

A simple access to ω -aminoalkyltrialkoxysilanes: Tunable linkers for self-organised organosilicas

Benoît P. Pichon, Michel Wong Chi Man *, Catherine Bied, Joël J.E. Moreau *

Laboratoire Architectures Moléculaires et Matériaux Nanostructurés, Hétérochimie Moléculaire et Macromoléculaire (UMR-CNRS 5076), Ecole Nationale Supérieure de Chimie de Montpellier, 8, rue de l'école normale, 34296 Montpellier cedex 05, France

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Abstract

A simple route to ω -aminoalkyltriethoxysilanes with variable alkylene chain lengths, $(\text{EtO})_3\text{Si}(\text{CH}_2)_n\text{NH}_2$ ($n = 5, 11$) is described. These silyl linkers have been used to prepare urea-based compounds with H-bonding and hydrophobic interactions which enable the self-assembly of the molecules. These molecular precursors are suitable for the obtention of nano-structured hybrid silicas.

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1. Introduction

We are currently interested in the synthesis of bulk nano-structured hybrid silicas. In this context, sol-gel chemistry constitutes a simple and easy approach for hybrid silica materials synthesis [1–3]. Bridged silsesquioxanes [4,5] composed of an organic fragment covalently bonded to a silica network, are receiving much attention owing to the possibility to introduce a large variety of organic fragments leading to hybrids for diverse applications [6–9]. Efforts are being made to synthesize well-defined structured hybrid materials. Using external supramolecular templates or taking advantage of intermolecular interactions between organic fragments allowed the formation of nano-structured materials [10,11]. We showed that hydrogen bonds interactions between urea groups [12] attached to the organic fragment permit to direct the organisation in the silica network and the transcription of a designed supramolecular architecture within the solid material. An essential step for the creation of nano-structured hybrid with various functionalities, consists in the

synthesis of appropriate precursors containing both functional organic groups and hydrolysable trialkoxysilyl moieties. We already emphasised the interest of new trialkoxysilyl reagents for the synthesis of the required precursors [5a,13].

Numerous trialkoxysilanes functionalised by organic groups are now commercially available and are used for many applications such as surface modifiers, coupling agents and cross-linkers [14]. Aminoalkyl functional silanes are of particular interest and offer a broad array of applications owing to their chemical activity, their ability to form hydrogen bonds and also to complex metallic species. Among these, 3-aminopropyltriethoxysilane represents one of the most versatile functional silane which is used as coupling agent for surface treatments. It has been used for the derivatization of solid support media for covalent bonding on DNA-microchips [15], as side groups for the molecular imprinting of bulk, mesoporous silica [16] and also for the formation of self-assembled monolayers (SAM) on a surface active reagent [17]. However in the latter case, the formation of monolayers was not always reproducible. A better self-assembly of the organics was obtained with longer alkyl chains of the aminoalkylsilane facilitating the controlled deposition of self-assembled monolayers [18]. This observation shows that additional organic groups

* Corresponding authors. Tel.: +33 467147219; fax: +33 467144353.
E-mail addresses: Michel.wong-chi-man@enscm.fr (M. Wong Chi Man), Joel.moreau@enscm.fr (J.J.E. Moreau).

with self-association properties such as long alkylene chain favor the self-assembly and hence the organisation of the organic functionalities in the solid materials.

Our current interest in self-assembled organo-bridged silicas [12] led us to use alkylene chain with various lengths as linker to generate bisureido units for forming organogels the structure of which was then transcribed into hybrid silicas [19]. Appropriate tuning of the self-organisation properties can result by use of hydrogen bonding or hydrophobic interactions. This led us to envisage a direct and simple route to ω -aminoalkyltrialkoxysilanes $(\text{EtO})_3\text{Si}(\text{CH}_2)_n\text{NH}_2$, with variable chain length ($n = 5, 11$) suitable to synthesize molecular precursors of self-organised hybrids. The triethoxysilyl group undergoes the hydrolysis-condensation reaction and the amino group allows the attachment to organic molecules which will bring intrinsic properties to the material.

2. Results and discussion

ω -Aminoalkyltrialkoxysilanes [20,21] have already been described but the synthetic route involved a protecting-deprotecting strategy with multiple steps leading to a moderate over-all yield [21]. With the aim to improve the over-all yields and to reduce the number of steps, we looked for a general method using commercially available 1-bromo- ω -alkenes, $\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{Br}$ ($m = 3, 9$) (**1**) as starting compounds (Scheme 1).

