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Research Article

A Synthetic Route to Quaternary Pyridinium Salt-Functionalized Silsesquioxanes

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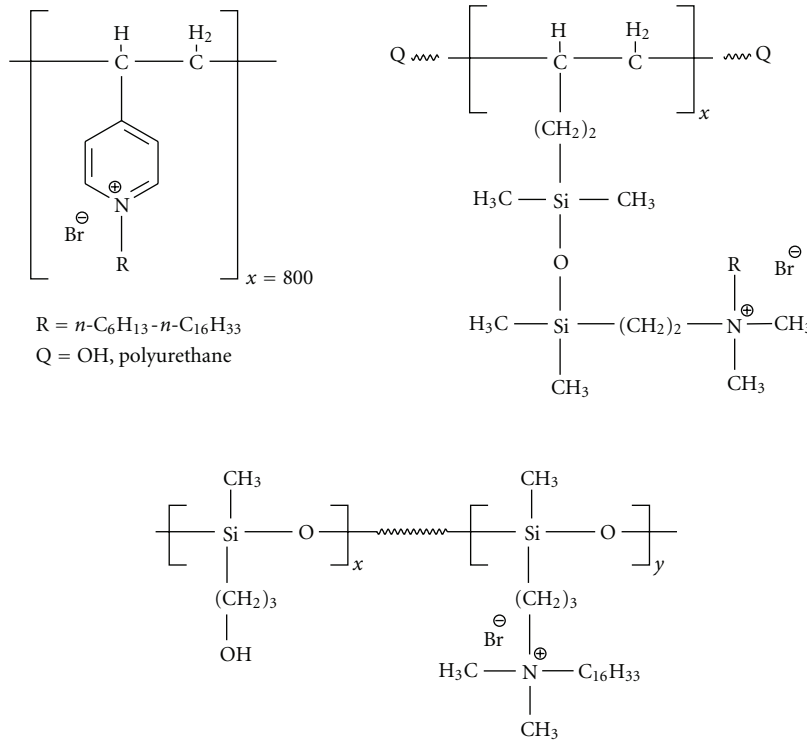
A synthetic route to potentially biocidal silsesquioxanes functionalized by quaternary pyridinium functionalities has been developed. *N*-Alkylation reactions of the precursor compounds 4-(2-(trimethoxysilyl)ethyl)-pyridine (**5**) and 4-(2-trichlorosilylethyl)pyridine (**6**) with iodomethane, *n*-hexylbromide, and *n*-hexadecylbromide cleanly afforded the corresponding *N*-alkylpyridinium salts (**7**–**10**). The synthesis of a 4-(2-ethyl)pyridine POSS derivative (**2**) was achieved by capping of the silsesquioxane trisilanol $Cy_7Si_7O_9(OH)_3$ (**1**) via two different preparative routes. Attempts to use compound **2** as precursor for quaternary pyridinium salt-functionalized POSS derivatives were met with only partial success. Only the reaction with iodomethane cleanly afforded the new *N*-methylpyridinium salt **12** in high yield, whereas *n*-hexylbromide and *n*-hexadecylbromide failed to react with **2** even under forcing conditions.

1. Introduction

Over the past fifty years a broad variety of new classes of polymers have been prepared and studied which should provide advances in developing a new family of compounds for antibacterial surface treatments [1]. Such polymeric materials or films which kill or inactivate microorganisms upon their direct contact are known as *biocidal (antimicrobial) polymers* or also *polymeric biocides*. During the 1990s the interest in biocidal polymers arose rapidly due to their potential ability to keep surfaces and materials *permanently* antiseptic. This continues to be of current importance for a wide range of applications. Biocidal polymers are used, for example, in cartridge filters for the disinfection of potable and recreational water supplies, in filter units for air disinfection, as sterile bandages, clothing, surgical gloves for medical uses, as biocidal polymeric coatings on surfaces of ship hulls, shower walls and many other kinds of tubing. The ideal biocidal polymer should possess at least the following characteristics: (1) it should be easily and inexpensively synthesized; (2) it should be stable in long-term usage and storage at the temperature of its intended application; (3) it should be not soluble in water in the case of water disinfection applications; (4) it should not decompose to and emit toxic products; (5) it should not be toxic or irritating to those handling it; (6) it should be regenerable upon loss of activity; and (7) it should be biocidal to a broad spectrum of pathogenic microorganisms in brief times of contact [1–4].

By now various biocidal polymers have been produced and tested in different fields, but the achievement of a polymer which combines all of these characteristics continues to be elusive. In accordance with literature reviews there are several classes of biocides which possess great potential for the development of the ideal biocidal polymers for their sufficiently high activity against the two major classes of bacteria and fungi, Gram-positive and Gram-negative. They will not be removed from surfaces on washing, they remain capable of continually acting against the bacteria, they are not toxic or irritating, and one of the very attractive advantages is that they cause no antibiotic resistance [1–4]. Their approximate composition is represented in Scheme 1.

Such biocidal polymers always comprise three essential structural parts: the *carrying surface*, usually the



Scheme 1

carbohydrate-base (cotton cloth, wood, paper, or bulk cellulose, etc.), and also glasses and silica, and the *polymer films* (in Scheme 1 polyethylene, polyurethane, and polysiloxane) which contain anchored *polyquat moieties* (the quaternary nitrogen) and which directly contact to a cell membrane and cause its disruption. It has been experimentally proven that low antiseptic activity already reveals for the moieties with *N*-alkyl chains from three to eight carbon units in length and is very high for the moieties containing a 16-carbon lipophilic chain [1–4].

