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Dumbbell-Shaped T₈-POSS with Functional Organic Linkers.

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Abstract: New dumbbell-shaped octasilsesquioxanes (T₈-POSS) are obtained by the condensation of organobridged silane precursors with partially condensed T₇-triol. The synthesis based on corner-capping proceeds under mild reaction conditions (60°C in toluene) upon a nucleophilic fluoride-catalyzed condensation of the T₇-triol with the alkoxy-silyl organics. Two dumbbell-type T₈-POSS, one with a non-symmetrical urea-thiourea linker and the other one with a symmetrical malonamide linker, are described. Their formation is monitored by FTIR, their structures are investigated by NMR spectroscopies (¹H, ¹³C and ²⁹Si) and confirmed by mass spectrometry.

Introduction

Organosilsesquioxanes are of general formula RSiO_{1.5} where R represents an organic group. They are easily obtained by hydrolysis-condensation of trichlorosilanes or trialkoxysilanes, most often catalyzed by a base, an acid, or a nucleophile such the fluoride anion.^[1,2] Using alkoxy-silanes may be beneficial, since only the corresponding alcohol group is released compared to corrosive HCl which evolves upon hydrolysis of Si-Cl bonds in the case of chlorosilanes. In addition, while base-catalyzed or acid-catalyzed reactions may be quite aggressive, fluoride-catalyzed reactions can be conducted in neutral medium. The uncontrolled hydrolysis of organotrialkoxysilanes often leads to undefined polymeric species and many efforts have been devoted to achieving well-defined molecular silsesquioxane structures. Two families of such compounds have been identified: fully and partially condensed silsesquioxanes. Indeed well-defined polyhedral or cage-like molecular structures known as polyhedral oligosilsesquioxanes (POSS)^[3] are now commonly prepared by the hydrolysis of trialkoxysilanes. These compounds are denoted T_n-POSS depending on the number of silicon atoms in the polyhedral cage (e.g. T₆, T₈, T₁₀, T₁₂, T₁₄, etc), with T₈ being the most commonly obtained structure.^[4] Ladder-like silsesquioxanes, prepared via a stepwise synthesis, are also known, eg. with gecko-like tricyclic shapes and caterpillar-like pentacyclic forms.^[5,6] In the case of partially condensed silsesquioxanes, several cyclic systems have already been isolated with good yields. As depicted in Figure 1, the cyclic trisiloxane^[7] and tetrasiloxane (Figure 1a and Figure 1b), respectively)^[8] both consist of isomers which are not easily separated. The last two exhibit only silanol moieties, which are produced in high yields^[9–11]

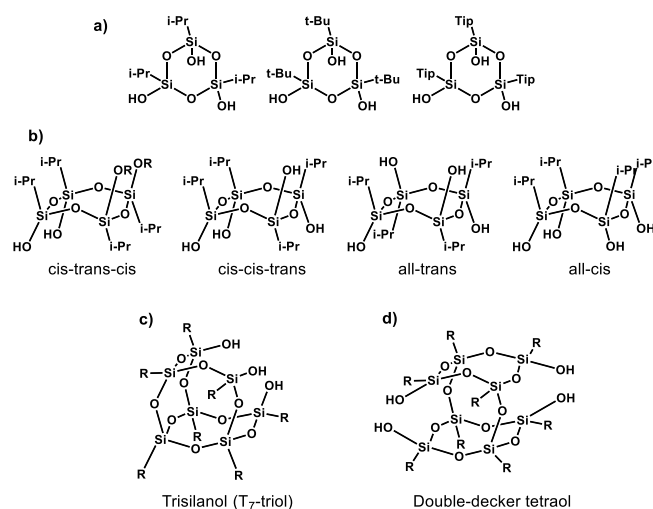
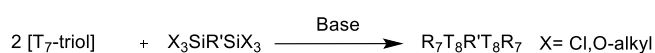


Figure 1. Partially condensed silsesquioxanes.

For the trisilanol (T₇-triol), (Figure 1c), the corner-capping reaction is often exploited to obtain monofunctional T₈-POSS^[12]. The sandwich-like tetraol (Figure 1d) was also more recently used to proceed by end-capping leading to “double-decker” silsesquioxanes.^[13,14]

Since T₈-POSS-based structures are mostly obtained POSS, it has predominantly been used and exploited in organic-inorganic hybrid materials for proton-exchange membranes,^[15] catalyst supports,^[16] polymers reinforcement,^[17] encapsulation^[18] and photoluminescence devices^[19]. POSS can be simply embedded as functional, single cage-like entities in a polymeric segment or within a hard template such as lamellar silica. Moreover, it can also be used as a building block for structured assembly. Recently, controlled reaction of *t*-butyl alcohol with the octahydridosilsesquioxane, a bifunctional T₈-POSS, was reported, with only two hydrido groups being substituted by two *t*-butoxy groups, thus leading to three isomers which could be purified.^[20] These dual functionalities at the silicon sites should open the way to constructing new materials made uniquely of T₈-POSS structures. T₈-POSS can also be arranged into particular structures such as dumbbell-shaped silsesquioxanes. These were described for the first time in 2004.^[21,22] However, until now, there were only limited reports on the synthesis of dumbbell-shaped T₈-POSS.^[21-24] Moreover, single-crystal X-ray structures were already obtained and their thermal stability studied.^[23,24] Dumbbell-shaped T₈-POSS can be prepared by using three main synthetic pathways: (i) hydrosilylation^[25] with either a telechelic double-bonded linker or another telechelic linker (e.g. dicarboxylic end groups) reacting with amino groups on POSS;^[26] (ii) cross-coupling of POSS bearing a functional terminal triple bond with POSS bearing an aryl halide (I or Br), through Sonogashira's reaction.^[27] In this case, non-symmetrical dumbbell POSS can be envisioned; and (iii) by corner-capping reaction of partially-condensed silsesquioxane T₇-triol (Scheme 1) with bistrichloro- or bistrichlorosilanes. The partially condensed silsesquioxane species are known since the work of Brown and Vogt in the mid 60's^[9] and this synthetic pathway has rarely been exploited.^[28]



Scheme 1. Corner capping of partially condensed POSS.

