Functionalization of Polyhedral Oligomeric Silsesquioxane (POSS) via Nucleophilic Substitution

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Abstract: Octakis(3-chloropropyl)octasilsesquioxane, obtained recently by a new method, has enabled a highly efficient synthesis of a whole family of cube-like T_8 silsesquioxanes by nucleophilic substitution of chlorine atom with appropriate nucleophilic agents. Five functionalized silsesquioxanes, i.e., octakis[3-(methacryloyloxy)propyl]-, octakis(3-acetoxypropyl)-, octakis[3-(phenylamino)propyl]-, and octakis[3-(4-methylpiperazin-1-yl)propyl]octasilsesquioxane as well as octakis{3-[(2-hydroxyethyl)dimethylammonio]propyl}octasilsesquioxane chloride were synthesized and characterized by spectroscopic methods and elemental analysis.

Key words: functionalized silsesquioxanes, nucleophilic substitution, POSS, polyhedral oligosilsesquioxanes

Polyhedral oligosilsesquioxanes (POSS) are a class of versatile building blocks for the production of inorganic–organic hybrid materials with designed properties due to the three-dimensional highly symmetrical nature of the POSS core.[1–7] The most important POSS materials are the cube-like T_8 derivatives, which have found a wide range of technological application. The reasons for their dominance are ease of handling and useful properties such as thermal stability, ease of chemical modification, and nano-sized dimension. POSS have also emerged as a new class of nanofillers for the preparation of nanostructured composites of higher performance.[8] They have been used extensively as catalysts,[9] dendrimers,[10] biocompatible materials, and scaffolds for the development of liquids crystals.[11,12]

Although the cubic T_8 arrangement is achieved by the hydrolysis/condensation reactions of many simple silicon compounds such as $RSiCl_3$ or $R^1Si(OR^2)_3$, only a few of the known T_8R_8 derivatives can be prepared directly in this manner.[1–4]

Several variants of this method were tested by performing reactions in aqueous or nonaqueous media using acid-base catalysis. In most cases, however, the process requires a long time (several weeks), the final yield is low and the desired product (POSS) is accompanied by amorphous silsesquioxanes and those with a ladder structure.[6,13–22]

During the last few years a number of brilliant reviews concerning synthesis, characterization, and applications of POSS have been published.[1,2,23–27] Especially, the article by Paul Lickiss,[1] which has been published very recently, and references included in it, discuss all the aspects concerning cube-like POSS in detail.

About 90 POSS compounds with T_8 cores have been structurally characterized using diffraction methods and about 50 of them are of T_8R_8 composition.[1] The synthesis of the majority of new T_8R_8 compounds is based on the modification of a few simple precursors having such reactive groups as Si–H, Si–CH=CH_2, Si$(CH_2)_3$X, or Si–Ph. High yields of functionalized POSS can be obtained by three essential catalytic methods: (a) hydrosilylation,[1,4,20] (b) nucleophilic substitution,[2,20] and (c) metathesis/silylative coupling (Scheme 1).[28–30]

As usual there are some limitations with each of these methods. In some instances, direct hydrosilylation of an olefin derivative of the intended functional group can lead to serious side reactions. Moreover, hydrosilylation is an exothermic reaction and can lead to an uncontrolled increase in temperature, which may cause, in the case of some functional groups (e.g., methacryloyl), undesirable reactions. Finally, both hydrosilylation as well as metathesis are catalyzed by transition metal complexes that are very sensitive to poisoning caused by the presence of certain functional groups. The choice of functionalization method depends also on the availability of the starting raw material. For example, T_8H_8 is obtained in five weeks in 19% yield.[28–30]

The method based on the nucleophilic substitution of halogens in halogen derivatives of silsesquioxane is one of the most versatile, enabling the syntheses of various functionalized POSS. The above process is well known and frequently applied to the synthesis of organofunctional silanes.[31] The starting material used in this method is a 3-halopropyl-substituted silsesquioxane.

