Functionalization of Nanocrystalline Porous Silicon Surfaces with Aryllithium Reagents: Formation of Silicon−Carbon Bonds by Cleavage of Silicon−Silicon Bonds

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Abstract: Reaction of nanocrystalline ("porous") silicon with phenyllithium and lithium phenylacetylide results in functionalization of the silicon surface with phenyl and phenylacetylene moieties, respectively. The reaction proceeds by addition of the aryllithium reagent across a surface Si−Si bond, resulting in a Si−aryl bond and Si−Li species. The highly reactive Si−Li surface species is readily hydrolyzed by water, resulting in significant surface oxidation. The surface-bound Li can also be replaced with H or acyl species by addition of trifluoroacetic acid, acetyl chloride, heptanoyl chloride, or 4-butylbenzoyl chloride. These latter treatments significantly reduce the rate of air oxidation of the porous silicon surface. The nanocrystalline silicon samples used display visible photoluminescence arising from quantum confinement effects. Functionalization with phenyllithium preserves some of the photoluminescence, while the lithium phenylacetylide reaction results in almost complete loss of photoluminescence from the silicon nanocrystallites.

Introduction

Interest in photoluminescent porous silicon for potential display and chemical sensor applications has led to considerable development of the surface chemistry of this nanocrystalline material.[1,2] Hydrogen-terminated porous silicon is obtained by electrochemical oxidation and dissolution of silicon in fluoride-containing media.[3−6] Under the appropriate conditions, a matrix of photoluminescent silicon nanocrystallites results.[3,7] The photoluminescence has been attributed to quantum confinement effects within the silicon nanocrystallites.[3,8−12] The hydrogen-terminated silicon material oxidizes slowly in air, often resulting in loss of photo- or electroluminescent properties. Many studies have been directed at understanding the chemical properties of H-terminated silicon surfaces in order to protect porous Si from loss of its luminescent properties. Most efforts to stabilize the material focus on formation of silicon oxide species, either with thermal, electrochemical, or chemical oxidation reactions.[13−18] Although this approach has met with some success, oxidation of the interface is not desirable for many applications. For example, electroluminescent device efficiency is hindered if the luminescent silicon nanocrystallites are covered with an insulating oxide layer.[19] For sensor applications, attachment of chemical species is desired to impart specificity.[1,20] This can be accomplished through alkoxide or ester linkages, although the Si−O bond in this case is readily hydrolyzed, limiting the stability and applicability of such sensors.[21,22] It is highly desirable to prepare porous Si surfaces with modified chemical characteristics that are chemically stable.

The attachment of species to silicon surfaces by formation of Si−C bonds has been shown to provide greater stability toward oxidation. For example, Linford and Chidsey have shown that single-crystal silicon surfaces can be derivatized with alkyl monolayers by photolysis of diacyl peroxides at 90−100 °C.[23,24] Similarly, Lewis and co-workers have functionalized silicon with an alkyl layer in a two-step reaction in which the

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H-terminated Si surface is first chlorinated with PCl_5 and then treated with a Grignard reagent at 80 °C for 30 min to 8 days.[25] Finally, Chazalviel and co-workers have grafted methyl groups to porous silicon surfaces directly using an anodic electrochemical treatment in ether solutions containing either CH_3Li or CH_3MgCl.[26] In all of the above cases, the Si−C bonded species have been observed to significantly impede the rate of surface oxidation of the silicon. In this paper, we report the room-temperature functionalization of the surface of porous Si with aryllithium reagents. It is found that electrochemical anodization is not necessary to obtain measurable surface coverage, and that the aryl surface species also reduces the rate of air oxidation of porous silicon. The data indicate that a mechanism involving Si−Si bond cleavage occurs, generating surface aryl and Si−Li species. The surface Si−Li is very reactive and provides a convenient means for subsequent addition of electrophiles to the porous Si surface. A similar motif has recently been reported for the reaction of porous Si with Grignard reagents.[27]