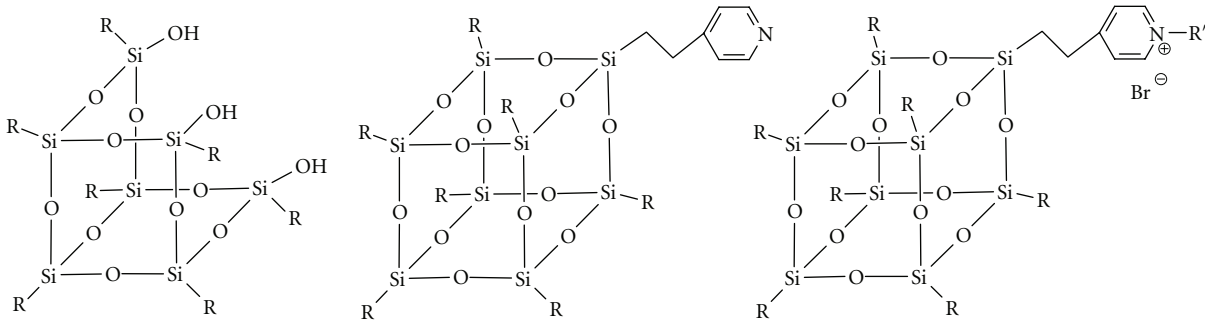
Polyhedral oligomeric silsesquioxanes (POSS) form an exciting class of hybrid organic-inorganic filler materials receiving considerable attention in recent years [5–17]. They represent several elements of novelty, for example, molecular diameters between 1 and 3 nm, low density, high thermal stability, and an array of side-chain functionalities [18] which accounts for compatibility with various host polymers. Thus is seemed of interest to synthesize and characterize a new class of biocidal materials based on polyhedral oligomeric silsesquioxanes by attaching distant quaternary ammonium functional groups to the POSS cage. In this contribution, we report the first synthetic approach eventually leading to POSS derivatives comprising a pendant quaternized 4-(2-ethyl)pyridyl group.

The key precursor **1** and the target molecules **2** and **3** are illustrated in Scheme 2. Trisilanol **1** was chosen as the best model for silica that has been developed to date for its close-range geometric similarity to known SiO_2 structures. It is a very useful model for both spectroscopic comparisons and chemical reactivity studies for it structurally resembles specific surface structures that occur on silica [19–23]. Alkylated quaternary 4-(2-ethyl)pyridyl groups containing 6- and 16-carbon chains are of considerable interest for their significant activity against a wide range of bacteria (**3a, b**, Scheme 2). The intended synthetic route involved capping of **1** with either 4-(2-(trimethoxysilyl)ethyl)-pyridine and 4-(2-trichlorosilylethyl)pyridine to give the 4-(pyridine)ethyl derivative **2** which could then be alkylated by treatment with appropriate alkyl halides to give the target compounds **3a** and **3b**.

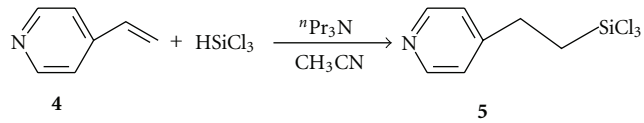
2. Results and Discussion

2.1. Preparation of the Starting Materials 4-(2-Trichlorosilylethyl)pyridine (5) and 4-(2-(Trimethoxysilyl)ethyl)-pyridine (6). The envisaged synthetic route for functionalizing the trisilanol precursor **1** first required the availability of the starting materials 4-(2-trichlorosilylethyl)pyridine (**5**) and 4-(2-(trimethoxysilyl)ethyl)pyridine (**6**). Both of them had been reported in the literature [24, 25]. The reported synthesis of **5** involves hydrosilylation of 4-vinylpyridine (**4**) with trichlorosilane according to Scheme 3. Through a slight modification of the original preparation reported in [25] the yield of **5** could be increased from 52% to 81%, making this compound readily available in large quantities.

The original preparation of 4-(2-(trimethoxysilyl)ethyl) pyridine (**6**) calls for treatment of the trichlorosilyl precursor **5** with trimethyl orthoformate in the presence of catalytic amounts of aluminum trichloride according to Scheme 4 [25].



Scheme 2



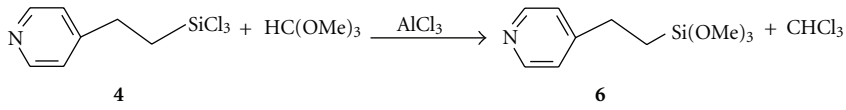
Scheme 3

Although the reaction outlined in Scheme 4 had been described only on a 1 g-scale, we found that by employing longer heating times up to *ca.* 10 g of **6** could be prepared without difficulties. As an alternative route to **6**, the direct hydrosilylation of vinylpyridine (**4**) with trimethoxysilane, $HSi(OMe)_3$, has also been investigated (Scheme 5). Such reactions of unsaturated substrates with trialkoxysilanes have been shown to work well in the presence of suitable hydrosilylation catalysts such as $H_2PtCl_6 \times H_2O$ (Speier's catalyst) or Karstedt's catalyst (= $Pt(LL)_2$, LL = $(CH_2{=}CHSiMe_2)_2O$) [26–31]. Reactions were carried out under various conditions (e.g., without solvent or in acetonitrile solution, without catalyst or in the presence of Speier's catalyst or Karstedt's catalyst), but surprisingly all these reactions failed to produce appreciable amounts of **6**. Thus the original preparation (Scheme 4) remains the best access to the trimethoxysilyl derivative **6**.

