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Frameworks Based on Polyhedral Oligomeric Silsesquioxanes

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FRAMEWORKS BASED ON POLYHEDRAL OLIGOMERIC SILSESQUIOXANES

A Major Qualifying Project Report:

submitted to the Faculty

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Degree of Bachelor of Science

by

_____

Oana-Raluca Luca

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Approved:

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Abstract

This work explores methods for the synthesis of polyhedral oligomeric silsesquioxanes (POSS) and their use in the design of organic and metal-organic framework materials. Specifically, this work focuses on the octameric POSS ($R_8Si_8O_{12}$) due to its unique cubic geometry, thermal stability, and multi-functionality. The Si_8O_{12} cage in POSS offers a rigid inorganic core on which additional organic functional groups can be placed in strategic locations. By tailoring the number and nature of these organic arms it is possible to generate silicious ligands previously unavailable for the framework materials. Three different POSS derivatives possessing cyano, pyridyl, and hydroxy functionalities are synthesized and applied as nodes for the preparation of extended materials using hydrogen bonding and metal-ligand interactions. Different methods of syntheses, characterization of POSS compounds, and attempts at the design of crystalline and polymeric materials are discussed.

1. Introduction

Polyhedral organic silsesquioxanes, also known as POSS compounds, are a class of silicon-oxygen compounds that contain a nucleus with $(SiO_{1.5})_n$ repetitive units in a perfect geometrical arrangement and organic fragments attached at some or all of the apex Si atoms. Because of their geometry, POSS compounds are also named spherosiloxanes. Allowed geometries of the Si-O arrangement permit n to differ from 6, to 8, 10, 12, 14, and 16.[1-3] The somewhat spherical core of these cage compounds is assigned the symbol T_n. The POSS compounds in all of these geometries have been isolated and their structures are shown in **Figure 1**.
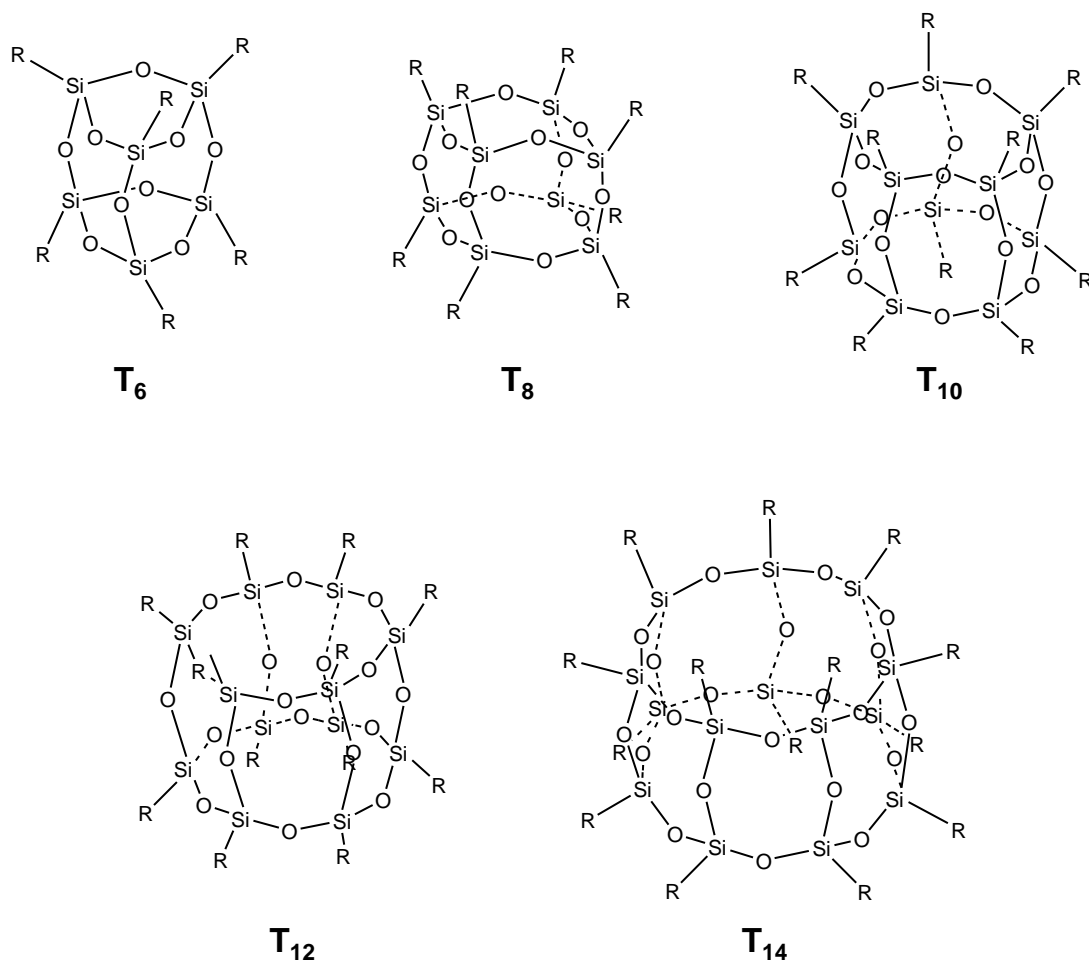
Figure 1. Molecular structures of silicious cores of T_n POSS. Notice the differences in geometries and the number and mutual orientation of organic arms (R groups) on different T_n cores.

It would appear that these molecules are cyclic analogues of 3, 4, 5, 6, 7 or 8 cyclotetrasiloxane rings fused together in a prismatic arrangement, while linear double chain silsesquioxane structures may also be regarded as homologous structures of the polyhedral T-type arrangements.

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The relative stability of these T_n compounds may be explained through geometry-induced strain that is generated by the distortion of the optimal Si-O-Si angle. The expected O-Si-O angle in any of the POSS compound is tetrahedral; while imposing the condition that all the Si-O-Si angles are equal in an ideal T_n geometry, calculations show that the Si-O-Si angles are 129.5^o, 148.5^o, 154°, 153° and 154 for the T_6, T_8, T_{10}, T_{12} and T_{14} structures respectively. The 155° optimal Si-O-Si angle is a direct indication of the low torsional strain and stability of the T_{10} compound. The slight deviation in angular geometry places the T_8 and T_{12} members of the T_n series at a somewhat lower stability, but still well within the synthetic reach. As one looks at the lower (T_6) and at the higher members of the sequence (T_6, T_{14}, and T_{16}), the strain becomes significant and accounts for the difficulty in preparing these polyhedral compounds.

