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Cyclic Azasilanes

SPECIAL ISSUE

Surface-Triggered Tandem Coupling Reactions of Cyclic Azasilanes

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Abstract: Cyclic azasilanes have been synthesized for the purpose of developing coupling agents appropriate for a variety of nanotechnologies including surface modification of nanoparticles, nanocrystals, mesoporous materials and substrates. *N*-Methyl-aza-2,2,4-trimethylsilacyclopentane is representative of this class of compounds. Preliminary data for the treatment of inorganic surfaces, including nanoparticles and oxidized silicon wafers, with cyclic azasilanes suggest high-density monolayer deposition by a ring-opening reaction. Cyclic azasilanes contain a cryptic amine functionality that can perform a subsequent tandem coupling reaction with functional molecules after the surface-triggered ring-opening reaction, allowing for a one-pot self-assembly route on nanostructures. Tandem coupling reactions are demonstrated via addition reactions of the cryptic amine with epoxy and acrylate systems.

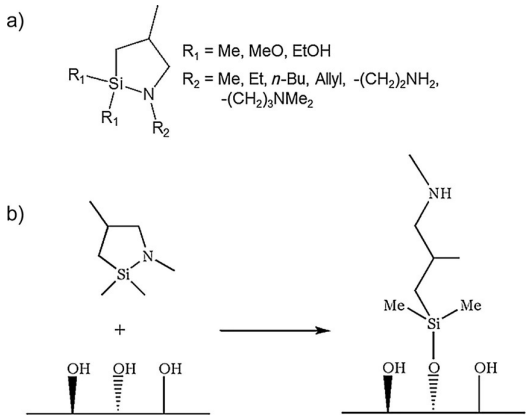

Figure 1. (a) General cyclic azasilane structure. (b) Reaction of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane with surface hydroxyls to yield an amine functional surface.

Surface modification of hydroxyl-containing surfaces with features less than 10 nm pose challenges for conventional alkoxysilane coupling agents. Byproducts of substrate reactions with alkoxysilanes and chlorosilanes can remain strongly adsorbed to the surface, interfering with the desired functional or chemical behavior of the modified surface. Most significantly, "nanoscale feature" modification is generally preferred in an environment free of water.

Cyclic azasilanes have been demonstrated to be highly effective reagents for surface modification of hydroxyl-containing surfaces, particularly inorganic surfaces associated with nanoparticles, mesoporous materials and substrates employed in the fabrication of microelectronic and optoelectronic devices (Figure 1).[1–3] The reaction of cyclic azasilanes proceeds at room temperature in vapor-phase or condensed-phase without co-reagents or byproducts.[4–6] Their high conversion efficiency offers a convenient and versatile route to surfaces with amine functionality (Figure 1 b). In the fabrication of surface nanoscale features, it is essential not only to effect a self-limiting functionalization of surface hydroxyl groups in high yield and at low temperatures but to do so on a time scale consistent with processing techniques such as MLD (molecular layer deposition) and SOD (spin-on deposition). Further, often an amine functionality may only provide a reactive starting point for a progressive series of reactions that proceed to an operational device or particle.

This work explores two issues associated with the expanding role of cyclic azasilanes in surface modification. Preliminary data on kinetics for substrate reactivity demonstrates that cyclic azasilane deposition is consistent with the time-scale requirements of nano-fabrication techniques. Examples are provided of the cyclic azasilane-modified substrates undergoing in situ tandem coupling reactions, facilitating the formation of a broad range of functional nanostructures (Scheme 1).

