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Large polyhedral oligomeric silsesquioxane cages – the isolation of functionalized POSS with an unprecedented $\text{Si}_{18}\text{O}_{27}$ core

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Abstract: The synthesis of organo-functionalized polyhedral oligomeric silsesquioxanes (POSS, $(\text{R-SiO}_{1.5})_n$, T_n) is currently an area of significant activity. To date, T_{14} is the largest such cage synthesized and isolated as a single isomer. Herein, we report the successful synthesis and isolation of an unprecedented, single-isomer styryl-functionalized T_{18} POSS. Unambiguously identified among nine possible isomers by multinuclear solution NMR (^1H , ^{13}C and ^{29}Si), MALDI-MS, FTIR and computational studies, this represents the largest single-isomer functionalized T_n compound isolated to date.

A ring strain model was developed to correlate the ^{29}Si resonances with the number of six-, five- and/or four-Si-atom rings that each non-equivalent Si atom is part of. The model successfully predicts the speciation of non-equivalent Si atoms in other families of T_n compounds, demonstrating its general applicability for assigning ^{29}Si resonances to silicon atoms in cage silsesquioxanes and providing a useful tool for predicting silicon-atom environments.

Introduction

The development of polyhedral oligomeric silsesquioxanes (POSS, $\text{R}-(\text{SiO}_{1.5})_n$, where $n=6, 8, 10, 12$, etc) is currently an area of intense activity within the materials chemistry community, due in part to the wide range of fields in which they can be applied, including polymer chemistry^[1-8], bio/nanomedicine^[9-14], catalysis^[15-18], optical and sensing applications^[3, 19-20], optoelectronics^[21], flame retardancy^[22], etc. Of these, the cage silsesquioxanes, which are composed of a well-defined $(\text{SiO}_{1.5})_n$ polyhedral core (T_n) covalently linked to organic moieties, have been of particular interest^[23], with $n=8$ being the most widely reported, studied and employed in several application fields. These hybrid molecules can be readily incorporated into nanostructured materials either via hydrolysis-condensation processes involving silanol groups^[24] or by polymerization on the organic moiety^[4, 25-26]. Porous materials can be readily obtained in such systems,^[24-25] where the porosity can either arise from the voids between the cages or the core of the cage (0.3 nm for T_8)^[25]. In addition, self-organized systems^[27-29], POSS micelles and templated POSS systems leading to mesoporous materials with T_8 cages embedded with the walls^[30], and organic polymer-based nanohybrids^[1, 3, 31-34] can be obtained through judicious selection of functional organics.

We recently described the synthesis of new styryl-functionalized T_8 , T_{10} and T_{12} POSS compounds, in which the styryl group was linked to the cage via the phenylene group as spacer rather than the vinyl group^[35]. Such functionalized T_n molecules bearing organic moieties that can be further modified via conventional and well-established reactions such as hydrosilylation, Heck coupling, thiolene click reactions, metathesis, etc, without modifying the structure of the T_n core, are particularly interesting. Indeed, they pave the way to an even wider range of potential applications. Accordingly, the availability of T_n precursors bearing styryl moieties grafted onto all “ n ” vertices usefully extends the range of versatile POSS precursors. However, most of the T_n precursors successfully isolated and unambiguously identified to date have exhibited values of $n = 6, 8, 10$, or 12 , with larger cages being comparatively rare. Indeed, to the best of our knowledge, the largest such cages isolated and unambiguously identified to date as pure compounds are the D_{3h} and C_{2v} isomers of

(H-SiO_{1.5})₁₄ [36]. The availability of such large, structurally well-defined cages would significantly extend the range of potential applications for POSS compounds as building blocks. In addition to providing the opportunity to modulate the size and shape of inorganic nodes in hybrid networks, the presence of functional organics bonded to each of the *n* vertices in (R-SiO_{1.5})_{*n*} with larger values of *n* would confer additional flexibility and degrees-of-freedom on organic networks constructed around the functional organics. However, their synthesis is complicated by the fact that increasing values of *n* lead to a corresponding increase in the number of possible theoretical isomers in the system. For example, while cage silsesquioxanes with *n*=8 or 10 are obtained as single isomers, those with *n*=12, 14 or 16 could theoretically yield up to two, four or seven isomers, respectively [36]. Individual isomers have been obtained for *n*=14 in the (H-SiO_{1.5})₁₄ system, although only mixtures have been obtained for *n*=16 [36].

