

Reaction of Photoluminescent Porous Silicon Surfaces with Lithium Reagents To Form Silicon–Carbon Bound Surface Species

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Exposure of photoluminescent porous Si to alkyllithium reagents results in grafting of the alkyl group to the silicon surface by formation of a Si–C bond. The reaction is proposed to proceed by addition of the alkyllithium reagent across a surface Si–Si bond, forming Si–alkyl and Si–Li surface species. The highly reactive Si–Li surface group is readily hydrolyzed by water, resulting in significant surface oxidation. The surface-bound Li can also be replaced with acyl or methyl groups by addition of acetyl chloride, heptanoyl chloride, 4-butylbenzoyl chloride, 3-(chloromethyl)benzoyl chloride, 3-chloropropionyl chloride, or methyl trifluoromethanesulfonate. The acylation or alkylation steps preclude surface oxidation. In all cases, the intensity of photoluminescence from the porous Si samples is reduced after functionalization.

Introduction

The desire to develop crystalline Si as a platform for displays, micromachines, and sensors has led to the discovery of several chemical methods to functionalize Si surfaces.^{1–13} As a surface linking group, the Si–O bond is readily hydrolyzed, limiting the stability and applicability of these surface species for many applications.^{14,15} It is highly desirable to prepare modified Si surfaces that are more chemically stable. The use of Si–C bonds is one such approach that has been shown to provide stable surface species.^{6–8,11,13,16,17} The reason for this greater stability arises from kinetic, rather than thermodynamic considerations. The highly electronegative oxygen atom polarizes silicon atoms involved in Si–O linkages, making them susceptible to attack by nucleophiles. In contrast, Si–C is not as highly polarized

and so is less susceptible to nucleophilic substitution. For example, tetramethoxysilane (TMOS) hydrolyzes rapidly in air to form SiO₂, whereas tetramethylsilane (TMS) is so air-stable that it is commonly used as an internal standard for NMR spectroscopy.

We have recently reported a room-temperature functionalization reaction using phenyllithium and lithium phenylacetylide as reagents to modify porous Si surfaces.¹⁷ The high surface area of porous Si makes the products of surface reactions easy to characterize.^{3,18,19} The arylation reaction is thought to proceed by addition of the aryllithium reagent across a surface Si–Si bond, resulting in Si–aryl and Si–Li species. The reaction is attractive because the highly reactive Si–Li species allows for further modification of the surface with electrophilic reagents. This two-step approach potentially provides a general method for introducing a wide range of stable functionalities to Si surfaces. In this article, we have explored the generality of this reaction using alkyllithium nucleophiles in the first step and alkyl or aryl electrophiles in the second.

Experimental Section

Sample Preparation and Treatment. Luminescent porous Si samples were prepared by galvanostatic photoetch¹ of polished crystalline n-Si [phosphorus doped; 0.58–0.59 Ω·cm resistivity; (100) orientation] supplied by International Wafer Service. The etching solution was prepared by adding an equal volume of pure ethanol (Quantum Chemicals) to an aqueous solution of hydrofluoric acid (48 wt %; Fisher Scientific). This composition was also used in the “aqueous ethanolic HF” rinse used to remove oxide after chemical functionalization. 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 cm² 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

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as a counterelectrode. Samples were illuminated during the etch with a 300-W tungsten lamp to supply a photocurrent for the corrosion reaction. Samples were etched at an anodic current density of 50 mA/cm² 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 before use. From this point on, standard inert atmosphere (nitrogen) techniques were used to avoid introduction of air or water.²⁰ This preparation produces material that displays strong photoluminescence, whose spectrum is centered at 660 nm under 435 nm irradiation.