To date, most of the known substituted partially condensed POSS have been described by Feher et al.^[12] seeking model systems for application in catalysis. The corner capping method involves the reaction of a partially-condensed T₇-triol with a chloro- or an alkoxy silane in the presence of a catalytic base such as triethylamine (NEt₃) or tetraalkylammonium hydroxide (NEt₄OH) (Scheme 1). In the case of the synthesis of dumbbell silsesquioxanes, trichlorosilanes were initially the preferred reagents for this specific type of reactions due to their high reactivity. Indeed, Naka et al.^[29] developed dumbbell-shaped trifluoropropyl-substituted POSS derivatives linked by simple aliphatic chains with various lengths by using the combination of trichlorosilane and trimethylamine, with a yield of up to 70% being achieved. Triethoxysilanes are also widely used for the synthesis of dumbbell silsesquioxanes. In 2014 and 2015, Bottino et al.^[23,24] described the synthesis of dumbbell-shaped cyclopentyl-substituted POSSs linked by aliphatic and aromatic bridges, using triethoxysilanes combined with tetramethylammonium hydroxide, with an average yield of 78 %. Base-catalyzed synthesis of fully condensed POSS has been successful in creating many new molecules with a variety of R-groups. Moreover, fluoride anion can also be used as a catalyst to favor the corner-capping-condensation reaction. Indeed, Bassindale et al.^[30] have successfully used tetrabutylammonium fluoride (TBAF) under scarce-water hydrolysis conditions as a catalyst, to increase the fully-condensed POSS yield when using triethoxysilane compounds. Compared to the first two synthetic pathways, the corner-capping reaction is a straightforward, single-step reaction while the former ones are performed in two steps.

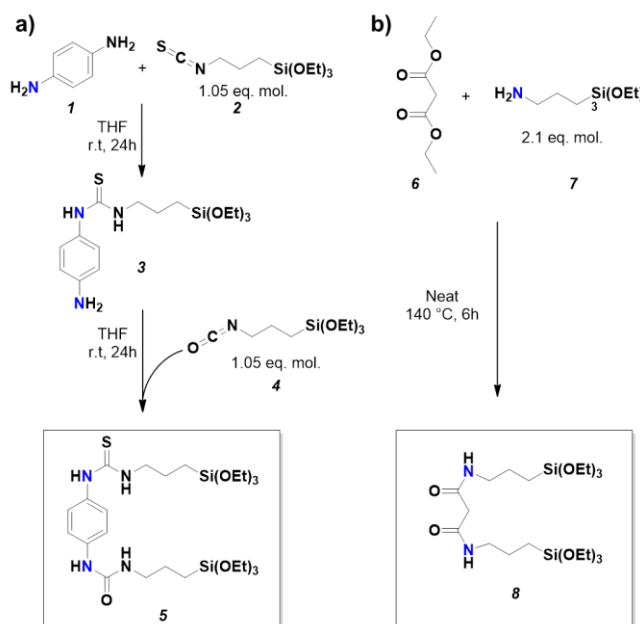
In this work, we report the successful syntheses of two new dumbbell-shaped T₈-POSS derivatives using the corner-capping method and fluoride anion (TBAF) as catalyst. Through this way, functional systems are shown to be easily accessible. Indeed, by using a non-symmetrical bis-silylated precursor, a dumbbell T₈-POSS bearing a urea-thiourea linker was obtained. Moreover, a bis-silylated malonamide precursor was used to synthesize a symmetrical dumbbell T₈-POSS.

Results and Discussion

Synthesis of the urea-thiourea bistrichlorosilane linker

The synthesis of the urea-thiourea precursor was based on the preparation of the bis-urea analogue described by Moreau and co-worker^[31] in 2001, which was obtained by reaction of 1,4-diaminobenzene with two molar-equivalents of 3-isocyanatopropyltriethoxysilane. In this case, there was no issue with the selectivity of the reaction, as the resulting bis-urea compound is symmetrical. Recent work within our group demonstrated that in the case of the corresponding thiourea reagent, the reaction did not proceed to completion for the substitution of both amino groups with urea derivatives.^[32] Instead, only one amino group was selectively transformed into the thiourea function, leaving the other one intact (Scheme 2a) to give the intermediate amino-urea compound **3** (90% yield). This selectivity is due to the deactivation of the second amino group after formation of the thiourea fragment. In a second step, 3-isocyanatopropyltriethoxysilane (**4**) reacted with **3** to give quantitatively the expected urea-thiourea precursor (compound **5**) with an overall yield of 85 %. Compared to the bis-urea compound,^[31] where mainly the self-structuring of the material was targeted through the H-bonding within the urea groups, compound **3** contains two functions (urea and thiourea) and thus can play a dual role due to these two different functions: urea, on one hand, can direct and induce structuring by H-bonding^[31] but it can also play the role of

complexing agent to bind heavy ions such as lanthanides.^[33] On the other hand, thiourea will have a targeted role for complexing transition metal cations (not discussed in this work).



Scheme 2. a) Synthesis of urea-thiourea linker, **5**. b) Synthesis of malonamide linker, **8**.

The synthesis of the linkers was followed by NMR spectroscopy (^1H , ^{13}C and ^{29}Si). The ^1H NMR spectrum of **5** (Figure 2), shows two sets of signals at 6.51 and 8.03 ppm and at 5.48 and 7.95 ppm which are assigned, respectively, to the two distinct NH protons of the thiourea and of the urea groups.

