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An examination of the substitution chemistry of di-*n*-hexyldichlorosilane

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Abstract

Various nucleophiles were reacted with the substrate di-*n*-hexyldichlorosilane as model reactions for the substitution of two geminal Si–Cl bonds on polymer backbone repeat units. The reactants examined were chosen on the basis of steric bulk, electronic factors, and resulting stability of the product. Linear and branched alcohol nucleophiles used in conjunction with an amine proton acceptor produced disubstituted products in moderate yields, whereas bulkier reagents substituted only one silicon–chlorine bond. Due to their vastly increased nucleophilicity, alkyllithium reagents were found to have increased activity and were found to produce very high yields. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Substitution; Alcohol; Nucleophile; Silyl ether

1. Introduction

The synthesis of functionalized silanes continues to be relevant, given the importance of silicon-based materials in both biomedical and commercial applications. Since chlorosilanes are readily produced by various means and commercially available, the efficient conversion of their reactive silicon–chlorine bonds to more hydrolytically stable bonds is of interest in order to produce a useful material. Nucleophilic substitution has long been shown to be a flexible route of modifying the properties of reactive silanes. Highly reactive silicon–halide bonds are readily attacked by a variety of nucleophiles, facilitating mild reaction conditions. In the case of alcoholysis reactions, the resulting silyl ethers can be used as protecting groups [1], reagents in organic syntheses [2], or as pendant groups in inorganic polymers [3]. Furthermore, these products are used as biomedical materials [1,4,5], elastomers, coatings, and fibers [3]. All silyl ethers are susceptible to slow hydrolysis, a reaction which kinetically is dependent upon the nature of the alkyl substituent, chemistry which is quite old and useful [5]. Polymers of this nature are usually made by either ring opening or polycondensation reactions [6–8]. An alternative route of functionalization of reactive silicon–chlorine bonds is alkylation reactions. The formation of a silicon–carbon bond via Grignard or alkyllithium substitution chemistry has been shown to be useful due to their ease of synthesis and thermodynamic stability [9]. This study encompasses both methods of Si–Cl functionalization.

In recent years, we have investigated methods of producing silicon-containing polymers of various architectures via acyclic diene metathesis (ADMET) polymerization [10], a transition metal catalyst-mediated condensation, and we now report on an extension of this chemistry in order to broaden the behavior of the materials that can be made in this fashion. In particular, we have synthesized unsaturated carbosilane polymer backbones possessing two highly reactive, but hydrolytically unstable Si–Cl bonds, which then can be converted to other materials via nucleophilic substitution reactions described above [11]. Substitution reactions on these polymer backbones require significant amounts of conversions to produce a useful material. This approach is advantageous since a common backbone can be altered such that a wide range of materials and properties behavior can be produced in this fashion.

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While extensive literature precedence for substitution on large groups such as polymer chains lies in phosphazene chemistry [12], substitution on a P–Cl bond is substantially different than on a Si–Cl bond because of both steric and electronic factors. In terms of substitution reactions used on silicon polymers, Interrante and coworkers [6] have synthesized dialkoxysilanes based on a dichlorocyclosilabutane ring, while Manners and coworkers [7] have incorporated similar chemistry on a ferrocenyldichlorosilane. However, the steric environments around the silicon atom in these reactions are entirely different from the linear dialkyldichlorosilane case, since these structures possess ring strain and are in a locked conformation about the site of substitution. West and coworkers [8] have used aromatic and alkyl based polymer substrates, while most other efforts have involved macromolecular substitution of only one Si–Cl bond per repeat unit [6,7].

Multiple substitutions at one silicon center are quite different from that of other atoms, and a paucity of data has been reported in comparison to analogous carbon and phosphorus chemistry, particularly on longer, linear substrates. Most of the literature concerning silicon substitutions has been focused on compounds containing either only one Si–Cl bond or three sites of substitution [9], but relatively few attempts have been made to describe reactions at a tetracoordinate silicon site containing two reactive chlorine atoms (Fig. 1). Furthermore, a majority of these studies concern cyclic species or involve substitution on either dimethyldichlorosilane or diphenyldichlorosilane, neither of which impose serious steric difficulties [13,14]. In this study, we are examining the substitution chemistry of the geminal dichlorosilane functionality in a linear polymer backbone model. Two significantly different nucleophile systems (alcohol–amine or alkyllithium reagents) were studied to evaluate their utility for the substitution of silicon–chlorine bonds on model compounds for polymer repeat units.