During subsequent work on the styryl-functionalized T_{*n*} system previously reported [35], we identified the presence of small quantities of an additional cage silsesquioxane compound, with *n* = 18. In this paper, we describe the synthesis, isolation and characterization of this large styryl-functionalized cage and demonstrate that it is obtained as a single isomer. A model relating the effect of ring strain in a series of styryl-functionalized T_{*n*} cages with *n*=8, 10, 12 and 18 to the ²⁹Si chemical shifts arising from non-equivalent silicon sites in the cages is also described and used to confirm the structure of the T₁₈ isomer obtained.

Results and Discussion

As indicated above, most studies of functionalized T_{*n*} cage silsesquioxane species to date have focused on the T₈ system, together with the less common T₁₀ and T₁₂ compounds. However, several studies have also used various chromatographic techniques to isolate larger functionalized T_{*n*} systems. Frye and Collins first reported the preparation of a mixture of (HSiO_{1.5})_{*n*} (*n* = 10, 12, 14 and 16) cage silsesquioxanes, together with a resin-like product, and their separation by gas chromatography [37]. The resulting materials were characterized by ¹H NMR and IR spectroscopy, although their structures were not determined. Agaskar et al. described the isolation and characterization by single-crystal X-ray diffraction of two isomers of (HSiO_{1.5})₁₄ with D_{3h} and C_{2v} symmetry [36, 38]. A subsequent chromatographic study by the same authors [36] revealed evidence for the presence of (HSiO_{1.5})_{*n*} with all possible values of *n* from 16 to 32 (in steps of 2). In this work, the authors succeeded in isolating a mixture of isomers for *n* = 16, although it was not possible to isolate and identify the individual compounds within the mixture. Bürgy and Calzaferri employed size exclusion chromatography to obtain (HSiO_{1.5})_{*n*} for values of *n* up to 18 [39], although no structural data were presented.

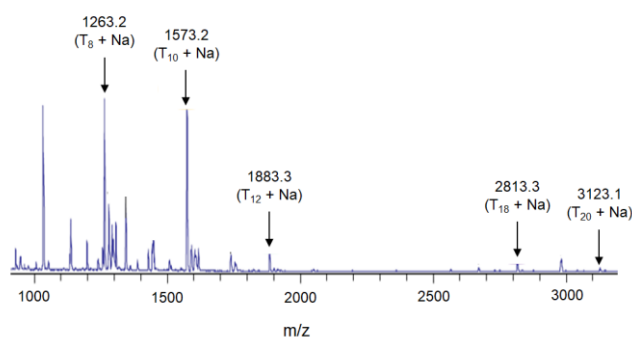


Figure 1. MALDI-TOF mass spectrum of the product mixture from which styryl-functionalized T_{*n*} compounds were isolated.

The approach used by us to synthesize and isolate styryl-functionalized T_{*n*} compounds for *n* = 8, 10 and 12 has been previously described. These compounds were isolated from a complex mixture, which was characterized by MALDI MS, as illustrated in **Figure 1**. Peaks arising from M+Na adducts of the T₈, T₁₀ and T₁₂ compounds (each separated by the expected 310 m/z, corresponding to two R-SiO_{1.5} groups [35]) are clearly seen, together with weaker peaks associated with larger cages. Thin layer chromatography was used to isolate the various fractions present in the mixture. Apart from the T₈, T₁₀, and T₁₂ components, most of the other fractions obtained exhibited broad ¹H NMR signals, which often arise from polymeric species and were thus discarded. However, one fraction, which was obtained with a yield of 4.5 %, consistently exhibited narrow and well-defined ¹H NMR signals and was thus characterized in detail. The MALDI mass spectrum of this compound, **Figure 2**, revealed a strong peak at 2813.4 m/z, which is attributed to the presence of a styryl-functionalized T₁₈ cage (expected m/z = 2813.4 for T₁₈+Na, higher by 3 x 310.1 m/z than the mass peak for the corresponding T₁₂ cage compound). It is intriguing that no T₁₄ or T₁₆ compounds could be identified by MALDI-MS, with a single, pure fraction of T₁₈ being obtained. We note that two isomers in the H-T₁₄ series have previously been isolated as pure products and characterized by single crystal X-ray diffraction (with D_{3h} [38] and C_{2v} [36] symmetry), suggesting that substituent effects, such as steric interactions, may play a role in controlling the formation and stabilization of the silsesquioxane cages in such large POSS systems. Unfortunately, attempts to crystallise the styryl-functionalized T₁₈ compound from a variety of solvents were unsuccessful.

