■ Siloxane Nanoparticles

# High-Yield Synthesis of Amido-Functionalized Polyoctahedral Oligomeric Silsesquioxanes by Using Acyl Chlorides

Mateusz Janeta, Łukasz John,* Jolanta Ejfler, and Sławomir Szafert[a]

**Abstract:** Homosubstituted amido-functionalized polyocta-hedral oligomeric silsesquioxanes (POSS) have been synthe-sized by using acyl chlorides in high yields (ca. 95%). The method proved to be superior over "conventional" syntheses applying carboxylic acids or acid anhydrides, which are much less efficient (ca. 60% yield). A palette of aryl and alkyl groups has been used as side-chains. The structures of the resulting amide-POSS are supported by multinuclear $^1$H, $^{13}$C, $^{29}$Si NMR and FTIR spectroscopy and their full conversion into octasubstituted derivatives was confirmed using mass spectrometry. We also demonstrate that the functionalized silsesquioxanes with bulky organic side-chains attached to cubic siloxane core form spherical-like, well-separated nano-particles with a size of approximately 5 nm.

## Introduction

Polyoctahedral oligomeric silsesquioxanes (POSS) constitute a group of organosilicon compounds with the basic structure of general formula $(RSiO_{3/2})_8$.[1] Their attractiveness derives from the fact that they can contain numerous functional groups as side-chains, spawning various possibilities to attach organic fragments. These groups—the so-called organic shell—can be varied from alkyl to alkylene or arylene. Thus, such molecules can fundamentally be regarded as truly inorganic core/shell structures that are able to bind organic moieties, polymers, and natural biomaterials. Moreover, the presence of the three Si—O bonds together imparts superior thermal, mechanical, and chemical stability, which makes these compounds ex-tremely interesting from an industrial point of view.[2]

Many interesting examples that illustrate these remarkable properties have already been described.[3] For example, porous hybrid materials based on "click" chemistry or polymerization methodology can be obtained from vinyl-POSS-derivatives that constitute building blocks for 3D networks.[4,5] Schwab et al. described a synthetic approach to easy-to-scale-up modifica-tion of POSS cages that allows for their incorporation into ther-moplastic resins resulting in increased oxygen permeability, re-duced flammability, and mechanical properties effectively closer to relative conventional organic systems.[6] Copper and co-workers reported on soluble ramified aryl-like conjugated microporous polymers (CMP) based on POSS architecture that open a new range of applications of CMPs that exploit a unique combination of conjugation and porosity.[7] Fluorinat-ed POSS (F-POSS) also constitute an interesting class of com-pounds for, among others, the construction of superamphi-phobic and flexible macroporous monoliths,[8] self-healing, su-perhydrophobic, and superoleophobic surfaces,[9,10] or transpar-ent, flexible and superomniphobic surfaces.[11] Furthermore, amide-derivatives of octa(3-aminopropyl)silsesquioxanes (OAS) play a crucial role in the field of biomaterials.[12,13]

Within this class of cage-like organosilicons, considerable at-tention is focused on aminopropyl-functionalized POSS (OAS-POSS) prepared by a sol-gel process based on the hydrolytic condensation of 3-aminopropyltrialkoxysilane, for example, 3-aminopropyltriethoxysilane (APTES) or aminopropyltrimethoxy-silane (APTMS). However, the synthesis of cage-like octa(3-ami-nopropyl)silsesquioxane is cumbersome and gives relatively low yields (ca. 30%) and requires a long reaction time (up to 6 weeks) when conducted in a mixture of MeOH/HCl at 25°C.[14] Moreover, the products usually contain contaminations of other polyhedral silsesquioxanes such as $(RSiO_{3/2})_n$ ($n \neq 8$) or open cage-like structures.[15–17]

Some modifications have been reported that have led to better synthetic efficacy for OAS-POSS preparation; for exam-ple, the use of tetraethyl ammonium hydroxide $Et_4NOH$ as cat-alyst (yields < 70% after 24 h).[18] Some improvement has also been achieved by optimization of the standard reaction condi-tions (ca. 30%, 5–10 days).[19] Kaneko and co-workers devel-oped another valuable approach to the synthesis of such sys-tems.[20] They investigated the hydrolytic condensation of APTMS by using a number of different acid catalysts. The most effective approach proved to involve the use of trifluorometha-nesulfonic acid. OAS-POSS-$CF_3SO_3$ was prepared after 5–6 h in approximately 90% overall yield. However, the authors ob-served the presence of decasubstituted polyhedral silsesquiox-ane as a minor by-product.[21] Nevertheless, such a novel strat-egy opened a new way for the preparation of a range of so-phisticated OAS-POSS-based derivatives.

[a] M. Janeta, Dr. Ł. John, Dr. J. Ejfler, Dr. S. Szafert
Faculty of Chemistry, University of Wrocław
14 F. Joliot-Curie, 50-383 Wrocław (Poland)
Fax: (+48) 71-328-23-48
E-mail: lukasz.john@chem.uni.wroc.pl
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Laine et al. investigated a valid strategy for the synthesis of imide-derivatives of OAS-POSS starting from acyl anhydrides.[19] In this paper, we present a new synthetic approach that allows a high-yield synthesis of OAS-POSS from ionic precursors and describe its modification to access various amide-derivatives starting from acyl chlorides. We have also been able to obtain nanoparticles of amido-functionalized OAS-POSS-like species containing aryl and alkyl side-chains (Figure 1), which were synthesized in high yield and purity while avoiding the formation of other ($n \neq 8$) polyhedral silsesquioxanes or polymeric/oligomeric compounds.
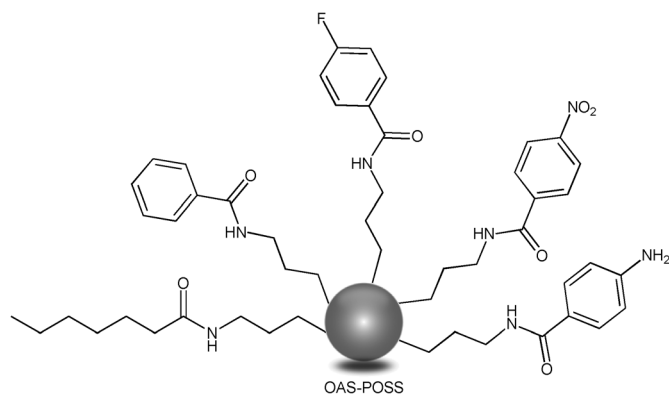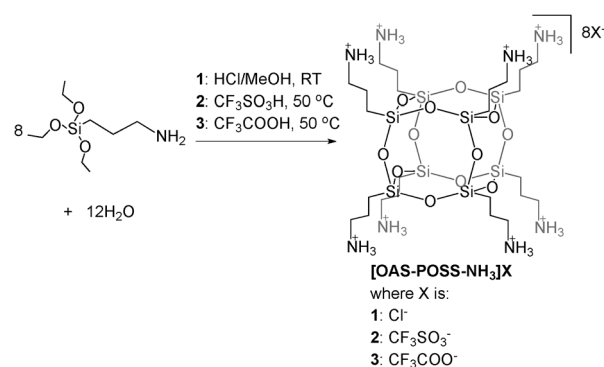


**Scheme 1.** Synthesis of [OAS-POSS-NH₃]X.



**Figure 1.** Alkyl, aryl, and fluorinated side-chains utilized in an amido-functionalized OAS-POSS.

## Results and Discussion

Looking for a stable cage scaffold for further preparation of octa-amido-functionalized POSS derivatives, in the first approach we obtained three OAS-POSS-based salts, [OAS-POSS-NH₃]Cl (**1**), [OAS-POSS-NH₃]CF₃SO₃ (**2**), and [OAS-POSS-NH₃]CF₃COO (**3**), as shown in Scheme 1.

Compounds **1**–**3** were obtained in a one-step hydrolytic condensation by using commercially available (3-aminopropyl)-triethoxysilane (APTES) and an appropriate amount (relative to APTES) of hydrochloric HCl (3.6 equiv), trifluoromethanesulfonic CF₃SO₃H (1.5 equiv), or trifluoroacetic CF₃COOH (1.5 equiv) acid. Their structures were unambiguously confirmed with high-resolution mass spectrometry and multinuclear (¹H, ¹³C, ²⁹Si) NMR spectroscopy (see Experimental Section and the Supporting Information). The chemical shifts of ²⁹Si NMR signals were within the expected region for alkyl-substituted cubic POSS[3] at $\delta = -66.52$, $-66.53$, and $-66.65$ ppm (single, sym-

metrical peak) for **1**, **2**, and **3**, respectively, and confirmed the presence of only one type of Si nucleus. The characteristic peaks ($\delta = 8.23$, 2.79, 1.74, 0.75 ppm for **1**, $\delta = 7.57$, 2.75, 1.56, 0.66 ppm for **2**, and $\delta = 7.97$, 2.79, 1.61, 0.62 ppm for **3**) in the ¹H NMR spectra indicated the formation of cage-like structures with terminal -PrNH₃⁺ moieties (Table 1). In the FTIR spectra of **1**–**3**, the Si-O-Si stretching gave strong absorptions around 1116, 1136, and 1132 cm⁻¹ for **1**, **2**, and **3**, respectively. Siloxane absorption, compared those obtained with conventional hybrid materials obtained by sol-gel method, were much narrower in **1**–**3**, supporting a high symmetry of the resulting products.