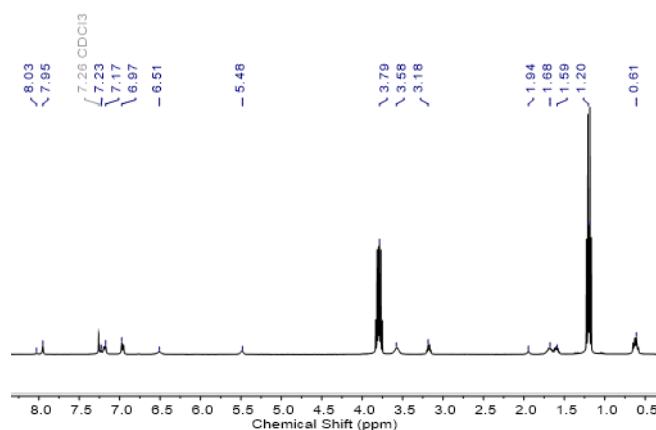


Figure 2. ^1H NMR spectrum of the urea-thiourea bistrithoxysilane linker **5** in CDCl_3 .

The AB system is unambiguously attributed to the aromatic protons (6.97 and 7.17 ppm) indicating that the urea and thiourea groups have different electronegativity which affects and differentiates the aromatic protons. Indeed, oxygen has an electronegativity of 3.44 while sulfur possesses an electronegativity of 2.58. This effect is even visible in the ^{29}Si spectrum (Figure 3), which clearly exhibits two sharp peaks at -45.43 and -45.86 ppm assigned, respectively, to the thiourea-side and urea-side silicon atoms. The ^{13}C NMR spectrum exhibits fourteen peaks consistent with the following assignments: 180.8 (C=S), 155.89 (C=O), 138.37, 134.07, 126.85, 120.87 (C_{ar}), 58.6, 18.41 (OCH_2CH_3), 58.5 (CH_2NHCS), 42.77 (CH_2NHCO) 23.61, 22.64, 7.78, 7.71 (NCH_2CH_2).

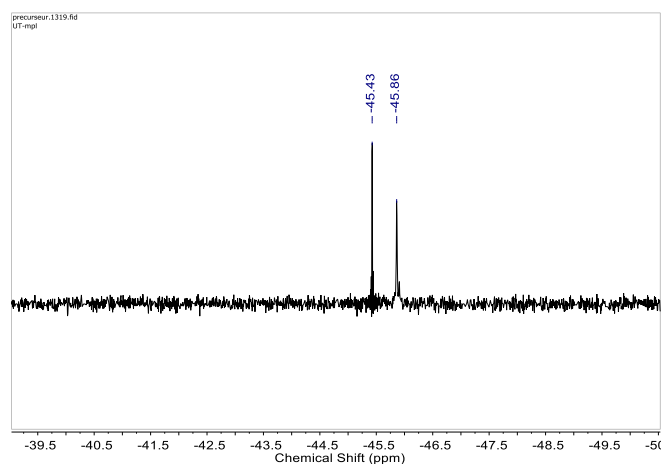


Figure 3. ^{29}Si NMR spectrum of the urea-thiourea linker **5**.

Synthesis of the malonamide bistrithoxysilane linker

Syntheses of malonamide compounds are usually based on the high reactivity of acyl chloride, and are performed under strict conditions as described by Conocar et al.^[34] in their work on new hybrid silica-based materials for the solid/liquid extraction of actinides. Indeed, malonamides are good complexing agents for actinides and lanthanides.^[35] Lately, a modified synthesis of silylated malonamide groups, based on tetraethyl ethanetetra-carboxylate, has been developed by Freitas et al.^[36] to obtain luminescent hybrid materials. In our work, we used diethyl malonate as a starting molecule (Scheme 2b). The synthetic route consists in two consecutive substitution reactions. The ether group of the malonate is substituted by APTES to form the malonamide group. By optimizing the reaction which was done at 140 °C for 6 h in a sealed flask, we obtain compound **8** with a high yield of 90% after purification. Although the temperature of the reaction is higher than the condition used with acyl chloride, no decomposition occurred and the purification only involves evaporation of the excess of APTES and other volatiles at 100 °C for 24 h under vacuum. The synthesis of the linker was investigated by liquid NMR (^1H , ^{13}C and ^{29}Si). The ^1H NMR spectrum (Figure 4) exhibits a chemical shift at 7.30 ppm corresponding to the NH proton of the amide function. The ethoxy protons are assigned to the chemical shifts at 3.78 and 1.17 ppm. The sharp peak at 3.1 ppm is attributed to the two protons of the central carbon of the malonamide group and finally the three propylene CH_2 groups are located at 3.21, 1.59 and 0.58 ppm, with respective integration of 1:6:9:1:2:2:2, as expected.

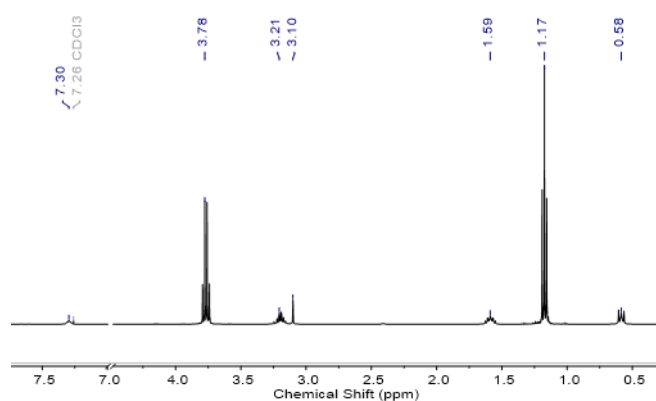


Figure 4. ^1H NMR spectrum of the malonamide bistrithoxysilane linker **8** in CDCl_3 .