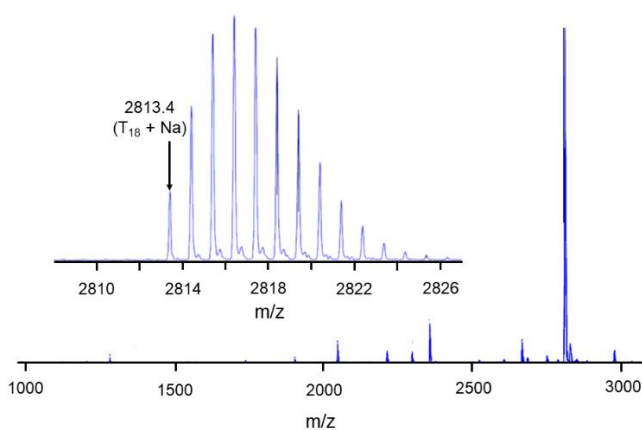


Figure 2. MALDI-TOF mass spectrum of styryl-functionalised T_{18} .

Apart from its attribution to styryl-functionalized T_{18} cage silsesquioxane, other possible attributions for the 2813.4 m/z peak were also considered but were discounted. As discussed below, a feature of the compound is that the ^{29}Si spectrum is consistent with all Si sites having T^3 speciation, with no T^2 or T^1 sites being evident. This is consistent with a closed-cage structure and excludes the possibility of open or partially-condensed cages terminated by hydroxyl or bridging oxo species, since all such compounds would exhibit either T^2 signals around 10 ppm downfield from the observed T^3 features (see **Table S1**) or T^1 signals around 20 ppm downfield. The potential formation of open or partially-condensed cages terminated by hydroxyl groups is further excluded by the IR spectrum of the compound (**Figure S1**), which does not exhibit any evidence of $\nu_{(\text{O-H})}$ modes above 3200 cm^{-1} . No other ^{29}Si signals were observed in the range from +50 to -150 ppm that might arise from other Si(IV) or pentacoordinated moieties (such as $\equiv\text{Si-F}$). Finally, the ^1H and ^{13}C spectra (**Figures S2** and **S3**, respectively, discussed in more detail below) are consistent with functionalization of all Si sites with styryl moieties, with no other organic moieties covalently bonded to Si being evident. This precludes the presence of pendant methoxy groups in the compound, which would give rise to signals near 3.5 and 50 ppm in the ^1H and ^{13}C solution NMR spectra, respectively.

As indicated above, Agaskar and Klemperer^[36] previously reported the identification of a mixture of isomers of $(\text{H-Si}_{18}\text{O}_{27})$ via chromatographic separation of a mixture of HT_n species (where $n=14-32$), although no pure T_{18} compounds were isolated or characterized in their study. They proposed nine possible isomers in the HT_{18} system (**Figure 3**), which differ mainly in the number of 6-, 5- and 4-silicon-atom rings and in the corresponding silicon environments. The isomers proposed by Agaskar and Klemperer exhibit between four and seven non-equivalent silicon atoms, and hence it would be anticipated that ^{29}Si NMR spectroscopy would provide useful insights into the structure of the isomer obtained in our work.