2. Results and discussion

In order to gain a better understanding of the substitution chemistry on large and flexible, sterically encumbered silicon sites, we have examined the reaction between a range of carbon- and oxygen-based nucleophiles and di-*n*-hexyldichlorosilane, a compound that models our polymer repeat unit [11a]. A variety of

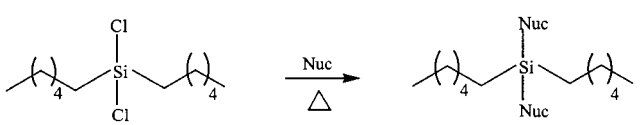


Fig. 1. Substitution of geminal di-*n*-hexyldichlorosilane.

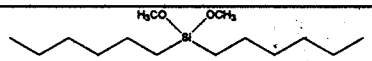
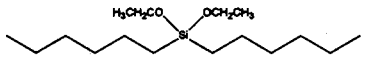
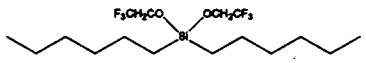
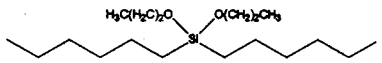
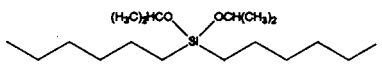
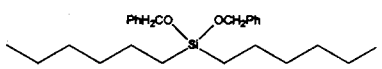
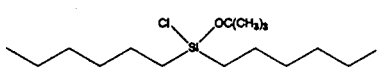
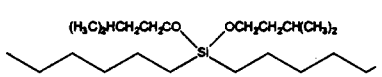
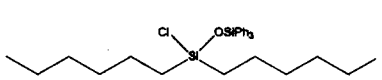
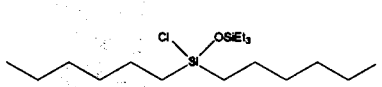
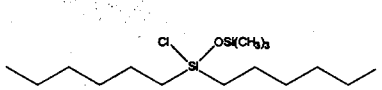
different nucleophiles were used in this study and each was selected on the basis of steric bulkiness, electronic factors, and the ultimate hydrolytic stability of the resulting bond. We have observed that when larger, flexible alkyl chains such as *n*-hexyl groups are bonded to the reaction site, the Si–Cl bonds become less reactive than with methyl and phenyl groups, and that quantitative disubstitution is not trivial.

The substitution reaction of a Si–Cl bond has been established in the literature as proceeding in an S_N2-like fashion [2,15]. It has been discovered that the atoms bonded to silicon control the nature of the substitution [9]. In the case of chlorine, the substitution reaction proceeds with inversion of configuration. Therefore, limitations of the S_N2 reaction, particularly sterics, apply to the substitution of dialkyldichlorosilanes as well. Since this reaction has been shown to occur stepwise, large substituents on the silicon atom sterically encumber the backside attack by the second equivalent of nucleophile, often slowing or completely hindering the second substitution. Consequently, it is often difficult to obtain the desired product. Careful choice of both size and strength of nucleophile is required to induce complete substitution on the silicon atom. The results of our study show that disubstitution of dichlorosilyl groups is possible, but that optimal reaction conditions vary for differing substrates (Table 1). Both systems we examined will produce disubstituted products, given the correct conditions.

Alcoholysis reactions have long been used in the functionalization of chlorosilanes. Even though alcohols are considered to be mild nucleophiles, they still readily substitute silicon–chlorine bonds. Due to the acidic by-products of the reaction, it is common to use a soluble base, such as hindered amine or pyridine, as a proton acceptor. In our example, we used triethylamine, previously established in the literature as an effective promoter for the alcoholysis of silicon–chlorine bonds. Although Et_3N is quite basic, with a pK_b of 3.36, it is considered to be non-nucleophilic due to steric considerations, so there is no competing reaction for substitution of the silicon–chlorine bond [14,15]. However, it does interact with the alcohol, accepting the proton from the nucleophile and promoting the substitution reaction. This is particularly important when other groups, such as olefin sites, which are acid-sensitive, are present. We observed that a wide variety of alcohols do indeed substitute both silicon–chlorine bonds, producing a dialkoxy derivative (Table 1).