Kinetic and Characterization Studies of Surface Triggered Coupling Reactions. Surface modification using *N*-methyl-aza-2,2,4-trimethylsilacyclopentane was investigated on glass, copper, and silicon surfaces. The fast reaction kinetics could be evaluated by the reaction with the terminal hydroxyl groups

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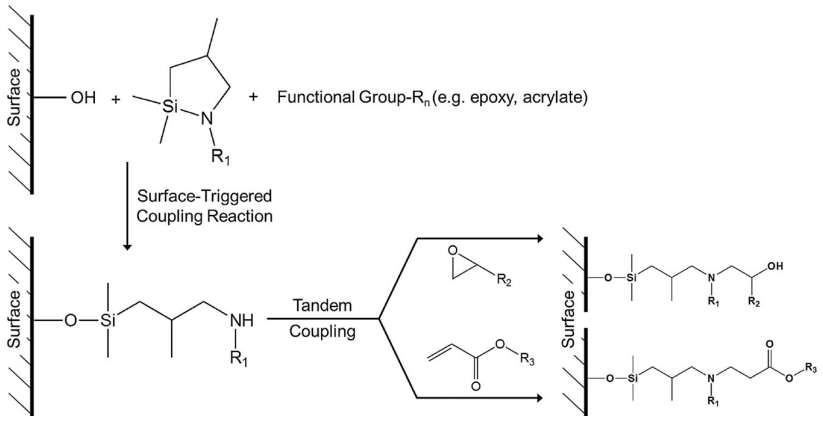


Scheme 1. Rapid ring-opening reaction of cyclic azasilane is triggered by surface hydroxyls yielding an amine functional monolayer surface. An in situ tandem coupling reaction then proceeds between the amine and a broad range of functional groups. These one-pot coupling reactions proceed at low temperatures with high yield, allowing for a facile approach to form self-assembled nanostructures.

on the surface of amorphous fumed silica as analyzed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The chemical and surface analysis was conducted using X-ray photon spectroscopy (XPS) and ellipsometry.

Cyclic azasilanes, such as *N*-methyl-aza-2,2,4-trimethylsilacyclopentane, have favorable structures for surface modification of hydroxyl-containing surfaces. The substrate reaction of cyclic azasilanes is thermodynamically driven because of the Si–N ($\approx$410 kJ mol^{-1}) and Si–O ($\approx$569 kJ mol^{-1}) bond energy differences and the release of ring strain. The ring-opening reaction occurs via cleavage of the Si–N bond by a hydroxyl group. The concomitant transfer of a hydrogen atom affords an organofunctional secondary amine, available for further reaction. When reacted with a hydroxyl-rich surface, cyclic azasilanes undergo this process to yield the 1,5-insertion product.

The progress and extent of the cyclic azasilane surface modification reaction of fumed silica on pulsed exposure to solutions of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane in dichloromethane was determined by spectral means. The silica surface was treated with 0.5 wt% cyclic azasilane solution in anhydrous dichloromethane. The solution was passed through a fixed-bed of silica in an 8 second pulse, followed immediately with a solvent wash to remove residual unbound silane. After each silane solution pulse, a sample of the silica was collected and analyzed by DRIFT spectroscopy. Infrared spectral analysis of silane-modified silica surfaces is well established.[7–14] The reaction of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane with terminal surface hydroxyl groups on the amorphous silica was complete in approximately 35 seconds at 25 °C, as determined by DRIFT spectroscopy. Amorphous fumed silica has three diagnostic hydroxyl peaks: terminal (3745 cm^{-1}), geminal (3650 cm^{-1}) and vicinal (3560 cm^{-1}) in the IR region.[15] It is known that organofunctional trialkoxysilanes preferentially react with terminal hydroxyl groups on silica, and thus the peak area of the terminal hydroxyl group affords a convenient method for monitoring the kinetics of this surface reaction with cyclic azasilanes. When *N*-methyl-aza-2,2,4-trimethylsilacyclopentane was reacted with amorphous fumed silica, consumption of terminal hydroxyls was monitored by the observation of the terminal hydroxyl peak at 3745 cm^{-1} (Figure 2).