Several synthetic methodologies and extensive literature resources are available for the prepration of T_8R_8. The focus of our work is therefore placed on the synthesis and characterization of octafunctionalized T_8R_8, whose core contains 12 O-atoms bridging eight apical Si-atoms, in an almost cubical arrangement. Our ultimate goal in this project is to employ these stable materials as octadentate ligands towards the construction of extended coordination and supramolecular frameworks. **Figure 2** shows some of the compounds we attempted to synthesize in this research.
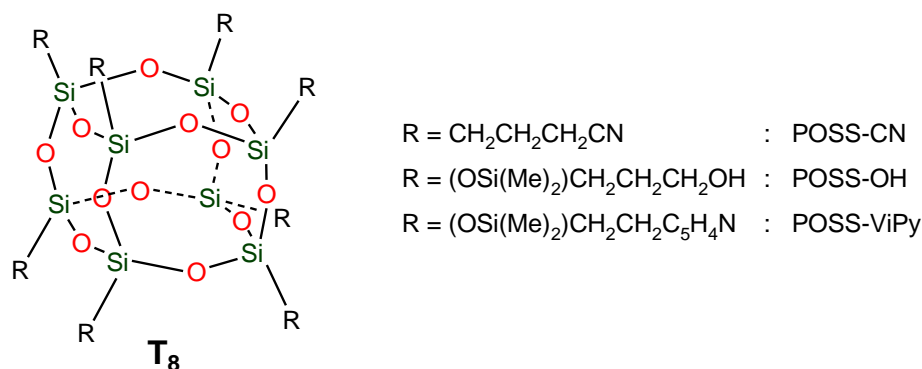

R = CH$_2$CH$_2$CH$_2$CN : POSS-CN
R = (OSi(Me)$_2$)CH$_2$CH$_2$CH$_2$OH : POSS-OH
R = (OSi(Me)$_2$)CH$_2$CH$_2$C$_5$H$_4$N : POSS-ViPy

Figure 2. T_8 POSS compounds synthesized in this work. The cyano POSS is prepared using condensation method (**Scheme 1**) and hydroxy and vinylpyridyl POSS are made from hydrosilylation reactions (**Scheme 2** and **4**).

2. Background in POSS Chemistry

The synthetic chemistry of siloxanes is extensive and an understanding of basic reactions in this realm is essential to the selection of appropriate processes for obtaining the POSS cage compounds. We have selected two distinct routes to the preparation of the POSS shown in **Figure 2**. In one method, the POSS are made from the siloxane condensation of monomers (**Scheme 1**). The reactions and methodologies are further elaborated in **Section 4**. It is useful and advantageous to avoid extensive synthetic procedures for the preparation of POSS. In the second method, we use hydrosilylation reactions (**Scheme 2**) on commercially available $T_8(OSiMe_2H)_8$, referred to as OSLO from here on, that would offer a synthetic process with fewer steps and potentially better yields.

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Scheme 1. Synthesis of T_8R_8 compounds by siloxane condensation used in Method 1.

1. $RSiX_3 + 3H_2O \rightarrow RSi(OH)_3 + 3\,HX$
2. $8\,RSi(OH)_3 \rightarrow (RSiO_{1.5})_8 + 12H_2O$
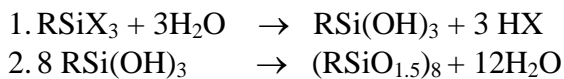
Scheme 2. Hydrosilylation reaction used in Method 2.
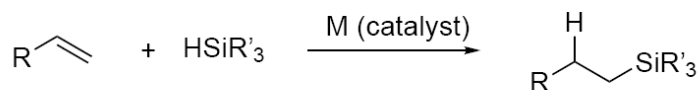
The condensation reactions used in Method 1 are sensitive to several factors. These include the nature of the solvent, concentration of the initial monomer, catalyst selectivity, identity of the substituent R, identity of the X groups in the monomer, the rate of water addition, pH, and the temperature and solubility of the polyhedral compounds formed. These factors do not operate independently and must therefore be considered simultaneously; making general assessments of the first method is therefore a difficult task.

In the case of the condensation of silanes (**Scheme 1**), it is known that the bulkier R groups favor the formation of incompletely condensed cages, whereas small R groups like H and Me normally favor the completion of the silane condensation. On the other hand, the nature of the X group is not significant to the reaction path, since X is depleted in (1) which usually fast. Halogenated silanes react more rapidly than the alkoxy analogues, but their use in synthetic procedures can be facilitated by the presence of a selective catalyst.[4] The mineral acids produced in step (1) may also perform the function of further catalyzing other condensation reactions.

POSS compounds with n=4 and 6 are selectively obtained through condensation in nonpolar and weakly polar solvents at 0-20 °C, while alcoholic solvents interfere with condensation and prevent the formation of the POSS cages. In a different situation, the synthesis of aryl POSS (e.g., T_8Ph_8) is favored by solvents such as benzene, nitrobenzene and pyridine at high temperatures.[3] Further views on the effects of solvent polarity are discussed in a recent review.[4]

Initial concentrations of $RSiX_3$ are also known to influence reaction kinetics of the condensations. While the extent of this concentration effect is not yet known, it has been inferred that a high initial monomer concentration favors polymerization as opposed to the oligomeric condensation. The rate of water addition to the reaction also remains a kinetic factor that has not yet been elucidated, water being observed to act as both reagent and catalyst. Temperature is an intrinsic reaction factor, but its influence on reaction kinetics and the solubilities of reagents and products has not yet been fully investigated. Nevertheless, some reports indicate that reactions carried out at high temperatures are more likely to yield completely condensed species.[4]

A recent review describes the effect of pH on the syntheses of POSS compounds using the first method.[5] Highly acidic environments are known to favor the formation of oligosilsesquioxanes, whereas in basic environments, polymeric species prevail.

The three known catalysts for hydrosilylation involving OSLO cages with available Si-H functionalities are Pt(dvs) (platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex), Pt(dcp) (platinum dicyclopentadienyl dichloride), and hexachloroplatinic acid. The efficiency of these three catalysts has been compared in the study of the reactions of OSLO and T_8H_8 with unsaturated compounds. The catalyst Pt(dvs) has been found to yield the least number of side products and has reaction times up to six times shorter than the other two Pt catalysts.