Very recently, we reported a new method for the synthesis of octakis(3-chloropropyl)octasilsesquioxane (**1**), based on a two-stage hydrolytic condensation of (3-chloropropyl)trimethoxysilane.[32,33] This approach enables selective formation of the desired product in a shorter time (4 days), compared to the previous methods (5 weeks), while the yield (35%) is comparable. The process is conducted in methanolic solution with acid hydrolysis as the first stage

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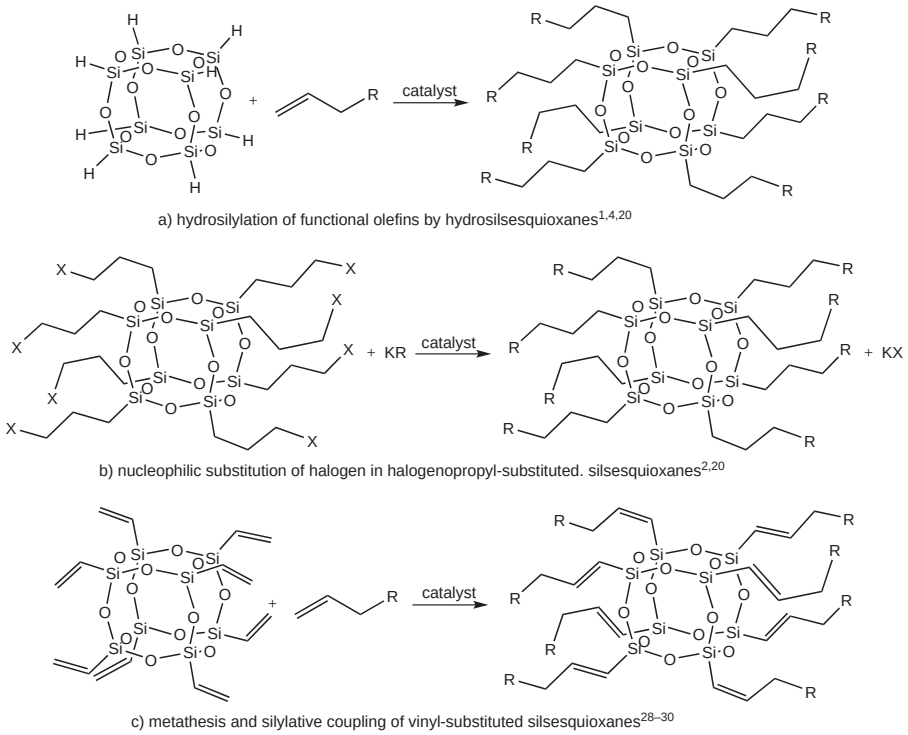


Scheme 1 Most common routes for the functionalization of POSS

and condensation in the presence of dibutyltin dilaurate as a catalyst in the second stage.

Our method enables the product to be obtained with similar yield, but in a much shorter period of time. Moreover, it is the optimal time, during which octakis(3-chloropropyl)octasilsesquioxane (**1**) is selectively formed. This was confirmed by X-ray crystal structure analysis and ^{29}Si NMR (only the signal at $\delta = 67.28$ is observed, which is typical for cubic POSS). Prolonging the process would result in the formation of ladder-like and random POSS, which are not desired in this case.

The above method, due to easy access to octakis(3-chloropropyl)octasilsesquioxane (**1**), enables the synthesis of a whole family of functionalized silsesquioxanes by nucleophilic substitution of the chlorine atom. This is why the present work is aimed at the synthesis of new functionalized T_8 silsesquioxanes on the basis of the reactions of the silsesquioxane **1** with different nucleophilic agents such as potassium methacrylate, sodium acetate, aniline, 1-methylpiperazine, and 2-(dimethylamino)ethanol as well as at characterization of the products obtained. Functional groups present in the above compounds are frequently employed to functionalize siloxanes.