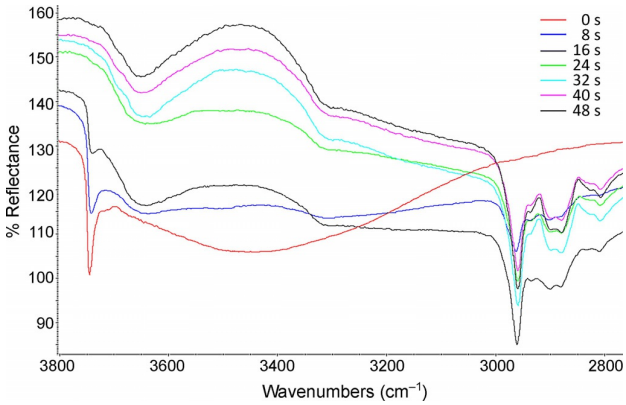


Figure 2. DRIFT spectra of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane treated fumed silica from 2800 to 3800 cm^{-1} over 48 seconds. Surface modification of amorphous fumed silica at 25 °C was complete in less than 1 minute.

Rapid surface interaction (< 1 minute) of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane with all of the terminal hydroxyl sites on amorphous fumed silica was observed. This site-specific reaction with no byproducts demonstrates an example of surface "click chemistry" because of its speed, specificity, and high yield.

In order to further probe the chemical characteristics of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane surface modification, treated surfaces of silicon, glass and copper were analyzed by XPS. Contact angle was measured to confirm functionality of the surfaces. The relevant XPS spectra are presented in Figure 3. The C 1s spectrum of borosilicate glass treated with *N*-methyl-aza-2,2,4-trimethylsilacyclopentane depicted a symmetric peak at 284.1 eV with a secondary C–N amine peak at 287.5 eV (Figure 3a). This observed characteristic was consistent with the C 1s spectra of 1.0% treated silicon wafer and 1.0% treated copper (Figure 3c,d), respectively, with the observed C–N peak at 286.2 eV (on silicon) and 287.8 eV (on