3. Synthetic Routes for T_8R_8 Compounds

3.1 Condensation of Trihalosilanes

3.1.1 Amberlite Catalyzed Synthesis of Octameric Silsesquioxanes

For the synthesis of and octacyano-T_8-silsesquioxane we performed a procedure similar to the one of octavinylsilsesquioxane.[6] In this procedure, acid Amberlite (RSO_3-H^+, IR-120 PLUS) was initially washed with concentrated HCl, followed by water and methanol. The washed resin was added to a round bottom flask with 150 mL methanol. Vinyltrichlorosilane (0.04 mol) was added to the flask and the mixture was stirred for 10 h. The methanol solution was decanted into a flask and allowed to evaporate. The small white crystals formed on the walls of the flask were dissolved and recrystallized from dichloromethane. Amberlite was removed from the flask and used in further experiments.

3.1.2 $FeCl_3$ Catalyzed Condensation Reaction

Anhydrous ferric chloride along with HCl were dissolved in methanol and toluene and stirred vigorously. Hexane solutions of trichlorosilanes were added slowly over a period of 9-10 h. The organic layer was transferred to a different flask and $CaCl_2$ was added and stirred overnight. After filtration, the solution was reduced by evaporation. Crystals were formed through slow evaporation of a dichloromethane solution.[7]

3.1.3 Synthesis of Silsesquioxanes by Heating at Low Pressure[8]

The trichlorosilanes were dissolved in diethyl ether. To this solution, 0.5 L of water was added slowly, while keeping the temperature constant (25°C) using a cooling bath. The ether solution was washed, concentrated over a steam bath and then heated at 22 mmHg pressure. The product of this process was a viscous oily material. 3.45 g of the oil with 7.7 g powdered sodium hydroxide was heated at 300-380 °C at 0.1-0.15 mmHg. After foaming and violent boiling, the volatile polymers were distilled at 200-270 $^{\circ}$C. The residue was dark and spongy. Crystals were obtained from recrystallization from acetone.

3.2 Condensation of Trialkoxysilanes

3.2.1 Synthesis of Octakis(3-mercaptopropyl)silsesquioxane $T_8(PrSH)_8$

To 0.4 moles of 3-mercaptopropylsilane was added to 1.8 L methanol along with 60 mL HCl.[4] This mixture was stirred for 5 weeks to get a colorless oily liquid. The solution was decanted and

the oil was washed with methanol. The remaining residue was dissolved in warm acetone. The solution was kept for three days at -15 °C until colorless crystals were formed. The solid product was washed with warm acetone and dried in vacuum.

3.2.2 Synthesis with TBAF[9-11]

The trialkoxysilane (1.75 mmol) was treated with a solution of tetrabutylammonium fluoride, TBAF (0.001 mmol in THF with 5% water). The solution was stirred for a day at room temperature after having added 40 mL dichloromethane. The product was obtained after removal of the solvent under vacuum. This reaction can be considered a mild hydrolysis method.

The crude products were either purified by column chromatography with SiO_2-hexane (for octaisobutyl POSS, octaphenyl POSS, octahexyl POSS, octaoctyl POSS or SiO_2-hexane-dichloromethane (for octa(4-carboxymethyl-3,3-dimethylbutyl) POSS). The pure products were all crystallized from a mixture of acetone and dichloromethane.

3.3 Functionalization of T_8R_8 Scaffolds

3.3.1 Chlorination of T_8H_8 and Synthesis of $T_8(OCH_3)_8$

Clorination of T_8H_8 was be performed in CCl_4 under light with a 95% yield.[12] The T_8Cl_8 product underwent further reactions with methyl nitrite. After sublimation and crystallization from toluene, the $T_8(OCH_3)_8$ product was be obtained in 45% yield.

3.3.2 Synthesis of Octakis(3-hydroxypropyl)silsesquioxane

The $T_8(PrOH)_8$ compound was synthesized through the reaction of T_8H_8 and allyl acohol in distilled dichloroethane.[13] A 2.78 mM solution of the hexachloroplatinic acid was used as catalyst. The resulting solution was refluxed under nitrogen for 2 days. The product was crystallized from 1,2-dichloroethane.

3.3.3 Syntheses from T_8H_8 or $T_8(Me_2SiHO)_8$ − Karstedt versus Spiers catalyst

$$H_8T_8 + 8\ CH_2=CH-CH_2-X \xrightarrow{\textbf{Pt(dvs)Cl}_2\ \textbf{or}\ \textbf{H}_2\textbf{PtCl}_6} T_8(Pr-X)_8$$
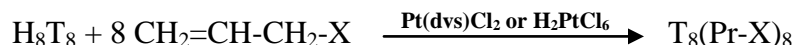
The role of the nature of reagents in the choice of the catalytic process is emphasized as vital in the use of α-substituted allylic compounds.[4,14] When X is a weak electron withdrawing group, the reaction undergoes full condensation and there are no side products when using a hexachloroplatinic acid catalyst (Spiers catalyst). However, when facing an electronwithdrawing group, such as -CN or -OPh, the use of H_2PtCl_6 yields a large amount of polymer side products and the reaction has no significant yield. To stop these side reactions, the use of large amounts of allylic coumpound, along with a very small amount of Karstedt's catalyst (Pt(dvs)) reported to give yields as high as 95% at 70°C.

3.3.4 Allylic Reactions with T_8Vi_8

3.3.4.1 Syntheses of Octa(γ-mercaptopropyldimethylmethoxysilane)silsesquioxane

$$T_8(CH=CH_2)_8 + 8SiHX_3 \xrightarrow{\textbf{Pt olefin catalyst}} T_8(CH_2-CH_2-SiX_3)_8$$
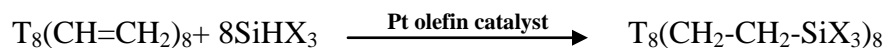
The T_8Vi_8 may also be used as scaffold for T_8 octafunctionalization reactions with silanes (trihalo or ethoxy) in the presence of a Pt-olefin catalyst. An example would be the reactions with γ-mercaptopropyldimethylmethoxysilane (free radical addition).