The ^{13}C NMR spectrum shows seven peaks assigned to $\text{C}=\text{O}$ (167.45), CH_2 and CH_3 of the ethoxy groups (respectively at 58.5 and 18.34), central C (42.95) and the propylene carbons (42.12, 22.81 and 7.85). The corresponding ^{29}Si spectrum (Figure 5) exhibits a single peak at -45.86 ppm which corresponds to a triethoxysilyl group bonded to a carbon sp^3 , indicating that no hydrolysis occurred even at temperatures as high as those of the synthesis (140 °C).

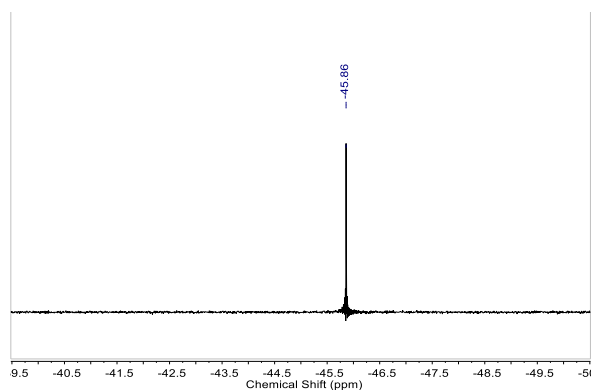
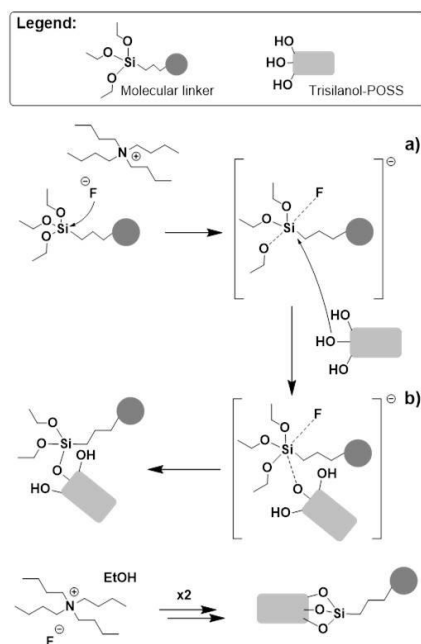


Figure 5. ^{29}Si solution NMR spectrum of the malonamide bistrithoxysilane linker **8**.

Synthesis of the dumbbell-shaped POSS

In 2003, Severn et al.^[37] reported the synthesis of silsesquioxane-bonded zirconocene complexes by reacting partially condensed silsesquioxane with triethoxysilane-substituted molecules to afford the corner-capped POSS substituted compound. Applying this synthetic route to compounds **5** and **8** failed to produce the corresponding dumbbell-shaped POSS and no reaction occurred probably because the reactivity towards partially condensed T_7 -triol is lower than these with the zirconocene derivative.



Scheme 3. Fluoride-catalyzed condensation of alkoxy silane. a) Reversible formation of a pentavalent silicon intermediate. b) Nucleophilic attack of the silanol on the hypervalent silicon leading to nucleophilic substitution by proton transfer and elimination of Et-OH.

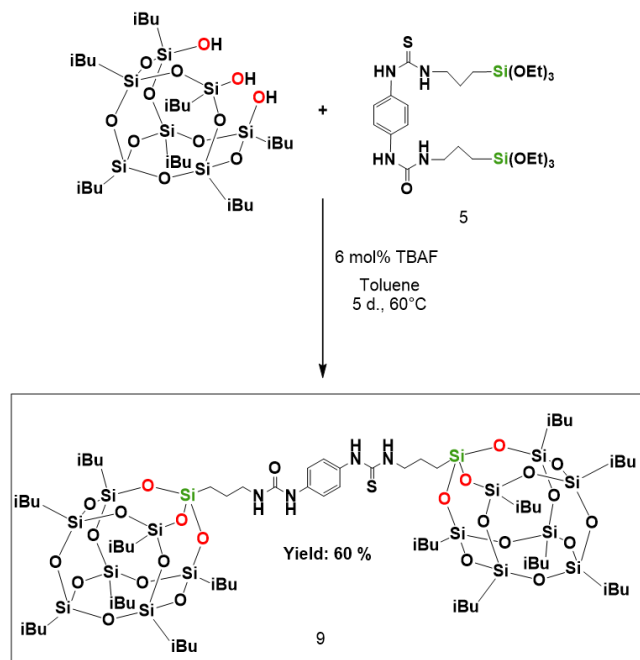
Therefore, in the case of the urea-thiourea compound **5** and of the malonamide compound **8**, a catalyst was required to activate the corner-capping reaction. Three catalysts were tested and compared in terms of efficiency: (i) acetic acid as an acid-based catalyst; (ii) triethylamine as a base catalyst; and (iii) tetrabutylammonium fluoride (TBAF) as a nucleophilic-based catalyst.

In contrast with literature reports for the synthesis of dumbbell-shaped T_8 -POSS in the presence of triethylamine as base catalyst, the reaction did not occur, irrespectively of the linker unit employed (urea-thiourea or malonamide). Likewise, no reaction was observed with acetic acid. Only TBAF allowed the reaction to proceed. Indeed ^1H NMR was found to be a good tool to monitor the corner-capping reaction. The disappearance of the ethoxy groups of the linker precursor (peaks at 3.78 (O- CH_2 - CH_3) and 1.17 ppm (O- CH_2 - CH_3)) together with that of the Si-OH from the partially condensed silsesquioxane demonstrates that the reaction was proceeding.