The first objective in this study was to evaluate the effect of the size of the nucleophile on these disubstitution reaction systems. Methanol readily formed a disubstituted product due to its small size, as evidenced by ^{29}Si-NMR; only one silicon signal is present at -2.4 ppm, which correlates with the literature for a silicon

Table 1
Substitution of di-*n*-hexyldichlorosilane with alcohols

Nucleophilic Group Employed	Silane Product Observed	Isolated % Yield of Disubstituted Product
CH_3O-		37
CH_3CH_2O-		64
CF_3CH_2O-		64
$CH_3CH_2CH_2O$-		50
$(CH_3)_2CHO$-		32
$PhCH_2O$-		62
$(CH_3)_3CO$-		0
$(CH_3)_2CH(CH_2)_2O$-		59
Ph_3SiO-		0
Et_3SiO-		0
Me_3SiO-		0

atom bonded to two alkyl groups and two methoxy groups [16]. Larger, linear nucleophiles such as ethanol and propanol also produce a completely disubstituted product. Complete characterization by NMR, mass spectrometry, and elemental analysis confirmed the expected structures. It is evident that small, linear, alcohol nucleophiles fit into the sterically hindered silicon–chlorine site that results after the first substitution and thus the second substitution occurs quite readily.

Linear, aliphatic substituents of silyl ethers result in silicon–oxygen bonds which are vulnerable to atmospheric hydrolysis. Fluorination of alkyl groups on the linkage is an effective means of suppressing this reaction. Minimizing hydrolysis is important in our work, so we focused attention on the synthesis of more hydrolytically stable molecules. CF_3CH_2OH was chosen as a nucleophile due to its inherent hydrophobicity, and previous use in reducing hydrolysis rates of analogous phosphorus ethers [6,12]. The incorporation of an electron-poor trifluoromethyl group reduces the nucleophilicity of the alcohol; even so, we find that disubstitution occurs quite readily (vide infra).

Another method of slowing the hydrolysis of a silyl ether is to use larger aliphatic groups on the linkage. It has been established that use of bulkier nucleophiles can reduce hydrolysis rates of the product significantly, but they are much less reactive in S_N2-like substitution reactions due to the inability of the reagent to reach the substrate due to steric inhibitions. We find that the bulky nucleophile systems, with tertiary or neopentyl-type structures about the oxygen atom, $(CH_3)_3COH$–NEt_3, Et_3SiOH–NEt_3, $NaOC(CH_3)_3$, $NaOSiMe_3$, and

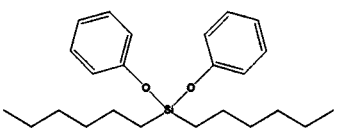
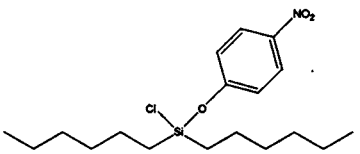
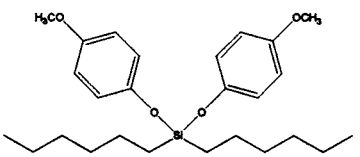
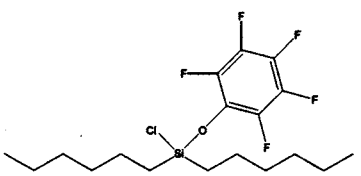
$NaOSiPh_3$, lead to incomplete substitution. Consequently, a compromise between steric bulk (reduced hydrolysis) and accessibility was desired to synthesize products with slower atmospheric degradation rates. We found that, by using secondary alcohols (2-propanol) and primary alcohols with methylene spacer units between the branch point and nucleophilic site (3-methyl-1-butanol), we were able to effectively substitute both silicon–chlorine bonds in moderate yields. Increased steric bulk around the backbone, as in the case of 2-propanol, has been shown to be advantageous because of the fact that the silyl ether linkage is even able to survive mildly basic aqueous workup.

Phenolic nucleophiles were also used in this study, since the products of this substitution reaction have been shown to be hydrolytically stable [6,7]. In contrast to the previous results, all attempts to disubstitute di-*n*-hexyldichlorosilane with excess phenol–NEt_3 or with NaOPh failed. This is most likely due to the decreased nucleophilicity of phenols (pK_a 8–11) compared to alcohols (pK_a 15–17) [17]. Disubstitution using these nucleophiles did occur however, when a catalytic amount of 4-dimethylaminopyridine (DMAP) was added, in keeping with the literature, which shows that a small amount of this reagent accelerates more difficult substitution reactions [14,15]. Consequently, DMAP was added in the reaction using phenol as a nucleophile.