3.3.4.2 Hydrosilylation of OSLO with Allyl Alcohol and Acrylonitrile[15]

$$T_8(OSiMe_2H)_8 + CH_2=CH-CH_2-X \longrightarrow T_8(OSiPrX)_8$$

Hydrosilylation of Allyl Alcohol:[16] T_8(dimethylsiloxy)$_8$ (4.91 mmol) was placed in a 100-mL flask (Schlenk) previously equipped with a reflux condenser and a magnetic stirrer. 25 mL of toluene was added to dissolve the POSS compound and 49.1 mmol allylalcohol was added (1:10 ratio). The reaction flask was evacuated and refilled with N three times. 1.2mL Pt(dvs) (Karstedt's catalyst) was added through a syringe. The exothermic hydrosilylation was done in approx. 30 minutes. Triphenylphosphine was added to the two layers formed to deactivate the Pt catalyst and the mixture was further stirred for an hour. The product was present in the bottom layer. Excess allyl alcohol and toluene was removed under N stream and then under vacuum. Product was soluble in methanol, THF, acetone and dichloromethane. Low Pt concentration required.

Hydrosilylation of Acrylonitrile:[17,18] Acrylonitrile was added with a syringe (0.078 mmol) slowly to a stirred solution of $T_8(OSiMe_2H)_8$ (3.3g, 9.7 mmol) in 15mL anhydrous diethylether and three drops of hexachloroplatinic acid in DMF (Spiers catalyst) over 6 hours. Residual acrylonitrile and organic solvent were removed under N_2 and then under vacuum. The mixture was refluxed for 6 days. It was then cooled and filtered through a celite bed, washed with methanol and vacuum dried. Product was a white solid.

4. Experimental Methods, Results and Discussion

Several studies have reported attaining the monofunctionalization of POSS compounds. This was succeeded through corner capping reactions of the compounds resulting from the controlled hydrolysis-condesantion reactions of trialkoxy and trihalogenated silanes that yield heptameric reaction products.[3,19-20] Substitution reactions on the functionalized T_8 cage were also possible, as well as hydrolysis of the appropriate stoichiometric quantities of required trihalogenated silanes.[19] Reports are also available for the selective multifunctionalization of T_8H_8 and $T_8(OSiMe_2H)_8$ through Pt catalyzed stoechiometric alkene hydrosilylation reactions.[21]

4.1 Synthesis of POSS-CN

We began our work in the synthesis of T_8 compounds with octafunctionalized POSS-CN (Figure 2). The silane monomer used in the synthesis of POSS-CN was readily available, it had the ligand functionality (cyano) that did not interfere with the condensation process, and it contained a relatively non-bulky linear alkyl chain. We adopted the synthesis of octavinyl-T_8 for the synthesis of POSS-CN. Among the several synthetic strategies applied, the acid amberlite catalyzed reaction was proven to be successful in our hands. Acidic Amberlite (**Figure 3**) is a resin made of polystyrene beads that contain sulfonic acid functionalities on their surface; it facilitates the mild hydrolysis of trichlorosilanes so as to form condensation products.

Figure 3. Left: A photograph of acid Amberlite ion exchange resin showing the polystyrene beads. The surfaces of these beads contain sulfonic acid functionalities in the form of sodium salt. Right: Single crystals of POSS-CN viewed under crossed-polarizers.

For the synthesis (**Scheme 3**), acid Amberlite ($RSO_3\text{-}H^+$, IR-120 PLUS) was washed with conc. HCl, water and methanol. The washed resin was added to a flask that had 150 mL methanol. ω-Cyanopropyltrichlorosilane (0.04 mol) was added to the flask and the mixture was stirred at rt for 10 h. The methanol solution was decanted; after a while small white crystals (**Figure 3**) were formed on the walls of the flask. These crystals were further recrystallized from CH_2Cl_2 for X-ray data collection.

Scheme 3. Synthesis of POSS-CN using Method-1 and Amberlite catalyst.
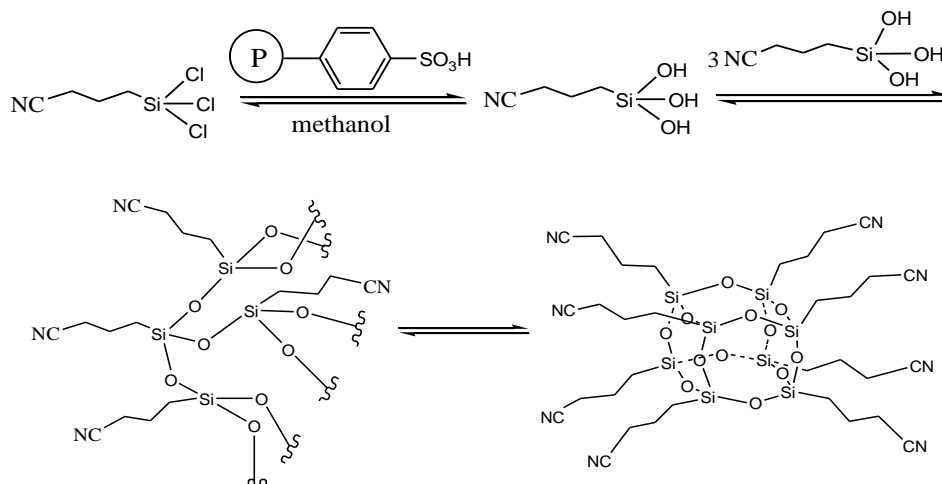
4.2 Structural Description of POSS-CN

The best single crystals of POSS-CN are typically small (0.10 mm in largest dimension) and have bipyramidal morphology. A single crystal of POSS-CN was carefully mounted on a glass fiber with the help of paratone oil and placed into a cold nitrogen stream. The X-ray data were collected on a Bruker Kappa-APEX II diffractometer using ω and ϕ scans. The data were integrated using Bruker SAINT and corrected for absorption by empirical methods using the program SADABS.