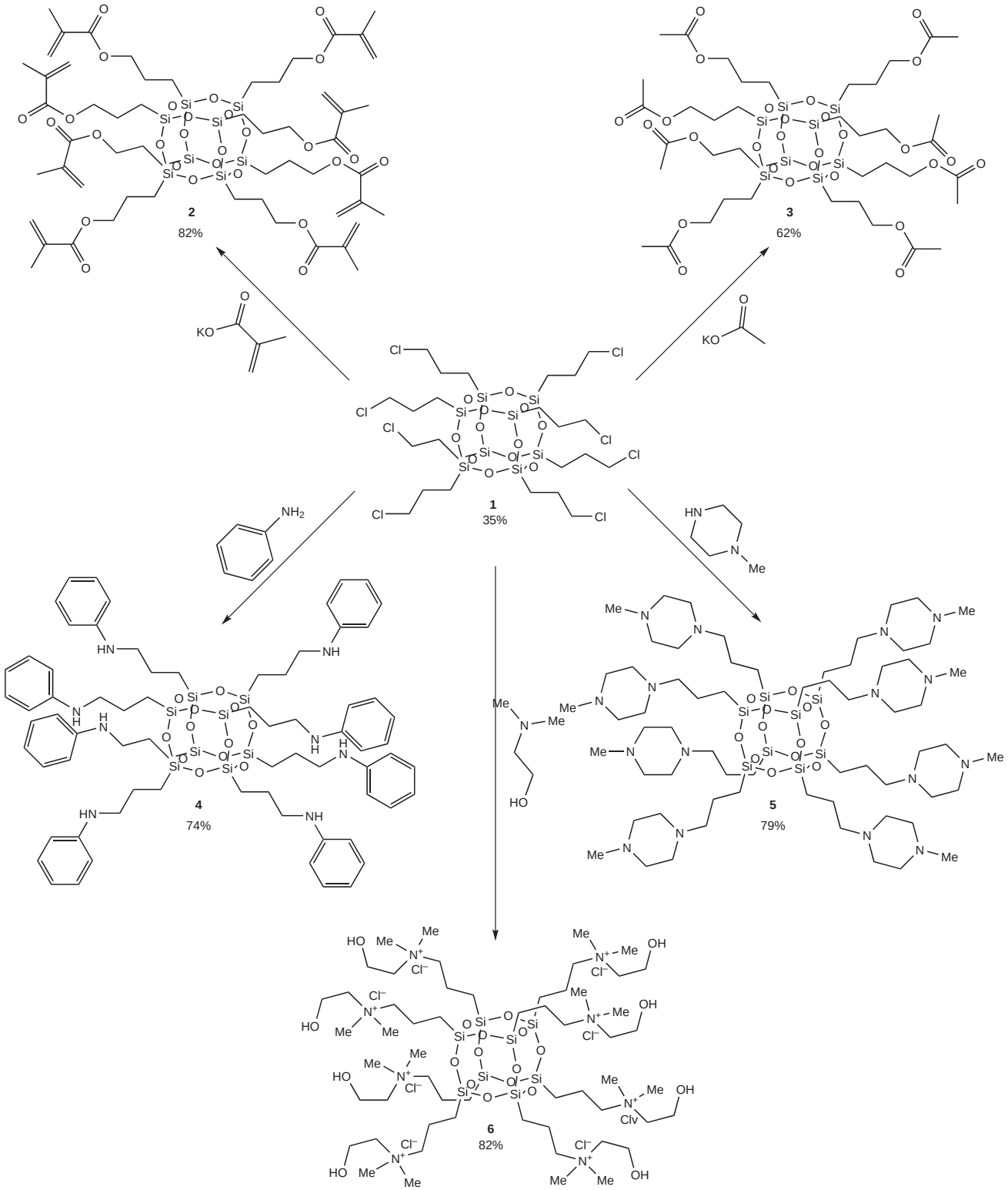
All reactions were performed in the same way, i.e. in *N*,*N*-dimethylformamide medium, except for the reaction with 2-(dimethylamino)ethanol, where the latter operates also as a solvent. Potassium iodide was employed as a catalyst for the reaction with potassium methacrylate and sodium acetate, whereas in all other cases the amines used in the reactions acted autocatalytically. Moreover, potassium chloride and sodium chloride were byproducts in the first two reactions, respectively, whereas in the reactions with aniline and 1-methylpiperazine, the relevant amine hydrochloride was a byproduct, therefore while carrying out these reactions, it was reasonable to use 100% amine excess. The reaction with 2-(dimethylamino)ethanol is, as a matter of fact, a quaternization reaction as a result of which octakis{3-[(2-hydroxyethyl)dimethylammonio]propyl}octasilsesquioxane chloride (**6**) was obtained. However, it was included in the study because of the great similarity of the reaction course.