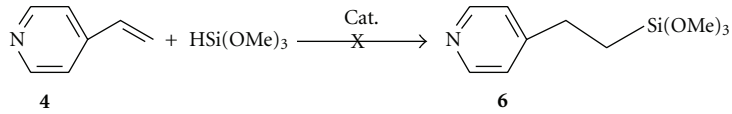
*2.2. Quaternization of 4-(2-Trichlorosilylethyl)pyridine (**5**) and 4-(2-(Trimethoxysilyl)ethyl)-pyridine (**6**) with Different Alkyl Halides.* Next, quaternization reactions of the precursors **5** and **6** with different alkyl halides were studied. In quaternization reactions of tertiary amines with alkyl halides the reactivity of the latter generally decreases in the series RI > RBr > RCl, for example, MeBr > EtBr > *n*-$C_6H_{13}Br$ > C_{16} $H_{33}Br$. Although for application reasons we were particularly interested in the reactivity of alkyl halides with longer chains, for example, with six or sixteen carbon atoms, reactions with methyl iodide as the simplest and most reactive alkyl halide were also included. Usually *N*-alkylation reactions of tertiary amines are performed in polar solvents (acetonitrile, methanol, ethanol, etc.). The highest reaction rates are normally observed in bipolar aprotic solvents (DMF, DMSO), but when using these solvents difficulties in product isolation and purification can became apparent. Quaternization reactions of **5** and **6** were carried out in anhydrous organic solvents (e.g., methanol, acetonitrile, THF) as illustrated in Scheme 6. Owing to the very high solubility of 4-(2-trichlorosilylethyl)pyridine (**5**) and iodomethane in all organic solvents, the *N*-alkylation with iodomethane was possible to perform in pentane, diethyl ether, THF, DMSO, acetonitrile, ethanol, and methanol. The highest reaction rates were observed in the more polar solvents and the slowest in nonpolar solvents. The pure product, the *N*-methylpyridinium salt **7**, was isolated as a white solid after recrystallization from diethyl ether in nearly quantitative yield (98%).

As expected, the analogous quaternization reactions with *n*-hexyl and *n*-hexadecyl bromide (Scheme 7) were much slower than the CH_3I reactions. *N*-alkylation of **6** with *n*-hexylbromide could readily be performed in those polar solvents (acetonitrile, methanol) in which the highest reaction rates were observed for iodomethane, but the *N*-alkylation with *n*-hexadecylbromide could only be carried out in diethyl ether or THF because of its poor miscibility with the more polar solvents. Accordingly, in both cases the reaction rates and isolated yields were so low that even after 5–7 days of refluxing the reactions were less than 30% completed.

Much better yields (69–78%) were obtained in a second series of *N*-alkylation experiments which were performed under solvent-free conditions by just stirring a mixture of the reagents at temperatures of 100–130°C for 48–72 h. Under these conditions the pure *N*-*n*-hexylpyridinium salt **9** was isolated from diethyl ether as a pale greenish oil and the *N*-*n*-hexadecylpyridinium salt **10** as a very pale greenish solid. The structures of all prepared pyridinium salts **7**–**10** were confirmed by ^1H and ^{13}C NMR data. In particular, *N*-alkylpyridinium salt formation was proven by the long range



Scheme 4



Scheme 5

coupling between the protons in the positions 1,1′ and 4 in the HQBC NMR experiment (Scheme 8).

2.3. Capping of Trisilanol ***1*** *with the Pyridine-4-ethyl Functionality.* For the preparation of the 4-(2-ethyl)pyridine derivative of silsesquioxane trisilanol **1** two different synthetic procedures have been developed. The first route, illustrated in Scheme 9, first involved *in situ* preparation of $Cy_7Si_7O_9(OLi)_3$ (**11**) by deprotonation of **1** with 3 equivelant of $LiN(SiMe_3)_2$ according to the literature [32, 33]. This was immediately followed by treatment with equimolar amounts of 4-(2-trichlorosilylethyl)pyridine (**5**). This method was highly efficient and gave the highest yields of the target product **2** (up to 92–96%).

The second route was performed in toluene and involved the reaction of **1** with **4** in the presence of triethylamine (Scheme 10). This method was also found to be quite straightforward and afforded the desired compound **2** in good yields around 68–72%.

The pure product **2** was isolated as a white solid by the recrystallization from a toluene/acetonitrile mixture. The crystalline material is moderately soluble in pentane, toluene, diethyl ether and highly soluble in THF, but insoluble in DMSO, acetonitrile, methanol, and water. The constitution of **2** was confirmed by its ^{1}H, ^{13}C, and ^{29}Si NMR spectra and elemental analysis.

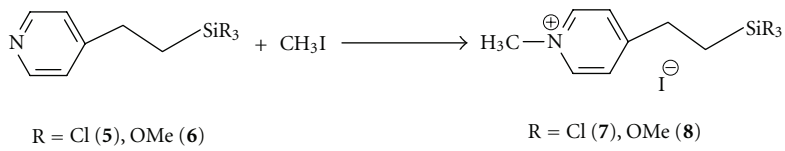
2.4. Attempted Quaternization Reactions of Compound ***2****.* As mentioned above, the final step towards the target compounds **3a** and **3b** would be the quaternization reaction of **2** with the appropriate alkyl bromides. While such reactions using the model compounds **5** and **6** were successful (*cf.* Section 2.2), nearly all attempts to carry out *N*-alkylation reactions with the pyridine-4-ethyl-functionalized POSS derivative **2** failed. Only with iodomethane it was possible to isolate the new N-methylpyridinium iodide **12**. Since compound **2** is insoluble in DMSO, acetonitrile and methanol, its *N*-alkylation with iodomethane (Scheme 11) could not be carried out in these very polar solvents which would have been desirable. While in less polar THF and nonpolar toluene solubility of **2** is very high, the quaternization rates with iodomethane were so low that even under reflux conditions over 5–7 days the product (methylpyridinium salt **12**) content in the reaction mixture did not exceed 5–8%. It was, however, found that the yield of **12** could be drastically improved (up to 92%) by prolonged heating of the precursor **2** in neat iodomethane. The resulting white solid was characterized by NMR spectroscopy. It dissolves in $CDCl_3$ but is insoluble in diethyl ether and hydrocarbons. Unfortunately, *n*-hexyl bromide and *n*-hexadecylbromide did not react with **2** even under forcing reaction conditions (e.g., extended heating of **2** in the neat alkylbromide). Thus the target compounds **3a** and **3b** thus far remain elusive. It also remains to be examined in the course of a future study if compounds like **12** exhibit biocidal properties.