Experimental Section

Sample Preparation and Treatment. Luminescent porous Si samples were prepared by galvanostatic photoetch of polished crystalline n-Si (phosphorus doped; 0.58 Ω•cm resistivity; (100) orientation) supplied by International Wafer Service.[1] The etching solution was prepared by adding an equal volume of pure ethanol (Quantum Chemicals) to an aqueous solution of HF (48 wt %; Fisher Scientific). The etching cell was constructed of Teflon and was open to air. Si wafers were cut into squares with a diamond scribe and mounted in the bottom of the Teflon cell with a Viton O-ring seal, exposing 0.2 cm^2 of the Si surface. Electrical contact was made to the backside of the Si wafer with a strip of heavy Al foil. A loop of Pt wire was used as a counter electrode. Samples were illuminated during the etch with a 300 W tungsten lamp in order to supply a photocurrent for the corrosion reaction. Samples were etched at an anodic current density of 50 mA/cm^2 for 5 min. After etching, the samples were rinsed in methylene chloride, dried under a stream of dry $N_{2(g)}$, and then dried in vacuo for 30 min prior to use. From this point on, standard inert atmosphere (nitrogen) techniques were used to avoid introduction of air or water.[28]

Functionalization with Aryllithium Reagents. The functionalization reactions were carried out in standard Schlenk flasks in a nitrogen-filled glovebox.[28] In a typical reaction, the freshly prepared porous silicon sample was added to the Schlenk flask and 1 mL of the reagent of interest (phenyllithium, 1.8 M solution in cyclohexanes−ether, or lithium phenylacetylide, 1.0 M solution in tetrahydrofuran, Aldrich Chemicals) was added by syringe. The flask was sealed and removed from the glovebox. Reaction was allowed to proceed for 160 min at room temperature, at which point the flask was attached to a Schlenk line and the solution removed by syringe. The flask containing the functionalized sample was then cooled to −78 °C in an acetone/dry ice bath and 3 mL of the desired quenching reagent (acetyl chloride (99+%), heptanoyl chloride (99%), 4-butylbenzoyl chloride (97%), trifluoroacetic acid (99%), or trifluoroacetic acid-*d* (99.5 atom % D, Aldrich Chemicals)) was added by syringe. The acetone/dry ice bath was removed and the mixture allowed to return to room temperature. After 90 min the liquid reagent was removed by syringe and the sample rinsed with 3 mL aliquots of dry tetrahydrofuran (previously distilled from sodium benzophenone ketyl solution) three times. The sample was then removed from the Schlenk flask and dried under a stream of dry nitrogen.