Since the synthesis of the starting material **1** was hitherto difficult, nucleophilic substitution has not been frequently applied to POSS functionalization (to octafunctionalized POSS synthesis of chlorine in **1** in particular). A few authors have reported chlorine atom substitution in **1** with I, SCN, PPh_2, and SMe.[2,16,34] The reactivity of chlorine atom in **1** was also used in the functionalization of POSS compounds with silver oxide or silver nitrate to obtain hydroxy functionality,[35,36] with 2-methyl-4,5-dihydrooxazole,[37,38] or with *N*,*N*-dimethyloctylamine.[16]

Of all the functional groups used by us for silsesquioxane functionalization (Scheme 2), only the methacryloyl group had been employed earlier to synthesize organofunctional organosilicon compounds, i.e. to synthesize [3-(methacryloyloxy)propyl]trimethoxysilane, one of the most important silane promoters of adhesion.[31]

The methacryloyl group easily undergoes free radical polymerization. Its reactivity is frequently exploited to obtain hybrid materials or organic-inorganic copolymers. On the other hand, the synthesis of derivatives with methacryloyl groups has a potentially undesirable side reac-

tion, polymerization, therefore, it is necessary to carry out this reaction in a controlled way, i.e. under relatively mild conditions. One of the methods that forms methacryloyloxy-functionalized silanes as well as silsesquioxane is hydrosilylation of allyl methacrylate. However, contrary to nucleophilic substitution, the former reaction is exothermic, leading to uncontrolled polymerization. On the other hand, polycondensation of [3-(methacryloyloxy)propyl]trimethoxysilane in the presence of formic acid, resulting in the formation of a mixture of oligo- and polysilsesquioxanes, has also been reported in the literature.[17]



Scheme 2 General methodology for the functionalization of POSS via nucleophilic substitution

The application of the reaction of nucleophilic substitution has made it possible to obtain the product **2** with a high yield (82%) in a relatively short time (8 h). The compound **2** is a yellowish liquid of considerable viscosity. NMR and FT-IR analyses unambiguously confirmed the structure assumed for compound **2**. Another example of carboxy group addition to the silsesquioxane core is the synthesis of octakis(3-acetoxypropyl)octasilsesquioxane (**3**). The final yield of the latter product is the lowest (62%), compared to all remaining silsesquioxanes, which can be explained by the difficult isolation of the product from sodium chloride that is formed as a byproduct.

The other functionalized silsesquioxanes contain amino derivatives. Amino-functional polysiloxanes are of considerable practical importance for different industrial branches, among others the textile and cosmetic industries. The synthesis of silsesquioxanes with analogous groups opens the possibility of expanding their application.

To the best of our knowledge, compounds **4**–**6** have not been previously obtained. An analogous reaction to that with 2-(dimethylamino)ethanol (which gives product **6**), was carried out by the use of polysiloxane substituted with chloropropyl groups to get water soluble and amphiphilic silicone.[39] Significant practical importance of compounds of this type has encouraged us to perform the synthesis of analogous silsesquioxanes. Quaternization of tertiary hydroxyalkylamine [2-(dimethylamino)ethanol] with 3-chloropropyl groups attached to POSS gave quaternary (hydroxyalkylammonio)alkyl-substituted silsesquioxane **6**, well soluble in water, with high yield (82%).