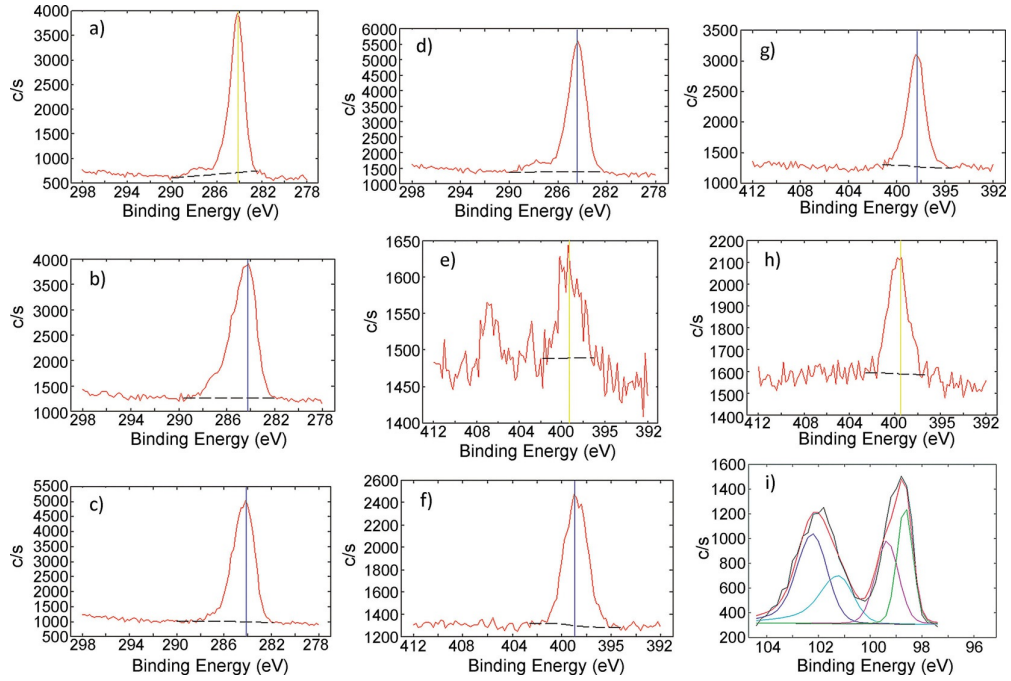


Figure 3. XPS spectra of surfaces treated with *N*-methyl-aza-2,2,4-trimethylsilacyclopentane by condensed phase deposition: C 1s (a) 0.5 wt% on glass, (b) 0.5 wt% on Si wafer, (c) 1.0 wt% on Si wafer, and (d) 1.0 wt% on copper; N 1s (e) 0.5 wt% on glass, (f) 0.5 wt% on Si Wafer, (g) 1.0 wt% on Si wafer, and (h) 1.0 wt% on copper; (i) Si 2p of 0.5 wt% on a Si wafer deconvoluted for the determination of the Si–O binding energy difference.

copper). The peaks observed in the N 1s spectra were symmetric with binding energies below 400 eV, which is indicative of the presence of a neutral amine species on each borosilicate glass, silicon, and copper. In the N 1s spectrum on glass, an additional peak was observed at 406.9 eV, which is consistent with the presence of a protonated amine species on or near the silicate surface (Figure 3e). Such a protonated amine peak is consistent with a protonated amine peak previously observed[16,17] along with the variety of binding modes exhibited by aminosilanes on hydroxylated silica substrates.[18]

A Si–O binding energy difference of greater than 429.6 eV on glass is consistent with complete silane coverage, while a binding energy difference of less than 429.6 eV suggests a lack of uniform silane coverage with the underlying glass silicate structure being exposed. The value of 429.5 eV presented in Table 1 for glass showed a high degree of coverage of the glass surface. On a silicon wafer, the underlying silicon metal causes a shift in the Si–O binding energy (generally considered as 2.4 eV higher at 432.0 eV than that for glass).[19] The detection of a Si signal on a copper surface indicates that *N*-methyl-aza-2,2,4-trimethylsilacyclopentane reacted with the surface, and the Si–O binding energy difference of 428.09 eV establishes a comparative standard for looking at other silane coverages on copper surfaces. Clearly, the cyclic azasilane has reacted in a high-yield conversion with hydroxyl on each substrate.

Table 1. Calculated Si–O binding energy differences of cyclic azasilane-modified substrates from binding energies collected at a 45° incident angle by XPS.

Concentration of cyclic azasilane [wt%]	Substrate	Si–O [eV]
0.5	Si wafer	433.0
0.5	Si wafer	433.1
1.0	Si wafer	433.0
1.0	Si wafer	433.0
1.0	Cu	428.1
1.0	borosilicate glass	429.5
0.5	silica	430.0[a]

[a] The binding energy for silica was collected at a 20° incident angle.

The reaction of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane on silicon wafers was confirmed by ellipsometry. Ellipsometry affords the ability to determine the thickness of the film on the substrate surface. The measured thickness of the silicon wafers treated with 0.5 wt% *N*-methyl-aza-2,2,4-trimethylsilacyclopentane for 5 min was 1.5(±0.28) nm. Silicon wafers treated with organofunctional trialkoxysilanes for 1 hour under optimal conditions[20] also have an ellipsometric film thicknesses of 1.5 nm. Film thicknesses reported for organofunctional trialkoxysilanes can range from 1.5 nm to 16.3 nm depending on the reaction conditions implemented. The wide range of film thicknesses of organofunctional trialkoxysilanes on surfaces is indicative of the formation of multi-layers as opposed to self-limiting monolayer deposition of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane. It has been demonstrated that the reaction of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane on glass, copper, and silicon surfaces proceeds rapidly at room temperature at high yield without the formation of any byproducts.

Tandem Coupling Reactions. The ring-opening of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane on a surface reveals the cryptic amine functionality of the cyclic azasilane structure,

which can be used in an in situ tandem coupling reaction. This rapid surface-triggered route to amine functional surfaces offers the opportunity to immobilize DNA and proteins directly to a substrate[21–26] or to couple with molecules containing complimentary functionalities (e.g., epoxy, acrylate, isocyanate and thiocyanate) to generate self-assembled nanostructures.