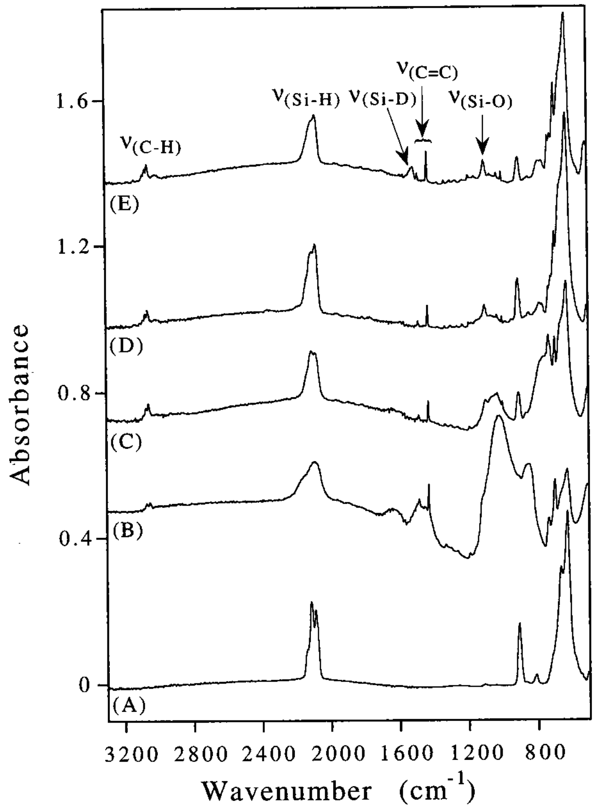

Figure 1. Infrared spectra representing the reaction of porous Si with phenyllithium. (A) Spectrum of a freshly etched porous Si sample before functionalization, displaying the Si−H stretching modes characteristic of freshly etched, hydrogen-terminated porous Si. (B) Spectrum of a porous Si sample after treatment with phenyllithium and exposure to air, showing the presence of surface-bound phenyl. Significant oxidation of the sample is also apparent. (C) Spectrum of the sample from (B) after treatment with ethanolic HF to remove surface oxide. Bands characteristic of the phenyl group are still apparent, indicating the phenyl group is still bound to the surface. (D) Spectrum of a different porous Si sample that has been functionalized with phenyl but treated with trifluoroacetic acid before exposure to air. In this case the phenyl group has still become attached but the oxidation reaction has been eliminated. (E) Same reaction as in (D), but with D-substituted trifluoroacetic acid, showing that the deuteration step produces an Si-D species. Spectra are offset along the *y*-axis for clarity.

Photoluminescence Measurements. Steady-state photoluminescence (PL) spectra were obtained with an Acton 0.275 m monochromator, 450 nm cutoff filter, and a UV-enhanced Princeton Instruments liquid nitrogen-cooled charge coupled device (CCD) detector. The excitation source was the 435 nm emission line (filtered through two identical narrow-band-pass interference filters) from an Oriel 250 W Hg arc lamp. Incident power at the sample was always below 1.25 mW/cm^2. PL measurements were performed on samples in air. The PL intensities were normalized to a measured standard phosphor (ZnS: Cu) in order to provide an accurate measurement of intensity changes before and after each functionalization reaction.

Infrared (FTIR) Spectroscopic Measurements. Fourier transform infrared spectra were collected on a Nicolet Magna 550 operating in the transmission mode. Spectral resolution was 4 cm^{-1}, and typically 128 interferograms were acquired per spectrum. Although the sample chamber was purged with dry nitrogen, sample transfers were usually performed in air.

Results and Discussion

Reaction with Phenyllithium. The transmission infrared spectrum (FTIR) of freshly etched porous Si (Figure 1A) displays absorptions characteristic of surface SiH, SiH_2, and

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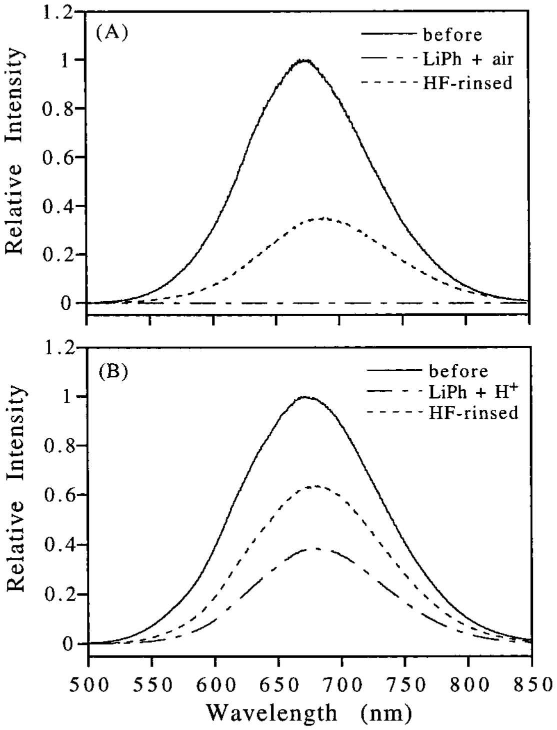
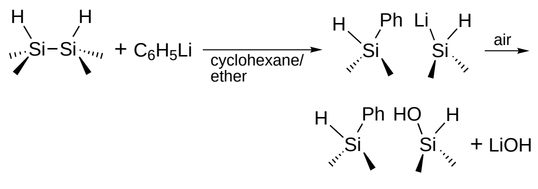


Figure 2. Comparison of the steady-state PL spectra (435 nm excitation) from porous Si samples functionalized with phenyllithium and the effect of protonating the sample before exposing it to air. (A) Spectrum from a freshly etched sample ("before") after phenylation and exposure to air ("LiPh + air") and after rinsing with ethanolic HF ("HF-rinsed"). (B) Spectrum from a freshly etched sample ("before"), after phenylation and low-temperature protonation ("LiPh + H$^+$"), and after rinsing with ethanolic HF ("HF-rinsed").