The corresponding ω -bromoalkyltrialkoxysilanes **2** were synthesized by hydrosilylation of **1** with $\text{HSi}(\text{OEt})_3$ using Karstedt platinum catalyst at room temperature under N_2 atmosphere. **2** were isolated by distillation under reduced pressure in good yields. The synthesis of the corresponding ω -aminoalkyltrialkoxysilanes **4** was achieved via an azide intermediate **3**. This approach permits the synthesis of the amino group under dry medium to preserve the triethoxysilane group from hydrolysis. The bromine substitution by an azide was realised upon treatment of **2** with 2.5 equiv. of sodium azide in dry acetonitrile. Reduction under hydrogen atmosphere in the presence of palladium activated on charcoal catalyst led to an amine function. This simple approach avoids the protection-deprotection strategy and the final products are obtained in less steps with excellent over-all yields.

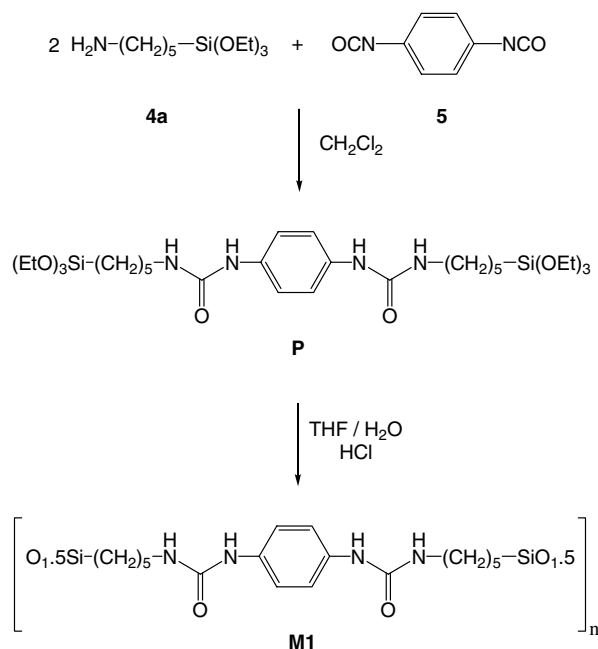
The treatment of these silylated compounds with organic molecules consisting of isocyanato groups can lead to hybrid silsesquioxanes molecular precursors with urea functions capable of self-assembling through the hydrogen bonding interactions. To illustrate this approach we synthesize precursor **P** by the reaction of 5-aminopentyltriethoxysilane

4a with 1,4-diisocyanatobenzene **5** in dichloromethane (Scheme 2).

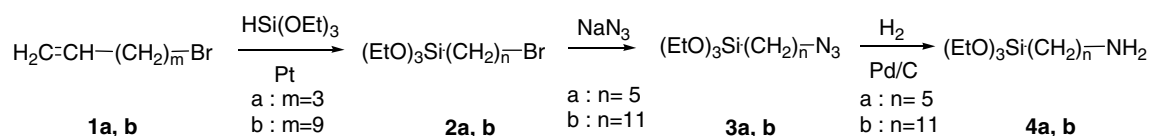
The hydrolysis of **P** was performed in solution in the presence of HCl in a 1:1 (v:v) mixture of THF and water. After few minutes a white precipitate appeared. The reacting mixture was left standing for 2 days at 60 °C under static conditions. The material **M1** was obtained after elimination of solvents followed by filtration and washing with water and ethanol. The white solid was then air-dried at 110 °C. The solid state ^{13}C and ^{29}Si NMR spectra showed that the silica network is covalently bonded to the organic fragment. The ^{29}Si NMR indicates peaks corresponding to T^1 [$[\text{C}-\text{Si}(\text{OSi})(\text{OR})_2]$, 8%), T^2 [$[\text{C}-\text{Si}(\text{O}-\text{Si})_2(\text{OR})]$, 59%) and T^3 [$[\text{C}-\text{Si}(\text{OSi})_3]$, 33%) units showing **M1** to be a highly condensed solid material. The scanning electron microscopy (SEM) image (Fig. 1) shows **M1** to consist of entangled fibers (length up to 2 μm , width up to 0.15 μm).

Fig. 2 represents the X-ray powder diffractogram of **M1** with sharp peaks corresponding to a long range-ordered structure.