Crystalline compounds **1** and **2** were selected as the most promising materials for subsequent investigations. Compound **3** was excluded because it continued to form a highly hygroscopic glassy product, which appeared to be more difficult to hand in further studies. The crystalline nature of **1**–**3** and other compounds was confirmed by using powder XRD analysis (Figure 2 and the Supporting Information). We also investigated the compounds by TEM analysis combined with selected area electron diffraction (SAED) analysis (Figure 3). Particles were found to form in the nanometer size range (5–10 nm). TEM images clearly showed that **3** constituted a shapeless product.

Ionic compounds **1** and **2** were next utilized to obtain cube-like neutral aminopropylsilsesquioxane **4** (OAS-POSS). From a synthetic perspective, it is much better to generate **4** in a one-pot transformation from crystalline, air-stable compounds **1** or **2** directly before the synthesis of the target OAS-POSS derivatives because pure, liquid **4** is constantly evolving in solution. It is worth noting here that the synthesis of **4** and its derivatives requires strictly anhydrous conditions, otherwise

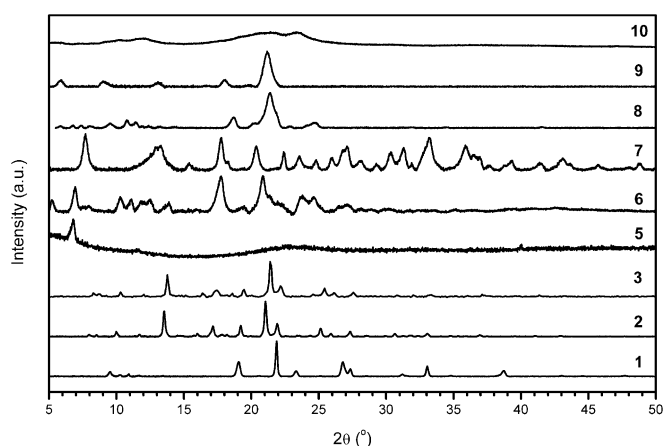| Table 1. NMR Data for **1-4**. | | | |
|---|---|---|---|
| Compound | ¹H NMR (NH₃⁺), (CH₂NH₃⁺), (-CH₂-), (SiCH₂) | ¹³C NMR (CH₂NH₃⁺), (-CH₂-), (SiCH₂) | ²⁹Si NMR[a] |
| **1** | 8.23, 2.79, 1.74, 0.75[a] | 41.7, 20.6, 8.7[c] | −66.52 |
| **2** | 7.57, 2.75, 1.56, 0.66[a] | 122.5 (CF₃SO₃⁻), 44.4, 23.3, 11.3[c] | −66.53 |
| **3** | 8.04, 2.80, 1.62, 0.62[a] | 159.5 (CF₃COO⁻), 117.4 (CF₃COO⁻), 41.4, 21.0, 8.6[a] | −66.65 |
| **4** | 2.60, 1.54, 0.63[b] | 44.4, 26.6, 9.8[a] | −66.53 |
| [a] Measured in DMSO. [b] Measured in CD₃OD. [c] Measured in D₂O. | | | |

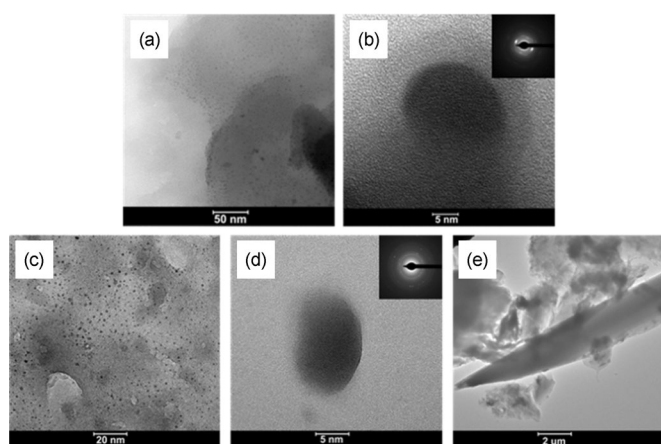**Figure 2.** Powder XRD patterns for **1–3** and **5–10**.



**Figure 3.** TEM Images of **1** (a, b), **2** (c, d), and **3** (e), and selected area diffraction patterns (Insets in b and d). Scale bars: a) 50 nm; b) 5 nm; c) 20 nm; d) 5 nm; e) 2 μm.

the formation of open cage-like **5** can be postulated as shown in Scheme 2.

As mentioned above, during the synthesis of **4** from **1** or **2** under hydrous conditions, we noticed decomposition of the cage-like structure. To investigate this effect, 5% aqueous solution of sodium hydrocarbonate was added to **1** in a controlled way. To inhibit degradation of **5** in solution, this compound
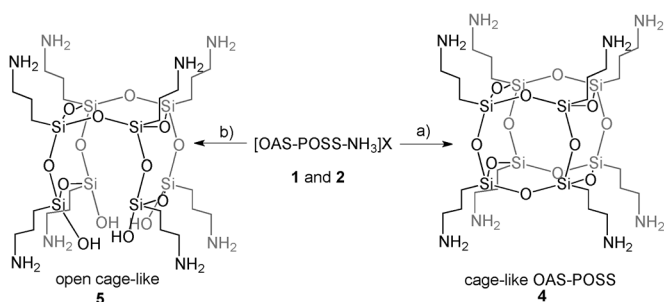


**Scheme 2.** The formation of cage-like OAS-POSS and open cage-like structures depending on reaction conditions: a) anhydrous conditions; b) hydrous conditions.

was transformed into a stable salt through the addition of a methanol solution of hydrochloric acid (0.5 M). In the proton NMR spectrum of the resulting white precipitate of **5**, a broad signal at $\delta = 3.64$ ppm for the silanol group was observed; in the NOESY spectrum, this signal gave an NOE cross-peak with the -$NH_3^+$ signal (Figure S19). An open cage-like structure was proposed based on the $^{29}Si$ NMR spectra (Figure 4).
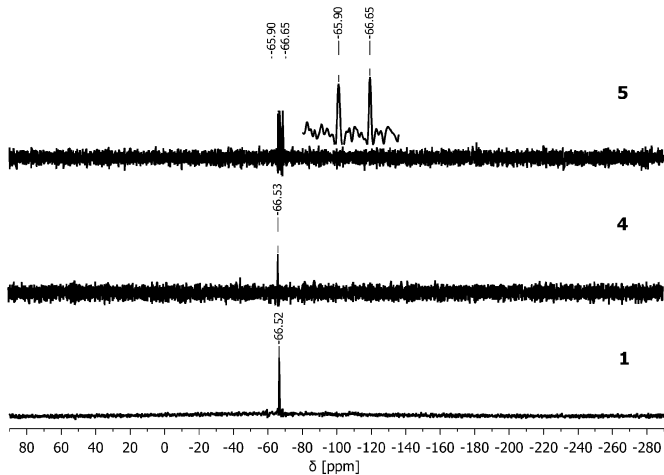


**Figure 4.** $^{29}Si$ NMR (59.6 MHz, [$D_6$]DMSO, 20 °C) spectra of **1**, **4**, and **5**.

For OAS-POSS **4** and its salt **1**, only one signal assigned to the Si nucleus at approximately $\delta = -66.5$ ppm was observed. In the case of open cage-like compound **5**, two signals from silicon nuclei were localized at $\delta = -65.90$ and $-66.65$ ppm. The first signal derives from the silicon atom with three Si-O-Si moieties, and the second from signals with two Si-O-Si and one Si-OH groups (see Scheme 2). Both signals possess similar intensity, because they correspond to four silicon atoms each. Moreover, in the $^{13}C$ NMR spectra of **5**, the carbon atoms directly bound to the silicon (signals at $\delta = 9.0$ and 8.7 ppm) have a different chemical shift compared with those from the cage-like structures (one signal at $\delta = 9.8$ ppm for **4**). Furthermore, the presence of silanol groups, which are characteristic for open cage-like structure, can be easily identified by using infrared spectroscopy. The ν(Si-OH) vibration was observed at 990 cm$^{-1}$. Furthermore, the structure of **5** was additionally supported by mass spectrometry (see the Supporting Information). Based on the previous reports, the mechanism of opening of cage-like compound **4** involves attack by an amine nitrogen on the silicon atom, which further reacts with water to produce a silanol moiety.[22] It should be emphasized that the core opening is caused not by the presence of a hydroxyl group but by an aliphatic amine. This conclusion is supported by the fact that during further synthesis of the amide-derivatives, the final product was washed with an aqueous solution of NaHCO$_3$ and if the amine group was blocked such an opening did not occur.

The presence of -PrNH$_2$ side-chains of neutral **4** was confirmed by using $^1H$ NMR spectroscopic analysis. Signals of identical integration localized at $\delta = 2.60$, 1.54, and 0.63 ppm were

assigned to -C$H_2$N$H_2$, -SiC$H_2$C$H_2$C$H_2$N$H_2$, and -SiC$H_2$- fragments, respectively. Given that these chemical shifts would be similar for all the "aminopropyl" compounds, in Table 1 we show these data for other species.

The $^{29}$Si NMR spectrum exhibited only one symmetrical peak, as expected for a cubic structure, which strongly indicates the presence of only one type of silicon atoms in the molecule of **4**, comprised of three siloxane -Si-O-Si- moieties. No silanol groups were observed. The mass spectrum {HRMS (ESI+, TOF/CH$_3$OH): m/z (%): 881.2916 (45) [M+H]$^+$ (calcd 881.2871), 441.1635 (100) [M+2H]$^{2+}$ (calcd 441.1469), 294.4442 (20) [M+3H]$^{3+}$ (calcd 294.4339)} confirmed the formation of a closed frame structure composed of eight silicon atoms possessing terminal aminopropyl side-chains.