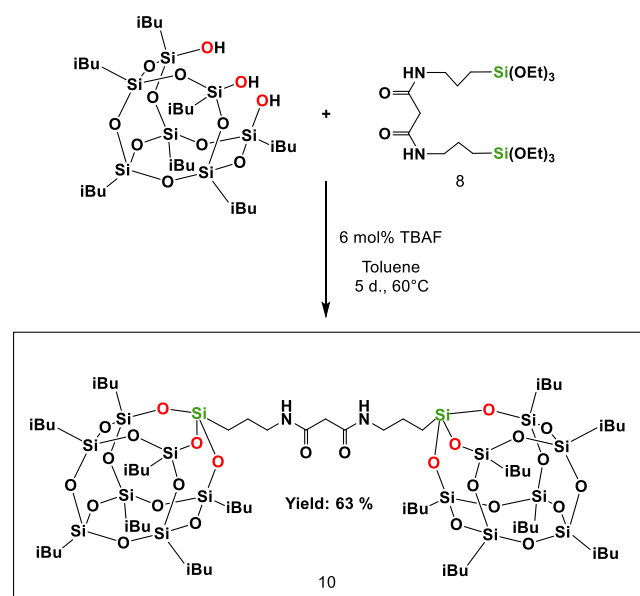
Thus, fluoride anion was selected as catalyst. In this case, it is likely that the hydrolysis-condensation reaction occurs via the fast and reversible, formation of a pentavalent silicon anion intermediate^[1,38] (Scheme 3a) that stretches and weakens

the surrounding Si-OEt bonds which thus becomes more reactive towards electrophiles. The subsequent condensation step therefore corresponds to the nucleophilic attack (Scheme 3b) of the hydroxyl group present in the trisilanol T7-triol on the hypervalent silicon species, leading to the nucleophilic substitution by proton transfer and elimination of ethanol. Due to the proximity of the other silanols in the partially condensed intermediate and since F⁻ fits reasonably well in the cubic system,^[30] it is reasonable to expect that the corner-capping would proceed accordingly, thus favoring the dumbbell formation.

Schemes 4 and 5 represent the synthetic route to dumbbell compounds **9** and **10** obtained, with compounds **5** and **8**, respectively, used as functional linkers with TBAF as catalyst and toluene as solvent. The reaction, which was monitored by ¹H NMR, proceeded for five days, with complete disappearance of the peaks of the ethoxysilane observed at that time.



Scheme 4. Synthesis of urea-thiourea dumbbell, **9**



Scheme 5. Synthesis of malonamide dumbbell, **10**

Following the complete disappearance of the ethoxy groups, ^{29}Si NMR spectra (Figures 6 and 8) were measured on the crude product, to confirm the full condensation of the triol and capping of the corner. As found in Figure 6, the starting reagents (triol and bistrithoxysilyl linker, respectively spectra 6b and 6c) were not observed in the spectrum of the crude product (6a), indicating that the reactant was fully reacted.

The ^{29}Si NMR spectrum of **9** (Figure 6a) exhibits five peaks in a very narrow range from -67 ppm to -70 ppm. The three central peaks (see inset) at -67.61 ppm (red dot), -67.83 ppm (purple dot) and -67.91 ppm (blue dot) correspond to the chemical shifts of the silicon atoms linked to the isobutyl groups.

Two additional weak peaks are also present in the spectrum 6a (see inset). These are located at -67.09 ppm (green dot) and -68.91 ppm (yellow dot) and are assigned to the silicon atoms directly linked to the thiourea side and to the urea side, respectively, of the bridging linker. The presence of these two weak peaks is due to the non-symmetry of the urea-thiourea bridging unit and is consistent with a successful corner-capping of the POSS to form the dumbbell silsesquioxane.

The FT-IR spectrum shows the extinction of the band due to Si-OEt (1065 cm^{-1}) for compound **9** (Figure 7e). This observation in addition to the increase in the intensity of the band (1089 cm^{-1}) due to Si-O-Si stretching vibrations of POSS show that the capping has occurred.

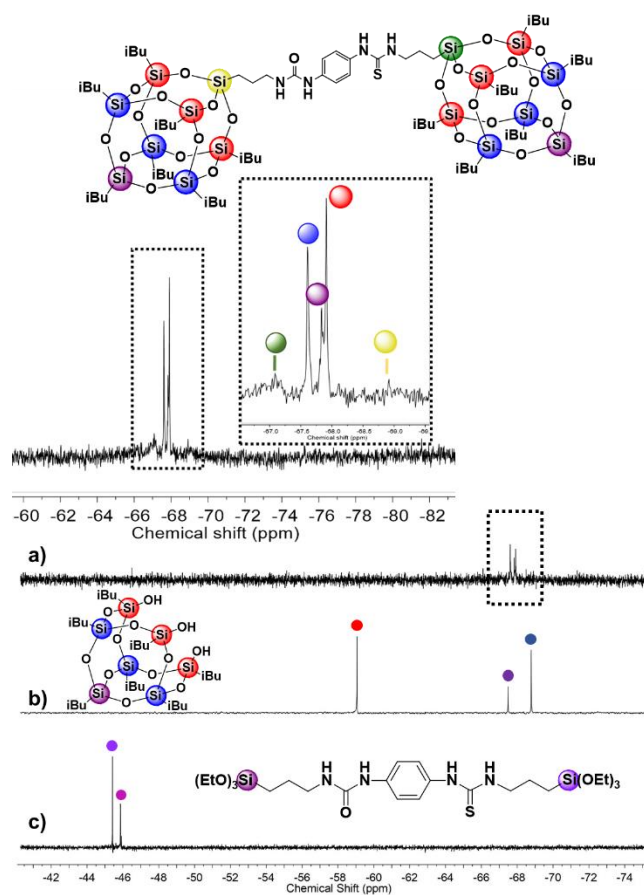


Figure 6. ^{29}Si solution NMR spectra of a) urea-thiourea dumbbell, **9**, b) partially-condensed T_7 -triol and c) urea-thiourea bistrithoxysilane linker, **5**

Moreover, the appearance of the two bands due to Si-C antisymmetric vibrations (950 cm^{-1}) and Si-C symmetric vibrations (762 cm^{-1}) within the spectra of compound **9** (Figure 7e) is attributed to the grafting of the linker to the partially condensed T_7 -triol.