The application of other amine derivatives in the nucleophilic substitution of the chlorine atom in **1** gave an effective synthesis of products **4** and **5** with high yields (74% and 79%, respectively). The reactions were conducted in the same way by using 100% excess of amine in order to combine HCl (released during the reactions) by forming amine hydrochloride that can be easily separated from the desirable product by washing with appropriate solvents. In both cases, products **4** and **5** form solids and NMR and FT-IR analyses fully confirmed their structures.

In conclusion, octakis(3-chloropropyl)octasilsesquioxane (**1**) obtained according to the new effective method,[32,33] is a very important and attractive precursor for synthesis of a wide range of functionalized silsesquioxanes, prepared by nucleophilic substitution of the chlorine atoms in **1** with appropriate organic groups. This reaction enables highly efficiently syntheses of five functionalized silsesquioxanes: octakis[3-(methacryloyloxy)propyl]silsesquioxane (**2**), octakis(3-acetoxypropyl)octasilsesquioxane (**3**), octakis[3-(phenylamino)propyl]silsesquioxane (**4**), octakis[3-(4-methylpiperazin-1-yl)propyl]silsesquioxane (**5**), and octakis{3-[(2-hydroxyethyl)dimethylammonio]propyl}octasilsesquioxane chloride (**6**). The reaction proceeded under considerably milder conditions than those needed when using other well-known methods and therefore, it can be applied from synthetic and economic point of view to synthesis of a variety of functionalized POSS.

^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), and ^{29}Si NMR (59 MHz) spectra were recorded on a Varian XL 300 spectrometer at r.t. using $CDCl_3$, C_6D_6, or D_2O as solvents. FT-IR spectra were recorded on a Bruker Tensor 27 Fourier transform spectrophotometer equipped with a SPECAC Golden Gate diamond ATR unit. In all cases 16 scans at a resolution of 2 cm^{-1} were used to record the spectra. Elemental analyses were made on an Elementar Analyser Vario EL III. Melting point measurements were carried out on a Stuart Scientific SMP3 apparatus. (3-Chloropropyl)trimethoxysilane, benzene, $CHCl_3$, MeOH, DMF, 1-methylpiperazine, 2-(dimethylamino)ethanol, dibutyltin dilaurate (DBTL), and HCl were used as received (Aldrich) without further purification. KI was dried overnight at 120 °C and aniline was distilled under vacuum and stored over KOH. Potassium methacrylate was synthesized from KOH and methyl methacrylate.

Octakis(3-chloropropyl)octasilsesquioxane (1)[32,33]

Anhyd MeOH (119 g, 150 mL, 3.71 mol) and concd HCl (5.94 g, 5 mL) were placed in a two-necked round-bottomed flask equipped with a condenser, addition funnel, and magnetic stirring bar. Then (3-chloropropyl)trimethoxysilane (15 g, 13.9 mL, 75.5 mmol) was added dropwise through the addition funnel over 10 min with vigorous stirring, which was maintained for 2 h until the soln cooled down to r.t. The mixture was allowed to stand at r.t. for an additional 48 h without stirring. After 2 d, DBTL as a condensation catalyst (150 mg, 140 μL, 0.24 mmol) was added with stirring. Then the mixture was left for a further 2 d to give a white crystalline precipitate. The supernatant liquid was filtered off and the collected crystals were washed several times with MeOH and dried in a vacuum to give **1** (3.68 g, 35%); mp 206–208 °C.

IR (ATR): 2996–2875, 1457–1274, 1230–940, 552 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (t, 16 H, $SiCH_2$), 1.84 (quint, 16 H, CH_2), 3.53 (t, 16 H, CH_2Cl).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.9, 26.4, 47.1.

^{29}Si NMR (59 MHz, $CDCl_3$): δ = –67.28.