In the next step, homo-octafunctionalized **1** and **2** were used for the preparation of a diverse set of hybrid materials. This demonstrates that **1** and **2** constitute attractive scaffold platforms for the controlled synthesis of well-defined amido-functionalized homo-polyoctasilsesquioxanes. First, to modify **1** and **2**, we used benzoyl chloride and its 4-nitro- and 4-fluoro-derivatives as well as hexanoyl chloride, as presented in Scheme 3. Next, the resulting 4-nitrobenzoyloamide-POSS was utilized to prepare 4-aminobenzoyloamide-POSS as shown in Scheme 4. The use of acyl chlorides led to higher yields (ca. 90%) compared with those observed in the "conventional" re-
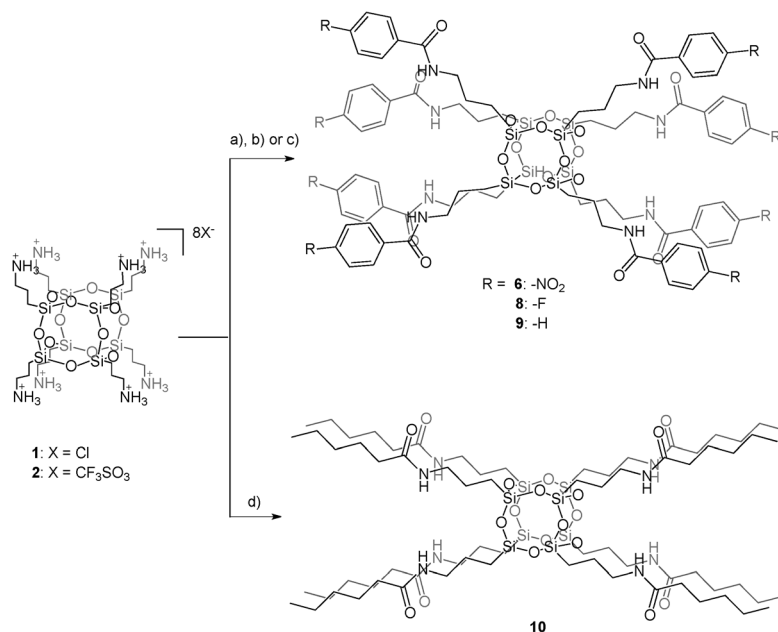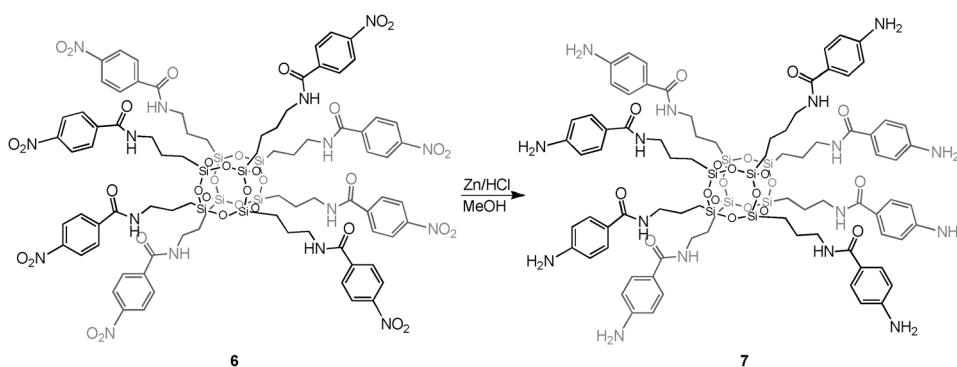


Scheme 4. Synthesis of 7 by reduction of 6 with hydrogen.

actions through the use of carboxylic acids or acid anhydrides (ca. 60%).[21]

Initially, benzoylation reactions were carried out according to the Schotten–Baumann[23] reaction by using sodium hydroxide as base. However, NaOH proved to be too strong, causing decomposition of the polyoctasilsesquioxane core. Furthermore, application of a weaker base (an aqueous solution of sodium hydrogencarbonate), did not work. Only the use of the weak base triethylamine avoided destruction of the siloxane core. An excess of triethylamine was used 1) to generate amine **4** in situ, which further reacted with benzoyl chloride and 2) to neutralize HCl, which was liberated from appropriate acyl chloride, during the reaction with **1** or **2**. This procedure allowed the synthesis of various benzamido-derivatives of octaaminopropylsilsesquioxanes (**6**, **8**, and **9**). During the reaction, 1.1 equiv of acid chloride was used and reaction was performed in N,N-dimethylformamide at 0 °C. Notably, in the reaction with an excess of aryl acid chloride, the presence of tertiary amide was not observed, which contrasts with the reactions with alkyl amide. NMR spectra that confirmed this phenomenon are presented in Figure S24. The product yields were successfully increased by leaving the reaction mixture in a freezer overnight.

Next, 4-amino compound **7** was obtained by reduction of nitro-derivative **6** with hydrogen generated in situ, as shown in Scheme 4. Compound **7** is stable even when NaOH was used to remove Zn(OH)$_2$ and neutralize an excess of acid (use of a strong base did not lead to destruction of the cubic core). This stability was confirmed by $^{29}$Si NMR spectroscopic analysis (Figure 5), which revealed only one chemical shift at $\delta = -68.0$ ppm.



Scheme 3. Syntheses of homoocta-functionalized POSS-based hybrid materials. a) 6: 4-nitrobenzoyl chloride 8.8 equiv, NEt$_3$ 18.5 equiv, DMF, 0 °C; b) 8: 4-fluorobenzoyl chloride 8.8 equiv, NEt$_3$ 18.5 equiv, DMF, 0 °C; c) 9: benzoyl chloride 8.8 equiv, NEt$_3$ 18.5 equiv, DMF, 0 °C; d) hexanoyl chloride 16.3 equiv, NEt$_3$ 26.4 equiv, DMF, 0 °C.
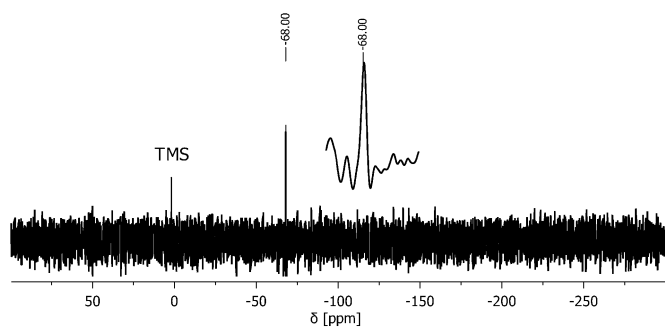
**Figure 5.** $^{29}$Si NMR (59.6 MHz, [D$_6$]DMSO, 20 °C) spectrum of **7**.



**Figure 7.** FTIR of **10** possessing a narrow absorption band assigned to Si-O-Si stretching.

In contrast, the reaction of **1** or **2** with hexanoyl chloride in a mixture of NEt$_3$ and *N,N*-dimethylformamide (DMF) gave hexanoamide derivative **10** as shown in Scheme 3. After purification by silica gel column chromatography, more than one product was identified by mass spectrometry; these products differed in the number of attached C$_6$H$_{11}$O groups (Figure 6) and their final separation was possible by passing the mixture twice through a flash silica gel column. The purity of homoocta-substituted **10** was confirmed by NMR and FTIR spectroscopic methods and by mass spectrometry (see the Experimental Section and the Supporting Information).

To ascertain the presence of aminopropyl side-chains, all reactions were tested by using ninhydrin. Given that none of the tests resulted in a violet color (in contrast to the to so-called control), the presence of a primary amine was excluded. Pure homoocta-substituted final product was confirmed by available spectroscopic methods and by mass spectrometry (see the Experimental Section and the Supporting Information).

All amido-functionalized POSS compounds were characterized by using FTIR and multinuclear NMR ($^1$H, $^{13}$C, $^{29}$Si) spectroscopy, and mass spectrometry. In the infrared spectra, the amide group gave specific absorption bands, for example, for **6** vibrations at 1649, 1547, and 1301 cm$^{-1}$ can be clearly as-
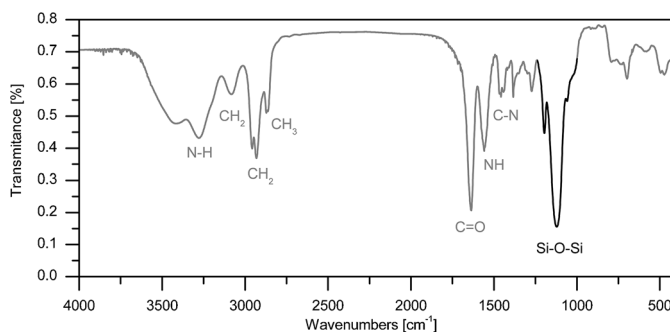
signed to ν(C=O), δ(N-H), and ν(C-N) modes. Furthermore, ν(Si-O-Si) stretching appeared at 1222 cm$^{-1}$. It is also worth noting that the absorption band in the range of siloxane Si-O-Si bond vibrations was narrow, as shown in Figure 7. This phenomenon is not common and is extremely important from the application point of view.