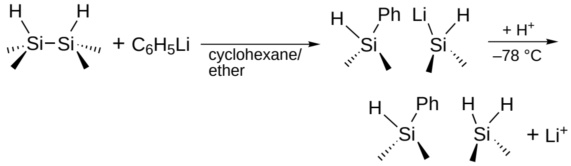
SiH_3 species at 2085, 2110, and 2140 cm^{-1}, respectively.[29] There is also a very small signal at 1060 cm^{-1} due to interstitial oxygen in the silicon lattice, typical of Czochralski-grown silicon wafers. The PL from this sample is strong and centered around 660 nm (Figure 2). After treatment of the sample with phenyllithium and subsequent air hydrolysis (eq 1), the infrared spectrum exhibits bands characteristic of silicon-bound phenyl at 1490 and 1430 cm^{-1},[30] aromatic $\nu_{(\mathrm{C-H})}$ stretching absorptions between 3080 and 3030 cm^{-1}, and a strong broad silicon oxide stretching mode at 1100 cm^{-1} (Figure 1B).



(1)

A new Si–H band, assigned to an oxide-back-bonded Si–H stretching mode, appears at 2260 cm^{-1}.[29] The data indicate that functionalization is accompanied by significant oxidation of the silicon surface, and bands characteristic of surface-OH or adsorbed water are also evident at 1460 and 1600 cm^{-1}. The intensity of the steady-state PL spectrum from phenyllithium-derivatized porous silicon is reduced to 0.2% of the original value (of freshly etched porous Si) (Figure 2A). The surface oxide can be removed by exposure of the sample to HF/ethanol (4 × 1 mL), which results in a loss of the 1100 cm^{-1} $\nu_{(\mathrm{Si-O})}$ band in the infrared spectrum (Figure 1C). The broad bands associated with adsorbed H_2O at 1460 and 1600 cm^{-1} also disappear, indicating that the surface is now hydrophobic. There is no concomitant loss in intensity of the $\nu_{(\mathrm{C-H})}$ and $\nu_{(\mathrm{C-C})}$ IR bands associated with the phenyl group, indicating that the HF/ethanol treatment leaves this species intact on the Si surface. Removal of the silicon oxide by the HF/ethanol wash results in recovery of 37% of the original steady-state PL intensity (Figure 2A).

Reaction of the Lithiated Surface with Trifluoroacetic Acid. To minimize surface oxidation during the alkylation reaction, the phenyllithium-treatment was followed with a low-temperature protonation step using trifluoroacetic acid (eq 2).



(2)

Under these conditions, the surface oxidation reaction is completely suppressed, as determined from the infrared spectrum (Figure 1D). The FTIR spectrum displays no increase in the silicon oxide region (ca. 1100 cm^{-1}), while still displaying bands characteristic of the surface-attached phenyl moiety. To determine the role of the acid, deuterated trifluoroacetic acid was used to quench the phenyllithium reaction. The FTIR spectrum displays a peak at 1519 cm^{-1} due to the formation of surface Si–D (Figure 1E).

The protonation step also produces a less defective Si surface, as indicated by the PL spectra (Figure 2). Thus the intensity of the PL spectrum of a porous Si sample that is exposed to air immediately after the phenylation step is reduced by a factor of 500 (Figure 2A), while phenylation followed immediately by low-temperature protonation leads to only a factor of 3 reduction in the PL intensity, relative to the freshly etched sample (Figure 2B). The data indicate that air hydrolysis of the Si–Li surface species leads to a very electronically defective surface, while displacement of the surface-bound Li atom with H provides a significantly more passive surface.