3. Conclusions

In summarizing the results reported here, a possible synthetic route to new quaternary pyridinium salt-functionalized silsesquioxane (POSS) derivatives has been outlined. Such compounds could be of interest as potential POSS-based biocides. Judging from the initial results reported here it appears that the proposed synthetic route to *N*-alkylpyridinium-functionalized POSS derivatives such as **3a** and **3b** is principally feasible. Thus far, however, only with iodomethane a clean reaction to give the quaternized product **12** has been achieved, while under the chosen reaction conditions *n*-hexyl bromide and *n*-hexadecylbromide failed to react with **2** to give the corresponding *N*-alkylpyridinium salts.

4. Experimental

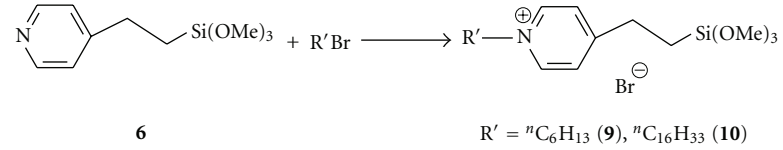
4.1. General Information. All reactions were carried out in an atmosphere of dry nitrogen with the use of standard Schlenk techniques or in a dry box (M. Braun, Labmaster 130 and MB 150B-G). NMR spectra were recorded on a Bruker DPX-NMR spectrometer (^{1}H 400 MHz, ^{13}C{^{1}H} 101 MHz, ^{29}Si{^{1}H} 79.5 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (^{1}H, ^{13}C) or an internal standard (^{1}H, ^{29}Si: TMS = 0 ppm). 4-Vinylpyridine (**4**), iodomethane, trimethylorthoformate, trichlorosilane, hexachloroplatinic acid (Speier's catalyst), and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex (Karstedt's catalyst) were obtained commercially (Aldrich or Acros) and used as received. The silsesquioxane precursor **1** was prepared in our laboratory according to the published procedure [19]. *n*-Pentane, *n*-hexane, toluene, diethyl ether, and THF were dried over sodium/benzophenone and freshly distilled under nitrogen prior to use. The other solvents and



R = Cl (**5**), OMe (**6**)

R = Cl (**7**), OMe (**8**)

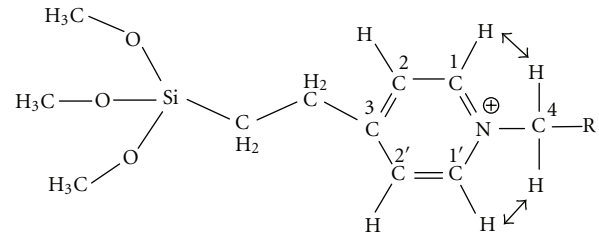
Scheme 6



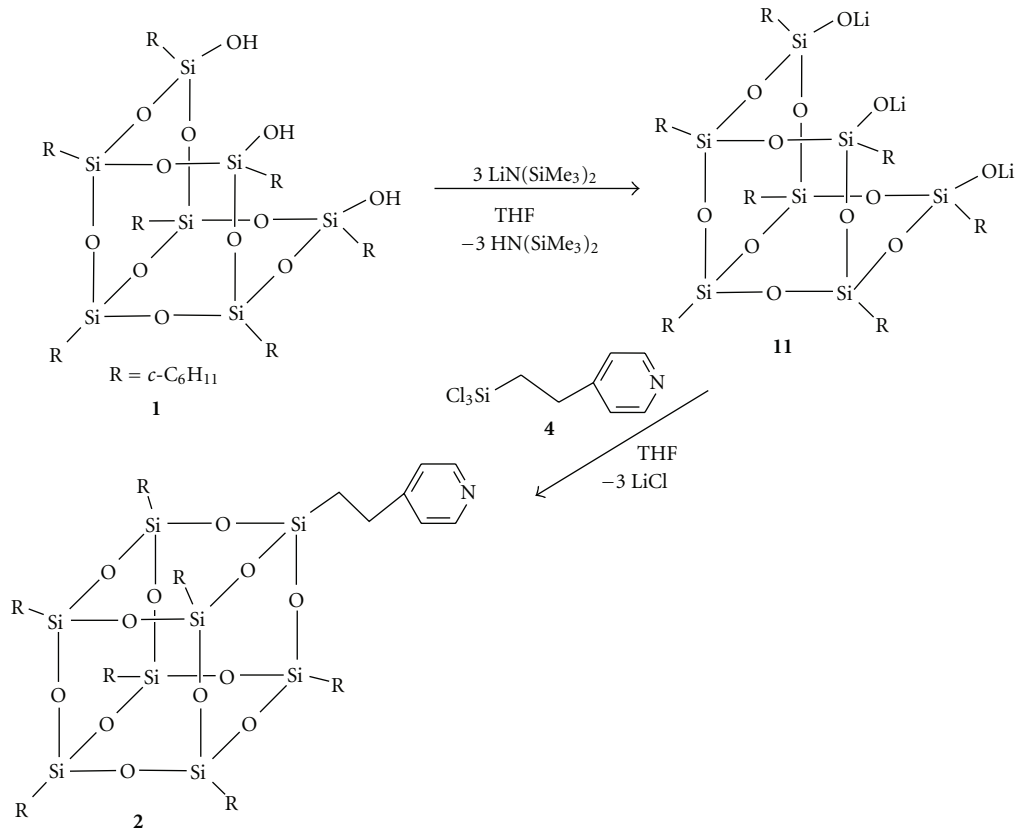
6

R′ = $^{n}C_6H_{13}$ (**9**), $^{n}C_{16}H_{33}$ (**10**)