The electronic character of the nucleophile was also studied in order to evaluate the effect of electron-donating and electron-withdrawing groups on phenol-based nucleophiles. For example, the electron donating methoxy group in 4-methoxyphenol leads to complete disubstitution in di-*n*-hexyldichlorosilane, whereas electron-withdrawing groups produce entirely different results (Table 2). Use of either pentafluorophenol or 4-nitrophenol failed to produce the disubstituted product, only the monosubstitution product formed. Since the size of the nucleophilic sites for these three phenols is similar, the decreased nucleophilic strength must be the reason for this observation.

Carbon-based nucleophiles are an essential part of the model study because the resulting silicon–carbon bond in the products possesses hydrolytic stability. Since Grignard reagents are not useful in the efficient synthesis of tetraalkylsilanes [6,18], significantly stronger alkyllithium nucleophiles were employed instead. The rationale behind using an alkyllithium reagent as a nucleophile instead of Grignard reagent is that they are more potent nucleophiles, and hence, tend

Table 2
Phenolic nucleophiles used in the substitution reaction

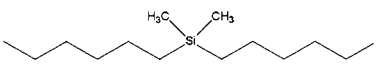
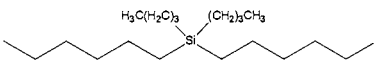
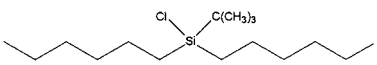
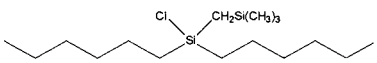
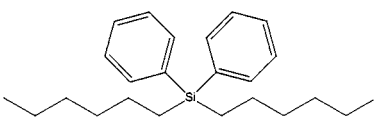
Nucleophilic Group Employed	Silane Product Observed	Isolated % Yield of Disubstituted Product
ArO-		53
4-NO_2ArO-		0
4-CH_3OArO-		67
Ar(F_5)O-		0

to promote more complete substitution of silicon–chlorine bonds [9]. Careful addition of the alkyllithium reagents under controlled conditions ($< 0°C$) and in stoichiometric amounts enables the reagent to perform as a nucleophile and not as a base, preventing α-lithiation of the C–H bond adjacent to silicon [19]. The resulting silicon–carbon bonds are thermodynamically stable and do not hydrolyze at kinetically appreciable rates. The use of small alkyl groups, as in methyllithium, does not impose considerable steric factors on the substitution reaction. However, larger and more bulky alkyllithium reagents must also be evaluated. The longer, straight-chain lithium reagent, *n*-butyllithium, was reacted with di-*n*-hexyldichlorosilane, resulting in the disubstituted product. Phenyllithium was also used in the same fashion to evaluate the effect of using aromatic carbon-based nucleophiles and yielded the disubstituted product as well. However, we found that sterics still govern this reaction, as *t*-butyllithium and (trimethylsilylmethyl)lithium were not able to produce the desired disubstituted product. In spite of the considerable increase of nucleophile strength used with these reagents, it is apparent that steric factors are the dominant aspect of the disubstitution reaction (Table 3).

3. Conclusions

We have demonstrated that the nucleophilic disubstitution of hindered dialkyldichlorosilane silicon–chlorine bonds is indeed plausible if the reagents selected meet certain requirements such as steric size and nucleophile strength. We have shown that small alcohol and alkyllithium reagents react readily, producing completely substituted products, but weaker and sterically bulky nucleophiles produce monosubstituted species. The size of the incoming nucleophiles in an S_N2-like reaction appears to play the dominant role in determining the selectivity of the reaction and in the case of silyl ethers, also the hydrolysis rate of the products. We have also shown that nucleophilicity, hence electronic factors of the reaction, can play an important role in the reaction for weaker nucleophiles when disubstitution is sterically possible. However, even in the case of extreme strength of nucleophile, as with alkyllithium reagents, it is evident that sterics play a central role in the feasibility of this reaction. The clear extension of our study is to use the characteristics of this substitution reaction and apply them to the synthesis of new, functionalized, silicon-containing polymers. We will report on these new polymers in a future publication.

Table 3
Alkyllithium nucleophiles promote substitution reaction over alkylation

Nucleophilic Group Employed	Silane Product Observed	Isolated % Yield of Disubstituted Product
Me-		61
^{n}Bu-		79
^{t}Bu-		0[a]
$(CH_3)_3SiCH_2$-		0
Ph-		87

[a]multiple products, including α-lithiation observed.