Functionalization with Alkylolithium Reagents. The functionalization reactions were carried out in standard Schlenk flasks in a nitrogen-filled glovebox.²⁰ In a typical reaction, the freshly prepared porous silicon sample was added to the Schlenk flask and 1 mL of the reagent of interest (methylolithium 1.4 M solution in diethyl ether, or butyllithium 1.6 M solution in hexanes, Aldrich Chemicals) was added by syringe. The flask was sealed and removed from the glovebox. Reaction was allowed to proceed for 120 min at room temperature, at which point the flask was attached to a nitrogen 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%), 3-(chloromethyl)benzoyl chloride (98%), 3-chloropropionyl chloride (98%), or methyl trifluoromethanesulfonate (99+%), Aldrich Chemicals] was added by syringe. The acetone/dry ice bath was removed and the mixture allowed to return to room temperature. After 60 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 (in air) and dried under a stream of dry nitrogen.

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 less than 1.25 mW/cm². PL measurements were performed on samples in air. The PL intensities were normalized to a measured standard phosphor (ZnS:Cu) to account for excitation source fluctuations and slight geometry changes in the optical bench before and after each functionalization reaction.

Infrared Spectroscopic Measurements. Fourier transform infrared (FTIR) spectra were collected on a Nicolet Magna 550 operating in transmission mode. Spectral resolution was 4 cm⁻¹, and 128 interferograms typically were acquired per spectrum. To correct for baseline curvature, the automatic baseline correction in the Nicolet OMNIC version 1.1 software package was applied to all the FTIR spectra presented in this article.

Electron Microscopy and Energy Dispersive Spectrometry (EDS) Measurements. Scanning electron microscopy (SEM) images were obtained using a Cambridge 360 SEM operating at 20 kV in secondary electron imaging mode. X-ray analysis (EDS) was performed with an integration time of 90 s.

Results and Discussion

Reaction of Porous Si with Nucleophiles. Porous Si and Methylolithium. The alkylolithium reactions generally were found to proceed similarly to those previously reported for aryllithium reactions with porous Si.¹⁷ Before the functionalization reaction, the transmission infrared spectrum (FTIR) of porous Si displayed absorptions characteristic of surface SiH, SiH₂, and SiH₃ stretching vibrations at 2085, 2110, and 2140 cm⁻¹, respectively,^{21–23} and Si–H and Si–H₂ bending vibrations at 810 and 904 cm⁻¹, respectively, a small signal at 1060 cm⁻¹ assigned to interstitial oxide in the bulk of the Si sample, and modes at

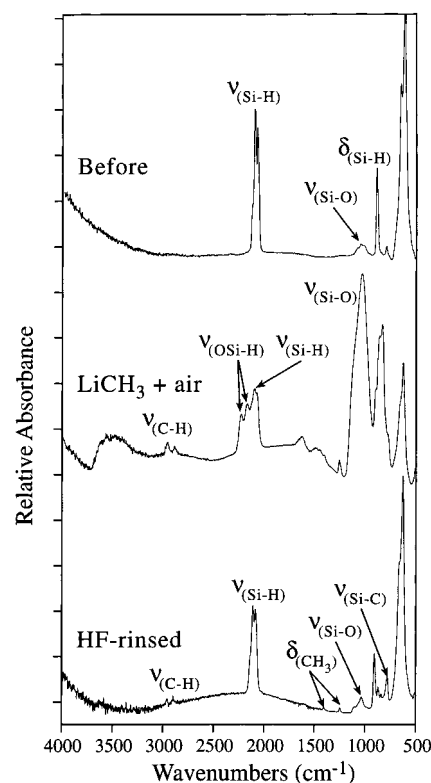


Figure 1. Transmission-mode infrared absorbance spectra of a porous Si sample before and after treatment with methylolithium. Before treatment (“Before”), the spectrum displays the Si–H vibrational modes characteristic of hydrogen-terminated porous Si, a small Si–O mode due to interstitial oxide, SiH_x bending, and Si–Si lattice modes. After methylation and exposure of the sample to air (“LiCH₃ + air”), the spectrum shows bands characteristic of surface-bound methyl groups and silicon oxide. The surface oxide can be removed by soaking the sample in aqueous ethanolic HF (“HF-rinsed”). The data show that the HF rinse removes oxide but not the methyl group. Spectra are offset along the y-axis for clarity.