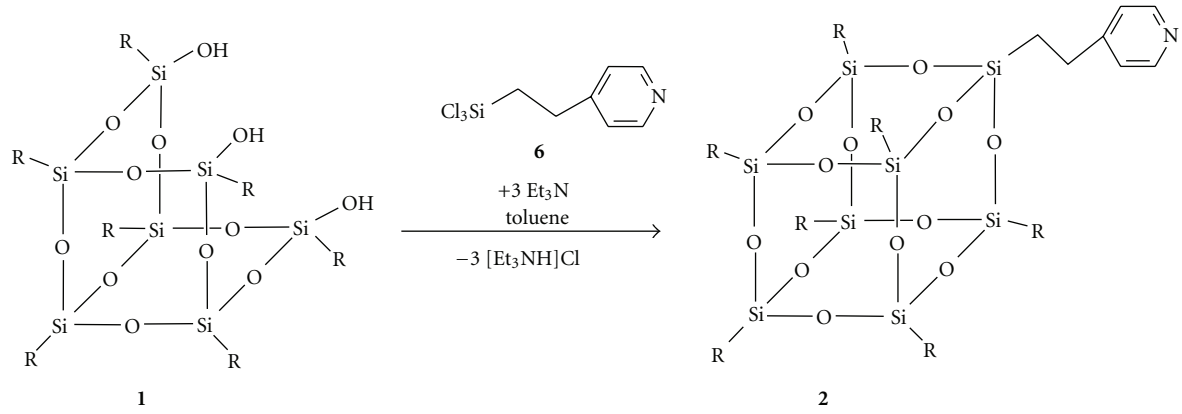
Scheme 7



Scheme 8

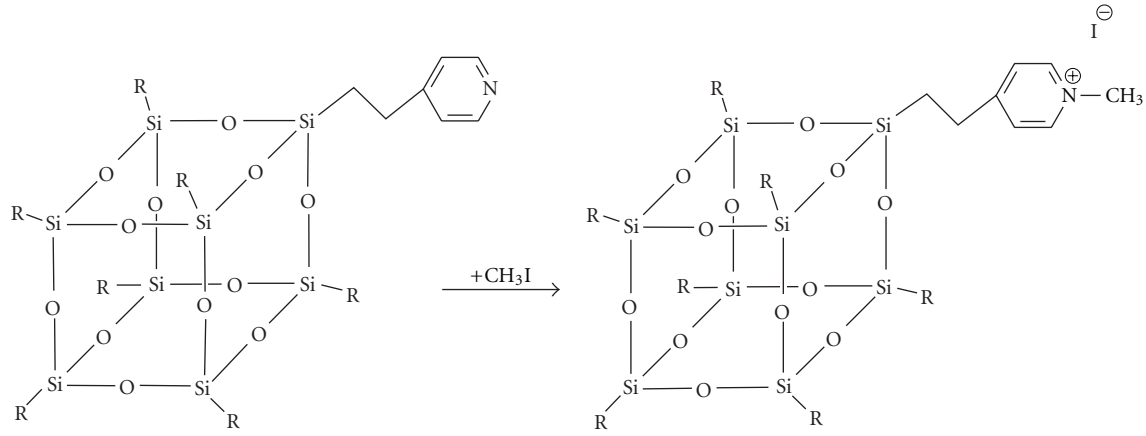


Scheme 9



1 **2**

Scheme 10



2 **12**

Scheme 11

reagents were first dried over the appropriate drying agent, then distilled and kept in the refrigerator. Chloroform was dried over phosphorus pentoxide (P_2O_5), acetone over boric anhydride (B_2O_3), acetonitrile over potassium carbonate (K_2CO_3), and triethylamine and tri-*n*-propylamine over calcium hydride (CaH_2). It was found that commercially available 4-vinylpyridine (**4**) had to be fractionally distilled under reduced pressure (5 mbar, b.p. 35-36°C) prior to use in order to achieve a reasonable purity and to remove polymeric material.