The ^{29}Si solution NMR spectrum of the styryl-functionalized T_{18} silsesquioxane, **Figure 4**, exhibits five distinct signals at -77.40, -78.35, -79.12, -79.18 and -79.35 ppm, suggesting the presence of five distinct T^3 Si sites in our product. Of the possible isomers suggested by Agaskar and Klemperer^[36], only two of the nine possess five non-equivalent Si sites (isomers **E** and **F** in **Figure 3**). The first of these contains six Si in 6^15^2 , four Si in $6^15^14^1$, two Si in 6^14^2 , two Si in 5^3 , and four Si in 5^24^1 sites, while the second contains four Si in 6^25^1 , four Si in 6^24^1 , four Si in $6^15^14^1$, four Si in 6^14^2 and two Si in 5^14^2 sites. Here, the notation $6^x5^y4^z$, where $x,y,z \geq 0$ and $x+y+z=3$, refers to the number of six-, five- and/or four-Si-atom rings that each non-equivalent Si atom is part of (see coloured Si assignments in **Figure 3**). In order to unambiguously identify the isomer, quantitative ^{29}Si NMR was performed. A zg30 pulse with a relaxation time, $D_1 = 100\text{ s}$, was used to ensure complete relaxation of the silicons between each acquisition. The integrated intensities of the proton-decoupled signals presented in **Figure 4** are consistent with the second possibility, indicating that the structure of the T_{18} isomer obtained in our work is that illustrated in **Figure 3-F**. It is interesting to note that modelling studies (see Experimental) indicated that there is only around 5 kJ/mol difference in the calculated energies of the optimized structures of isomers **E** and **F** in **Figure 3**, indicating that purely thermodynamic considerations alone cannot explain the formation of one isomer instead of the other. This suggests that the formation of isomer **F** is favored kinetically rather than thermodynamically, since only isomer **F** is observed in our study.

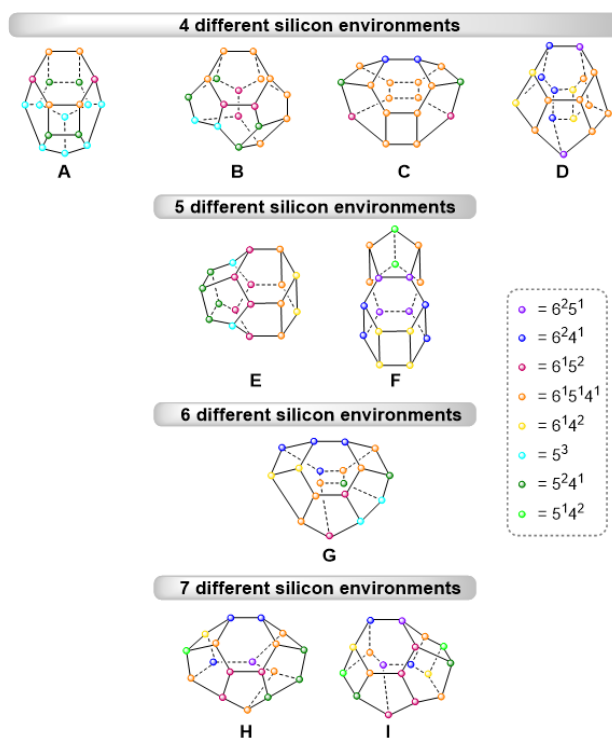


Figure 3. Proposed isomers in the T_{18} system.

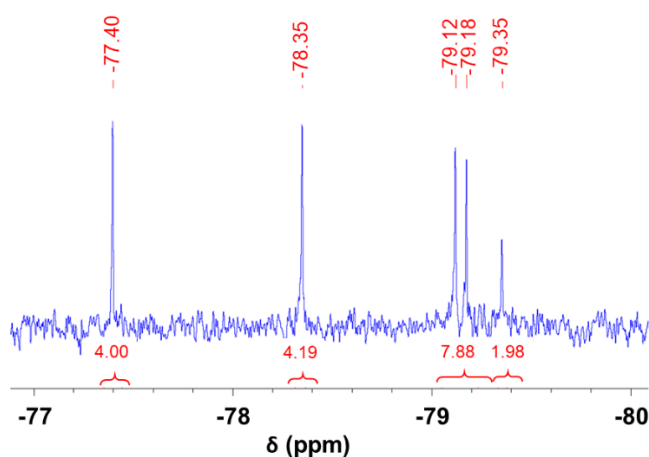


Figure 4. Quantitative ^{29}Si NMR spectrum of the styryl T_{18} cage silsesquioxane