626 and 665 cm⁻¹, assigned to either Si–Si lattice^{24,25} or Si–H_x vibrations^{22,26,27} (Figure 1, “Before”). After treatment of the sample with methylolithium and subsequent air hydrolysis, the infrared spectrum (Figure 1, “LiCH₃ + air”) exhibits bands characteristic of a methyl group (aliphatic ν(C–H) stretching modes between 2850 and 2960 cm⁻¹) and several broad silicon oxide-related bands centered at 1060 and 850 cm⁻¹. New Si–H bands, assigned to oxide-back-bonded Si–H stretching modes, appear at 2260 and 2200 cm⁻¹.²³ Bands characteristic of surface-OH or adsorbed water are also evident at 1460 and 1600 cm⁻¹. The FTIR data indicate that functionalization is accompanied by significant oxidation of the silicon surface.

The surface oxide formed during the functionalization procedure can be removed by exposure of the sample to an aqueous ethanolic HF solution. The infrared vibrational bands

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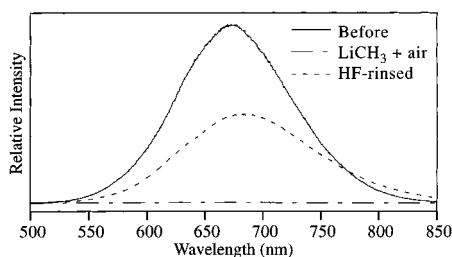


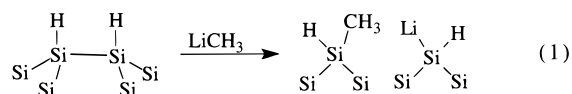
Figure 2. Comparison of the steady-state photoluminescence spectra (435 nm excitation) from a porous Si sample functionalized with methyl lithium. Spectrum from a freshly etched sample (“Before”), after methylation and exposure to air (“LiCH₃ + air”), and after rinsing with ethanolic HF (“HF-rinsed”). The data show that PL intensity from porous Si is reduced upon methylation, and that part of the PL intensity can be recovered upon removal of surface oxide with the HF rinse. Spectra were all normalized to a phosphor standard to allow accurate intensity comparisons.

associated with Si–O disappear after HF treatment (Figure 1, “HF-rinsed”). The broad bands associated with adsorbed H₂O at 1460 and 1600 cm⁻¹ also disappear upon HF exposure, indicating that the surface is now hydrophobic. There is only a slight loss in intensity of the ν_(C–H) IR bands associated with the methyl group, and weak symmetric δ_(CH₃) (1250 cm⁻¹) and asymmetric δ_(CH₃) (1409 cm⁻¹) bands become discernible,²⁸ indicating that the HF/ethanol rinse leaves this methyl species intact on the Si surface. After removal of the oxide, a strong vibrational band is apparent at 781 cm⁻¹. This 781 cm⁻¹ mode is assigned to a surface ν_(Si–C) vibration that was previously obscured by the Si–O bands. This assignment is in reasonable agreement with the assignments that have been made by Chazalviel (770 cm⁻¹, CH₃ species),⁹ Tobias (865–750 cm⁻¹, CH₃ species),²⁵ and Yates (761 cm⁻¹, CH₃ species),²⁶ although it is significantly higher than the ν_(Si–C) assignment of George and co-workers for a surface-bound ethyl species (698 cm⁻¹).²² It should be noted that Yates observed two vibrational bands in this region, at 775 and 761 cm⁻¹. Only the 761 cm⁻¹ band is sensitive to isotopic substitution of the surface CH₃ group with ¹³C. We consistently observed only one band in this region.

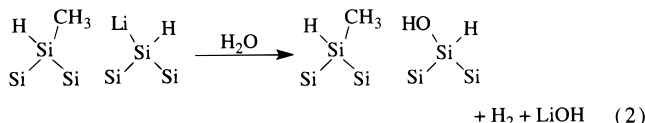
The intensity of the steady-state photoluminescence spectrum from the methyl-modified porous Si sample is reduced to 0.1% of the original value of the freshly etched porous Si sample (Figure 2). The removal of the Si oxide upon HF treatment results in recovery of 48% of the original steady-state PL intensity. This result suggests that the oxide formed in the functionalization procedure is highly defective and provides nonradiative recombination centers that are accessible to the Si nanocrystallites.^{29–32} These species are removed in the HF rinse, and so the PL recovers somewhat. The HF wash results in only partial recovery of PL; therefore, other nonradiative recombination centers that cannot be removed by an HF rinse are apparently also introduced in the methylation reaction.