4.2. Preparation of 4-(2-(Trichlorosilyl)ethyl)pyridine (5) (Modified from [25]). In a 100 mL round-bottom Schlenk flask with a stirring bar, trichlorosilane (10.0 mL, 12.56 g, 92.6 mmol) was mixed with tri-*n*-propylamine (0.9 mL, 0.66 g, 4.6 mmol). Then, 4-vinylpyridine (**4**, 10.0 mL, 9.75 g, 92.7 mmol) was added very slowly and dropwise, waiting every time until heat evolution had ceased. At the end of adding the 4-vinylpyridine the reaction mixture completely turned into white solid and mixing was not possible. Then, *ca.* 20 mL of acetonitrile were added and the reaction mixture was refluxed at 60°C with the cooling condenser held at −26°C for 36 h until the white solid completely turned into a yellow-orange solution. This solution was fractionally distilled under reduced pressure (2 mbar), collecting the fraction boiling at 105–110°C as a colorless, slightly hazy liquid which on standing at r.t. reversibly tended to crystallize into a white solid with a light green tint. During purification of the product by distillation, gentle warming of the distillation bridge with a heating gun was necessary in order to avoid clogging. Yield 17.02 g (81%). Analysis calcd. for $C_7H_8Cl_3NSi$ (240.59): C 34.95, H 3.35, N 5.82; found: C 35.66, H 3.30, N 6.22%. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25°C) δ 8.52-8.51 (m, 2H-*pyr*), 7.14-7.13 (m, 2H-*pyr*), 2.87 (m, 2H, $-CH_2-$py), 1.74 (m, 2H, $-CH_2-Si(OMe)_3$); $^{13}C\{^1H\}$NMR (100.61 MHz, $CDCl_3$, 25°C) δ 149.52 (s, C), 149.50, 122.78 (s, CH), 27.09, 24.12 (s, CH_2). MS (relative intensity) *m/e* 239 (M^+, 28%), 203 (M^+-Cl, 12%), 106 ($M^+-Cl-SiCl_2$, 100%), 92 ($M^+-Cl-SiCl_2-CH_2$, 24%).

4.3. Preparation of 4-(2-(Trimethoxysilyl)ethyl)pyridine (6) (Modified from [25]). A 100 mL Schlenk-flask was charged with a small amount (*ca.* 20 mg) of powdered anhydrous $AlCl_3$ and a stirring bar. Then, 4-(2-(trichlorosilyl)ethyl)-pyridine (**5**, 12.39 g, 51.5 mmol) was added. Trimethylorthoformate (22.5 mL, 21.86 g, 0.206 mol) was then added in

small portions of 3–5 mL, each time waiting 25–30 min until the vigorous gas evolution had stopped and the reaction mixture had cooled down to room temperature. (*Caution*: a more rapid addition of trimethylorthoformate causes intensive warming of the system which could lead to instantaneous splashing). At first, the yellow reaction mixture developed a pink and then an orange-brown color. After that the reaction mixture was refluxed at +80°C (oil bath) for 24–36 h until the refluxing stopped and the color had changed to deep green. The reaction mixture was fractionally distilled under reduced pressure (2 mbar), collecting the colorless fraction boiling at 118–120°C. When the product was distilling it was also necessary to gently heat the distillation bridge with a heating gun. Yield 8.43 g (72%). Analysis calcd. for $C_{10}H_{17}NO_3Si$ (227.34): C 52.83, H 7.54, N 6.16; found: C 51.31, H 7.45, N 5.73%. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25°C) δ 8.48-8.47 (m, 2H-*pyr*), 7.13-7.12 (m, 2H-*pyr*), 3.55 (s, 9H, $-OCH_3$), 2.70 (m, 2H, $-CH_2-$py), 0.97 (m, 2H, $-CH_2-Si(OMe)_3$); ^{13}C{^{1}H}NMR (100.61 MHz, $CDCl_3$, 25°C): δ 152.25 (s, C), 148.91, 122.48 (s, CH), 49.62 (s, CH_3), 27.36, 9.36 (s, CH_2); ^{15}N {^{1}H} NMR (40.56 MHz, $CDCl_3$, 25°C): $\delta-152.65$ (s). MS (relative intensity): *m/e* 226 (M^+, 100%), 121 ($M^+-Si(OMe)_3$, 51%), 91 ($M^+-Si(OMe)_3-CH_2$, 21%).

4.4. Preparation of N-Methyl-4-(2-(Trichlorosilyl)ethyl) pyridinium Iodide ***(7)***. In a 100 mL Schlenk flask equipped with a stirring bar, 4-(2-(trichlorosilyl)ethyl)pyridine (**5**, 1.0 g, 4.4 mmol) was dissolved in 5 mL of acetonitrile and iodomethane (0.5 mL, 0.63 g, 4.4 mmol) was added. The reaction mixture was stirred at room temperature for 1 h, the solvent was removed under vacuum, and the powdery yellow residue was twice washed with 10 mL of diethyl ether to give the pure product. Yield 1.66 g (98%). Analysis calcd. for $C_8H_{11}Cl_3INSi$ (382.53): C 25.12, H 2.90, N 3.66; found: C 24.12, H 3.31, N 3.50%. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25°C) δ 9.22-9.21 (m, 2H-pyr^+), 7.99–7.97 (m, 2H-pyr^+), 4.67 (s, 3H, $-CH_3$), 3.20 (m, 2H, $-CH_2-py^+$), 1.89 (m, 2H, $-CH_2-SiCl_3$); ^{13}C{^{1}H}NMR (100.61 MHz, $CDCl_3$, 25°C) δ 161.21 (s, C), 145.36, 127.67 (s, CH), 49.08 (s, CH_3), 28.51, 23.42 (s, CH_2).