In addition, the three bands at around 3290 cm^{-1} are assigned to stretching vibrations $\nu(\text{NH})$ from the urea and thiourea groups. While this NH vibration is clearly seen in the case of the urea-thiourea linker (Figure 7c) it is much less intense in the urea-thiourea dumbbell (Figure 7b). This may be attributed to the possible stronger H-bonding between the urea-thiourea groups in the former compared with the dumbbell compound holding two bulky POSS moieties at both ends of the latter structure.^[32] The bands due to the stretching vibrations $\nu(\text{C}=\text{O})$ at 1654 cm^{-1} and $\delta(\text{NH})$ at 1524 cm^{-1} are also observed.^[32] These results were confirmed by HR-ESI Mass Spectroscopy with the molecular peak at m/z 1925 being very close to the expected theoretical value of 1922.

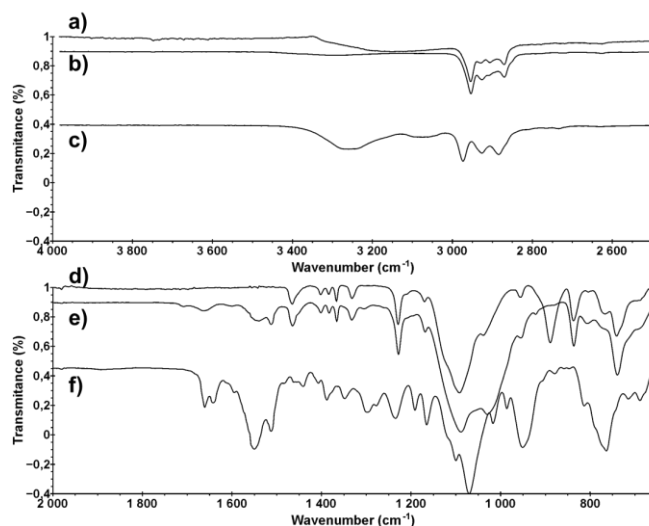


Figure 7. FT-IR spectra (4000-2000 cm^{-1}) of a) Partially-condensed T_7 -triol, b) Urea-thiourea dumbbell, **9**, and c) Urea-thiourea linker, **5**. FT-IR spectra (2000-600 cm^{-1}) of d) Partially-condensed T_7 -triol, e) Urea-thiourea dumbbell, **9**, and f) Urea-thiourea linker, **5**.

In the case of compound **10**, the ^{29}Si NMR spectrum (Figure 8a) shows only three peaks in the same narrow range from -67 ppm to -68 ppm. The simplified spectrum is due to the symmetry of the malonamide linker compared with compound **5**. The two peaks at -67.91 ppm (red dot) and -67.64 ppm (blue dot) correspond to the chemical shifts of the silicon atoms linked to the isobutyl groups. The signal located at -67.08 ppm corresponds to the silicon atom directly linked to the molecular linkers (yellow dot).^[39] Similarly to compound **9**, the disappearance of the silanol Si-OH peaks (-59.06 ppm) of the starting POSS (Figure 8b) and of the triethoxysilyl groups, $\text{Si}(\text{OEt})_3$ of the molecular linker **8** (-45.86 ppm) (Figure 8c) confirms that the reaction had proceeded.

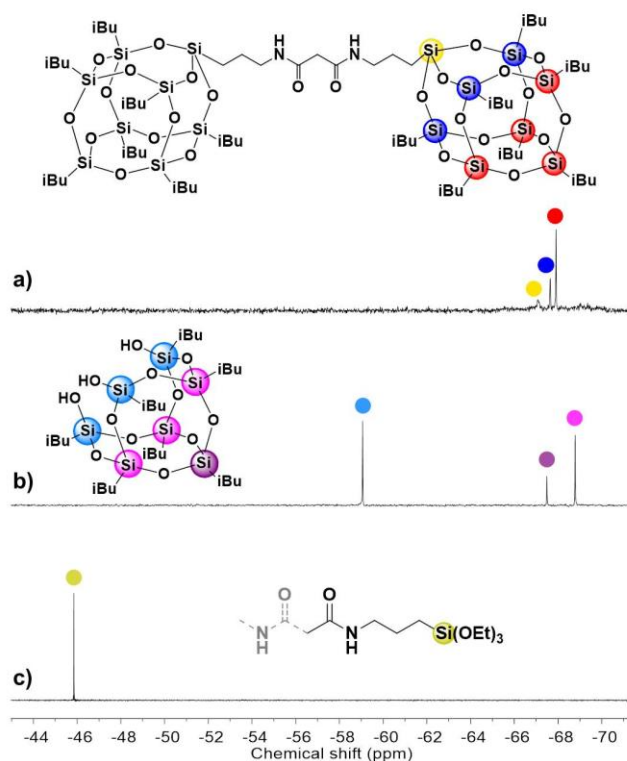


Figure 8. ^{29}Si solution NMR spectra of a) malonamide dumbbell, **10**, b) partially condensed T_7 -triol and c) malonamide linker, **8**

The corresponding FT-IR spectra show the extinction of the band associated with Si-OEt (1068 cm^{-1}) in compound **10** (Figure 9e), as expected. The extinction of this band and the increase in the intensity of the band (1083 cm^{-1}) due to Si-O-Si stretching vibrations of POSS showed that the capping reaction has occurred. Moreover, the appearance of the two bands due to Si-C antisymmetric vibrations (949 cm^{-1}) and Si-C symmetric vibrations (732 cm^{-1}) within the spectrum of

compound **10** (Figure 9e) is explained by grafting of the linker with the partially condensed T7-triol. In addition, the presence of the band profile at 3300 cm^{-1} is due to the stretching vibration of the NH from the amide group. The bands due to the stretching vibrations of the C=O (1643 cm^{-1}) are also observed.