To establish the potential for one-pot tandem coupling reactions, *N*-methyl-aza-2,2,4-trimethylsilacyclopentane was mixed in a 1:1 molar ratio with epoxy and acrylate materials under anhydrous and wet conditions. 3-Glycidoxypropylbis(trimethylsiloxy)methylsilane and acryloxypropyltris(trimethylsiloxy)silane were used as the model compounds for the tandem coupling reactions. No reaction was observed under the anhydrous conditions due to failure of the cyclic azasilane to ring-open and the preservation of the amine as a cryptic functionality. When water was added to the mixture or the mixture was exposed to ambient moisture, cleavage of the Si–N bond was observed, affording a free secondary amine that performed a ring-opening addition with an epoxy functionality and a Michael addition with an acrylate functionality (Scheme 2).

Kinetic data of the coupling reactions of the ring-opened *N*-methyl-aza-2,2,4-trimethylsilacyclopentane derivative with 3-glycidoxypropylbis(trimethylsiloxy)methylsilane and acryloxypropyltris(trimethylsiloxy)silane were obtained at 25 °C and 50 °C using ^{1}H NMR spectroscopy (Figure 4). The coupling reactions with glycidoxypropylbis(trimethylsiloxy)methylsilane and acryloxypropyltris(trimethylsiloxy)silane were complete at 25 °C after 8 hours. Improved kinetics were observed at 50 °C, and the timescale for completion of the epoxy addition and Michael addition acrylate system was ≈2 hours.

Dry fumed silica was exposed to combinations of the cyclic azasilane with epoxy and acrylate functional compounds in heptane solvent for 4 hours at 50 °C. DRIFT spectroscopic analysis indicated the successful tandem coupling reaction: surface hydroxyl triggered ring-opening of the cyclic azasilane followed by reaction with the epoxy or acrylate functional materials. The structural features of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane that enable surface-triggered tandem coupling reactions extend to the broad class of cyclic azasilanes. The ability of cyclic azasilane systems to undergo tandem coupling reactions at high yield, under mild conditions, without byproducts opens new pathways for nanofabrication of complex biomolecule and polymer heterostructures.

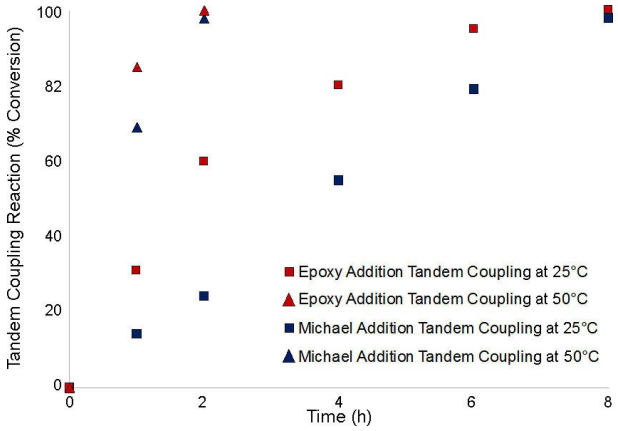
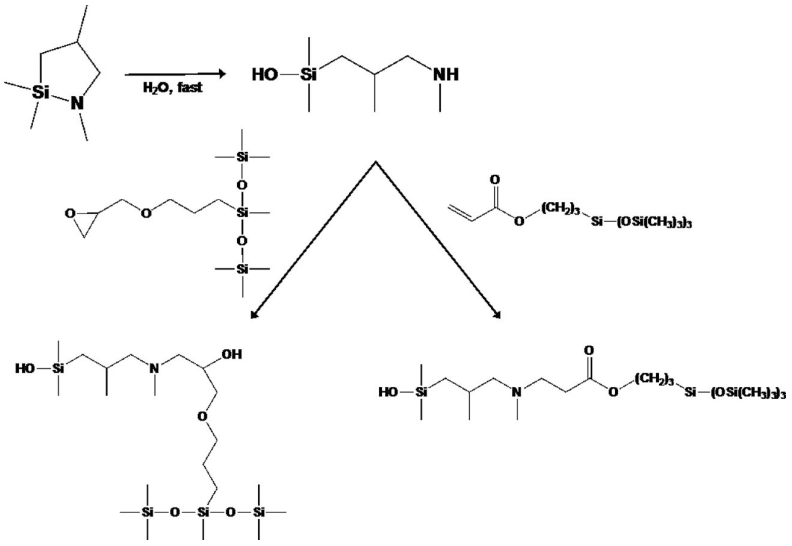