4. Experimental

4.1. Materials

Di-*n*-hexyldichlorosilane was purchased from Gelest, distilled under reduced pressure (b.p. = 113°C/6 mmHg), and stored over activated 4 Å molecular sieves under argon. Triethylamine and 1,5-hexadiene were purchased from Aldrich and dried by distillation over CaH_2. 4-Methoxyphenol was purchased from Aldrich and purified by vacuum sublimation and dried in vacuo. Methanol, ethanol, 2-propanol, pentafluorophenol, 2,2,2-trifluoroethanol, 3-methyl-1-butanol, and benzyl alcohol were purchased from Aldrich, dried over $Mg–I_2$, and stored over activated 3 Å or 4 Å molecular sieves. Phenol (Aldrich) was azeotropically distilled from benzene; 1 M CH_3Li in Et_2O, 1.8 M C_6H_5Li in cyclohexane–ether, and 2.5 M *n*-BuLi in hexanes were also purchased from Aldrich and used without further purification. The lithium reagents were titrated according to the method by Suffert [20]. Diethyl ether (Fisher) was dried and distilled over NaK–benzophenone ketyl.

4.2. Instrumentation

All NMR spectra, ^1H (300 MHz), ^{13}C (75 MHz), ^{19}F (282 MHz), and ^{29}Si (60 MHz) were conducted on either a Varian VXR or Varian Gemini series superconducting spectrometer system and referenced to residual C_6H_6, DMSO, or $CHCl_3$ solvent signals. ^{19}F-NMR spectra were internally referenced to $CFCl_3$. For the ^{29}Si-NMR spectra, a heteronuclear gated decoupling pulse sequence with a pulse delay of 30 s was used with an internal tetramethylsilane reference added. Mass spectral data were conducted on a Finnegan 4500 gas chromatograph–mass spectrometer using either electron ionization (EI) or chemical ionization (CI) mode. Gas chromatography was performed on a Shimadzu GC-17A gas chromatograph equipped with a 15 m Restek RTX-5 crossbonded 5% diphenyl–95% dimethyl siloxane column using He as the carrier gas and a FID detector. Elemental analyses were performed by Atlantic Microlab (Norcross, GA).

4.3. General procedure for synthesis of dialkoxydialkylsilanes

In a 250-ml three-neck round bottom flask, flame-dried and equipped with a stir bar and reflux condenser, 100 ml of Et_2O was added by cannula in an inert atmosphere. Using a syringe, 7.8 ml (0.056 mol) of Et_3N was added followed by 2.3 ml (0.056 mol) of anhydrous alcohol. Di-*n*-hexyldichlorosilane, 3.4 ml (0.014 mol), was then added dropwise; a precipitate formed immediately from the generation of triethylamine hydrochloride salts. The reaction mixture was refluxed under Ar for 18 h, cooled to room temperature (r.t.), and filtered through a Schlenk filter frit containing Celite to remove the organic salts. The solvent was removed under reduced pressure, and the product was distilled in vacuo (1 mmHg) using a microscale one-piece distillation apparatus containing a Vigreux column. Percent yields of the isolated products were calculated post distillation. The product isolated was a clear, light yellow liquid.

4.4. Synthesis of di-n-hexyldimethoxysilane (**1**)

Isolated yield: 37%. ^1H-NMR (δ, $CDCl_3$): 0.59 ($SiCH_2$)(t, 4H), 0.88 (CH_3)(t, 6H), 1.59 (CH_2)(br, 16H), 3.50 (OCH_3)(s, 6H). ^{13}C-NMR (δ, $CDCl_3$): 11.9 ($SiCH_2$), 14.1 (CH_3), 22.5, 22.7, 31.5, 33.1 (CH_2), 50.3 (OCH_3). ^{29}Si-NMR (δ, C_6D_6): −2.4 ($R_2Si(OCH_3)_2$). HRMS (CI): Anal. Calc. for $C_{14}H_{33}O_2Si$: 261.2250. Found: 261.2217. Elemental analysis for $C_{14}H_{32}SiO_2$: Calc. (Found) C, 64.55 (64.43); H, 12.38 (12.47%).