Octakis[3-(methacryloyloxy)propyl]octasilsesquioxane (2); Typical Procedure

All functionalized silsesquioxanes **2**–**6** were synthesized in a similar way. Syntheses were carried out in a two-necked round-bottomed flask equipped with condenser, thermometer, magnetic stirring bar, and heater. Octakis(3-chloropropyl)octasilsesquioxane (**1**, 300 mg, 0.27 mmol) was dissolved in DMF (5.68 g, 6 mL, 77.6 mmol) and placed in the reaction flask. Next potassium methacrylate (261 mg, 2.12 mmol) and KI (28 mg, 0.169 mmol) were added to this soln. The reaction was carried out at 100 °C for 8 h with stirring. Then the mixture was filtered in order to remove KCl that precipitated during the reaction and the obtained filtrate was subjected to concentration by vacuum evaporation of DMF. The remaining viscous liquid was filtered again, washed with distilled H_2O to remove all residual potassium salts and dissolved in $CHCl_3$. The organic layer was then separated and evaporated under vacuum to give **2** (330 mg, 82%).

IR (ATR): 2957, 2896, 1716, 1639, 1454–1297, 1250–939 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.68 (t, 16 H, $SiCH_2$), 1.74 (s, 24 H, CH_3), 1.92 (quint, 16 H, CH_2), 4.08 (t, 16 H, CH_2O), 5.53 (s, 8 H, CH_2=C), 6.07 (s, 8 H, CH_2=C).

^{13}C NMR (75 MHz, $CDCl_3$,): δ = 8.2, 18.3, 22.3, 66.3, 125.3, 136.4, 167.3.

^{29}Si NMR (59 MHz, $CDCl_3$): δ = –68.69.

Anal. Calcd for $C_{56}H_{88}O_{28}Si_8$: C, 46.90; H, 6.19. Found: C, 46.83; H, 6.18.

Octakis(3-acetoxypropyl)octasilsesquioxane (3)

DMF (6.63 g, 7 mL, 90.5 mmol), octakis(3-chloropropyl)octasilsesquioxane (**1**, 300 mg, 0.27 mmol), NaOAc (174 mg, 2.12 mmol) and KI (28 mg, 0.169 mmol) were placed in a reaction flask. The reaction was carried out at 100 °C for 24 h with stirring. After cooling to r.t., the mixture was filtered in order to remove NaCl that precipitated during the reaction and the obtained filtrate was subjected to concentration by vacuum evaporation of DMF. The solid residue was washed with distilled H_2O to remove all residual potassium and sodium salts and dissolved in benzene. The organic layer was then separated and evaporated under vacuum to give **3** (200 mg, 62%) as a light yellow oil

IR (ATR): 2950–2880, 1738, 1457–1350, 1238, 1114–1000, 519 cm^{-1}.

^1H NMR (300 MHz, C_6D_6): δ = 0.85 (t, 16 H, $SiCH_2$), 1.35 (quint, 16 H, CH_2), 1.82 (s, 24 H, CH_3), 4.05 (t, 16 H, CH_2O).

^{13}C NMR (75 MHz, C_6D_6): δ = 11.1, 20.5, 22.7, 65.9, 170.2.

^{29}Si NMR (59 MHz, C_6D_6): δ = –69.49.

Anal. Calcd for $C_{40}H_{72}O_{28}Si_8$: C, 39.20; H, 5.92. Found: C, 39.15; H, 5.91.