Figure 4. Tandem coupling kinetic data from the ^{1}H NMR spectra. Epoxy addition and Michael addition with ring-opened *N*-methyl-aza-2,2,4-trimethylsilacyclopentane derivative were monitored at 25 °C and 50 °C.

Experimental Section

Chemicals and Materials. *N*-Methyl-aza-2,2,4-trimethylsilacyclopentane [SIM6501.4], 3-aminopropyltrimethoxysilane [SIA0611.0], amorphous silica [SIS6960.0], and hexamethyldisilazane [SIH6110.0], 3-glycidoxypropyl-bis(trimethylsiloxy)methylsilane [SIG5820.0], and acryloxypropyl-tris(trimethylsiloxy)silane



Scheme 2. Demonstration of one-pot tandem coupling reactions of cyclic azasilane with epoxy and acrylate systems. 3-Glycidoxypropyl-bis(trimethylsiloxy)-methylsilane and acryloxypropyl-tris(trimethylsiloxy)silane were used as model compounds. Water was added to the system to trigger the rapid ring-opening of the cyclic azasilane (< 1 minute).

[SIA0210.0] were supplied by Gelest, Inc. and used without further purification. Benzyl glycidyl ether was supplied by Sigma–Aldrich and used without further purification. Silicon wafers [W-SI-76-0.4] were also obtained from Gelest, Inc. The silicon wafers were cut into 1.5 cm × 1.0 cm samples and rinsed with copious amounts of deionized water. After drying in a clean oven (in air) at 120 °C for 15 min, the wafers were treated with oxygen plasma (Harrick Plasma Cleaner) for 5 min at ≈50 mtorr. Silanization reactions were carried out immediately after treating the wafers in this fashion. Copper panels were obtained from McMaster–Carr, cut to the appropriate size, and wiped with acetone and a Kimwipe prior to use. Filter paper was treated with hexamethyldisilazane, dried at ambient temperature and pressure, and rinsed with dichloromethane prior to use. Potassium bromide (KBr) was obtained from Sigma–Aldrich, dried overnight in an oven at 110 °C and then used without additional purification. Solvents were obtained from Quaker City Chemicals and stored over 3 Å molecular sieves purchased from Alfa–Aesar. Borosilicate glass slides D263T were purchased from Schott Nexterion (Nexterion US Inc.) and M3504-E were purchased from Capitol Scientific. Borosilicate glass slides were acid etched in a 4% HCl solution for 45 min, rinsed with deionized water, ethanol, and acetone until a neutral pH was obtained, and dried under a stream of nitrogen prior to treatment with *N*-methyl-aza-2,2,4-trimethylsilacyclopentane. The slides were used within 10 minutes of acid-etching.

Treatment of Amorphous Silica. A sample of fumed silica (0.50 g) was placed on a piece of silanized filter paper in a Büchner funnel under dynamic vacuum. The volume of a 0.5 wt% solution of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane (0.10 g, 0.70 mmol) in dichloromethane (19.90 g, 234.3 mmol) was determined and passed in pulses through a bed of the silica, with a total contact time of 8 seconds. The supernatant was recovered and initial volume restored if needed by adding more dichloromethane. The treated solid was immediately pulsed with a dichloromethane rinse and a sample of dry silica extracted for FTIR analysis. The supernatant was passed in successive pulses through the bed of the silica five additional times in the same manner, with samples of the treated silica removed for FTIR analysis after each supernatant wash. All samples were cured at 110 °C for 30 min and cooled prior to FTIR and TGA analysis.