These results were confirmed by HR-ESI Mass Spectroscopy, with the peak at a m/z value of 1815.56 comparable to the expected theoretical value of 1815.62.

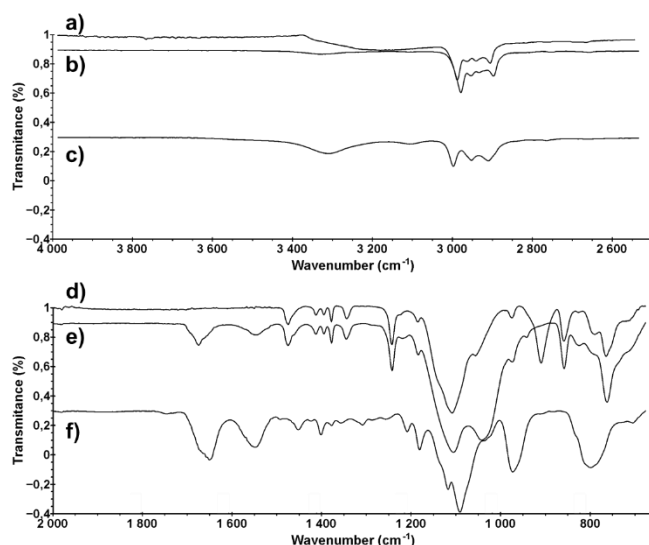


Figure 9. FT-IR spectra ($4000\text{-}2500\text{ cm}^{-1}$) of a) Partially condensed T7-triol, b) Malonamide dumbbell, **10** and c) Malonamide bistrithoxysilane linker, **8**. FT-IR spectra ($2000\text{-}600\text{ cm}^{-1}$) of d) Partially condensed T7-triol, e) Malonamide dumbbell, **10** and f) Malonamide bistrithoxysilane linker, **8**.

Conclusions

In summary, here we report a new type of functionalized, dumbbell-shaped T_8 -POSS, prepared via an unconventional corner capping reaction using two different linkers. The products are obtained in good yields, irrespective of the linker used, thus suggesting the possible use of our approach with more complex linkers. Until now the few reported examples of dumbbell silsesquioxanes synthesized by corner-capping reaction always involved the use of a base as a catalyst. However, bases can be detrimental to functional groups such as thiourea, thereby limiting the range of moieties that can be incorporated in functionalized dumbbell T_8 -POSS. Indeed, in our work, both base- and acid-catalyzed reactions were unsuccessful whereas with fluoride anion as catalyst, it was possible to circumvent such difficulties. This offers an alternative approach to the synthesis of functionalized dumbbell-shaped T_8 -POSS.

The preparation of these functional moieties is the first step towards developing more complex MOF-like or polymer-like architectures, and to complex within these architectures rare earth and transition metals cations to create new supported catalysts and other functional nanostructures with potential applications in optics, optoelectronics and nanomedicine.

Experimental Section

Chemicals and Solvents. Diethylmalonamide (FluoroChem), 3-isocyanatopropyltriethoxysilane and 3-aminopropyltriethoxysilane (ABCR), Partially-condensed T7-triol (POSS, Hybrid Plastics) and tetra-*n*-butylammonium fluoride (TBAF, Sigma Aldrich) were used without any further purification. (3-isothiocyanatopropyl)triethoxysilane was synthesized as reported previously. 1,4-Diaminobenzene (DAB, Acros) was sublimed before use. Toluene, tetrahydrofuran and pentane were dried using a MBraun SPS-800 apparatus.

Materials Characterization. Nuclear Magnetic Resonance (NMR) Spectroscopy. ^1H , ^{13}C and ^{29}Si liquid NMR spectra were recorded on a Bruker 400 MHz at room temperature and are reported relative to the chemical shifts of TMS. ^1H NMR spectra: Peak notations are used as follows: s (singlet), d (doublet), t (triplet), q (quadruplet), qt (quintuplet) and m (multiplet). ^{13}C NMR and ^{29}Si NMR spectra were recorded with ^1H decoupling. High resolution electrospray ionization (HR-ESI) mass spectroscopy were obtained using a JEOL MS-DX 300 apparatus. Fourier-transform infrared (FTIR) spectra were obtained using a Perkin-Elmer FTIR Spectrum BX spectrophotometer equipped with a Gladia-ATR accessory.

Synthesis of urea-thiourea bistrithoxysilane linker, 5. DAB (500 mg, 4.62 mmol) was dissolved in 60 ml of dry THF in a 90 ml Schlenk tube equipped with a magnetic stirrer. 3-isothiocyanatopropyl triethoxysilane (1.95 g, 7.40 mmol) was then added and the mixture was vigorously stirred at room temperature for 24 h to form the intermediate compound **3**. The crude product was washed with dry pentane to remove the excess of 3-isothiocyanatopropyltriethoxysilane and after filtration under inert atmosphere, the resulting intermediate compound **3**, 1-(4-aminophenyl)-3-(3-(triethoxysilyl)propyl)thiourea, was dried under reduced pressure for 2 h. Then, **3** (1.16 g, 3.14 mmol) was dissolved in 60 ml of dry THF in a 90 ml Schlenk tube equipped with a magnetic stirrer. 3-Isocyanatopropyltriethoxysilane **4** (1.01 g, 4.08 mmol) was then added and the mixture was stirred at room temperature for 24 h to form compound **5**. The excess of 3-isocyanatopropyltriethoxysilane was removed after washing with dry pentane and filtering under an inert atmosphere. The resulting compound **5** was dried under vacuum for 2 h. Yield: 85%. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 8.02 (s, C_{ar}NH, 1H), 7.89 (s, C_{ar}NH, 1H), 7.23 (d, CH_{ar}, 2H), 7.01 (d, CH_{ar}, 2H), 6.39 (s, C_{ar}NH 1H), 5.45 (m, C_{ar}NH 1H), 3.80 (q, OCH₂, 12H), 3.68 (m, NHCOCH₂, 2H), 3.18 (m, NHCSCCH₂, 2H), 1.65 (m, NCH₂CH₂, 4H), 1.21 (t, CH₃, 18H), 0.61 (m, SiCH₂, 4H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 180.80 (C=S), 155.89 (C=O), 138.37 (C_{ar}NHCS), 134.07, (C_{ar}NHCO), 126.85 (C_{ar}), 120.87 (C_{ar}), 58.60 (OCH₂), 58.50 (CH₂NHCS), 42.77 (CH₂NHCO), 23.61 (NCH₂CH₂), 22.64 (NCH₂CH₂), 18.41 (CH₃), 7.78 (SiCH₂), 7.71 (SiCH₂). ²⁹Si NMR (80 MHz, CDCl₃, δ, ppm): -45.43 (s), -45.86 (s) (integration ratio respectively 1:0.93).