In all cases, except **5**, the presence of silanol groups was excluded. This was confirmed by the high stability of amide-derivatives in the alkaline environment, in which the siloxane network was maintained. This can be explained by the presence of side-chains with large steric bulk. This contrasts with OAS-POSS for which there is a high probability of the formation of open cage-like structures depending on the environment. Therefore, from the synthetic point of view, the amide-derivatives possessing extended substituents stay in competition to non-ramified octaaminopropylsilsesquioxanes structures, which are prone to decomposition in solution.

Moreover, all compounds were purified by using column chromatography, which allowed for the separation of the target compounds from side-products that do not hold fully substituted side-chains. Such homo-substitution was unambig-
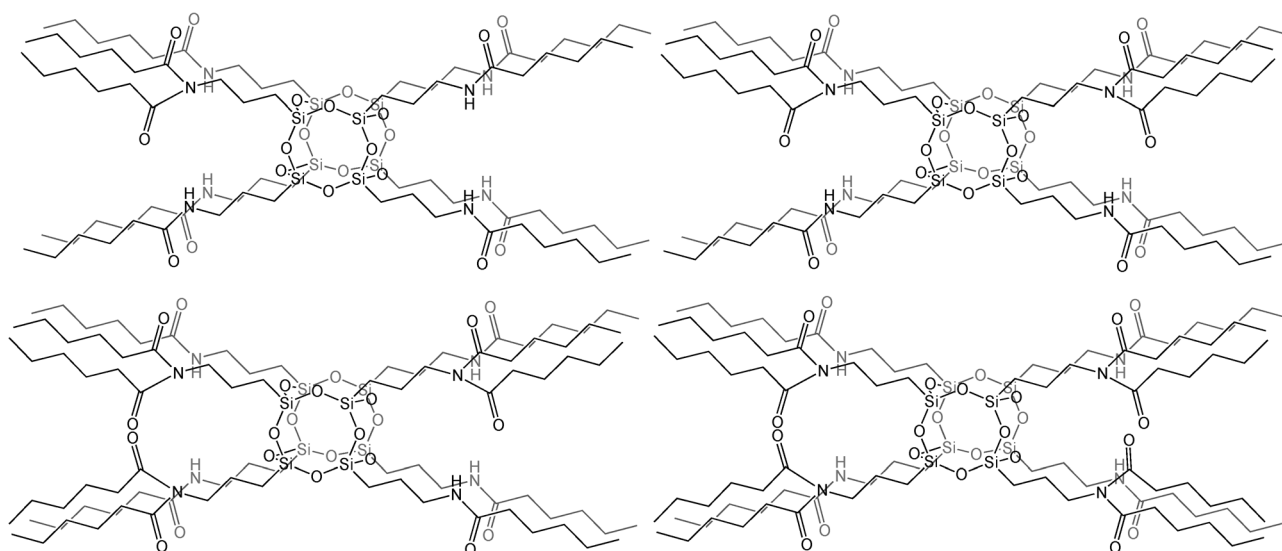


**Figure 6.** Examples of by-products identified during the reaction of hexanoyl chloride with **1** or **2**.

uously verified by mass spectrometry (see the Supporting Information).

Thermal stability of amide-POSS **6**–**10** was also examined under aerobic conditions (for TGA-DTA details see the Supporting Information). Generally, thermal decomposition occurred in two steps. The first mass-loss corresponded to extrusion of the side-chains. In the second step ($>400\,^{\circ}$C), the siloxane cage decomposed to $SiO_2$, which was confirmed by FTIR spectroscopy. For **9**, extrusions of side-chains occurred at lower temperature ($165\,^{\circ}$C), but substitution of aryl ring in the *para*-position increased this temperature, which, for **8**, approached $396\,^{\circ}$C. Decomposition temperatures for 4-substituted amide-derivatives, and for hexanoamide **10**, were higher compared with **1** and **2**. For instance, decomposition of **1** occurred at $314\,^{\circ}$C. No MS analysis of the volatiles was performed.

Compounds **6**–**10** were next used to obtained crystalline nanoparticles. The resulting species were dissolved in dimethyl sulfoxide (DMSO) and precipitated with deionized water. Such suspensions were centrifuged at a speed of 5800 rpm and the resulting powders were sonicated in methanol. The resulting particles had a diameter of approximately 5 nm, spherical-like (aryl substituents) shape, and did not form agglomerates as shown in Figure 8. The only exception was nanoparticles of **10**, which had a fibrous-like morphology. This could be explained by the presence of carbon side-chains attached to the POSS core. The composition of all nanoparticles was confirmed by EDS analysis (see the Supporting Information) and their crystallinity was examined by powder XRD and SAED measurements.
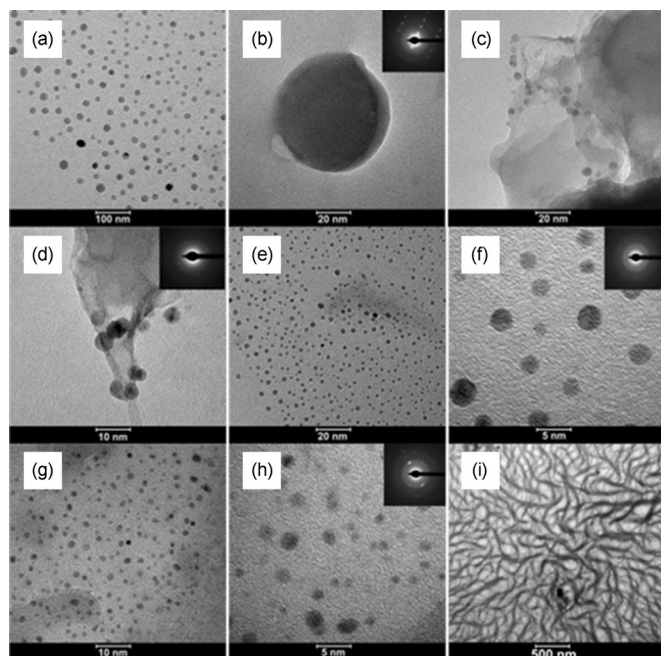


**Figure 8.** Selected HR-TEM Images of **6** (a, b), **7** (c, d), **8** (e, f), **9** (g, h), and **10** (i) particles. Selected area electron diffraction patterns are placed as insets in b, d, f, h images. Scale bars: a) 100 nm; b) 20 nm; c) 20 nm; d) 10 nm; e) 20 nm; f) 5 nm; g) 10 nm; h) 5 nm; i) 500 nm.

## Conclusion

We have shown that salts derived from OAS-POSS containing anions such as $Cl^-$ and $CF_3SO_3^-$ constitute ideal starting materials for the controlled assembly of well-defined homooctaamido-functionalized POSS. By using sulfonide salt, we noticed higher yields in the synthesis of amide-derivatives; for example, for **6**, yields of up to 97% were obtained. The applied synthetic approach allowed various organic substituents (alkyl and aryl) to be bound to the siloxane cage-like core. Careful optimization of the reaction conditions enabled the formation of unwanted by-products such as open cage-like polysilsesquioxanes to be avoided. We also demonstrated that by using the wide range of organic substituents, it is possible to prepare functionalized nanoparticles that are difficult to obtain by using pure organic molecules without their attachment to the siloxane core. Notably, the spherical-shaped particles do not form agglomerates and are nicely separated. Such organic-inorganic nanohybrids open up a wide field of applications, for instance as a column fillers for advanced organic and inorganic synthesis or efficient drug delivery systems. These kinds of material can effectively replace functionalized silica, and add unique characteristics including superior thermal, mechanical, and chemical properties.

## Experimental Section

**General procedures and chemicals**: All reactions were conducted under $N_2$ with the use of standard Schlenk techniques. Hexanes and diethyl ether were distilled from Na, tetrahydrofuran was pre-dried with NaOH and then distilled from Na/benzophenone; acetone was distilled from $P_2O_5$; ethanol (anhydrous, J. T. Baker), methanol, and chloroform (HPLC grade) were used as received. Dimethyl sulfoxide and dimethylformamide (99.8% anhydrous, Aldrich) were dried over activated 4 Å molecular sieves prior to use. Benzoyl chloride (98%, Aldrich), 4-nitrobenzoyl chloride (98%, Aldrich), 4-fluorobenzoyl chloride (98%, Aldrich), hexanoyl chloride (99%, Merck), (3-aminopropyl)triethoxysilane (99%, Aldrich), trifluoroacetic acid (98%, Aldrich), trifluoromethanesulfonic acid (98%, Aldrich), triethylamine (99.5%, Aldrich), zinc dust (99,99%, Fluka), HCl (36–38%, Avantor Performance Materials Poland S.A.), $NaHCO_3$ (Avantor Performance Materials Poland S.A.) were used without further purification unless stated otherwise. Chromium(III) acetylacetonate was prepared by following the described procedure.[24]