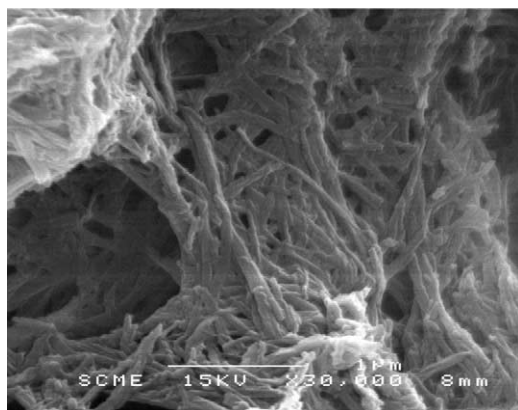
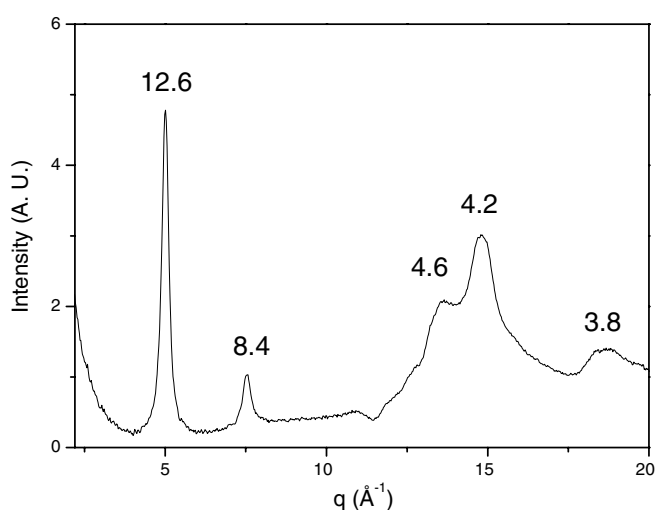
The two peaks at long distances (12.6 and 8.4 Å) can be assigned respectively to the second and the third order of a lamellar structure with d spacing of 25.2 Å. This distance is related to the bridging organic group between the two silicon atoms [12a,12b,12c]. The d spacing of the lamellar



Scheme 2. Synthesis of precursor **P** and hybrid material **M1**.

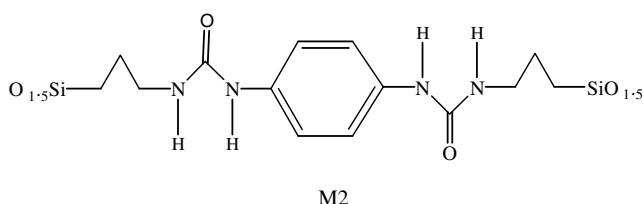


Scheme 1. Synthesis of ω -aminoalkyltrialkoxysilanes ($n = 5, 11$).

Fig. 1. SEM image of **M1**.Fig. 2. X-ray powder diffraction (XRD) pattern of **M1**.

structure in **M1** (25.2 Å) is greater than in a formerly reported hybrid material **M2** (19.6 Å) with shorter C₃ alkylene linkers between the urea groups and the silicon atoms (Scheme 3) [12a]. This is in accord with the longer organic fragment in material **M1** with four additional C–C single covalent bonds compared with that of **M2**.

The peak at 4.6 Å can be attributed to the intermolecular distance between two neighbouring urea groups in agreement with that of **M2** (4.5 Å) [12a]. This distance indicates that hydrogen bonds are formed between the urea groups leading to the auto-association of organic fragments in the silica network.

Scheme 3. Structural representation of **M2** with C₃ linkers between the urea groups and the silicon atoms.

3. Conclusions

In conclusion, we report a simple and direct synthesis of ω-aminoalkyltrialkoxysilanes without any protection or deprotection of the amino function which is generated at the last step. These reagents can be used to synthesize urea-based hybrid silica precursors with variable alkyl chain length between the urea groups and the silicon atoms. Aminoalkylsilanes with adjustable alkylene chain lengths can be exploited for other applications such as surface modifiers with proximal organic functions due to the self-assembling possibility of the long alkylene chains.