An unequivocal attribution of the ^{29}Si NMR signals in **Figure 4** to Si atoms in the five non-equivalent sites illustrated in **Figure 3-F** is non-trivial. Agaskar and Klemperer presented correlations between the number of 4-Si-atom rings around each silicon site in selected HT_n -systems and the corresponding ^{29}Si chemical shifts^[36], although these correlations could not be successfully applied to our system. Rikowski and Marsmann also presented empirical correlations between the ^{29}Si chemical shifts in organofunctionalized T_8 , T_{10} and T_{12} compounds,^[40] which were attributed to differences in the strain in 4- and 5-Si-atom rings. However, again, these correlations could not be successfully applied in our case; moreover, no correlations for compounds containing 6-Si-atom rings were presented. Accordingly, we have developed an empirical “ring-strain” model to predict the chemical shifts in styryl-functionalized T_8 , T_{10} , T_{12} and T_{18} cages and to assign the signals in the ^{29}Si T_{18} spectrum to specific Si atoms in each of the five non-equivalent sites. As discussed above, it has previously been established that 4-Si-atom rings in cage silsesquioxane systems are more strained than 5-Si-atom rings, although no such correlations have previously been reported in the case of 6-Si-atom rings. Indeed, the only reports of chemical shifts in 6-Si-atom ring systems appear to be in the case of less-constrained cyclic polysilanol such as $[\text{PhSi}(\text{O})(\text{OH})]_6$ ^[41] and silsesquioxanes such as $[\text{PhSi}(\text{O})(\text{OSiMe}_2\text{R})]_6$ ^[42]. The assignments of signals in the ^{29}Si NMR spectra of T_8 (-78.19 ppm, 4³), T_{10} (-79.59 ppm, 5¹4²) and T_{12} (-79.45 ppm, 5¹4²; -81.04 ppm, 5²4¹) have already been established using ring-strain correlations, as indicated previously and are consistent with the relative abundance observed by ^{29}Si NMR

spectroscopy. The chemical shifts of the signals in the T_{18} spectrum are largely bounded by the values established in the T_8 , T_{10} and T_{12} systems, although one signal (-77.40 ppm) appears more downfield than that of the single resonance in the T_8 spectrum (-78.35 ppm, 4^3). This suggests that the former is associated with a more constrained system than the T_8 (which contains only 4^3 silicon sites). Although not previously observed, one explanation of this effect would be to postulate that 6-Si-atom rings are more constrained than 4-Si-atom rings in cage silsesquioxane systems. Accordingly, the T_{18} signal at -77.40 ppm would logically be assigned to $6^2 4^1$ sites, which would then be identified as the most constrained Si environments in the T_n systems. Based on the integrated intensities shown in **Figure 4**, the signal at -79.35 ppm is directly attributable to the (two) $5^1 4^2$ sites in the T_{18} cage, in close agreement with the chemical shifts of Si atoms in $5^1 4^2$ sites in the T_{10} and T_{12} compounds (-79.59 and -79.45 ppm, respectively).

Table 1. Assignments of signals in the ^{29}Si NMR spectra of T_n compounds and predicted chemical shifts based on the “ring-strain” model.

Cage type	Number of Si in ring			Chemical Shift (ppm)	Model (ppm)
	6-ring	5-ring	4-ring		
T_{18}	2	0	1	-77.40	-77.62
T_8	1	0	2	-78.19	-78.17
T_{18}	0	0	3	-78.35	-77.90
T_{18}	2	1	0	-79.12	-79.05
T_{18}	1	1	1	-79.18	-79.33
T_{18}	0	1	2	-79.35	-79.60
T_{12}	0	1	2	-79.45	-79.60
T_{10}	0	1	2	-79.59	-79.60
T_{12}	0	2	1	-81.29	-81.04