4.5. Preparation of N-Methyl-4-(2-(Trimethoxysilyl)ethyl)pyridine Iodide ***(8)***. In a 100 mL Schlenk flask with a stirring bar 4-(2-(trimethoxysilyl)ethyl)pyridine (**6**, 1.0 mL, 1.23 g, 5.411 mmol) was dissolved in 5 mL of acetonitrile, and iodomethane (0.34 mL, 0.77 g, 5.411 mmol) was added at room temperature. The reaction mixture was stirred at r.t for 1 h. Then the solvent was removed under vacuum and the yellow oily residue was washed with 5 mL of diethyl ether under stirring at room temperature until the oil turned into yellow solid. The solid was washed with 5 mL of diethyl ether once again and dried *in vacuo* giving the pure product. Yield 1.18 g (98%). The pure compound could be isolated as colorless thin needles by recrystallization from boiling diethyl ether. Analysis calcd. for $C_{11}H_{20}INO_3Si$ (240.59): C 34.95, H 3.35, N 5.82; found: C 35.66, H 3.30, N 6.22%. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25°C) δ 9.26-9.24 (m, 2H-pyr^+), 7.89–7.87 (m, 2H-pyr^+), 4.66 (s, 3H, $-CH_3$), 3.59 (s, 9H, $-OCH_3$), 2.99 (m, 2H, $-CH_2-py^+$), 1.02 (m, 2H, $-CH_2-Si(OMe)_3$); ^{13}C{^{1}H}NMR (100.61 MHz, $CDCl_3$, 25°C) δ 164.30 (s, C), 144.86, 127.27 (s, CH), 50.63, 48.59 (s, CH_3), 29.14, 9.28 (s, CH_2); ^{15}N {^{1}H} NMR (40.56 MHz, $CDCl_3$, 25°C) δ 28.00 (s).

4.6. Preparation of N-n-Hexyl-4-(2-(Trimethoxysilyl)ethyl) pyridine Bromide ***(9)***. In a 50 mL Schlenk flask with a stirring bar 4-(2-(trimethoxysilyl)ethyl)pyridine (**6**, 1.0 mL, 1.23 g, 5.4 mmol) was mixed with *n*-hexylbromide (5% excess, 0.79 mL, 0.93 g, 5.7 mmol). The reaction mixture was stirred at 80°C (oil bath) for 48 h. When the reaction mixture changed its color from deep green to orange-brown, the heating was stopped. The formed deep green oil was washed with 5 mL of diethyl ether and then dried under vacuum at +40°C to give **9** as a pale green oil. Yield 2.02 g (96%). Analysis calcd. for $C_{16}H_{30}BrNO_3Si$ (392,41): C 48.97, H 7.71, N 3.57; found: C 48.88, H 7.30, N 4.05%. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25°C): δ 9.59–9.57 (m, 2H-pyr^+), 7.95–7.93 (m, 2H-pyr^+), 4.92 (t, 2H, py^+-CH_2-*hexyl*), 3.59 (s, 9H, $-OCH_3$), 2.98 (m, 2H, $-CH_2-py^+$), 2.06 (m, 2H, $-CH_2-$*hexyl*), 1.40 (m, 2H, $-CH_2-$*hexyl*), 1.37–1.23 (m, 4H, $-(CH_2)_2-$*hexyl*), 1.02 (m, 2H, $-CH_2-Si(OMe)_3$), 0.86 (t, 3H, $-CH_3-$*hexyl*); ^{13}C{^{1}H}NMR (100.61 MHz, $CDCl_3$, 25°C): δ 163.72 (s, C), 144.32, 127.18 (s, CH), 60.60 (s, CH_2), 50.39 (s, CH_3), 31.48, 30.76, 28.83, 25.28, 21.98 (s, CH_2), 13.55 (s, CH_3), 9.11 (s, CH_2).

4.7. Preparation of N-n-Hexadecyl-4-(2-(Trimethoxysilyl) ethyl)pyridine Bromide ***(10)***. In a 50 mL Schlenk-flask with a stirring bar 4-(2-(trimethoxysilyl)ethyl)pyridine (1.0 mL, 1.23 g, 5.4 mmol) was mixed with *n*-hexadecylbromide (5% excess, 1.74 mL, 1.74 g, 5.7 mmol). The reaction mixture was stirred at 80°C (oil bath) for 72 h. The formed oily mixture when cooled down to room temperature turned into a deep green solid. The pure product could be isolated as colorless thin needles by the recrystallization from methanol. Yield 2.91 g (96%). Analysis calcd. for $C_{26}H_{40}BrNO_3Si$ (522.60): C 59.76, H 7.71, N 2.68; found: C 57.95, H 7.33, N 2.23%. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25°C) δ 9.36–9.34 (m, 2H-pyr^+), 7.87-7.86 (m, 2H-pyr^+), 4.94 (t, 2H, py^+-CH_2-*hexadec*), 3.58 (s, 9H, $-OCH_3$), 2.98 (m, 2H, $-CH_2-py^+$), 1.99 (m, 2H, $-CH_2-$*hexadec*), 1.33 (m, 2H, $-CH_2-$*hexadec*), 1.29–1.17 (m, 22H, $-(CH_2)_{11}-$*hexadec*), 1.01 (m, 2H, $-CH_2-Si(OMe)_3$), 0.88 (t, 3H, $-CH_3-$*hexadec*); ^{13}C{^{1}H}NMR (100.61 MHz, $CDCl_3$, 25°C) δ 164.25 (s, C), 144.32, 127.39 (s, CH), 61.22 (s, CH_2), 50.75 (s, CH_3), 29.63 (m, 6 CH_2), 29.60, 29.55, 29.47, 29.30, 29.22, 29.05, 26.01, 22.63 (s, CH_2), 14.07 (s, CH_3), 9.42 (s, CH_2); ^{15}N {^{1}H} NMR (40.56 MHz, $CDCl_3$, 25°C) δ 53.20 (s).