4.5. Synthesis of di-n-hexyldiethoxysilane (**2**)

Isolated yield: 64%. ^1H-NMR (δ, $CDCl_3$): 0.58 ($SiCH_2$)(t, 4H), 0.88 (CH_3)(t, 6H), 1.21 ($OCH_2\mathit{CH_3}$)(t, 6H), 1.28 (CH_2)(br, 16H), 3.73 (OCH_2)(q, 4H). ^{13}C-NMR (δ, $CDCl_3$): 12.6 ($SiCH_2$), 14.1 (CH_3), 18.5 ($OCH_2\mathit{CH_3}$), 22.6, 22.8, 31.5, 33.1 (CH_2), 58.1 (OCH_2). ^{29}Si-NMR (δ, $CDCl_3$): −5.62 (R_2SiOR_2). HRMS (CI): Anal. Calc. for $C_{16}H_{37}O_2Si$: 289.2563. Found: 289.2531. Elemental analysis for $C_{16}H_{36}SiO_2$: Calc. (Found) C, 66.60 (66.31); H, 12.58 (12.40%).

4.6. Synthesis of di-n-hexyldipropoxysilane (**3**)

Isolated yield: 50%. ^1H-NMR (δ, $CDCl_3$): 0.59 ($SiCH_2$)(t, 4H), 0.88 (CH_3)(t, 12H), 1.26 (CH_2)(br, 16H), 1.54 ($OCH_2\mathit{CH_2}$)(t, 4H), 3.61 (OCH_2)(t, 4H). ^{13}C-NMR (δ, $CDCl_3$): 10.3 ($O(CH_2)_2\mathit{CH_3}$), 12.6 ($SiCH_2$), 14.1 (CH_3), 22.6, 22.8, 31.5, 33.1 (CH_2), 25.9 ($OCH_2\mathit{CH_2}$), 64.2 (OCH_2). ^{29}Si-NMR (δ, $CDCl_3$): −6.01 (R_2SiOR_2). HRMS (CI): Anal. Calc. for $C_{18}H_{41}O_2Si$: 317.2876. Found: 317.2887. Elemental analysis for $C_{18}H_{40}O_2Si$: Calc. (Found) C, 68.29 (68.53); H, 12.73 (12.67%).

4.7. Synthesis of di-n-hexyldi(trifluoroethoxy)silane (**4**)

Isolated yield: 64%. ^1H-NMR (δ, $CDCl_3$): 0.70 ($SiCH_2$)(m, 4H), 0.87 (CH_3)(m, 6H), 1.31 (CH_2)(m, 16H), 3.99 (OCH_2)(q, 4H). ^{13}C-NMR (δ, $CDCl_3$): 12.0 ($SiCH_2$), 14.0 (CH_3) 22.1, 22.5, 31.4, 32.8 (CH_2), 61.0 (OCH_2), 124.0 (CF_3). ^{19}F-NMR: −77.3 (CF_3)(t, 3F). ^{29}Si-NMR (δ, $CDCl_3$): −2.4 (R_2SiOR_2). HRMS (CI): Anal. Calc. for $C_{16}H_{31}SiF_6O_2$: 397.1998. Found: 397.1992. Elemental analysis for $C_{16}H_{30}F_6O_2Si$: Calc. (Found) C, 48.46 (48.57); H, 7.63 (7.72%).

4.8. Synthesis of di-n-hexyldi(3-methyl-1-butoxy)silane (5)

Isolated yield: 59%. ^{1}H-NMR (δ, $CDCl_3$): 0.58 ($SiCH_2$)(t, 4H), 0.90 (CH_2CH_3), ($CH(CH_3)_2$)(m, 18H), 1.31 (CH_2), ($CH_2CH(CH_3)_2$)(br, 20H), 1.70 (CH)(m, 2H), 3.65 (OCH_2)(t, 4H). ^{13}C-NMR (δ, $CDCl_3$): 12.5 ($SiCH_2$), 14.1 (CH_2CH_3), 22.5, 22.6, 31.5, 33.1 (CH_2), 22.8 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 41.7 ($CHCH_2$), 60.9 (OCH_2). ^{29}Si-NMR (δ, $CDCl_3$): -5.9 (R_2SiOR_2). HRMS (CI): Anal. Calc. for $C_{22}H_{49}SiO_2$: 373.3502. Found: 373.3470. Elemental analysis for $C_{22}H_{48}O_2Si$: Calc. (Found) C, 70.90 (70.65); H, 12.98 (13.10%).