**Methods**: $^1$H and $^{13}$C NMR spectra were recorded with a Bruker Avance 500 or a Bruker Avance III 600 spectrometer. $^{29}$Si NMR spectra were recorded with a Bruker AMX-300 spectrometer using Wildmad's PTFE-FEP (polytetrafluoroethylene/fluorinated ethylene polypropylene copolymer) 5 mm tube liners. Cr(acac)$_3$ was added in a concentration of approximately $10^{-2}$ mol L$^{-1}$ as a shiftless relaxation agent. Chemical shifts are reported in parts per million ($\delta$) downfield from tetramethylsilane and are referenced to residual peaks of deuterated NMR solvents. Chemical shift values for $^{29}$Si{$^1$H} NMR spectra were referenced to TMS or DSS. Assignments are based on COSY, NOESY, HSQC, and HMBC correlation experiments. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates. Chromatograms were visualized by using UV light (254 nm). For the detection of amine, the chromatograms were first dipped in a 5% (w/v) solution of ninhydrin in 95% aqueous ethanol, and finally charred on a hotplate. Flash column chro-

matography was performed with Merck silica gel, grade 60, 230–400 mesh. Elemental analyses were performed with a Vario EL III element analyzer. Infrared spectra were recorded in a KBr cell with a Bruker Vertex 70 FTIR spectrometer. High-resolution and accurate mass spectra were recorded with a Bruker apex ultra FTMS and a Bruker microTOF-Q spectrometer using the electrospray technique. TG-DTA analyses were recorded with a Setaram SETSYS 16/18 instrument. Samples for thermogravimetric characterization were placed in open alumina crucibles in an air atmosphere. A heating rate of $10\,^{\circ}C\cdot min^{-1}$ was applied and all samples were studied between 40 and $1000\,^{\circ}C$. Samples for transmission electron microscopy (TEM) were prepared by dispersing the powder in ethanol and depositing the suspension on a holed carbon copper grid. The images were obtained with a FEI Tecnai G2 F20 X-TWIN Transmission Electron Microscope equipped with a Penta FET EDX detector. Powders were characterized by recording X-ray powder diffraction (XRD) patterns with a Bruker D8 ADVANCE diffractometer equipped with a copper lamp ($\lambda_{CuK\alpha} = 1.5406$ Å). Standard measurements were done for $2\theta = 5$–$50^{\circ}$ with a $2\theta$ step of $0.016^{\circ}$ and a counting time of 1 s.

**Synthesis of 1**: Concentrated HCl (200 mL) was carefully added to a continuously stirring solution of (3-aminopropyl)triethoxysilane (150 mL, 139.4 g, 0.641 mol) in MeOH (1.0 L) in a 2.0 L round-bottom flask. The flask was capped and the solution was stirred at RT for 4 weeks at $25\,^{\circ}C$. A product started to crystallize after 2 weeks. Pure **1** was obtained by filtering the reaction mixture, washing with cold MeOH, and drying under vacuum ($25\,^{\circ}C$, 0.5 mbar) in 45 % yield (42.3 g). An additional portion of **1** (6.58 g, 7 %) was collected by adding ethanol to the filtrate. Analytically pure product could be obtained as a white microcrystalline powder by recrystallization from hot MeOH. $^1$H NMR (500 MHz, [D$_6$]DMSO, $20\,^{\circ}C$): $\delta = 8.23$ (s, 24 H; NH$_3^+$), 2.79 (t, $^3J$(H,H) $= 7.9$ Hz, 16 H; CH$_2$NH$_3^+$), 1.74 (m, 16 H; SiCH$_2$CH$_2$CH$_2$NH$_3^+$), 0.75 ppm (t, $^3J$(H,H) $= 8.6$ Hz, 16 H; SiCH$_2$); $^{13}$C{$^1$H} NMR (126 MHz, D$_2$O, $20\,^{\circ}C$): $\delta = 41.7$ (s, SiCH$_2$CH$_2$CH$_2$NH$_3^+$), 20.6 (s, SiCH$_2$CH$_2$CH$_2$NH$_3^+$), 8.7 ppm (SiCH$_2$CH$_2$CH$_2$NH$_3^+$); $^{29}$Si{$^1$H} NMR ([D$_6$]DMSO, 59.6 MHz, $20\,^{\circ}C$): $\delta = -66.52$ ppm (s, $^1J$(Si,C) $= 45$ Hz; T$^3$); FTIR (KBr pellets): $\tilde{\nu} = 3041$ (s, $\nu_{N-H}$), 2935 (m, $\nu_{C-H}$), 2872 (m, $\nu_{C-H}$), 1615 (m, $\delta_{NH3}$), 1500 (m, $\nu_{C-N}$), 1237 (m, $\nu_{Si-C}$), 1116 (s, $\nu_{cage-asymSi-O-Si}$), 941 (m, $\nu_{cage-symSi-O-Si}$), 798 (w, $\delta_{Si-C}$), 701 (m, $\delta_{O-Si-O}$) cm$^{-1}$; HRMS (ESI+, TOF/MeOH): $m/z$ (%): 881.2898 (25) {calcd. for [$M$+H−8HCl]$^+$ 881.2871}, 441.1490 (100) {calcd. for [$M$+2H−8HCl]$^{2+}$ 441.1472}, 294.4340 (28) {calcd. for [$M$+3H−8HCl]$^{3+}$ 294.4339}; elemental analysis calcd (%) for C$_{24}$H$_{72}$O$_{12}$Si$_8$N$_8$Cl$_8$ (1173.18): C 24.57, H 6.19, N 9.55, Cl 24.18; found: C 24.51, H 6.15, N 9.54, Cl 24.10. Temperature of decomposition to SiO$_2$ (determined by TGA measurement), residue yield: $314\,^{\circ}C$, 40.70 % (calcd 40.97 %).

**Synthesis of 2**: CF$_3$SO$_3$H (0.5 M aqueous solution, 30 mL, 15.0 mmol) was added with stirring at RT to (3-aminopropyl)triethoxysilane (2.34 mL, 2.17 g, 10.0 mmol). The resulting solution was further stirred for 3 h and then heated to approximately $50\,^{\circ}C$ in an open beaker until the solvent had completely evaporated (3 h). The crude product was heated at $100\,^{\circ}C$ for 1 h, then cooled to RT and acetone (100 mL) was added. The precipitate was isolated by filtration, washed with acetone ($3 \times 10$ mL), and dried in a vacuum oven ($50\,^{\circ}C$, 20 mbar, 48 h) to give **2** (2.24 g, 95 %) as a white powder. $^1$H NMR (500 MHz, [D$_6$]DMSO, $20\,^{\circ}C$): $\delta = 7.57$ (s, 24 H; NH$_3^+$), 2.75 (t, $^3J$(H,H) $= 7.2$ Hz, 16 H; CH$_2$NH$_3^+$), 1.56 (m, 16 H; SiCH$_2$CH$_2$CH$_2$NH$_3^+$), 0.66 ppm (t, $^3J$(H,H) $= 8.6$ Hz, 16 H; SiCH$_2$); $^{13}$C{$^1$H} NMR (126 MHz, D$_2$O, $20\,^{\circ}C$): $\delta = 122.5$ (q, $^1J$(C,F) $= 317$ Hz; CF$_3$SO$_3^-$), 44.4 (s; SiCH$_2$CH$_2$CH$_2$NH$_3^+$), 23.3 (s; SiCH$_2$CH$_2$CH$_2$NH$_3^+$), 11.3 ppm (s; SiCH$_2$CH$_2$CH$_2$NH$_3^+$); $^{29}$Si{$^1$H} NMR (59.6 MHz, [D$_6$]DMSO, $20\,^{\circ}C$): $\delta = -66.53$ ppm (s, T$^3$); FTIR (KBr pellets): $\tilde{\nu} = 3041$ (s, $\nu_{N-H}$),

1615 (m, $\delta_{NH3}$), 1507 (m, $\nu_{C-N}$), 1267 (s, $\nu_{C-F}$), 1226 (m, $\nu_{Si-C}$), 1138 (s, $\nu_{Si-O-Si}$), 103 (s, $\nu_{SO3}$), 640 (s, $\nu_{S-N}$) cm$^{-1}$; HRMS (ESI+, TOF, 5 % AcOH/H$_2$O): $m/z$ (%): 881.2898 (30) {calcd. for [$M$+H−8CF$_3$SO$_3$H]$^+$ 881.2871}, 441.1572 (100) {calcd. for [$M$+2H−8CF$_3$SO$_3$H]$^{2+}$ 441.1472}, 294.4400 (20) {calcd. for [$M$+3H−8CF$_3$SO$_3$H]$^{3+}$ 294.4339}; elemental analysis calcd (%) for C$_{32}$H$_{72}$F$_{24}$N$_8$O$_{36}$S$_8$Si$_8$ (2081.67): C 18.46, H 3.49, N 5.38, S 12.32; found: C 18.40, H 3.46, N 5.37, S 12.30. Temperature of decomposition to SiO$_2$ (determining by TGA measurement), residue yield: $428\,^{\circ}C$, 23.00 % (calcd 23.09 %).