4.8. Preparation of $Cy_7Si_8O_{12}(CH_2)_2C_5H_4N$ ***(2)***. Freshly distilled hexamethyldisilazane $HN(SiMe_3)_2$ (1.96 mL, 9.2 mmol) was diluted with 5 mL of freshly distilled hexane. 5.78 mL of 1.6 M *n*-BuLi (9.2 mmol) solution were added dropwise at −35°C (2-propanol/liquid nitrogen mixture). The reaction mixture was stirred for 0.5 h. The thus prepared cold solution of $LiN(SiMe_3)_2$ was added slowly *via* a double-ended needle to the stirred solution of $Cy_7Si_8O_9(OH)_3$ (**1**,

3.0 g, 3.1 mmol) in 300 mL of freshly distilled THF at −35°C. The reaction mixture was stirred for 1-2 h allowing warming up slowly and then another 0.5 h at room temperature. Then the solvents were removed completely *in vacuo*. The white residue was washed twice with *n*-pentane. The solid was dried *in vacuo* once again and then dissolved in 300 mL of THF. Now 24.2 mL of a toluene solution (20 mL) of 4-(2-(trichlorosilyl)ethyl)-pyridine (0.74 g, 3.1 mmol) was added dropwise *via* a double-ended needle. The reaction mixture was stirred at room temperature for 6 h and 1 h at 60°C (oil bath) until a small amount of white solid started precipitating. Then the reaction mixture was concentrated to 150 mL, the solution was filtered from white sediment (LiCl) and the sediment was washed twice with 100 mL of THF. The solvent from the filtrate was removed completely and the white residue was dried *in vacuo* at +40°C. Yield 3.35 g (98%). Analysis calcd. for $C_{49}H_{85}NO_{12}Si_8$ (1104.90): C 53.27, H 7.75, N 1.27; found: C 53.01, H 7.29, N 2.12%. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25°C) δ 8.49-8.48 (m, 2H-*pyr*), 7.16-7.15 (m, 2H-*pyr*), 2.74 (m, 2H-*pyr*), 1.96–1.48 (complex m, 35H-*cycl*), 1.37–1.04 (complex m, 35H-*cycl*), 0.97 (m, 2H-*pyr*), 0.82–0.67 (complex m, 7H-*cycl*); ^{13}C{^{1}H}NMR (100.61 MHz, $CDCl_3$, 25°C) δ 153.60 (s, C-*pyr*), 149.27, 123.45 (s, CH-*pyr*), 28.61 (s, CH_2-*pyr*), 27.53, 27.44, 27.39, 26.85, 26.80, 26.63, 26.59 (s, CH_2-*cycl*), 23.08, 23.04 (s, 4 : 3 for CH-*cycl*), 12.81 (s, CH_2-*pyr*); ^{15}N {^{1}H} NMR (40.56 MHz, $CDCl_3$, 25°C) δ −158.81 (s); ^{29}Si {^{1}H}NMR (79.49 MHz, d_5-pyridine, 25°C) δ −65.59, −66.81, −66.86 (s, 1 : 4 : 3). ^{29}Si {^{1}H}NMR (79.49 MHz, $CDCl_3$, 25°C) δ −67.81, −68.58 (s, 1 : 7). MS (relative intensity) *m/e* 1103 (M^+, 100%), 1020 (M^+–C_6H_{11}, 32%), 938 (M^+–C_6H_{11}–C_6H_{11}, 7%).

*4.9. Alternative Preparation of $Cy_7Si_8O_{12}(CH_2)_2C_5H_4N$ (**2**).* Trisilanol $Cy_7Si_7O_9(OH)_3$ (**1**, 3.0 g, 3.1 mmol) was dissolved in 300 mL of freshly distilled toluene. When the stirred solution had become completely clear, triethylamine (1.28 mL, 9.2 mmol) was added. 4-(2-(trichlorosilyl)ethyl)-pyridine (0.74 g, 3.1 mmol) in toluene (60-70 mL) was added dropwise *via* a double-ended needle at room temperature. The reaction mixture was stirred for 5-6 h at room temperature and 1 h at 60°C (oil bath) until the transparent solution became cloudy white. Then the solution was concentrated to 150 mL and filtered off from the white sediment of $[Et_3NH]^+Cl^-$, and the sediment was washed twice with 100–150 mL of toluene. The solvent from the clear filtrate was removed completely and the white residue was dried under vacuum at +40°C. Yield 3.01 g (88%). The pure product could be obtained by slow diffusion of acetone into saturated chloroform solution.

*4.10. Preparation of $[Cy_7Si_8O_{12}(CH_2)_2C_5H_4N^+CH_3]I^-$ (**12**).* The 4-(2-ethyl)pyridine POSS derivative **2** (1.0 g, 0.837 mmol) was mixed with 5 mL of neat iodomethane. The mixture was refluxed at 80°C (oil bath) for 72 h. Then the iodomethane was removed under vacuum and the yellow residue was washed twice with diethyl ether giving the pure product. Yield 0.96 g (92%). Analysis calcd. for $C_{50}H_{88}INO_{12}Si_8$ (1246.83): C 48.17, H 7.11, N 1.12; found: C 49.39, H 6.83, N 1.41%. ^{1}H NMR (400.13 MHz, $CDCl_3$, 25°C) δ 9.19–9.17 (m, 2H-*pyr*), 7.82-7.81 (m, 2H-*pyr*), 4.70 (s, 3H, –CH_3), 3.52 (m, 2H-*pyr*), 1.96–1.52 (complex m, 35H-*cycl*), 1.46–1.09 (complex m, 35H-*cycl*), 1.02 (m, 2H-*pyr*), 0.84–0.21 (complex m, 7H-*cycl*); ^{13}C{^{1}H}NMR (100.61 MHz, $CDCl_3$, 25°C) δ 164.73 (s, C-*pyr*), 144.94, 127.13 (s, CH-*pyr*), 29.64 (s, CH_2-*pyr*), 27.38, 27.34, 26.79, 26.75, 26.63, 26.54, (s, CH_2-*cycl*), 22.99, 22.96 (s, 4 : 3 for CH-*cycl*), 12.02 (s, CH_2-*pyr*).

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