4.9. Synthesis of di-n-hexyl-di-2-propoxysilane (6)

Isolated yield: 32%. ^{1}H-NMR (δ, $CDCl_3$): 0.57 ($SiCH_2$)(t, 4H), 0.87 (CH_3)(t, 6H) 1.15 ($CH(CH_3)_2$)(d, 12H), 1.27 (CH_2)(br, 16H), 4.10 (OCH)(m, 2H). ^{13}C-NMR (δ, $CDCl_3$): 13.5 ($SiCH_2$), 14.1 (CH_3), 22.6, 27.0, 31.5, 33.2 (CH_2), 25.8 ($CH(CH_3)_2$), 64.5 (OCH). ^{29}Si-NMR (δ, C_6D_6): -2.6 (R_2SiOR_2). HRMS (CI): Anal. Calc. for $C_{18}H_{41}SiO_2$: 317.2876. Found: 317.2928. Elemental analysis for $C_{18}H_{40}O_2Si$: Calc. (Found) C, 68.29 (68.32); H, 12.75 (12.68%).

4.10. Synthesis of di-n-hexyldibenzoxysilane (7)

Isolated yield: 62%. ^{1}H-NMR (δ, $CDCl_3$): 0.74 ($SiCH_2$)(t, 4H), 0.87 (CH_3)(t, 6H), 1.23 (CH_2)(br, 16H), 4.83 (OCH_2)(s, 4H), 7.35 (arom CH)(m, 10H). ^{13}C-NMR (δ, $CDCl_3$): 12.6 ($SiCH_2$), 14.1 (CH_3), 22.6, 22.7, 31.5, 33.0 (CH_2), 64.4 (OCH_2), 126.3, 127.1, 128.2 (arom CH), 140.8 (arom C). ^{29}Si-NMR (δ, $CDCl_3$): -3.6 (R_2SiOR_2). HRMS (CI): Anal. Calc. for $C_{26}H_{41}SiO_2$: 413.2876. Found: 413.2832. Elemental analysis for $C_{26}H_{40}O_2Si$: Calc. (Found) C, 75.68 (75.56); H, 9.78 (9.97%).

4.11. General procedure for the synthesis of diphenoxydialkylsilanes

In a 250-ml three-neck round bottom flask equipped with a reflux condenser, 2.7 g (0.029 mol) of dry phenol was added, followed by cannulation of approximately 75 ml of diethyl ether. By syringe addition, the reaction vessel was charged with 4.0 ml (0.029 mol) of Et_3N and 2.0 ml (0.007 mol) of di-n-hexyldichlorosilane. Precipitation occurred, and the reaction mixture was stirred for 1 h. A catalytic amount of 4-dimethylaminopyridine (DMAP), 0.02 g (1.6×10^{-4} mol), was then added and the reaction flask was refluxed for 24 h. The ether was removed by rotary evaporation, the product was dissolved in hexane, and extracted 2×20 ml with H_2O followed by 2×20 ml with 1 M NaOH. The solution was dried over $MgSO_4$, filtered, and solvent removed by rotary evaporation. Purification of the product was achieved by column chromatography on silica gel with 3:1 (hexanes–methylene chloride) as the eluent, and the product was isolated as a pale yellow liquid.

4.12. Synthesis of di-n-hexyl(diphenoxy)silane (8)

Isolated yield: 53%. ^{1}H-NMR (δ, DMSO-d_6): 0.82 (CH_3),($SiCH_2$)(m, 10H), 1.21 (CH_2)(br, 16H), 6.97 (arom CH)(dd, 6H), 7.27 (arom CH)(t, 4H). ^{13}C-NMR (δ, DMSO-d_6): 12.5 ($SiCH_2$), 13.9 (CH_3), 21.7, 21.8, 30.7, 31.9 (CH_2), 119.4, 122.1, 129.8 (arom CH), 153.8 (arom C). ^{29}Si-NMR (δ, $CDCl_3$): -8.1 (R_2SiOPh_2). HRMS (CI): Anal. Calc. for $C_{24}H_{37}O_2Si$: 385.2563. Found: 385.2569. Elemental analysis for $C_{24}H_{36}O_2Si$: Calc. (Found) C, 74.95 (74.57); H, 9.44 (9.80%).