4. Experimental

4.1. General and techniques

The syntheses of the molecular precursors were carried out under nitrogen atmosphere by using vacuum line and schlenk techniques. 1-Bromopentene and 1-bromoundecene were purchased from Alpha Aesar, triethoxysilane and Karstedt catalyst from ABCR, sodium azide from Acros and palladium 10 wt% on activated carbon from Aldrich. Solvent were purchased from Prolabo. Acetonitrile and dichloromethane were distilled from CaH₂, ethanol from magnesium turnings and pentane from LiAlH₄ pellets. Water was distilled. Melting points were determined on an electrothermal apparatus (IA9000 series) and are uncorrected. IR data were obtained on a Perkin–Elmer 1000 FT-IR spectrophotometer. Elemental analysis were carried out by the “Service Central d’Analyse du CNRS” at Vernaison (France). ¹H and ¹³C NMR in solution spectra were recorded on Bruker AC-200 spectrometers respectively at 200 and 50 MHz. ²⁹Si NMR in solution were recorded on a Bruker AC-250 at 50 MHz. CDCl₃ and DMSO were used as NMR solvents and chemical shifts are reported as δ values in parts per million relative to Me₄Si (δ 0 ppm for ¹H). ¹³C and ²⁹Si solid-state NMR spectra were obtained from Bruker FT-AM 200 or FT-AM 400 spectrometers by using cross-polarization and magic angle spinning techniques (CP-MAS) and TMS as reference for the chemical shifts. Mass spectra were measured on JEOL MS-DX 300 mass spectrometer. X-ray diffraction spectra were carried out on a Philips PW goniometer (anticathode Cu) and registered from q = 1 to q = 2.3. The SEM images were obtained with JEOL 6300F microscope.

4.1.1. 5-Bromopentyltriethoxysilane (**2a**)

1-Bromo-5-triethoxysilylpentane (**2a**) was synthesized as already described [22] in similar conditions using Karstedt catalyst instead of Wilkinson catalyst. 5.5 mL of triethoxysilane (30 mmol) and 44.5 mL of Karstedt catalyst (1 mmol) were added to 2.37 mL of 1-bromopentene (20 mmol) placed under nitrogen atmosphere in a schlenk. The reaction was stirred overnight at 80 °C. Distillation under reduced pressure (69 °C at 4 × 10^{−2} bar) affords

compound **2a** as a colorless liquid (4.77 g, 70%); ^1H NMR (CDCl_3): $\delta = 0.59$ (t, 2H, $J = 7.0$ Hz, CH_2Si), 1.18 (t, 9H, $J = 6.9$ Hz, CH_3), 1.40 (m, 4H, CH_2), 1.81 (m, 2H, CH_2), 3.33 (t, 2H, $J = 6.8$ Hz, CH_2Br), 3.77 (q, 6H, $J = 6.9$ Hz, OCH_2); ^{13}C NMR (CDCl_3): $\delta = 10$ (CH_2Si), 18 (CH_3), 22, 31 and 32 (3CH_2), 34 (CH_2Br), 58 (CH_2O); ^{29}Si NMR (CDCl_3): $\delta = -45.4$; m/e MS FAB+ 314/312 (M^+ , 32); IR (CHCl_3): $\nu = 2976, 2929, 2891, 1102, 1077, 958, 792\text{ cm}^{-1}$.

4.1.2. 5-Azidopentyltriethoxysilane (**3a**)

1.7 g of sodium azide (28.5 mmol) was added to 3.56 g of 5-bromopentyltriethoxysilane (11.4 mmol) in acetonitrile (40 mL) under nitrogen atmosphere. The solution was stirred under reflux for 48 h. After removal of the solvent under vacuum, the crude mixture was diluted in pentane and the suspension was filtered. Solvent was removed from the resulting filtrate and the crude oil obtained was distilled under reduced pressure (65 °C at 3×10^{-2} bar) to give compound **3a** as a colorless liquid (2.66 g, 84%). ^1H NMR (CDCl_3): $\delta = 0.60$ (t, 2H, $J = 7.0$ Hz, CH_2Si), 1.18 (t, 9H, $J = 6.9$ Hz, CH_3), 1.25 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 1.58 (m, 2H, CH_2), 3.20 (t, 2H, $J = 6.7$ Hz, NCH_2), 3.77 (q, 6H, $J = 6.9$ Hz, OCH_2); ^{13}C NMR (CDCl_3): $\delta = 10$ (CH_2Si), 18 (CH_3), 22, 28 and 29 (3CH_2), 51 (CH_2N), 58 (CH_2O); ^{29}Si NMR (CDCl_3): $\delta = -45.4$; m/e MS FAB+ 275 (M^+ , 15); IR (CHCl_3): 2976, 2930, 2887, 2099, 1102, 1077, 959, 793 cm^{-1} ; Anal. Calc. for $\text{C}_{11}\text{H}_{25}\text{N}_3\text{O}_3\text{Si}$: C, 47.97; H, 9.15; N, 15.26. Found: C, 47.69; H, 9.24; N, 15.46%.