Based on these initial correlations, the proposed attributions of signals in the ^{29}Si NMR spectrum of the styryl-functionalized T_{18} cage are summarized in **Table 1**, together with the corresponding assignments for the T_8 , T_{10} , and T_{12} compounds. To further investigate the role of ring-strain in modulating the positions of the ^{29}Si signals, we then derived a simple linear relationship between the observed chemical shifts and the number of 4-, 5- and 6-Si-atom rings associated with each silicon site:

$$\delta_{\text{predicted}} = A.n_{4\text{-ring}} + B.n_{5\text{-ring}} + C.n_{6\text{-ring}} + D$$

where the values of A , B , C and D are obtained via non-linear regression using the data in **Table 1**. The results obtained are illustrated in **Figure 5**, which illustrates a reasonably good fit of the simple ring-strain model to the experimental data. The relative magnitudes of A , B and C suggest that the impact of 5-Si-atom rings on ^{29}Si chemical shifts is five-to-six-fold lower than that of 4- and 6-Si-atom rings. In addition, the impact of 6-Si-atom rings is around 15 % higher than that of 4-Si-atom rings. As far as we are aware, this is the first report of an empirical approach linking the relative strain in the various rings present in such cage silsesquioxanes to the positions of ^{29}Si NMR signals, with earlier studies^[40] not considering 6-Si-atom ring systems.

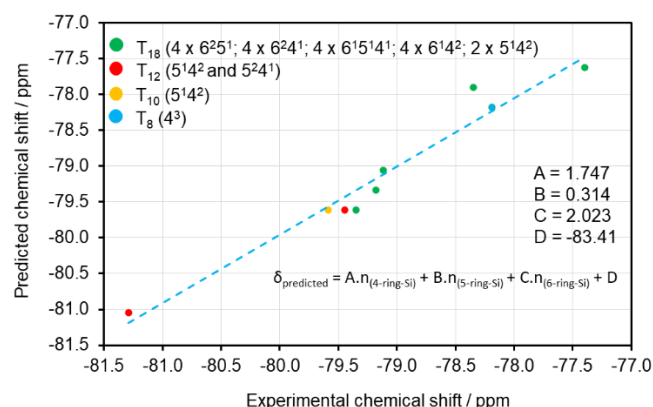


Figure 5. Experimental vs predicted chemical shifts for ^{29}Si signals in the styryl-functionalized T_n system ($n = 8, 10, 12$, and 18).

The proposed “ring-strain” approach is general, and hence the same values of A , B and C should be applicable to other functionalized T_n cage silsesquioxane families. However, the value of D would be expected to change with different organic moieties, to account for the different shielding of aliphatic and aromatic substituents, different NMR solvents, etc. To test this hypothesis, the comprehensive ^{29}Si NMR data for H- T_n (for $n = 8, 10, 12$ and 14 (both D_{3h} and C_{2v} isomers)) reported by Agaskar and Klemperer^[36] were modelled by using the values of A , B and C derived from the styryl system and varying the value of D via a least-squares minimization. The results obtained, **Figure 6**, demonstrate that the ring-strain model fits the data for the H- T_n system reasonably well, with the value of D being somewhat different to that for the styryl-functionalized system as expected.

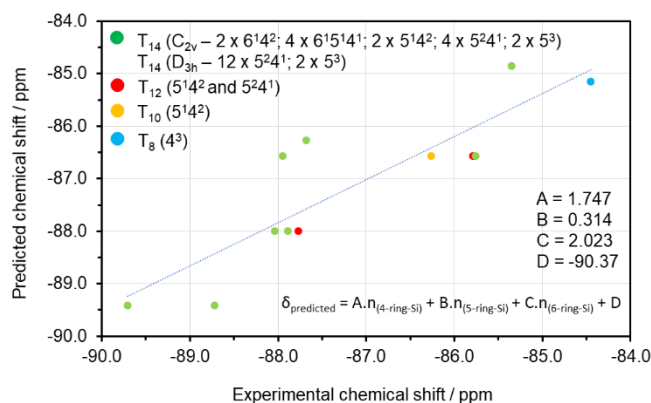


Figure 6. Experimental vs predicted chemical shifts for ^{29}Si signals in the H- T_n system ($n = 8, 10, 12$, and 14).