**Synthesis of 3**: Trifluoroacetic acid aqueous solution (5 %, 68.4 mL, 30.0 mmol) was added at RT to (3-aminopropyl)triethoxysilane (3.51 mL, 3.26 g, 15.0 mmol). The resulting solution was stirred for 2 h and then kept at $50\,^{\circ}C$ in an open system until the solvent completely evaporated (usually 2–3 h). The crude product was then maintained at $100\,^{\circ}C$ for 1 h. The product was washed with acetone ($4 \times 20$ mL), and then dried under vacuum ($25\,^{\circ}C$, 0.5 mbar) to give **3** (3.03 g, 90 %) as a hygroscopic glassy product. $^1$H NMR (500 MHz, [D$_6$]DMSO, $20\,^{\circ}C$): $\delta = 8.21$--7.86 (br, 24 H; NH$_3^+$), 2.87–2.72 (br, 16 H; CH$_2$NH$_3^+$), 1.70–1.54 (br, 16 H; SiCH$_2$CH$_2$CH$_2$NH$_3^+$), 0.74–0.50 ppm (br, 16 H; SiCH$_2$); $^{13}$C NMR (126 MHz, [D$_6$]DMSO, $20\,^{\circ}C$): $\delta = 159.5$ (q, $^2J$(C,F) $= 32$ Hz; CF$_3$COO$^-$), 117.4 (q, $^1J$(C,F) $= 297$ Hz; CF$_3$COO$^-$), 41.4 (s; SiCH$_2$CH$_2$CH$_2$NH$_3^+$), 21.0 (s; SiCH$_2$CH$_2$CH$_2$NH$_3^+$), 8.6 ppm (s; SiCH$_2$CH$_2$CH$_2$NH$_3^+$); $^{29}$Si{$^1$H} NMR (59.6 MHz, [D$_6$]DMSO, $20\,^{\circ}C$): $\delta = -66.65$ ppm (s, T$^3$); FTIR (KBr pellets): $\tilde{\nu} = 2944$ (s, $\nu_{N-H}$), 1674 (m, $\delta_{NH3}$), 1533 (s, $\nu_{co}$), 1473 (m, $\nu_{C-N}$), 1267 (s, $\nu_{C-F}$), 1132 (s, $\nu_{Si-O-Si}$) cm$^{-1}$; HRMS (ESI+, TOF/CH$_3$OH): $m/z$ (%): 881.2862 (24) {calcd. for [$M$+H−8CF$_3$COOH]$^+$ 881.2871}, 441.1475 (100) {calcd. for [$M$+2H−8CF$_3$COOH]$^{2+}$ 441.1469}; elemental analysis calcd (%) for C$_{40}$H$_{72}$F$_{24}$N$_8$O$_{28}$Si$_8$ (1793.76): C 26.78, H 4.05, N 6.25; found: C 26.75, H 4.01, N 6.21. Temperature of decomposition to SiO$_2$ (determining by TGA measurement), residue yield: $353\,^{\circ}C$, 26.70 % (calcd 26.60 %).

### Synthesis of 4

Method A: Amberlite IRA-400 ion-exchange resin (37.0 g) was prepared by washing with water ($4 \times 200$ mL), 1 M NaOH ($3 \times 200$ mL), water ($6 \times 200$ mL), and MeOH (elution solvent, $6 \times 200$ mL). The resin was suspended in MeOH (200 mL) and chilled ($-18\,^{\circ}C$, 5 h) before use. Half of the resin beads were loaded onto a column (3.0 cm outside diameter) and the other half was used to prepare a suspension of **1** (0.500 g, 0.426 mmol) in a minimum amount of eluent (ca. 5 mL) at $-18\,^{\circ}C$. Elution across the column produced a solution of **4**, which tested negative for chloride (by addition of AgNO$_3$). The solvent was removed with nitrogen flow at $0\,^{\circ}C$ and then evaporated ($0\,^{\circ}C$, 0.5 mbar) to afford **4** (50 %, 0.200 g) as a yellowish resin. Compound **4** should be freshly prepared before use and stored as a MeOH solution at $-18\,^{\circ}C$. $^1$H NMR (500 MHz, MeOD, $20\,^{\circ}C$): $\delta = 2.60$ (t, $^3J$(H,H) $= 7.9$ Hz, 16 H; CH$_2$NH$_2$), 1.54 (m, 16 H; SiCH$_2$CH$_2$CH$_2$NH$_2$), 0.63 ppm (t, $^3J$(H,H) $= 8.6$ Hz, 16 H; SiCH$_2$); $^{13}$C{$^1$H} NMR (126 MHz, [D$_6$]DMSO, $20\,^{\circ}C$): $\delta = 44.4$ (s; SiCH$_2$CH$_2$CH$_2$NH$_2$), 26.6 (s; SiCH$_2$CH$_2$CH$_2$NH$_2$), 9.8 ppm (s; SiCH$_2$CH$_2$CH$_2$NH$_2$); $^{29}$Si{$^1$H} NMR (59.6 MHz, [D$_6$]DMSO, $20\,^{\circ}C$): $\delta = -66.53$ ppm (s; T$^3$); FTIR (KBr pellets): $\tilde{\nu} = 3041$ (s, $\nu_{N-H}$), 2935 (m, $\nu_{C-H}$), 2872 (m, $\nu_{C-H}$), 1615 (m, $\delta_{NH2}$), 1500 (m, $\nu_{C-N}$), 1237 (m, $\nu_{Si-C}$), 1116 (s, $\nu_{ring-asym Si-O-Si}$), 941 (m, $\nu_{ring-sym Si-O-Si}$), 798 (w, $\delta_{Si-C}$), 701 (m, $\delta_{O-Si-O}$) cm$^{-1}$; HRMS (ESI+, TOF/CH$_3$OH): $m/z$ (%): 881.2916 (45) {calcd. for [$M$+H]$^+$ 881.2871}, 441.1635 (100) {calcd. for [$M$+2H]$^{2+}$ 441.1469}, 294.4442 (20) {calcd. for [$M$+3H]$^{3+}$ 294.4339}; elemental analysis calcd (%) for C$_{24}$H$_{64}$N$_8$O$_{12}$Si$_8$ (881.50): C 32.70, H 7.32, N 12.71; found: C 32.69, H 7.35, N 12.69, Cl 0. Temperature of decomposition to SiO$_2$ (determined by TGA), residue yield: $210\,^{\circ}C$, 54.60 % (calcd 54.53 %).

**Method B**: The procedure was analogous to that described in Method A with the use of **2** (0.510 g, 0.245 mmol) instead of **1**.

Yield: 0.190 g (88%). Elemental analysis calcd (%) for $C_{24}H_{64}N_8O_{12}Si_8$ (881.50): C 32.70, H 7.32, N 12.71; found: C 32.68, H 7.40, N 12.75.

**Synthesis of 5·8HCl**: A solution of **4** (0.150 g, 0.170 mmol) in MeOH (50 mL) was added to a solution of NaHCO₃ (2.50 g, 19.1 mmol) in double-distilled H₂O (50 mL), and the mixture was stirred for 6 h. MeOH and water were removed under vacuum (25 °C, 0.5 mbar) to afford a yellow resin of **5**. The product was washed with water (3×30 mL) and 0.5 M methanolic solution of HCl (0.34 mL, 0.170 mmol) was added to give **5·8HCl** (0.196 g, 95%). ¹H NMR (500 MHz, [D₆]DMSO, 20 °C): $\delta = 8.04$ (s, 24H; NH₃⁺), 3.64 (br, 4H; OH), 2.80 (br, 16H; CH₂NH₃⁺), 1.62 (br, 16H; SiCH₂CH₂CH₂NH₃⁺), 0.67 (br, 8H; HOSiCH₂), 0.64 ppm (br, 8H; O₃SiCH₂); ¹³C{¹H} NMR (126 MHz, [D₆]DMSO, 20 °C): $\delta = 41.7$ (s; SiCH₂CH₂CH₂NH₃⁺), 20.6 (s; SiCH₂CH₂CH₂NH₃⁺), 9.0 (s; O₃SiCH₂CH₂CH₂NH₃⁺), 8.7 ppm (s; HOSiCH₂CH₂CH₂NH₃⁺); ²⁹Si{¹H} NMR ([D₆]DMSO, 59.6 MHz, 20 °C): $\delta = -65.90$ (s; T²), $-68.55$ ppm (s; T³); FTIR (KBr pellets): $\tilde{v} = 3436$ (s, $v_{O-H}$), 3041 (s, $v_{N-H}$), 1610 (m, $\delta_{NH3}$), 1500 (m, $\delta_{NH3}$), 1136 (s, $v_{Si-O-Si}$), 990 (m, $v_{Si-OH}$), 799 (w, $\delta_{Si-C}$), 554 (w, $\delta_{O-Si-O}$) cm⁻¹; HRMS (ESI+, TOF): m/z (%): 917.230 (100) {calcd. for $[M+H-8HCl]^+$ 917.308}; elemental analysis calcd (%) for $C_{24}H_{76}O_{14}Si_8N_8Cl_8$ (1209.21): C 23.84, H 6.33, N 9.27, Cl 23.46; found: C 23.41, H 6.38, N 9.20, Cl 23.40. Temperature of decomposition to SiO₂ (determined by TGA measurement), residue yield: 324 °C, 41.00% (calcd 40.97%).