Similar to the mechanism proposed for reaction of porous Si with aryllithium reagents, we propose that the alkyllithium reagent adds across a Si–Si bond, cleaving the bond and forming neighboring Si–methyl and Si–Li surface species (eq

1). The highly reactive Si–Li group is expected to be hydrolyzed

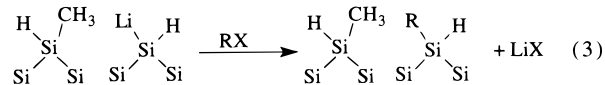


rapidly (eq 2), which accounts for the large amount of oxide observed if the sample is exposed to air at this point. It is also

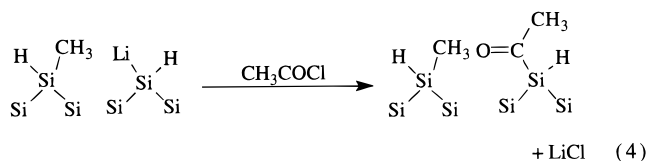


possible that the alkyllithium reagent abstracts surface hydrides as LiH, as has been proposed by Chazalviel and co-workers.^{9,11} In their research, Chazalviel and co-workers discovered that when an electrochemical bias is applied to porous Si in an electrolyte solution containing an alkyllithium or alkyl Grignard reagent, extensive removal of surface hydrides occurs. In the present study, it is found that a bias need not be applied to obtain observable Si-bound alkyls; although quantitative data comparing the relative surface coverage of the two techniques is not available.

Two-Step Reaction of Porous Si with Nucleophile/Electrophile Combinations. Reaction with Methyl lithium/Acetyl Chloride. To minimize oxidation and allow further modification of the reactive Si surface, the reactivity of the alkyllithiated surfaces toward carbocation reagents was explored. The general concept involves replacement of the highly reactive intermediate Si–Li species with a more stable Si–C bonded group (eq 3).



The scheme above was tested with several different nucleophile/electrophile combinations. For example, treatment of a porous Si sample with methyl lithium (1.4 M in diethyl ether) followed by neat acetyl chloride at –78 °C leads to the bifunctional surface shown in eq 4. The FTIR spectrum of this reaction



product (Figure 3, “LiCH₃ + CH₃COCl”) displays aliphatic C–H stretching modes between 2850 and 2980 cm⁻¹, methyl group deformation modes at 1248, 1373, and 1407 cm⁻¹, an acylsilane C=O stretching mode at 1641 cm⁻¹ (assigned to the surface-bound Si–acyl species),³³ and a Si–C stretching mode at 780 cm⁻¹. Only a small silicon oxide peak around 1060 cm⁻¹ is observed, indicating that the acetyl chloride treatment precludes surface oxidation. Treatment of the sample with ethanolic HF results in no significant change in the infrared spectrum, except for a reduction in intensity of the silicon oxide band at 1060 cm⁻¹.

The intensity of PL from porous Si samples functionalized with methyl lithium and acetyl chloride is reduced by 95% relative to the untreated material. Subsequent HF rinsing of these