The crystals of POSS-CN belong to the space group P$\bar{1}$ with two symmetry independent molecules located on two distinct crystallographic inversion centers. The central T_8 cages of both molecules are fully ordered and maintain their cubic topology (**Figure 4**). There are a total of eight symmetry independent cyanopropyl groups, each adopting a different conformation (fully extended to partially folded) so that the overall packing efficiency is close to 68%.
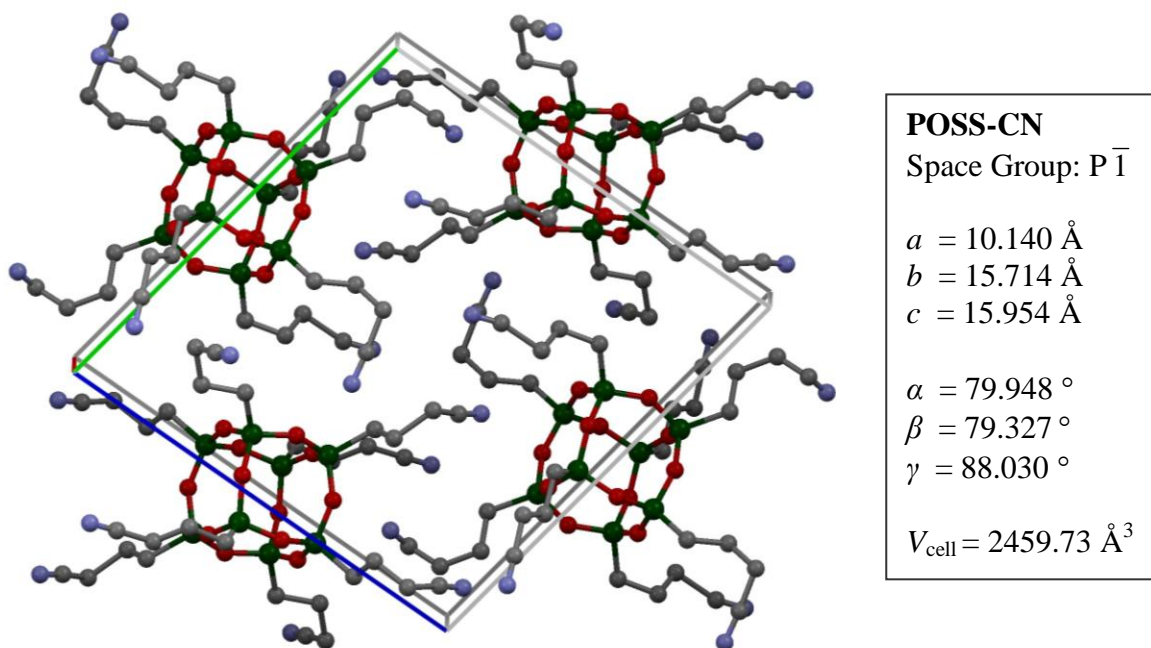

POSS-CN
Space Group: P$\bar{1}$

a = 10.140 Å
b = 15.714 Å
c = 15.954 Å

α = 79.948 °
β = 79.327 °
γ = 88.030 °

V_{cell} = 2459.73 Å^3

Figure 4. Crystal structure of POSS-CN showing the contents of the unit cell. Note the cubic geometry of the T_8 cage and different conformations of the cyanopropyl groups.

Each T_8 unit is connected to its neighboring T_8 units through C–H⋯N interactions. The presence of these interactions is inferred by the C⋯N close contacts. The overall structure (**Figure 5**) of this compound reveals that the symmetry independent molecules have slightly different packing patterns. Analysis of the packing by nodes (centroids of T_8 units) and nodal connectivities based on inter-nodal short contacts showed that the structure has an interwoven array of two simple cubic nets (**Figure 6**).
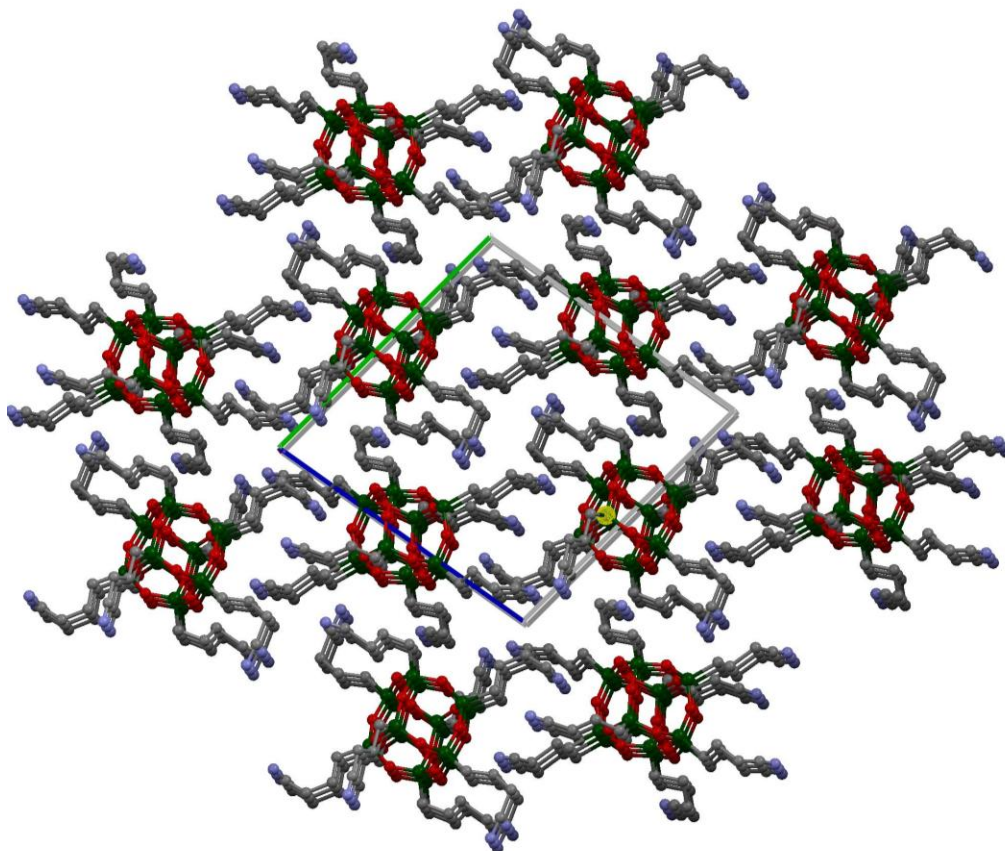
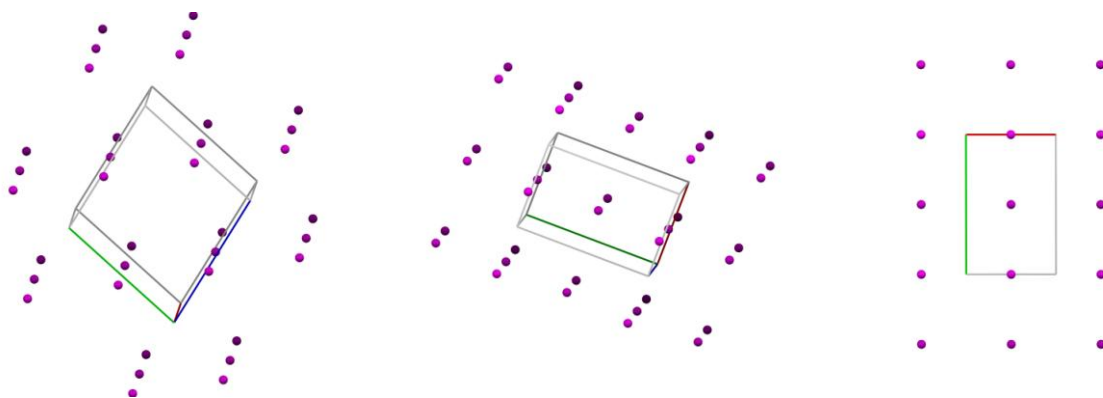**Figure 5.** Extended packing structure of POSS-CN.