As far as we are aware, there are currently no other examples of R- T_n cage silsesquioxane series for $n = 8$ to >14 against which to test our approach. However, it is of interest to use the correlations developed here to consider the stability of other potential isomers in the T_{12} , T_{14} and T_{16} systems. For example, the postulated D_{6h} T_{12} isomer has never been successfully isolated (despite being widely and incorrectly used as a model of the structure of the T_{12} cage silsesquioxanes), with the D_{2d} isomer always being exclusively obtained. Based on “ring-strain” considerations, this could arise from the fact that the D_{6h} isomer would consist of $12 \times 6^{24^1}$ Si species, and hence, would be highly strained compared to the D_{2d} isomer ($8 \times 5^{24^1}$ and $4 \times 5^{14^2}$).

The ^1H solution NMR spectrum of the styryl-functionalized T_{18} silsesquioxane, **Figure S2**, exhibits the series of overlapping signal clusters expected for five groups of non-equivalent styryl moieties, as discussed in detail in the **Supplementary Information**. Similarly, the ^{13}C solution NMR spectrum, shown in **Figure S3**, exhibits the expected chemical shifts of the styryl moieties, as previously described^[35]. The effect of the five non-equivalent Si environments can also be observed (expanded view in **Figure S3**), with the cluster of signals arising from the quaternary carbons directly bonded to the five non-equivalent Si atoms being evident.

Finally, the FTIR spectrum of the styryl-functionalized T_{18} is compared to the spectra of the corresponding T_8 and T_{10} compounds in **Figure 7**, with the intensities of peaks in the spectra normalized against the styryl modes. Apart from the characteristic features arising from the styryl function (e.g. ring C-C stretching at 1601 cm^{-1} and the C=C stretching at 1630 cm^{-1}), the comparison highlights a broader full-width at half-maximum in the Si-O-Si mode region for the T_{18} compound compared to the other cages. The T_8 and T_{10} cages are both highly symmetrical with equivalent Si-O-Si species in each cage, resulting in relatively narrow Si-O-Si band profiles in each case. In contrast, there are five non-equivalent Si environments in the T_{18} cage, and the broader profile observed in this region is entirely consistent with the presence of such non-equivalent sites.

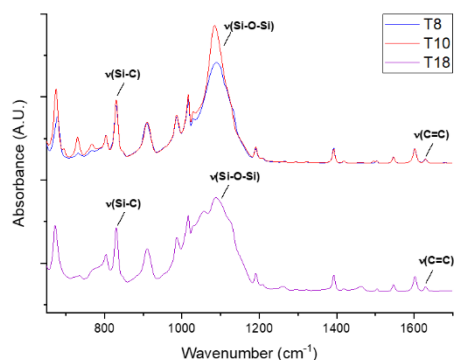


Figure 7. FTIR spectra of the styryl-functionalized T_8 , T_{10} and T_{18} cage silsesquioxanes.

Conclusions

In summary, we report the synthesis and characterization of an unprecedented styryl-functionalized T₁₈ cage silsesquioxane as a pure isomer, in which styryl groups are linked to all 18 vertices of the T₁₈ compound via the phenylene groups. Complementary analyses via MALDI mass spectrometry and multinuclear NMR enabled the particular isomer obtained to be identified from the nine possible isomers previously postulated for the T₁₈ system. To the best of our knowledge, this is the largest POSS compound synthesized and isolated to date as a pure, single-isomer product, thus extending the range of available organo-functionalized POSS compounds. Modelling studies are currently ongoing to better characterize the structure and properties of this novel cage silsesquioxane.

A ring strain model is presented that attributes observed ²⁹Si resonances in the styryl-functionalized T_n POSS family (where n=8, 10, 12, and 18) to non-equivalent Si atoms on the basis of their location in six-, five- and/or four-Si-atom rings (6^x5^y4^z, where x,y,z ≥ 0 and x+y+z=3). The model successfully predicted the speciation of non-equivalent Si atoms in other families of organo-functionalized T_n compounds, demonstrating its general applicability for assigning ²⁹Si resonances to silicon atoms in cage silsesquioxanes.

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Keywords: polyhedral oligomeric silsesquioxanes • styryl-functionalized POSS • T18 POSS cage • silsesquioxane • siloxane ring strain model.

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