4.13. Synthesis of di-n-hexyldi(4-methoxyphenoxy)silane (9)

Use of DMAP was unnecessary for this reaction. Isolated yield: 67%. ^{1}H-NMR (δ, $CDCl_3$): 0.85 ($SiCH_2$), (CH_3)(m, 10H), 1.23 (CH_2)(m, 16H), 3.74 (OCH_3)(s, 6H), 6.77, 6.83 (arom CH)(dd, 8H). ^{13}C-NMR (δ, $CDCl_3$): 12.7 ($SiCH_2$), 14.1 (CH_3), 22.3, 22.5, 31.3, 32.8 (CH_2), 55.6 (OCH_3), 114.5, 120.3 (arom CH), 148.2 (arom $COCH_3$), 154.4 (arom COSi). ^{29}Si-NMR (δ, $CDCl_3$): -7.9 (R_2SiOPh_2). HRMS (CI): Anal. Calc. for $C_{26}H_{41}O_4Si$: 445.2696. Found: 445.2768. Elemental analysis for $C_{26}H_{40}O_4Si$: Calc. (Found) C, 70.23 (70.33); H, 9.07 (9.05%).

4.14. General procedure for the synthesis of tetraalkylsilanes

Into a three-neck round bottom flask, 100 ml of dry Et_2O was added by cannula, followed by 5.0 ml (0.018 mol) of di-n-hexyldichlorosilane, by syringe addition. The reaction vessel was cooled to 0°C. An addition funnel was incorporated for the slow addition (dropwise over 15 min) of 30 ml (0.075 mol) of 2.5 M n-BuLi to the solution. Upon addition, a white precipitate was produced, and the reaction mixture was stirred for 12 h and slowly allowed to reach r.t. In order to quench any residual n-BuLi present, 10 ml of H_2O was added slowly under inert atmosphere, followed by an additional 100 ml of H_2O and ether. Two extractions with 100 ml of H_2O were completed, and the organic layer was dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel with 20:1 (hexanes–ethyl acetate) as the eluent. The product was isolated as a pale yellow liquid and dried in vacuo.

4.15. Synthesis of di-n-hexyldimethylsilane (**10**)

Isolated yield: 61%. ^{1}H-NMR (δ, $CDCl_3$): −0.06 ($SiCH_3$)(s, 6H), 0.47 ($SiCH_2$)(t, 4H), 0.89 (CH_3)(t, 6H), 1.28 (CH_2)(br, 16H). ^{13}C-NMR (δ, $CDCl_3$): −3.4 ($SiCH_3$), 14.2 (CH_3), 15.3 ($SiCH_2$), 22.6, 23.9, 31.6, 33.4 (CH_2). ^{29}Si-NMR (δ, $CDCl_3$): 1.9 (SiR_4). HRMS (CI): Anal. Calc. for $C_{14}H_{33}Si$: 229.2352. Found: 229.2352. Elemental analysis for $C_{14}H_{32}Si$: Calc. (Found) C, 73.59 (73.61); H, 14.12 (14.24%).

4.16. Synthesis of di-n-hexyl-di-n-butylsilane (**11**)

Isolated yield: 79%. ^{1}H-NMR (δ, $CDCl_3$): 0.47 ($SiCH_2$)(t, 8H), 0.87 (CH_3)(t, 6H), 1.26 (CH_2)(br, 24H). ^{13}C-NMR (δ, $CDCl_3$): 12.3, 12.5 ($SiCH_2$), 13.8, 14.2 (CH_3), 22.7, 23.9, 26.3, 26.9, 31.6, 33.7 (CH_2). ^{29}Si-NMR (δ, $CDCl_3$): 1.1 (R_4Si). HRMS (CI): Anal. Calc. for $C_{20}H_{45}Si$: 313.3291. Found: 313.3291. Elemental analysis for $C_{20}H_{44}Si$: Calc. (Found) C, 76.84 (76.55); 14.20, (14.09%).

4.17. Synthesis of di-n-hexyl-diphenylsilane (**12**)

Isolated yield: 87%. ^{1}H-NMR (δ, $CDCl_3$): 1.07 ($SiCH_2$)(t, 4H), 0.86 (CH_3)(t, 6H), 1.24 (CH_2)(br, 16H), 7.36 (arom CH)(m, 10H). ^{13}C-NMR (δ, $CDCl_3$): 12.5 ($SiCH_2$), 14.1 (CH_3), 22.6, 23.6, 31.4, 33.4 (CH_2), 127.7, 128.9, 134.8 (arom CH), 136.7 (arom C). ^{29}Si-NMR (δ, C_6D_6): −4.5 (R_2SiPh_2). HRMS (EI): Anal. Calc. for $C_{24}H_{36}Si$: 352.2586. Found: 352.2586. Elemental analysis for $C_{24}H_{36}Si$: Calc. (Found) C, 81.76 (81.28); H, 10.30 (10.35%).

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