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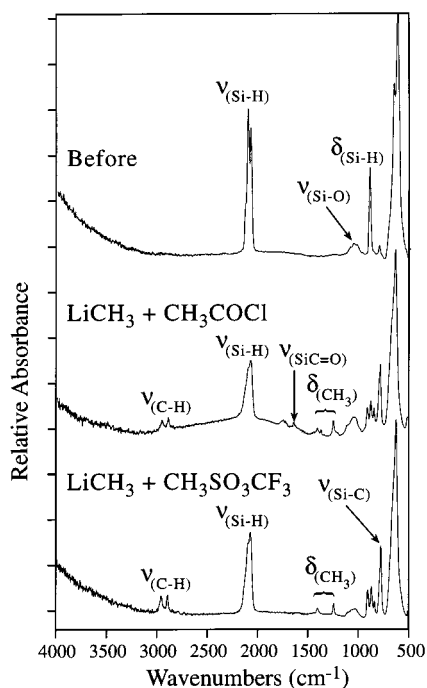
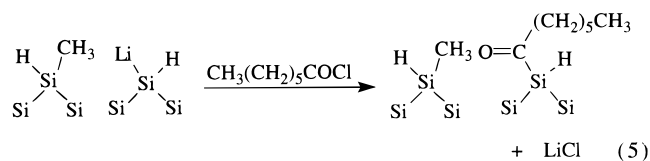


Figure 3. Infrared spectra of porous Si samples after treatment with methyllithium followed by acetyl chloride (“LiCH₃ + CH₃COCl”) or with methyl trifluoromethanesulfonate (“LiCH₃ + CH₃SO₃CF₃”). A representative spectrum of a sample before methyllithium exposure (“Before”) is included for comparison. These samples were not rinsed with HF, yet the bands associated with Si–O are very weak, indicating that little concomitant oxidation occurs in the reaction sequence. Spectra are offset along the y-axis for clarity.

doubly modified (methyl and acyl) samples leads to recovery of 20% of the original PL intensity (along with the small decrease in intensity of the Si–O band in the infrared spectrum already mentioned). It is proposed that the acylation reaction does not remove all the Si–Li groups generated in the first step, and so subsequent air exposure leads to oxidation of these remaining Si–Li species. The oxide contains an active nonradiative surface trap that is partially responsible for the loss of photoluminescence intensity. As in the methyllithium/air experiments, removal of the oxide in the HF rinsing step leads to recovery of some of the PL. Because PL is not completely recovered by the HF treatments, the above-mentioned interpretation does not account for all of the nonradiative processes introduced in these functionalization reactions. The two-step porous Si functionalization procedure appears to be a general approach. Several additional examples are outlined in the remaining sections of this paper, and relevant spectra are provided as Supporting Information.

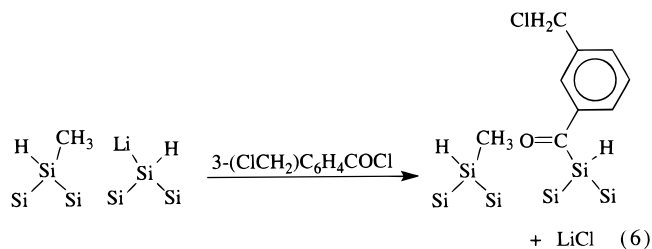
Reaction with Methyllithium/Heptanoyl Chloride. Reaction with methyllithium followed by a variety of electrophilic reagents results in a surface-derivatized product. For example, the FTIR spectrum of the reaction product involving heptanoyl chloride (eq 5) shows aliphatic C–H stretching modes between



2850 and 2980 cm⁻¹, methyl group deformation modes at 1249 and 1407 cm⁻¹, a methylene group deformation mode at 1473

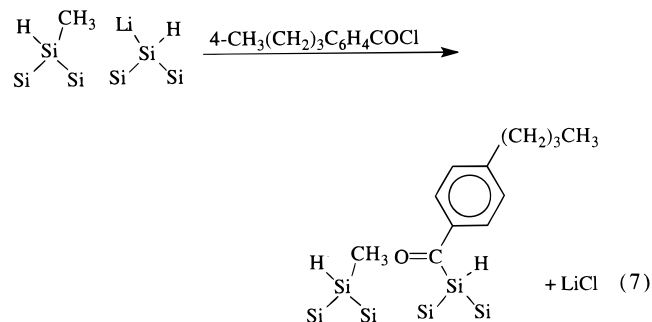
cm⁻¹, an acylsilane C=O stretching mode at 1641 cm⁻¹, and a Si–C stretching mode at 781 cm⁻¹. The intensity of the steady-state PL spectrum from the product of the two-step methyllithium/heptanoyl chloride reaction is reduced to 5% of the original value from freshly etched porous Si. Rinsing the derivatized porous Si surface with HF/ethanol results in a slight recovery of 30% of the original steady-state PL intensity.