4.1.3. 5-Aminopentyltriethoxysilane (**4a**)

The synthesis of 5-aminopentyl triethoxysilane (**4a**) has been already described [23]. 1.63 g of 5-azidopentyltriethoxysilane (5.9 mmol) and ethanol (40 mL) were placed in an autoclave. Palladium on activated carbon, wt. 10% (50 mg) was added and a pressure of hydrogen (1 bar) was applied and the mixture was stirred during 20 min at room temperature. The solution was filtered to eliminate the charcoal and the solvent was removed under vacuum. The crude oil obtained was distilled under reduced pressure to give compound **4a** (67 °C at 3×10^{-2} bar) as a colorless liquid (1.15 g, 78%). ^1H NMR (CDCl_3): $\delta = 0.60$ (t, 2H, $J = 7.0$ Hz, CH_2Si), 1.18 (t, 9H, $J = 6.8$ Hz, CH_3), 1.36 (m, 8H, CH_2 , NH_2), 2.63 (t, 2H, $J = 6.5$ Hz, NCH_2), 3.77 (q, 6H, $J = 6.8$ Hz, OCH_2); ^{13}C NMR (CDCl_3): $\delta = 10$ (CH_2Si), 18 (CH_3), 23, 30–33 (3CH_2), 42 (CH_2N), 58 (CH_2O); ^{29}Si NMR (CDCl_3): $\delta = -45.4$; m/e MS FAB+ 249 (M^+ , 100); IR (CHCl_3): 3323, 2976, 2930, 2887, 1102, 1077, 959, 793 cm^{-1} .

4.1.4. 11-Bromoundecyltriethoxysilane (**2b**)

The synthesis of 11-bromoundecyltriethoxysilane (**2b**) has already been described [24]. To 4.66 mL of 1-bromoundecene (20 mmol), were added 5.5 mL of triethoxysilane (30 mmol) and 44.5 mL of Karstedt catalyst (1 mmol) under nitrogen atmosphere. The reaction was stirred over-

night at 80 °C. Distillation under reduced pressure (90 °C at 4×10^{-2} bar) afforded compound **2b** as a colorless liquid (6.35 g, 80%). ^1H NMR (CDCl_3): $\delta = 0.59$ (t, 2H, $J = 7.2$ Hz, CH_2Si), 1.18 (t, 9H, $J = 6.9$ Hz, CH_3), 1.22 (m, 16H, CH_2), 1.81 (m, 2H, CH_2), 3.36 (t, 2H, $J = 6.8$ Hz, CH_2Br), 3.77 (q, 6H, $J = 6.9$ Hz, OCH_2); ^{13}C NMR (CDCl_3): $\delta = 10$ (CH_2Si), 18 (CH_3), 22 (CH_2), 28–33 (8CH_2), 34 (CH_2Br), 58 (CH_2O); ^{29}Si NMR (CDCl_3): $\delta = -45.4$; m/e MS FAB+ 398/396 (M^+ , 10); IR (CHCl_3): 2976, 2928, 2856, 1102, 1077, 908, 737 cm^{-1} .

4.1.5. 11-Azidoundecyltriethoxysilane (**3b**)

To a solution of 5.96 g of 11-bromoundecyltriethoxysilane (15.0 mmol) in acetonitrile (40 mL) placed under nitrogen atmosphere, was added 2.46 g of sodium azide (37.8 mmol). The solution was stirred under reflux for 48 h. The solvent was removed under vacuum, the crude mixture was diluted in pentane and the suspension was filtered. Solvent was removed from the obtained filtrate and the crude oil obtained is distilled under reduced pressure (111 °C at 5×10^{-2} bar) to give compound **3b** as a colorless liquid (4.80 g, 89%). ^1H NMR (CDCl_3): $\delta = 0.61$ (t, 2H, CH_2Si), 1.17 (t, $J = 6.9$ Hz, 9H, CH_3), 1.25 (m, 16H, CH_2), 1.58 (m, 2H, CH_2), 3.23 (t, 2H, $J = 6.7$ Hz, NCH_2), 3.78 (q, 6H, $J = 6.9$ Hz, OCH_2); ^{13}C NMR (CDCl_3): $\delta = 0$ (CH_2Si), 18 (CH_3), 23 (CH_2), 27–33 (8CH_2), 51 (CH_2N), 58 (CH_2O); ^{29}Si NMR (CDCl_3): $\delta = -45.4$; m/e MS FAB+ 314 [($\text{M} - \text{EtO}$), 27]; IR (CHCl_3): 2927, 2856, 2098, 1102, 1078, 909, 738 cm^{-1} ; Anal. Calc. for $\text{C}_{17}\text{H}_{37}\text{N}_3\text{O}_3\text{Si}$: C, 56.78; H, 10.37; N, 11.69. Found: C, 56.95; H, 10.42; N, 11.39%.