Mechanism of Aryllithium Addition. A reaction mechanism consistent with the above observations is outlined in Scheme 1. We propose that the aryllithium reagent adds across a Si–Si bond, cleaving the bond and forming neighboring Si–phenyl and Si–Li surface species. The highly reactive Si–Li group is expected to be rapidly hydrolyzed, which accounts for the large amount of oxide observed if the sample is exposed to air at this point (Figure 1B). The addition of a nonaqueous acid removes the surface-bound Li atom as Li$^+$, and caps the surface Si atom with H (or D, see Figure 1, spectra D and E). Thus generation of the new Si–H or Si–D species on the porous Si surface can be thought of formally as a result of protonation of a silyl anion produced in the Si–Si bond cleavage reaction.

Although the surface chemistry of porous Si is expected to be different from molecular silicon chemistry due to the large steric hindrance of the surface, there are solution analogues for

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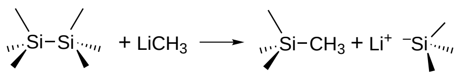
the proposed reaction. For example, reaction of hexamethyldisilane with methyllithium results in Si$-$Si bond scission (eq 3):[31]

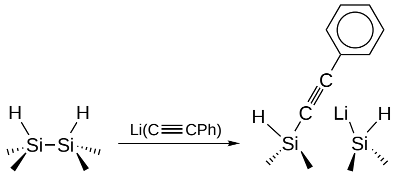


(3)

The cleavage of Si$-$Si bonds on the surface can also be rationalized by consideration of relative bond energies: Si$-$Si bonds are weaker than Si$-$H bonds by about 20 kcal/mol.[32] Although S$_N$2-type reactions cannot occur on a Si surface, the availability of energetically low-lying d orbitals make five-coordinate intermediates accessible in the Si system.

It should be noted that Chazalviel and co-workers have proposed an alternate reaction mechanism for alkyllithium and alkylgrignard reactions at porous Si surfaces, involving hydride abstraction followed by alkylation at a single Si surface atom.[26] This chemistry is electrochemically assisted, and under the appropriate conditions nearly complete replacement of the surface hydrides can be achieved.[33] The driving force for the reaction is the formation of a soluble metal hydride. The Chazalviel mechanism also has precedent in the molecular silicon chemistry literature,[34] and our data cannot completely rule out this possibility in the present system. However, Chazalviel's mechanism does not account for our deuterium or alkanoyl halide quenching results, or the high amount of oxidation that is observed if the reaction is not quenched.

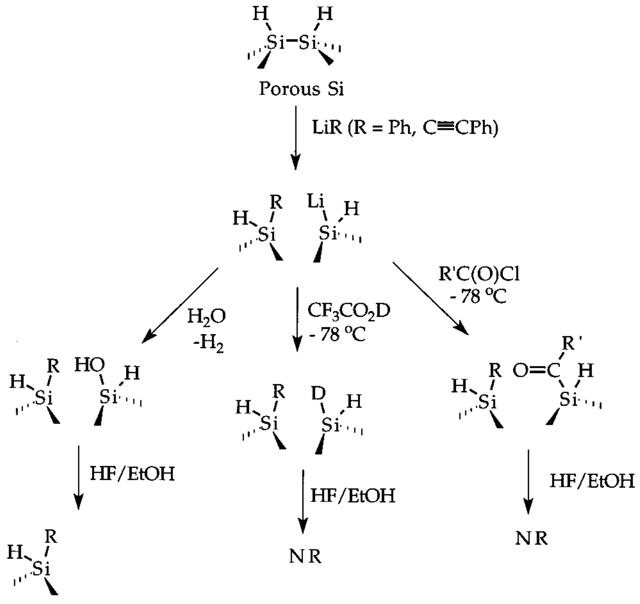
Reaction of Porous Si with Lithium Phenylacetylide. Modification of the porous Si surface can also be accomplished with lithium phenylacetylide (eq 4).