Reaction with Methyllithium/3-(Chloromethyl)benzoyl Chloride. The stability of the acyl-modified surfaces suggests a route for the rational functionalization of silicon surfaces using functionalized acyl species. An example is the reaction involving methyllithium followed by 3-(chloromethyl)benzoyl chloride (eq 6). The FTIR spectrum of the product of this reaction displays



an aromatic C–H stretching mode at 3070 cm⁻¹, aliphatic C–H stretching modes between 2850 and 2980 cm⁻¹, methyl group deformation modes at 1252 and 1404 cm⁻¹, a methylene group deformation mode at 1446 cm⁻¹, C=C stretching modes at 1588 and 1486 cm⁻¹, an acylsilane C=O stretching mode at 1605 cm⁻¹,³³ and a Si–C stretching mode at 779 cm⁻¹. The intensity of PL from porous Si samples functionalized with methyllithium and 3-(chloromethyl)benzoyl chloride is reduced to 2% of the original, untreated material. Subsequent HF rinsing of the modified sample leads to a slight recovery (to 8% of original intensity) of the original PL intensity.

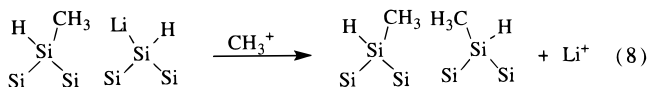
Reaction with Methyllithium/4-Butylbenzoyl Chloride. The FTIR spectrum of the reaction product of methyllithium/4-butylbenzoyl chloride treatment (eq 7) shows an aromatic



C–H stretching mode at 3026 cm⁻¹, aliphatic C–H stretching modes between 2850 and 2980 cm⁻¹, methyl group deformation modes at 1255 and 1420 cm⁻¹, a methylene group deformation mode at 1469 cm⁻¹, aromatic C=C stretching modes at 1597 and 1487 cm⁻¹, an acylsilane C=O stretching mode at 1617 cm⁻¹,³³ and a Si–C stretching mode at 780 cm⁻¹. The FTIR and PL results are similar to the other two-step reactions; the doubly modified porous Si material shows little surface oxidation, and bands characteristic of the surface-bound acyl species are present in the infrared spectrum even after an HF rinse. Additionally, the oxide band in the FTIR spectrum decreases in intensity and the intensity of photoluminescence slightly increases after the HF rinse. In all the acid chloride reactions there is a band at approximately 1750 cm⁻¹ in the infrared spectrum that we cannot assign. Subsequent HF/EtOH rinsing

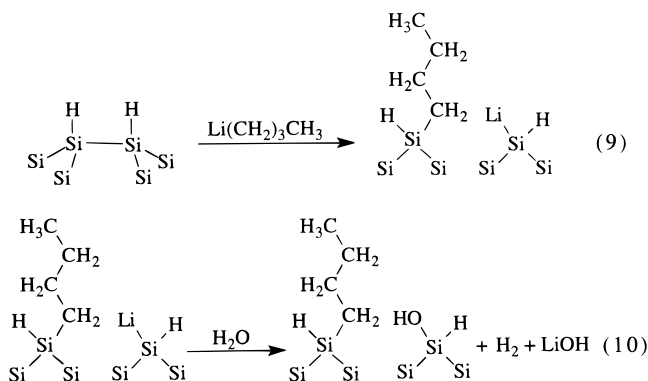
of all the derivatized porous Si surfaces results in either no or only slight changes in the infrared spectrum (and retention of the 1750 cm^{-1} band as well), indicating that the surface functionalities are quite stable toward HF.