4.1.6. 11-Aminoundecyltriethoxysilane (**4b**)

The synthesis of 11-aminoundecyltriethoxysilane (**4a**) has been already described [20]. A solution of 1 g of 11-azidoundecyltriethoxysilane (2.76 mmol) in ethanol (40 mL) was placed in an autoclave. 50 mg of palladium catalyst on activated carbon (10 wt%) was added and a pressure of hydrogen (1 bar) was applied. The reaction mixture was stirred during 20 min at room temperature. The charcoal was eliminated by filtration and the solvent was removed under vacuum. The crude oil obtained was distilled under reduced pressure (136 °C at 4×10^{-2} bar) to give compound **4b** as a colorless liquid (1.15 g, 78%). ^1H NMR (CDCl_3): $\delta = 0.61$ (t, 2H, $J = 7.0$ Hz, CH_2Si), 1.18 (t, 9H, $J = 6.9$ Hz, CH_3), 1.25 (m, 18H, CH_2), 2.66 (t, 2H, $J = 6.8$ Hz, NCH_2), 3.80 (q, 6H, $J = 6.9$ Hz, OCH_2); ^{13}C NMR (CDCl_3): $\delta = 10$ (CH_2Si), 18 (CH_3), 23 (CH_2), 27–33 (8CH_2), 42 (CH_2N), 58 (CH_2O); ^{29}Si NMR: $\delta = -45.4$; IR (CHCl_3): 3300, 2976, 2927, 2856, 1102, 1078, 909, 738 cm^{-1} .

4.1.7. 1,4-Bis[(triethoxysilyl)pentylureido]benzene (**P**)

To a solution of 96 mg of 1,4-diisocyanatobenzene (0.6 mmol) in dichloromethane (10 mL), was added dropwise 385 mg of 5-aminopentyltriethoxysilane (1.55 mmol) and the reaction was stirred overnight. The solvent was

removed under vacuum and the mixture was washed with pentane. Drying under vacuum affords compound **P** as a grey waxy solid (280 mg, 71%): m.p. 211 °C; ¹H NMR (DMSO): δ = 0.56 (t, 4H, *J* = 7.1 Hz, CH₂Si), 1.14 (t, 18H, *J* = 6.8 Hz, CH₃), 1.20–1.60 (2m, 12H, CH₂), 3.05 (m, 4H, N–CH₂), 3.72 (q, 12H, *J* = 6.8 Hz, OCH₂), 5.99 (m, 2H, NH), 7.20 (s, 4H, H_{ar}), 8.16 (s, 2H, NH); ¹³C NMR (DMSO): δ = 10 (CH₂Si), 18 (CH₃), 22, 29, 30 and 55 (5 CH₂), 57 (CH₂O), 118 and 134 (C_{ar}), 155 (CO); ²⁹Si NMR (DMSO): δ = –45.0; *m/e* MS FAB+ 658 (M⁺, 3); IR: 3323, 1635, 1579; Anal. Calc. for C₃₀H₅₈N₄O₈Si₂: C, 54.68; H, 8.87; N, 8.50. Found: C, 54.45; H, 8.52; N, 8.66%.

4.1.8. Preparation of hybrid silica (**MI**)

1,4-Bis[(triethoxysilyl)pentylureido]benzene (**P**) was heated until complete dissolution in THF. The solution was allowed to cool down to ambient temperature and water was added, a precipitate appeared. Then a solution of HCl (1 M) was added. These products were used in the molar ratio of **P**: 1, THF: 130, H₂O: 600, HCl: 0.2. The mixture was stirred for 2 h at 60 °C and then left standing for 2 days under static conditions. The resulting solid was filtered, washed successively with water, ethanol and acetone. Drying the precipitate overnight at 110 °C led to a white powder. ¹³C NMR (δ): 15.0, 21.7, 24.8, 31.7, 41.2, 124.3, 132.7, 157.5; ²⁹Si NMR (δ): –49, –57, –67 (T¹, T² and T³ units); IR: 1582 δ(CO), 1637 ν(CO), 3333 ν(NH); N₂. Anal. Found: C, 49.21; H, 6.25; N, 12.94; Si, 12.53.

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