mezari B, Van Santen RA, Li C (2007) Mesoporous organic-inorganic hybrid materials built using polyhedral oligomeric silsesquioxane blocks. *Angew Chem Int Ed* 46 (26):5003-5006. doi:10.1002/anie.200700640
43. Wang L, Guo R, Ren J, Song G, Chen G, Zhou Z, Li Q (2020) Preparation of superhydrophobic and flexible polysiloxane aerogel. *Ceram Int*. doi:10.1016/j.ceramint.2020.01.033
44. Li Y, Zhang WB, Hsieh IF, Zhang G, Cao Y, Li X, Wesdemiotis C, Lotz B, Xiong H, Cheng SZD (2011) Breaking symmetry toward nonspherical janus particles based on polyhedral oligomeric silsesquioxanes: Molecular design, "click" synthesis, and hierarchical structure. *J Am Chem Soc* 133 (28):10712-10715. doi:10.1021/ja202906m
45. Li Y, Dong XH, Guo K, Wang Z, Chen Z, Wesdemiotis C, Quirk RP, Zhang WB, Cheng SZD (2012) Synthesis of shape amphiphiles based on POSS tethered with two symmetric/asymmetric polymer tails via sequential "grafting-from" and thiol-ene "click" chemistry. *ACS Macro Lett* 1 (7):834-839. doi:10.1021/mz300196x
46. Rikowski E, Marsmann HC (1997) Cage-rearrangement of silsesquioxanes. *Polyhedron* 16 (19):3357-3361. doi:10.1016/S0277-5387(97)00092-2
47. Fidalgo A, Ilharco LM (2004) Chemical tailoring of porous silica xerogels: Local structure by vibrational spectroscopy. *Chem - Eur J* 10 (2):392-398. doi:10.1002/chem.200305079
48. Fidalgo A, Ilharco LM (2005) The influence of the wet gels processing on the structure and properties of silica xerogels. *Microporous Mesoporous Mater* 84 (1-3):229-235. doi:10.1016/j.micromeso.2005.04.021
49. Perry CC, Li X (1991) Structural studies of gel phases. Part 1. - Infrared spectroscopic study of silica monoliths; the effect of thermal history on structure. *Journal of the Chemical Society, Faraday Transactions* 87 (5):761-766. doi:10.1039/FT9918700761
50. Crupi V, Majolino D, Longo F, Migliardo P, Venuti V (2006) FTIR/ATR study of water encapsulated in Na-A and Mg-exchanged A-zeolites. *Vib Spectrosc* 42 (2):375-380. doi:10.1016/j.vibspec.2006.05.007

51. Crupi V, Longo F, Majolino D, Venuti V (2006) Vibrational properties of water molecules adsorbed in different zeolitic frameworks. *J Phys: Condens Matter* 18 (15):3563-3580. doi:10.1088/0953-8984/18/15/004
52. Falk M (1984) The frequency of the HOH bending fundamental in solids and liquids. *Spectrochim Acta Part A Mol Spectrosc* 40 (1):43-48. doi:10.1016/0584-8539(84)80027-6
53. Chaudhari A (2010) Hydrogen bonding interaction between 1,4-dioxane and water. *Int J Quantum Chem* 110 (5):1092-1099. doi:10.1002/qua.22143
54. Crupi V, Majolino D, Venuti V (2004) Diffusional and vibrational dynamics of water in NaA zeolites by neutron and Fourier transform infrared spectroscopy. *J Phys: Condens Matter* 16 (45):S5297-S5316. doi:10.1088/0953-8984/16/45/001
55. Blanco I, Abate L, Bottino FA (2017) Mono substituted octaphenyl POSSs: The effects of substituents on thermal properties and solubility. *Thermochim Acta* 655:117-123. doi:10.1016/j.tca.2017.06.019
56. Fan H, Yang R (2014) Thermal decomposition of polyhedral oligomeric octaphenyl, octa(nitrophenyl), and octa(aminophenyl) silsesquioxanes. *J Therm Anal Calor* 116 (1):349-357. doi:10.1007/s10973-013-3554-9
57. Zhang Z, Liang G, Lu T (2007) Synthesis and characterization of cage octa(aminopropyl)silsesquioxane. *J Appl Polym Sci* 103 (4):2608-2614. doi:10.1002/app.25304