### Synthesis of 6

**Method A**: 4-Nitrobenzoyl chloride (0.080 g, 0.422 mmol, 8.8 equiv) was added dropwise to a solution of **1** (0.0563 g, 0.0480 mmol) and NEt₃ (0.124 mL, 90.0 mg, 0.888 mmol, 18.5 equiv) in DMF (10 mL). After stirring overnight at −18 °C, the crude product was precipitated by slow addition to 1.0 M aqueous HCl (75 mL, 0 °C). Filtration, extraction into DMSO (10 mL), precipitation with cold, saturated NaHCO₃ (75 mL), washing with water, and drying in vacuo (25 °C, 0.5 mbar) afforded a yellow solid of crude **6** (0.0931 g, 93%), which was purified by flash column chromatography (hexane/ EtOH/MeOH, 8:1:1 v/v/v) to give **6** (0.090 g, 90% overall yield) as a yellowish solid ($R_f = 0.16$). ¹H NMR (600 MHz, [D₆]DMSO, 20 °C): $\delta = 8.72$ (s, 8H; 8NH), 8.13 (dd, $^3J(H,H) = 8.7$ Hz, $^5J(H,H) = 1.7$ Hz, 16H; 8m-Ph), 7.94 (dd, $^3J(H,H) = 8.8$ Hz, $^5J(H,H) = 1.3$ Hz, 16H; 8o-Ph), 3.21 (t, $^3J(H,H) = 6.9$ Hz, 16H; 8SiCH₂CH₂CH₂NH), 1.62 (m, 16H; 8SiCH₂CH₂CH₂NH), 0.68 ppm (t, $^3J(H,H) = 6.8$ Hz, 16H; 8SiCH₂CH₂CH₂NH); ¹³C{¹H} NMR (151 MHz, [D₆]DMSO, 20 °C): $\delta = 164.4$ (s, CO), 148.6 (s, CN), 140.2 (s, i-Ph), 128.6 (s, o-Ph), 123.2 (s, m-Ph), 41.9 (s, CH₂N), 22.4 (s, SiCH₂CH₂), 9.4 ppm (s, SiCH₂); ²⁹Si{¹H} NMR (59.6 MHz, [D₆]DMSO, 20 °C): $\delta = -68.03$ ppm (s; T³); FTIR (KBr pellets): $\tilde{v} = 3418$ (s, $v_{N-H}$), 2935 (m, $v_{C-H}$), 2872 (m, $v_{C-H}$), 1649 (s, $v_{C=O}$), 1598 (s, $v_{Ar}$), 1547 (s, $\delta_{NH}$), 1524 (s, $v_{asym\,N=O}$), 1488 (m, $v_{Ar}$), 1347 (s, $v_{sym\,N=O}$), 1301 (m, $v_{C-N}$), 1110 (s, $v_{ring-asym\,Si-O-Si}$), 1015 (m, $\delta_{Ar}$), 870 (m, $v_{C-NO2}$), 844 (m, $\delta_{Ar-NO2}$), 781 (w, $\delta_{Si-C}$), 718 (w, $\delta_{O-Si-O}$), 467 (w, $\delta_{Si-O-Si}$) cm⁻¹; HRMS (ESI+, TOF/MeOH): m/z (%): 2095.3525 (30) {calcd. for $[M + Na]^+$ 2095.3593}, 1059.1848 (100) {calcd. for $[M + 2Na]^{2+}$ 1059.1743}; elemental analysis calcd (%) for $C_{80}H_{88}N_{16}O_{36}Si_8$ (2074.32): C 46.32, H 4.28, N 10.80; found: C 46.36 H 4.24, N 10.76. Temperature of decomposition to SiO₂ (determining by TGA measurement), residue yield: 581 °C, 23.21% (calcd 23.17%).

**Method B**: The procedure was analogous to that described in Method A with the use of **2** (0.100 g, 0.0480 mmol) instead of **1**. Yield (crude): 0.0962 g (97%). Final yield: 0.0900 g (90%). Elemental analysis calcd (%) for $C_{80}H_{88}N_{16}O_{36}Si_8$ (2074.32): C 46.32, H 4.28, N 10.80; found: C 46.24, H 4.32, N 10.84.

**Synthesis of 7**: A 100 mL flask fitted with a reflux condenser was charged with **6** (0.100 g, 0.0480 mmol), zinc dust (0.032 g, 0.490 mmol, 10 equiv) and concentrated hydrochloric acid (36–38%, 0.127 mL, 1.47 mmol, 3 equiv). The mixture was heated in a water bath for 1 h, then the solution was neutralized by adding saturated NaHCO₃ (200 mL). Filtration followed by washing with a 1 M solution of NaOH to remove Zn(OH)₂, and a second filtration and washing with distilled water (3×35 mL), and drying in vacuo (25 °C, 0.5 mbar) afforded **7** (0.0790 g, 90%) as a yellow solid. ¹H NMR (500 MHz, [D₆]DMSO, 20 °C): $\delta = 8.11$ (t, $^3J(H,H) = 5.5$ Hz, 8H; 8NH), 7.57 (d, $J(H,H) = 8.7$ Hz, 16H; 8m-Ph), 6.51 (d, $J(H,H) = 8.7$ Hz, 16H; 8o-Ph), 5.59 (s, 16H; 8NH₂), 3.14 (dt, $^3J(H,H) = 6.5$ Hz, $^3J(H,H) = 5.9$ Hz, 16H; 8SiCH₂CH₂CH₂NH₂), 1.53 (m, 16H; 8SiCH₂CH₂CH₂NH₂), 0.58 ppm (t, $^3J(H,H) = 7.8$ Hz, 16H; 8SiCH₂CH₂CH₂NH₂); ¹³C{¹H} NMR (126 MHz, [D₆]DMSO, 20 °C): $\delta = 166.3$ (s, CO), 151.4 (s, CN), 128.6 (s, i-Ph), 121.3 (s, o-Ph), 112.5 (s, m-Ph), 41.5 (s, CH₂), 22.6 (s, SiCH₂CH₂), 8.8 ppm (s, SiCH₂); ²⁹Si{¹H} NMR (59.6 MHz, [D₆]DMSO, 20 °C): $\delta = -66.02$ ppm (s; T³); FTIR (KBr pellets): $\tilde{v} = 3418$ (s, $v_{N-H}$), 2935 (m, $v_{C-H}$), 2872 (m, $v_{C-H}$), 1649(s, $v_{C=O}$), 1598 (s, $v_{Ar}$), 1547 (s, $\delta_{NH}$), 1488 (m, $v_{Ar}$), 1301 (m, $v_{C-N}$), 1111 (s, $v_{ring-asym\,Si-O-Si}$), 1015 (m, $\delta_{Ar}$), 870 (m, $v_{C-NH2}$), 844 (m, $\delta_{Ar-NO2}$), 781 (w, $\delta_{Si-C}$), 718 (w, $\delta_{O-Si-O}$), 467 (w, $\delta_{Si-O-Si}$) cm⁻¹; HRMS (ESI+, TOF/ CH₃OH): m/z (%): 1855.5745 (6) {calcd. for $[M+Na]^+$ 1855.5660}, 1833.5829 (12) {calcd. for $[M+H]^+$ 1833.5840}, 939.2903 (100) {calcd. for $[M+2Na]^{2+}$ 939.2776}, 917.3066 (40) {calcd. for $[M + 2H]^{2+}$ 917.2956}; elemental analysis calcd (%) for $C_{80}H_{104}N_{16}O_{20}Si_8$ (1834.46): C 52.38, H 5.71, N 12.22; found: C 52.29, H 5.68, N 12.12. Temperature of decomposition to SiO₂ (determining by TGA measurement), residue yield: 594 °C, 26.14% (calcd 26.20%).

### Synthesis of 8

**Method A**: 4-Fluorobenzoyl chloride (0.051 mL, 0.0684 g, 0.423 mmol, 8.8 equiv), **1** (0.0563 g, 0.0480 mmol), and NEt₃ (0.124 mL, 0.0900 g, 0.888 mmol, 18.5 equiv) were combined in a procedure analogous to that for **6**. Analytically pure **8** was obtained by dissolving crude **8** in DMSO and precipitation with water. The white precipitate was centrifuged and dried in vacuo (25 °C, 0.5 mbar) to yield **8** (0.0400 g, 45%) as a white solid. ¹H NMR (500 MHz, [D₆]DMSO, 20 °C): $\delta = 8.44$ (s, 8H; 8NH), 7.85 (m, 16H; 8m-Ph), 7.20 (m, 16H; 8o-Ph), 3.19 (m, 16H; 8SiCH₂CH₂CH₂NH), 1.58 (m, 16H; 8SiCH₂CH₂CH₂NH), 0.64 ppm (t, $^3J(H,H) = 6.8$ Hz, 6H; 8SiCH₂CH₂CH₂NH); ¹³C{¹H} NMR (126 MHz, DMSO, 20 °C): $\delta = 165.2$ (s, CO), 163.7 (d, $^1J(C,F) = 249.7$ Hz; CF), 131.0 (s, i-Ph), 129.7 (d, $^3J(C,F) = 8.7$ Hz; o-Ph), 115.0 (d, $^2J(C,F) = 22$ Hz; m-Ph), 41.7 (s, CH₂N), 22.4 (s, SiCH₂CH₂), 8.9 ppm (s, SiCH₂); ²⁹Si{¹H} NMR (59.6 MHz, [D₆]DMSO, 20 °C): $\delta = -65.98$ ppm (s; T³); FTIR (KBr pellets): $\tilde{v} = 3320$ (s, $v_{N-H}$), 2934 (m, $v_{C-H}$), 2873 (m, $v_{C-H}$), 1639 (s, $v_{C=O}$), 1604 (m, $v_{Ar}$), 1548 (m, $\delta_{NH}$), 1504 (s, $v_{Ar}$), 1290 (m, $v_{C-N}$), 1236 (m, $v_{C-F}$), 1121 (s, $v_{ring-asym\,Si-O-Si}$), 849 (s, $v_{Ar-H}$), 765 (m, $\delta_{Si-C}$), 601 (m, $v_{Ar-F}$), 469 (w, $\delta_{Si-O-Si}$) cm⁻¹; HRMS (ESI+, TOF/CH₃Cl): m/z (%): 1857.4103 (14) {calcd. for $[M+H]^+$ 1857.4214}, 929.2262 (100) {calcd. for $[M+2H]^{2+}$ 929.2143}; elemental analysis calcd (%) for $C_{80}H_{88}N_8O_{20}Si_8F_8$ (1858.27): C 51.71, H 4.77, N 6.03; found: C 51.74, H 4.74, N 6.00. Temperature of decomposition to SiO₂ (determining by TGA measurement), residue yield: 463 °C, 25.84% (calcd 25.87%).