(4)

Reaction of porous Si with lithium phenylacetylide appears to follow the same mechanism as the phenyllithium reaction; exposure of the lithiated surface to air results in significant oxidation of the surface. If the oxidized material is subsequently treated with ethanolic HF, the surface oxide is selectively removed. The infrared spectrum of this product displays aromatic $\nu_{(C-C)}$ bands at 1599, 1490, and 1446 cm^{-1} and aromatic $\nu_{(C-H)}$ vibrational absorptions between 3080 and 3030 cm^{-1}.[30] The absorption for the asymmetric alkyne C$-$C stretch is expected to appear at 2050 cm^{-1}.[30] This region is obscured by the $\nu_{(Si-H)}$ vibrational bands, so we were unable to definitively identify an alkyne stretching band. In addition, the vibrational stretching mode for Si$-$C is expected to lie in the 680$-$760 cm^{-1} region.[26,35,36] There are two bands that could be assigned to this $\nu_{(Si-C)}$ mode at 696 and 757 cm^{-1} (Figure 3). In the absence of isotopic labeling experiments we are unable to make a definitive assignment. Similar bands were also observed in the infrared spectrum of the phenyl-terminated material (at 696 and 737 cm^{-1}). The degree of modification (or extent of coverage), which may be estimated from the intensity of the $\nu_{(Si-Hx)}$ bands relative to the intensity of the aromatic $\nu_{(C-H)}$ bands, seems to be a little greater for the lithium phenylacetylide reaction than for phenyllithium, although the difference may not be significant. Differing reactivities were expected due to the different steric requirements and reactivities of the two lithium reagents.

Scheme 1



The intensity of PL from the porous Si samples decreases significantly upon functionalization with phenylacetylide (Figure 4). The decrease is much greater than the decrease observed for a similarly prepared phenyl-terminated surface (Figure 2A), even though the FTIR data indicate that the relative coverages are comparable. Therefore it is concluded that the phenylacetylide species acts as a more efficient nonradiative surface trap than the phenyl species. Prior work has shown that aromatic molecules can quench PL from porous silicon by a mechanism involving energy transfer to the molecular triplet states.[37] Neither benzene nor phenylacetylene have accessible energy levels[38] for energy transfer quenching to be a reasonable mechanism in the present case. However, it is possible that the interaction of the phenylacetylide moiety with Si-based orbitals introduces states of the appropriate energy for non-radiative quenching to occur. In contrast, Chazalviel and co-workers noted little or no change in the intensity of PL from porous Si with anodically grafted methyl groups,[26] and Lewis and co-workers have reported that surface recombination velocities do not change significantly on single-crystal Si surfaces modified with alkyl groups (relative to the H-terminated surface).[25]

Reaction of the Lithiated Surface with Acyl Chlorides. To provide oxide-free surfaces and to allow for functionalization with distinct chemical species, the reactivity of the aryllithiated surfaces toward carbocation reagents was explored. The general