Synthesis of malonamide bistrithoxysilane linker, 8. 3-aminopropyltriethoxysilane, APTES, (6.36 g, 29 mmol) and diethylmalonamide (2.00 g, 12 mmol) were mixed in a 60 ml sealed Schlenk tube equipped with a magnetic stirrer and stirred at 140 °C for 6 h to form compound **8**. The excess of APTES was removed under reduced pressure at 120 °C for 24 h. Yield: 90 %. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.36 (t, NH, 2H), 3.75 (q, OCH₂, 12H), 3.19 (m, NCH₂, 4H), 3.10 (s, O=CCH₂C=O, 2H), 1.58 (m, NCH₂CH₂, 4H), 1.16 (t, CH₃, 18H), 0.56 (t, SiCH₂, 4H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 167.45 (C=O), 58.50 (OCH₂), 42.95 (O=CCH₂C=O), 42.12 (NCH₂), 22.81 (NCH₂CH₂), 18.34 (CH₃), 7.85 (SiCH₂). ²⁹Si NMR (80 MHz, CDCl₃, δ, ppm): -45.86 (s).

Synthesis of Urea-thiourea dumbbell, **9** Partially condensed T7-triol (1.47 g, 1.86 mmol) was dissolved in 5 ml of toluene in a 25 ml 2-necked flask equipped with a magnetic stirrer and a refluxing condenser. Then TBAF (14 µl, 0.05 mmol) was first added, followed by compound **5** (500 mg, 0.81 mmol). The mixture was stirred at 60 °C for 5 days under argon. The solvent was then removed under vacuum and the remaining solid was filtered over a silica gel plug and washed with a mixture of extraction solvent (cyclohexane/ dichloromethane/ trimethylamine 49.5/49.5/1). Then, the solvents were evaporated under vacuum, leading to compound **9** which was dried overnight under vacuum. Yield: 60 % (white powder, 942 mg, 0.49 mmol). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.40 (d, CH_{ar}, 2H), 7.10 (s, CH_{ar}, 2H), 3.57 (m, NCH₂, 2H), 3.23 (m, NCH₂, 2H), 1.85 (m, CH₂CH, 14H), 1.70 (m, NCH₂CH₂, 2H), 1.37 (m, NCH₂CH₂, 2H), 0.96 (m, CH₃, 84H), 0.59 (m, CH₂CH and SiCH₂, 32H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 181.21 (C=S), 178.13 (C=O), 126.88 (C_{ar}), 121.08 (C_{ar}), 118.75 (C_{ar}), 58.60 (CH-CH₂), 42.9 (NCH₂), 33.84 (NCH₂), 29.85 (CH₂-CH₂), 25.84 (CH₃), 24.03 (Si-CH₂), 22.64 (CH₂-CH₂), 18.57 (CH₂CH), 14.27 (Si-CH₂). ²⁹Si NMR (80 MHz, CDCl₃, δ, ppm): -68.91, -67.91, -67.83, -67.61, -67.09. HRMS (ESI⁺):m/z: calcd for C₇₀H₁₄₆N₄O₂₅SSi₁₆ (M+H): 1922.62; found: 1925.562

Synthesis of malonamide dumbbell, 10. Partially-condensed T7-triol (1.78 g, 2.25 mmol) was dissolved in 5 ml of toluene in a 25 ml 2-necked flask equipped with a magnetic stirrer and a reflux condenser. Then TBAF was added (15 µl, 0.06 mmol) followed by compound **8** (500 mg, 0.97 mmol). The mixture was vigorously stirred at 60 °C for 5 days under argon to form compound **10**. The solvent was then removed under vacuum and the resulting solid was filtered over a silica gel plug and washed with cyclohexane. The solvent was then removed under vacuum overnight to give compound **10**. Yield: 63 % (white powder, 1.11 g, 0.61 mmol). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.83 (m, NH, 2H), 3.20 (m, NCH₂, 4H), 3.11 (s, O=CCH₂C=O, 4H), 1.83 (m, CH₂CH, 14H), 1.60 (m, NCH₂CH₂, 4H), 1.42 (s, cyclohexane (purification solvent)), 1.39 (m, 4H), 0.94 (m, CH₃, 84H), 0.58 (m, 30H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 143.49 (C=O), 58.70 (CH-CH₂ and NH-CH₂), 27.17 (CH₂-CH₂-Si), 25.95 (CH₃), 24.10 (Si-CH₂), 23.31, 22.69 (CH₂-CH₂-NH), 18.69 (CH₂CH). ²⁹Si NMR (80 MHz, CDCl₃, δ, ppm): -67.91, -67.64, -67.08. HRMS (ESI⁺):m/z: calcd for C₆₅H₁₄₂N₂O₂₆Si₁₆ (M+H): 1815.62; found: 1815.562

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