Figure 6. Nodal representation of the structure of POSS-CN shown along *a*, *b*, and *c*-axes. Each pink sphere represents a T_8 cage.

4.3 Synthesis of POSS-OH

We have also tried to employ the second synthetic method discussed in **Section 2**. We worked with the pre-existing Si-O-Si cage of octakis(dimethylsiloxy)octasilsesquioxane (OSLO) and functionalized it with alkenic reagents. To date, we have been successful in completing this reaction with allyl alcohol. OSLO and allyl alcohol were taken 1:10 mol ratio in toluene. To this solution small amounts of Karstedt's catalyst (Pt(dvs)) were added under nitrogen purge. After ~30 min., PPh$_3$ was added to deactivate the Pt catalyst; the mixture was further stirred for an hour. The product was extracted from the bottom gel layer and crystals suitable for X-ray diffraction were grown in methanol.

Scheme 4. Synthesis of POSS-OH using Method-2 and OSLO.
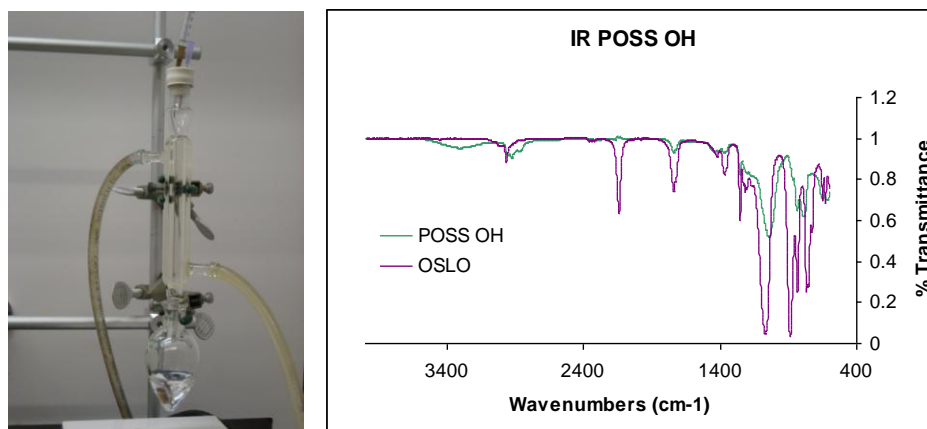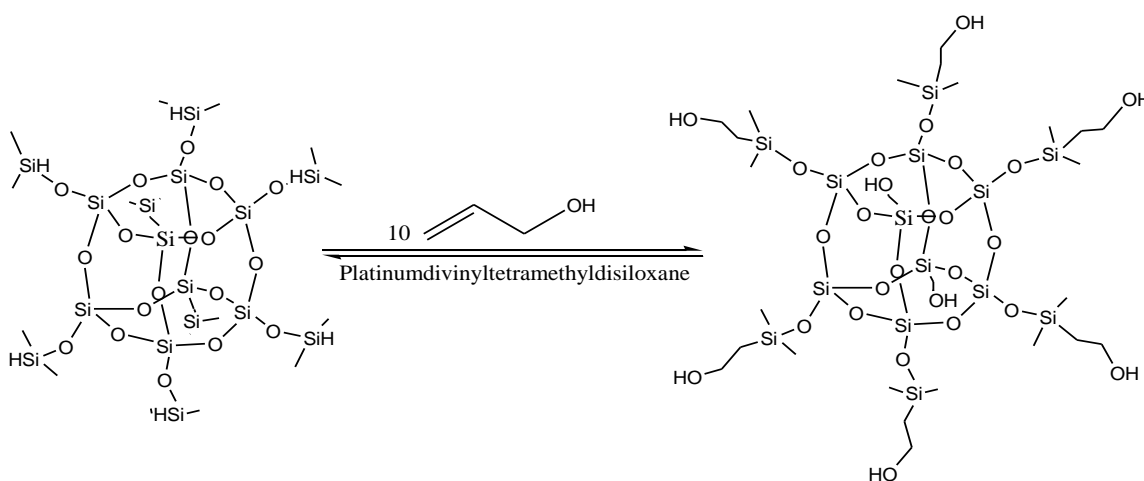

Figure 7. Left: Experimental Setup for the POSS-OH reaction. Right: IR Spectra of OSLO and POSS-OH; see text for details.

In the IR spectrum of POSS-OH, the peak at 780 cm^{-1} corresponds to Si-C stretch (**Figure 7**) and the broad absorption at 3100-3500 cm^{-1} represents O–H···O hydrogen bonding in the solid sate. In addition, the peak at 1254 cm^{-1} (corresponding to the O-Si-H band) that is distinct in the starting OSLO material has significantly diminished in the product, confirming the formation of the POSS-OH. The C-H stretches between 2900-3070 cm^{-1} have singnificantly changed after the functionalization, as well as Si-O-Si bands, now present at 1130 cm^{-1} for stretching, at 1030 cm^{-1} flexing of the cage and weak bending at 430-500 cm^{-1}.

4.4 Structural Description of POSS-OH

The crystal structure of POSS-OH has been determined using the same procedure as POSS-CN. Unlike the POSS-CN, this compound has only one symmetry independent molecule (**Figure 8**). At this stage the structure has not been fully refined because of the poor quality of the data; to the extent that this structure can be analyzed it can be represented as a simple cubic network in which the nodes of the network are coincident with the centroids of the T_8 cages.