Octakis[3-(phenylamino)propyl]octasilsesquioxane (4)

Octakis(3-chloropropyl)octasilsesquioxane (**1**, 400 mg (0.35 mmol) was dissolved in DMF (7.57 g, 8 mL, 103 mmol) and placed together with almost 100% excess of aniline (500 mg, 489 μL, 5.37 mmol) in a reaction flask. The reaction was carried out at 110 °C for 24 h with stirring. The mixture was filtered in order to remove aniline hydrochloride and the obtained filtrate was subjected to concentration by vacuum evaporation of DMF. The solid residue was washed with benzene several times to remove all remaining amine and byproduct (amine hydrochloride) followed by drying under vacuum to give **4** (410 mg, 74%); mp 100–103 °C.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.76 (t, 16 H, $SiCH_2$), 1.84 (quint, 16 H, CH_2), 3.13 (NH), 3.53 (t, 16 H, CH_2NH), 7.12–7.32 (m, 40 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.3, 26.2, 47.0, 113.1, 115.2, 129.2, 146.1.

^{29}Si NMR (59 MHz, $CDCl_3$): δ = –67.11.

Anal. Calcd for $C_{72}H_{96}N_8O_{12}Si_8$: C, 58.03; H, 6.49; N, 7.52. Found: C, 58.05; H, 6.50; N, 7.53.

Octakis[3-(4-methylpiperazin-1-yl)propyl]octasilsesquioxane (5)

Octakis(3-chloropropyl)octasilsesquioxane (**1**, 400 mg, 0.35 mmol) was dissolved in DMF (7.57 g, 8 mL, 103 mmol) and placed together with 100% excess of 1-methylpiperazine (570 mg, 631 μL, 5.7 mmol) in a reaction flask. The reaction was carried out at 100 °C for 48 h with stirring. Then the mixture was filtered in order to remove amine hydrochloride that was formed during the reaction and the obtained filtrate was subjected to concentration by vacuum evaporation of DMF. The solid residue was washed with $CHCl_3$ several times to remove the product from the remaining amine and its hydrochloride. All $CHCl_3$ portions were collected together. In the next step $CHCl_3$ was removed by vacuum evaporation to give **5** (460 mg, 79%).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, 16 H, $SiCH_2$), 1.25 (t, 16 H, CH_2N), 2.33 (quint, 16 H, CH_2), 2.43 (m, 24 H, NCH_3), 3.74 (s, 64 H, NCH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.0, 19.0, 44.4, 50.5, 52.9, 59.7.

^{29}Si NMR (59 MHz, $CDCl_3$): δ = –67.50.

Anal. Calcd for $C_{64}H_{136}N_{16}O_{12}Si_8$: C, 49.70; H, 8.86; N, 14.49. Found: C, 49.74; H, 8.87; N, 14.50.

Octakis{3-[(2-hydroxyethyl)dimethylammonio]propyl}octasilsesquioxane Chloride (6)

Octakis(3-chloropropyl)octasilsesquioxane (**1**, 300 mg, 0.27 mmol) and 2-(dimethylamino)ethanol with 100% excess (380 mg, 427 μL, 4.3 mmol) of were placed in a reaction flask. The reaction was carried out at 100 °C for 24 h with stirring. The excess of 2-(dimethylamino)ethanol was removed from the postreaction mixture by vacuum evaporation to give **6** (380 mg, 82%) as a white solid; the melting point of the obtained material is much higher then its decomposition temperature. The product changed its color from white to dark red during the measurement at about 230 °C.

IR (ATR): 3222, 2944–2775, 1469–1300, 1230–900, 698 cm^{-1}.

^1H NMR (300 MHz, D_2O): δ = 0.59 (t, 16 H, $SiCH_2$), 1.86 (quint, 16 H, CH_2), 2.84 (t, 16 H, CH_2N), 3.11 (s, 48 H, CH_3), 3.37 (t, 16 H, NCH_2), 3.47 (s, 8 H, OH), 3.75 (t, 16 H, CH_2O).

^{13}C NMR (75 MHz, D_2O): δ = 9.5, 16.5, 51.4, 55.3, 64.9, 67.3.

^{29}Si NMR (59 MHz, D_2O): δ = –67.31.

Anal. Calcd for $C_{56}H_{136}Cl_8N_8O_{20}Si_8$: C, 38.43; H, 7.83; N, 6.40. Found: C, 38.50; H, 7.85; N, 6.42.

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