**Method B**: The procedure was analogous to that described in Method A with the use of **2** (0.100 g, 0.0480 mmol) instead of **1**. Yield: 0.0424 g (48%). Elemental analysis calcd (%) for $C_{80}H_{88}N_8O_{20}Si_8F_8$ (1858.27): C 51.71, H 4.77, N 6.03; found: C 51.65, H 4.76, N 6.01.

### Synthesis of 9

**Method A**: Benzoyl chloride (0.100 mL, 0.121 g, 0.845 mmol, 8.8 equiv) was added dropwise to a solution of **1** (0.113 g, 0.0960 mmol) and NEt₃ (0.247 mL, 0.179 g, 1.78 mmol, 18.5 equiv) in DMF (8 mL, 0 °C). After stirring overnight, the crude product was precipitated by slow addition to 1 M HCl (aqueous, 140 mL, 0 °C). Filtration, dissolution in DMSO (16 mL), precipitation with cold sa-

turated NaHCO$_3$ (140 mL), washing with water and drying in vacuo (25 °C, 0.5 mbar) gave **9** (yield 1, crude product: 0.134 g, 81%) as a yellowish solid. The residue was purified by flash column chromatography (CH$_3$CN/EtOH, 1:1 v/v; $R_f$ = 0.38) to give **9** (yield 2, after purification using flash column chromatography: 0.091 g, 55%) as a white solid. $^1$H NMR (500 MHz, CDCl$_3$, 20 °C): $\delta$ = 8.33 (s, 8H; 8NH), 7.72 (dd, $^3J$(H,H) = 8.0 Hz, $^5J$(H,H) = 1.3 Hz, 16H; 8$o$-Ph,), 7.34 (t, $^3J$(H,H) = 7.4 Hz, 8H; 8$p$-Ph), 7.23 (m, 16H; 8$m$-Ph), 3.31 (m, 16H; 8CH$_2$N), 1.66 (m, 16H; 8SiCH$_2$CH$_2$), 0.62 ppm (t, $^3J$(H,H) = 6.8 Hz, 16H; 8SiCH$_2$); $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$, 20 °C): $\delta$ = 166.2 (s, CO), 134.5 (s, $i$-Ph), 130.9 (s, $p$-CH), 128.0 (s, $m$-Ph), 127.0 (s, $o$-Ph), 41.6 (s, CH$_2$N), 23.3 (s, SiCH$_2$CH$_2$), 8.7 ppm (s, SiCH$_2$); $^{29}$Si{$^1$H} NMR (CDCl$_3$, 59.6 MHz, RT): $\delta$ = −68.28 ppm (s; T$^3$); FTIR (KBr pellets): $\tilde{v}$ = 3410 (s, $v_{N-H}$), 2928 (m, $v_{C-H}$), 1638 (s, $v_{C=O}$), 1603 (m, $v_{Ar}$), 1544 (s, $\delta_{NH}$), 1488 (m, $v_{Ar}$), 1311 (m, $v_{C-N}$), 1119 (s, $v_{ring-asym\,Si-O-Si}$), 1028 (m, $\delta_{Ar}$), 802 (w, $\delta_{Si-C}$), 694 (w, $\delta_{O-Si-O}$), 473 (w, $\delta_{Si-O-Si}$) cm$^{-1}$; HRMS (ESI+, TOF/MeOH): $m/z$ (%): 1713.4890 (21) {calcd. for [$M$+H]$^+$ 1713.4968}, 879.2429 (12) {calcd. for [$M$+2Na]$^{2+}$ 879.2340}, 857.2631 (100) {calcd. for [$M$+2H]$^{2+}$ 857.2520}; elemental analysis calcd (%) for C$_{80}$H$_{96}$N$_8$O$_{20}$Si$_8$ (1714.40): C 56.05, H 5.64, N 6.54; found: C 56.09, H 5.67, N 6.66. Temperature of decomposition to SiO$_2$ (determining by TGA measurement), residue yield: 422 °C, 28.00% (calcd 28.04%).

**Method B**: The procedure was analogous to that described in Method A with the use of **2** (0.200 g, 0.0960 mmol) instead of **1**. Yield (crude): 0.148 g (90%). Final yield: 0.138 g (84%). Elemental analysis calcd (%) for C$_{80}$H$_{96}$N$_8$O$_{20}$Si$_8$ (1714.40): C 56.05, H 5.64, N 6.54; found: C 56.08, H 5.68, N 6.64.

### Synthesis of 10

Method A: Hexanoyl chloride (0.383 mL, 0.374 g, 2.77 mmol, 16.3 equiv) was added dropwise to a suspension of **1** (0.200 g, 0.170 mmol) and NEt$_3$ (0.626 mL, 0.455 g, 4.49 mmol, 26.4 equiv) in DMF (8 mL, 0 °C). After stirring overnight, the crude product was precipitated by slow addition to 1 M aqueous HCl (140 mL, 0 °C). Filtration, extraction with DMSO (16 mL), precipitation with cold saturated NaHCO$_3$ (140 mL), washing with water and drying in vacuo (25 °C, 0.5 mbar) afforded **10** (yield 1, crude product: 0.180 g, 64%) as a white solid. The residue was purified by flash column chromatography (Et$_2$O/hexane, 1:1 v/v) to afford **10** (yield 2, after purification using flash column chromatography: 0.178 g, 63%) as a white solid. $R_f$ = 0.56 (Et$_2$O/hexane, 1:1 v/v); $^1$H NMR (500 MHz, MeOD, 20 °C): $\delta$ = 7.92 (s, 8H; NH), 3.15 (t, $^3J$(H,H) = 7.0 Hz, 16H; CH$_2$NH), 2.19 (t, $^3J$(H,H) = 7.4 Hz, 16H; C(O)CH$_2$), 1.62 (m, 16H; SiCH$_2$CH$_2$CH$_2$NH), 1.59 (m, 16H; C(O)CH$_2$CH$_2$), 1.36, 1.32 (m, 32H; CH$_2$CH$_2$CH$_2$CH$_3$ and CH$_2$CH$_2$CH$_2$CH$_3$), 0.92 (t, $^3J$(H,H) = 7.0 Hz, 24H; CH$_3$), 0.65 ppm (t, $^3J$(H,H) = 8.4 Hz, 16H; SiCH$_2$); $^{13}$C{$^1$H} NMR (126 MHz, MeOD, 20 °C): $\delta$ = 176.2 (s, C=O), 43.0 (s, SiCH$_2$CH$_2$CH$_2$NH), 37.2 (s, C(O)CH$_2$), 32.6 (s, CH$_2$CH$_2$CH$_2$CH$_3$), 26.9 (s, C(O)CH$_2$CH$_2$CH$_2$CH$_3$), 24.1 (s, SiCH$_2$CH$_2$CH$_2$NH), 23.5 (s, CH$_2$CH$_2$CH$_2$CH$_3$), 14.5 (s, CH$_3$), 10.7 ppm (s, SiCH$_2$CH$_2$CH$_2$NH); $^{29}$Si{$^1$H} NMR (59.6 MHz, CDCl$_3$, 20 °C): $\delta$ = −66.29 ppm (s; T$^3$); FTIR (KBr pellets): $\tilde{v}$ = 3278 (s, $v_{N-H}$), 2931 (m, $v_{C-H}$), 2871 (m, $v_{C-H}$), 1636 (s, $v_{C=O}$), 1558 (s, $\delta_{NH}$), 1457 (w), 1383 (m, $v_{C-N}$), 1272 (w, $v_{C-C}$), 1122 (s, $v_{ring-asym\,Si-O-Si}$), 698 (w, $\delta_{O-Si-O}$), 472 (w, $\delta_{Si-O-Si}$) cm$^{-1}$; HRMS (ESI+, FT+MS/MeOH): $m/z$ (%): 1703.8530 (6) {calcd. for [$M$+K]$^+$ 1703.8283}, 1687.8586 (26) {calcd. for [$M$+Na]$^+$ 1687.8543}, 1665.8726 (10) {calcd. for [$M$+H]$^+$ 1666.8744}, 871.9043 (6) {calcd. for [$M$+2K]$^{2+}$ 871.8967}, 855.9257 (85) {calcd. for [$M$+2Na]$^{2+}$ 855.9228}, 833.4421 (100) {calcd. for [$M$+2H]$^{2+}$ 833.9408}, 577.9381 (5) {calcd. for [$M$+3Na]$^{3+}$ 577.9440}, 555.9649 (5) {calcd. for [$M$+3H]$^{3+}$ 555.9623}; elemental analysis calcd (%) for C$_{72}$H$_{144}$N$_8$O$_{20}$Si$_8$ (1666.64): C 51.89, H 8.71, N 6.72; found: C 51.88, H 8.72, N 6.75. Temperature of de-

composition to SiO$_2$ (determining by TGA measurement), residue yield: 444 °C, 28.85% (calcd 28.84%).

**Method B**: The procedure was analogous to that in Method A with the use of **2** (0.354 g, 0.170 mmol) instead of **1**. Yield (crude): 0.232 g (82%). Final yield: 0.213 g (75%). Elemental analysis calcd (%) for C$_{72}$H$_{144}$N$_8$O$_{20}$Si$_8$ (1666.64): C 51.89, H 8.71, N 6.72; found: C 51.92, H 8.75, N 6.68.

## Acknowledgements

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