POSS-OH
Space Group: P $\bar{1}$

a =11.728 Å
b =11.953 Å
c =13.718 Å

α =75.308 °
β = 82.427 °
γ = 84.318 °
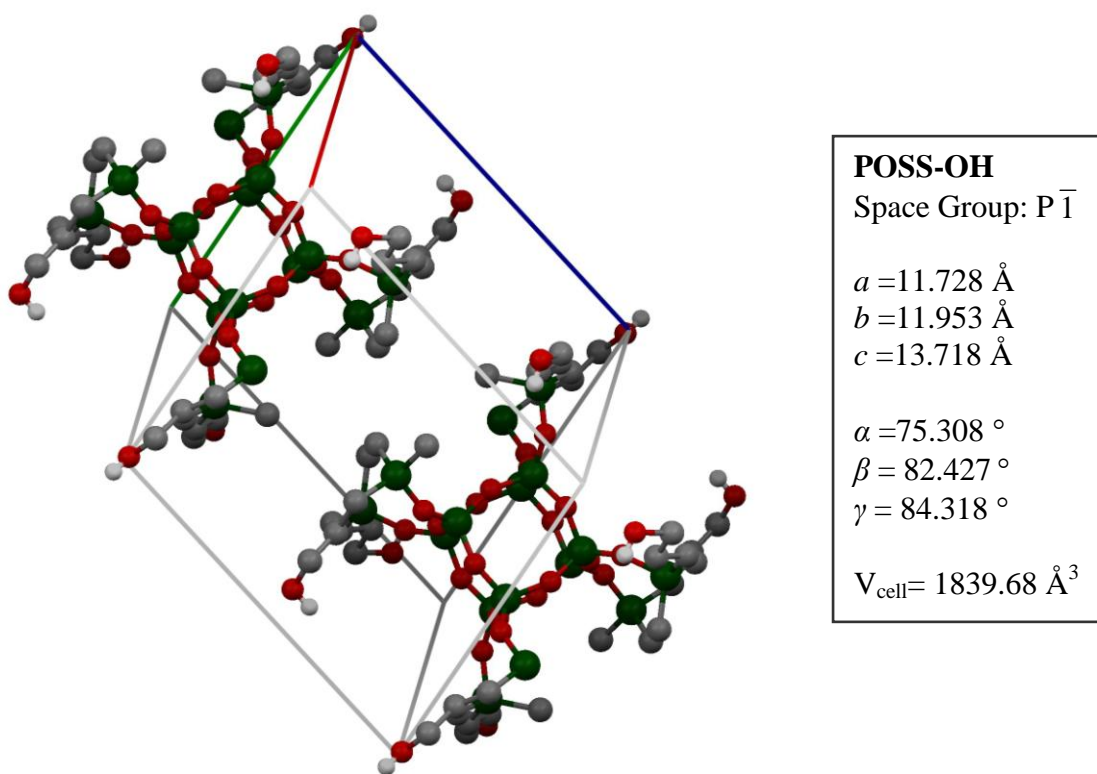
V_{cell}= 1839.68 Å^3

Figure 8. Crystal structure of POSS-OH showing the contents of the unit cell. Note the cubic geometry of the T_8 cage and different conformations of the hydroxypropyl groups. Note that there is only one symmetry independent molecule.

4.5 Attempted synthesis of POSS-ViPy

A synthetic procedure analogous to the previous POSS-OH methodology was attempted for the preparation of POSS-ViPy. Our target product was unfortunately has not yet been isolated. A rigorous mechanistic analysis of the Si-H functionalization reaction may bring to light the importance of the allylic carbon atom in the structure of the reactant, which would justify the unpromising behavior observed so far (separate crystallization of the starting material).

Figure 9. Experimental setup for the POSS-ViPy synthesis

4.6 Design and Synthesis of POSS Frameworks

We have attempted the synthesis of extended frameworks containing our products by several methods such as slow evaporation, vapor diffusion and solvothermal conditions. Slow evaporation experiments were carried out with specific covalent and metallic spacers.


Figure 10. Experimental setup for the solvothermal synthesis of frameworks.

We attempted to couple POSS-CN and POSS-OH with metal ions that are known to act as linear spacers such as Ag^+, Cu^+, as well as Zn^{2+}, Fe^{3+}, Co^{2+} who would provide octahedral coordination

modes. Coordination geometries of the latter group may be expected to provide discrete assemblies such as paddlewheel compounds with the large octadentate POSS ligand.

The POSS-OH cube has also been a central part in our attempts to exploit the aza-hydroxy and hydroxy-pyridyl synthons (**Scheme 5**) to allow for linear connectivities between the designed cubes.

Scheme 5. Hydrogen bonding in hydroxy···synthons used in this work.

Hydroxy-pyridyl synthon

Hydroxy- aza synthon
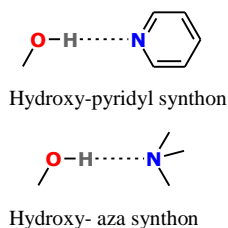
We have not yet succeeded in the synthesis of a crystalline extended framework. During our slow evaporations experiments we have, however, succeeded in obtaining polymeric materials. As many of the available characterization methods were not viable to this particular situation, only DSC (differential scanning calorimetry) and IR methods have been applied.
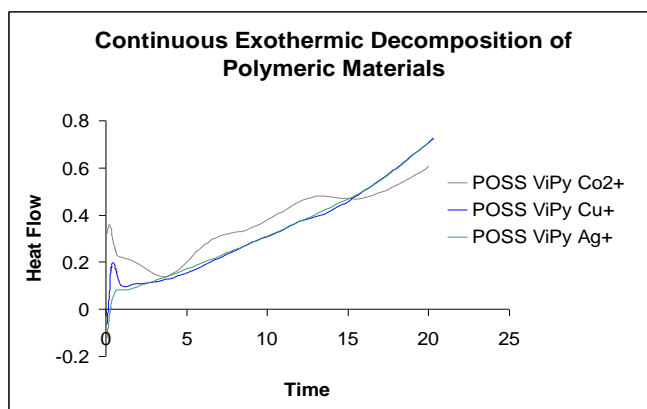
Figure 11. Experimental DSC traces obtained from the polymeric materials

We have noted that the polymeric materials obtained have either been elastomeric or ceramic; both types of polymers were subjected to DSC analysis. The DSC traces (**Figure 11**) reveal some unusual continuous exothermic decomposition throughout the heating range employed. We assumed that a continuous metal catalyzed polymerization reaction is being carried out. As seen in the figure, the behavior may be a function of the allowed coordination geometry of the metal cation.