Reaction with Methylolithium/Methyl Trifluoromethanesulfonate. To explore the feasibility of introducing electrophiles other than acid chlorides, methyl trifluoromethanesulfonate was used in the second step of the two-step procedure. The result is a doubly methylated surface (eq 8). The FTIR spectrum (Figure



3) displays methyl C–H stretching absorptions between 2850 and 2980 cm^{-1} , a methyl asymmetric bending absorption at 1409 cm^{-1} , a methyl symmetric bending absorption at 1250 cm^{-1} , and a Si–C stretching mode at 780 cm^{-1} . The intensity of the steady-state PL spectrum from the porous Si sample decreases to 10% of the original PL intensity after the double methylation reaction. As with the other two-step functionalization reactions, rinsing the functionalized sample with HF causes partial recovery of PL (to 22% of the intensity of the original, unfunctionalized material). The efficiency of the second step of the double methylation procedure can be discerned by comparison of the intensities of the $\nu_{(\text{C-H})}$ stretching modes in the FTIR spectrum with and without the second methylation step (Figures 3 and 1, respectively). When the methylolithium reagent is followed with methyl trifluoromethanesulfonate, characteristic infrared absorbance peaks from the surface-bound methyl group are approximately double the intensity of those obtained from the methylation/air hydrolysis reaction. The fact that very little oxidation is observed in the double methylation reaction indicates that removal of surface Si–Li species by the methyl trifluoromethanesulfonate reagent is nearly complete.

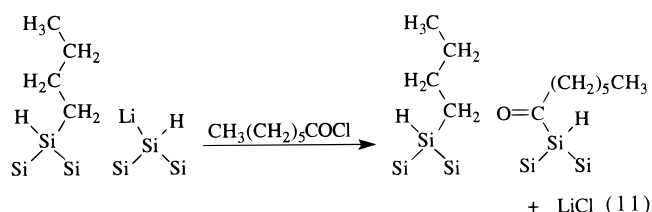
Reaction with Butyllithium. Functionalization of the porous Si surface can also be accomplished with butyllithium. Reaction of porous Si with butyllithium appears to follow the same mechanism as the methylolithium reaction (eq 9). Exposure of the lithiated surface to air results in significant oxidation (eq 10). Modification of porous Si with butyllithium and subsequent



air hydrolysis results in FTIR bands characteristic of alkyl $\nu_{(\text{C-H})}$ stretching absorptions between 2850 and 3000 cm^{-1} , an oxygen–back-bonded $\nu_{(\text{OSi-H})}$ stretching mode at 2260 cm^{-1} , and broad $\nu_{(\text{Si-O})}$ stretching modes at ca. 1060 and 850 cm^{-1} . As observed with the methylolithium reactions, 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 butyl-derivatized

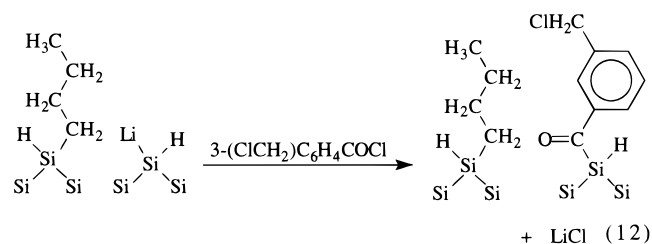
porous silicon is reduced to 0.2% of the original value (of freshly etched porous Si). The surface oxide can be removed by rinsing the sample with HF/ethanol (4 \times 1 mL), which results in a loss of the 1060 cm^{-1} $\nu_{(\text{Si-O})}$ band in the infrared spectrum. The broad bands associated with adsorbed water at 1460 and 1600 cm^{-1} are also removed with the HF rinse. There is little concomitant loss in infrared intensity of the C–H stretching modes associated with the butyl group, indicating that the HF/ethanol treatment leaves this species intact on the Si surface. Weak bands that can be assigned to alkyl bending modes appear between 1470 and 1380 cm^{-1} after the HF rinse. These bands were presumably obscured by the strong H₂O-related modes in the spectrum of the original butylated material. Removal of the silicon oxide also results in recovery of 38% of the original steady-state PL intensity.