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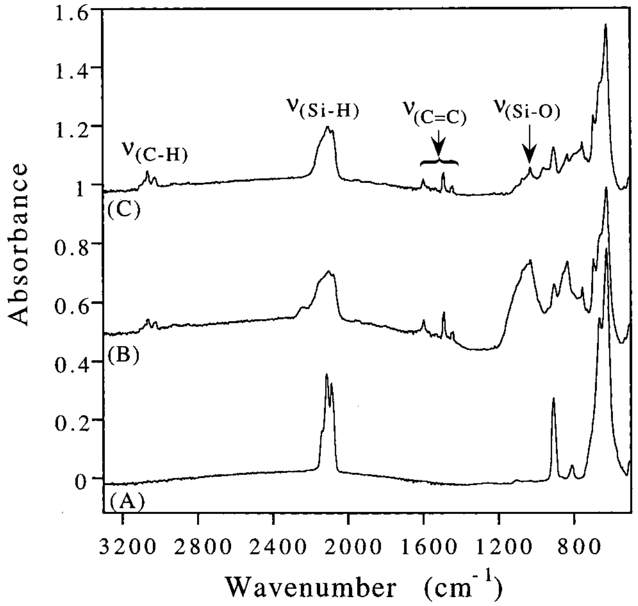
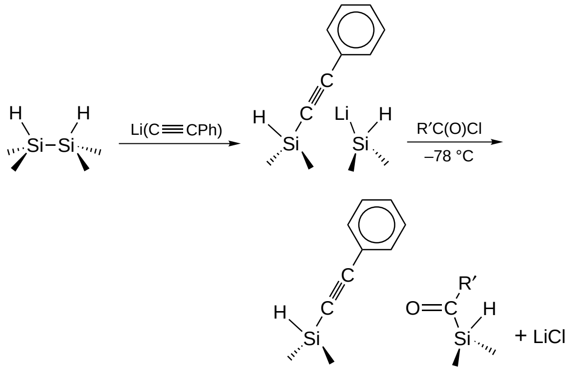


Figure 3. Infrared spectra representing the reaction of a porous Si sample with lithium phenylacetylide. (A) Spectrum of a freshly etched porous Si sample before functionalization. (B) Spectrum of the porous Si sample after treatment with lithium phenylacetylide and exposure to air, showing bands indicative of the presence of surface-bound phenyl moieties and oxide. (C) Spectrum of the sample from (B) after treatment with ethanolic HF to remove the surface oxide. Bands characteristic of the phenylacetylide group are still apparent, indicating that it is still bound to the surface. Spectra are offset along the *y*-axis for clarity.

concept involves replacement of the highly reactive intermediate Si−Li species with a more stable Si−C bonded group (eq 5).



(5)

Figure 5 displays the difference FTIR spectrum of a porous Si sample before and after treatment with lithium phenylacetylide (1.0 M in THF) followed by neat heptanoyl chloride. The spectrum shows alkyl C−H stretching absorptions between 2850 and 2950 cm^{-1}, an alkyl bending mode absorption at 1373 cm^{-1}, and an acylsilane C=O stretching mode at 1641 cm^{-1}, assigned to the surface-bound Si−acyl species.[39] Bands assigned to the surface phenylacetylide species are observed at 1599, 1490, and 1446 cm^{-1} (aromatic modes) and 3080 and 3030 cm^{-1} (aromatic C−H stretches). Only a small silicon oxide peak around 1100 cm^{-1} was observed, indicating that the acyl chloride treatment is similar to the protonation reaction discussed above in that it precludes surface oxidation. Brook and co-workers have reported that acyltris(trimethylsilyl)silanes can be prepared in yields of 60−70% by the coupling of tris(trimethylsilyl)silyllithium with a large excess of the acid chloride at −70 °C.[39] The fact that little oxidation is observed in the present study implies that removal of surface Si−Li species is nearly complete. Similar reactivity is observed if acetyl chloride or 4-butylbenzoyl chloride are substituted for the heptanoyl chloride used in the reaction. In all cases, subsequent washes with ethanolic HF do not remove either the phenylacetylide or acyl species.