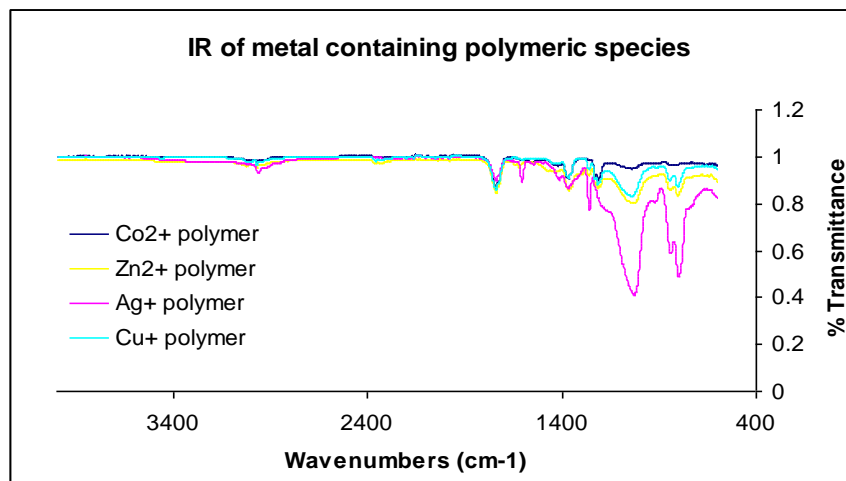**Figure 12.** IR spectra of metal containing POSS polymers obtained in solvothermal synthesis.

The IR spectra of the polymers (**Figure 12**), whose composition is yet to be determined, show a similar peak pattern. A significant Si-C stretch is present at 780 cm^{-1}, as well as the Si-O-Si stretching (1130 cm^{-1}), flexing (1030 cm^{-1}), and bending (500-400 cm^{-1}). The presence of the silsesquioxane cage is indicated by the peaks around 1400 cm^{-1} (symmetric Si-R deformation absorptions). The band below 3070 cm^{-1} indicated the presence of the aliphatic C-C bonds coming from the vinyl pyridine reaction. More structural investigations are needed to draw more specific structural conclusions.

5. Applications of POSS compounds

The fundamental aspect of this work is the application of POSS based materials. Much research has focused on obtaining polymers with custom-made properties. POSS monomers are unique because they contain relatively large, robust Si-O cages that can be functionalized according to their intended incorporation in the thermoplastic resin large-scale preparations. This would be feasible without modification of the manufacturing process.

POSS based polymers are known to show increased glass transition and decomposition temperatures, a fantastic oxygen permeability and reduced flammability and heat evolution. This makes them excellent candidates for enhancing polymers, such as polyurethanes by increasing wear-and-tear resistance. Other applications of these materials are also pursued by both US Airforce and National Aeronautics and Space Administration.[22]

The US Airforce has identified the atomic oxygen resistance of POSS polymers (they form a glassy, passivating SiO_2 layer that prevents further decay of the underlying polymer in the hyperthermal presence of atomic oxygen / Low Earth Orbit condition simulations). NASA is also researching their properties as flame retardants and is considering using these materials as film coatings for cabin items during space missions.

Epoxy resins based on POSS analogues are being studied for their potential as insulating "glues" to hold together the several metal layers of substrate printed circuit boards. These resins would also offer a response to the demand for materials with coefficients of thermal expansions between the values of the Si chip and the circuit board (to minimize shear stress). Silsesquioxanes based resins are expected to offer an alternative to the expensive doping of the traditional epoxy resin with silica nanoparticles.[23]

The safety of the use of silicone-containing materials in the context of biomedical devices needs to be addressed. Proteins have been known to bind to silicone surfaces; therefore compromising results of silicone based medical devices. Along with this, protein deposition on silicone-based contact lenses is known to reduce both their comfort and medical performance. The nature of these interactions has been deemed somewhat controversial, but a solution to address this issue is necessary. Functionalized silsesquioxane polymer coatings allow for inferences to correlate POSS/silicone–protein interactions and offer information about the distinct nature of these weak, but important interactions.[24]

Their different mechanical and chemical properties bring the POSS cages forward as a solution to the problem of higher temperature and oxidation resistance materials that the industry is currently seeking. POSS monomers offer a simple alternative to forming high-resistance and tough hybrid materials (between ceramics and polymers). They are also available as both blendable resins (ceramics), as well as simple organic monomers (polymers). They are easily soluble in most organic solvents and are highly thermally stable. They can be easily polymerized using radical, condensation, ring opening polymerizations (standard organic polymerization reactions).

On the other hand, a porous three-dimensional array of cubes may harbor extensive catalytic properties. Metal organic frameworks are being explored for their ability to participate in chemical reactions[25] because of their catalyst encapsulation properties. It may be that the extended framework structures based on POSS allow for a more efficient entrapment of the desired catalyst. These properties need to be further investigated.

One of the current trends in research involving metal-organic frameworks is their exploration towards gas sorption, storage and separation.[26-28] While their sorption rates may be promising,[29] optimal structural, thermal, and mechanical stability has not yet been achieved. We believe that the coordination and hydrogen bonded POSS polymeric materials[30] may produce a more efficient gas storage material, due to the high porosity and stability of the Si-O cages incorporated in the frameworks.

6. Summary and Conclusion

We explored two distinct approaches for constructing the scaffold of POSS derivatives. In one method, the POSS scaffold is built from eight separate linear trialkoxy or trihalo silanes. In the second method, a pre-built cubic core is used for further substitution reactions. In the first method, we explored four different types of reactions. These included processes such as heating in trace amounts of water, TBAF activation, and catalytic condensation. In our hands, the

condensation reaction with acidic Amberlite resin gave highest yields with two different POSS derivatives. In the second method, we used the pre-built core of octakis(dimethylsiloxy)-octasilsesquioxane (OSLO) to perform C-hydrosilylation/Si-H bond functionalization. Using this method, we added alkenic functional groups on the cubic core of OSLO. Specifically, we prepared POSS-pyridyl and POSS-OH derivatives and characterized them with IR spectroscopy. We also determined the crystal structures of two separate octafunctionalized POSS derivatives. Both these compounds have functionalities, cyano and hydroxy, that are useful starting groups for forming metal-ligand or hydrogen bond synthons. Our preliminary work on creating coordination polymers using POSS derivatives and metal cations (Ag^+, Cu^{2+}, Co^{3+}, Zn^{2+} etc) led to both elastic as well as ceramic type polymers. We are currently exploring the effect of metal ion on polymerization and also on the thermal properties of these polymers. Our attempts to create hydrogen bonded complexes of POSS with pyridyl acceptor ligands did not yet yield crystals suitable for X-ray diffraction analysis. We believe that the functionalized POSS compounds described here will pave the path toward a new class of framework materials for applications such as gas sorption and storage.

7. Bibliography

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