Reaction with Butyllithium/Heptanoyl Chloride. The FTIR spectrum of a porous Si sample that has been treated with butyllithium followed by neat heptanoyl chloride (eq 11)



displays strong alkyl $\nu_{(\text{C-H})}$ absorptions between 2850 and 3000 cm^{-1} , alkyl bending absorptions at 1381 and 1468 cm^{-1} , and an acylsilane $\nu_{(\text{C-O})}$ mode at 1642 cm^{-1} , assigned to the surface-bound Si–acyl species.³³ A silicon oxide $\nu_{(\text{Si-O})}$ peak at about 1060 cm^{-1} and a shoulder corresponding to the oxygen–back-bonded $\nu_{(\text{OSi-H})}$ stretching mode at 2260 cm^{-1} are also observed.²³ Treatment of the sample with ethanolic HF results in no significant change in the infrared spectrum, except for a reduction in intensity of the silicon oxide–related bands. The intensity of the steady-state PL spectrum of the material after the two-step butyllithium/heptanoyl chloride reaction is reduced to 0.5% of the original intensity of freshly etched porous Si. Rinsing the derivatized porous Si surface with HF/ethanol results in a very slight recovery of 2% of the original steady-state PL intensity.

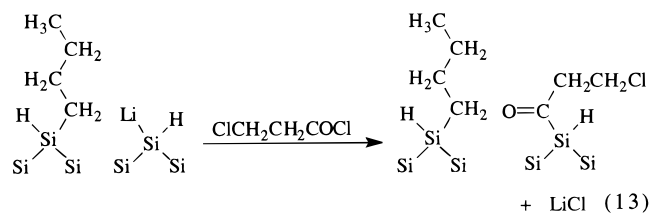
Reaction with Butyllithium/3-(Chloromethyl)benzoyl Chloride. The FTIR spectrum of the two-step reaction product of butyllithium/3-(chloromethyl)benzoyl chloride (eq 12) shows



an aromatic $\nu_{(\text{C-H})}$ stretching mode at 3045 cm^{-1} , aliphatic $\nu_{(\text{C-H})}$ modes between 2850 and 2980 cm^{-1} , and several weaker bands in the fingerprint region. The intensity of PL from the porous Si sample functionalized with butyllithium and 3-(chloromethyl)benzoyl chloride is reduced to 1% of the original (untreated) intensity. In this case, a subsequent aqueous ethanolic HF rinse of the modified sample does not lead to detectable PL recovery.

Reaction with Butyllithium/3-Chloropropionyl Chloride. Use of 3-chloropropionyl chloride in the second step of the two-

step procedure (eq 13) attaches a readily modified linker



molecule to the surface. Introduction of the halide-containing aliphatic linker to the porous Si surface may be of use for the modification of porous Si with protein or other biological species.⁴ The FTIR spectrum of this reaction product shows bands assigned to alkyl bending modes at 1384 and 1467 cm^{-1} , alkyl C–H stretching absorption modes between 2850 and 3000 cm^{-1} , a surface-bound Si–acyl C=O stretching mode at 1644 cm^{-1} , and no observable silicon oxide at 1060 cm^{-1} . The presence of chlorine (from the chlorine-containing linker) on the porous Si surface was confirmed by elemental analysis using an EDS attachment on a scanning electron microscope.

Conclusions

The reactions studied here demonstrate the generality of the two-step nucleophile/electrophile addition procedure for func-

tionalizing Si surfaces. The reactions all proceed to detectable products, although we have not quantified the degree of surface coverage. Following the nucleophile with an electrophile before the sample is exposed to air significantly reduces oxidation in this procedure. Unlike Si–O bonded compounds, the carbon-bound alkyls are not removed by an aqueous ethanolic HF rinse. The reaction is proposed to proceed by addition of the alkyl-lithium reagent across a Si–Si surface bond, generating the stable Si–alkyl species and a highly reactive Si–Li species. The Si–Li species is then alkylated in the second step. In all cases, photoluminescence intensity from the porous Si sample is reduced upon functionalization, which can be partially recovered with a postreaction rinse in ethanolic HF. The partial recovery of photoluminescence suggests that the oxidation side reaction introduces some (but not all) of the nonradiative recombination traps produced in the reaction sequence.

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Supporting Information Available: Infrared and photoluminescence spectra of porous Si alkylation products of eqs 4–13. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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