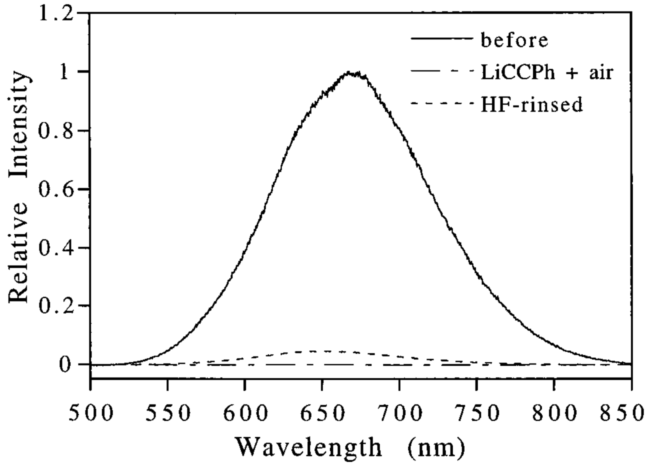


Figure 4. Comparison of the steady-state PL spectra (435 nm excitation) from a porous Si sample functionalized with phenylacetylide. Spectrum from a freshly etched sample ("before") after phenylacetylide functionalization and exposure to air ("LiCCPh + air") and after rinsing with ethanolic HF ("HF-rinsed"). Note the PL intensity from the phenylacetylide-terminated material is significantly weaker than that from the corresponding phenyl-terminated material (Figure 2).

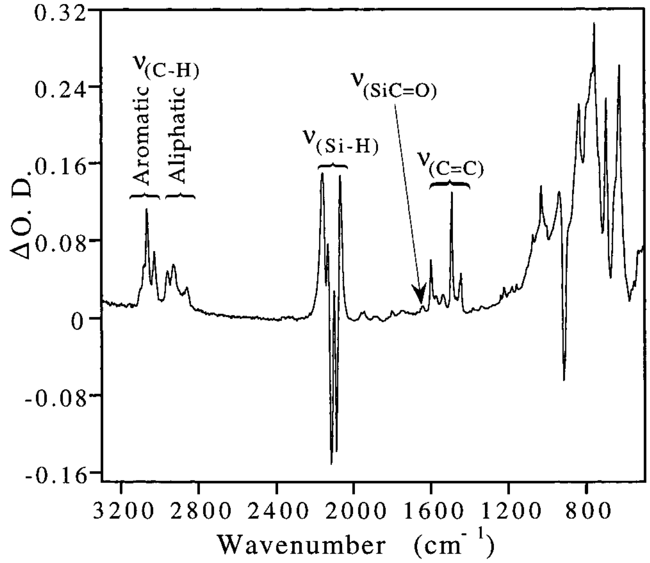


Figure 5. Difference FTIR spectrum showing the effect of functionalization of porous Si with lithium phenylacetylide followed by heptanoyl chloride. Bands assigned to surface phenylacetylide and heptanoyl groups are both apparent.

Comparison of the relative intensities of the FTIR bands associated with the phenylacetylide species and the acyl species indicates that they are not present on the surface in a 1:1 ratio as would be expected from eq 5. Rather, the acyl species are less abundant than the phenylacetylide species on the porous Si surface. This deficit is particularly apparent on comparison of the aromatic and aliphatic C−H stretching bands in the difference FTIR spectrum of Figure 5. On the basis of the FTIR spectrum of a model organic compound such as 1-phenylhexane, only one-fourth of the proposed Si−Li species have been acylated. The discrepancy may be due to protonation of the

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Si−Li species rather than acylation, which could occur if the acylating agents were hydrolyzed by trace water prior to the porous Si surface reaction. It is also possible that a competing hydride abstraction mechanism (as proposed by Chazalviel et al.) is operative.[26,33]

As stated above, the PL intensity from phenylacetylide-modified porous Si is significantly lower than that from freshly etched porous Si. The acid chloride (acetyl chloride, heptanoyl chloride, or 4-butylbenzoyl chloride) treatments do not lend any additional PL intensity to the material. Subsequent HF rinsing of these doubly modified (phenylacetylide and acyl) samples leads to a slight (5%) recovery of PL, although no change can be observed in the infrared spectra upon HF rinse.

Conclusions

A summary of the reactivity patterns explored in this work is outlined in Scheme 1. Exposure of porous Si to phenyllithium or lithium phenylacetylide results in grafting of the corresponding aryl to the silicon surface by formation of a Si−C bond. Unlike Si−O bonded compounds, the carbon-bound aryls cannot be removed by an ethanolic HF rinse. The reaction is proposed to proceed by addition of the aryllithium reagent across Si−Si surface bonds, generating the stable Si−aryl species and a highly reactive Si−Li species. The generation of silyl anions by this reaction provides a convenient means of covalently attaching electrophiles to the surface of porous Si.

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