Treatment of Borosilicate Glass Slides. Solutions of two concentrations of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane in hexanes were prepared in a 120 cc plastic bottle. For each set of conditions (A1, A2, B1, B2) presented in Table 1, three glass slide samples were prepared and analyzed. The acid etched glass slides were immersed for the designated time, rinsed with hexanes, dried under a stream of N_2, cured at 110 °C for 30 min, and cooled in a desiccator.

Treatment of Silicon Wafers. A 0.5 wt% and 1.0 wt% solution of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane (0.025 g, 0.17 mmol; 0.050 g, 0.35 mmol) in cyclohexane (5.00 g, 59.4 mmol; 5.00 g, 59.4 mmol) were prepared in glass vials. The silicon wafer was immersed in the solution for 5 min, removed, rinsed with cyclohexane, and cured at 110 °C for 30 min. The sample was removed and cooled prior to analysis.

Treatment of Copper Panels. A 1.0 wt% solution of *N*-methyl-aza-2,2,4-trimethylsilacyclopentane (0.80 g, 5.6 mmol) in cyclohexane (79.20 g, 941.1 mmol) was prepared in a 120 cc plastic bottle. The copper panel was immersed in the solution for 5 min, removed, rinsed with cyclohexane, and cured at 110 °C for 30 min. The sample was removed and cooled prior to analysis.

Tandem Coupling Reaction. Two scintillation vials were charged with a 3.0 wt% solution of fumed silica (0.15 g) in heptane (5.0 g). Benzyl glycidyl ether (0.50 g) was added to each vial and shaken for 5 s. *N*-Methyl-aza-2,2,4-trimethylsilacyclopentane (0.30 g) was added to the second vial. The vials were stirred for 4 h and vacuum filtered through a Büchner funnel with a Whatman 55 mm grade 42 filter paper (2.5 μm retention, ashless). The solid was rinsed with heptane and dried with active air flow through the Büchner funnel for 5 minutes. The solid was collected and dried at 110 °C for 5 min. The resulting solid was analyzed by DRIFT spectroscopy using a 2% KBr powder solution.

Characterization. Contact angles were measured on a Ramé-Hart Goniometer using deionized water. Infrared spectra were collected on a Thermo Scientific Nicolet iS10 FT-IR spectrometer with a Thermo Spectra Tech Avatar diffuse reflectance adapter using the supplied OMNIC software. Diffuse reflectance samples were prepared using a 2 wt% sample in a KBr solution, 0.2 g total weight. XPS was collected on a Physical Electronics Quantum 2000 spectrometer with a 200 μm spot size and monochromatic $Al_{K\alpha}$ radiation (1486.68 eV). The X-ray source was operated at 50 W and 15 kV with the analyzer's constant pass energy at 29.35 eV. A 45° incident XPS beam angle was used on the wafer-like surfaces and a 20° incident beam angle was used on the powders. The pressure in the analysis chamber was ca. 6×10^{-9} Pa during measurements. The binding energy (BE) scales were referenced to 284. 6 eV as determined by peak maxima of the C 1s spectra of adventitious hydrocarbon (CH_x). Surface compositions were determined by the corresponding core-level spectral area ratios calculated using the relative sensitivity factor method. The relative error for all XPS data used to determine surface composition is estimated to be ±2%. Each sample was analyzed at two different points, and the average composition was calculated. In addition to wide-energy-range spectra, high-energy resolution spectra of the characteristic peaks of the elements Si 2p, C 1s, O 1s and N 1s were recorded through a narrow energy range. From the shape and shift of the energy of the XPS spectra, the chemical bonding of surface elements was inferred. The XPS spectra were processed by using the MultiPak software. An ellipsometer (Philips, PZ2000) equipped with a He-Ne laser (632.8 nm) with its incident angle fixed at 70° was used to determine the thicknesses of the monolayers. Kinetic characterization of the coupling reactions of ring-opened *N*-methyl-aza-2,2,4-trimethylsilacyclopentane derivative with 3-glycidoxypropyl-bis(trimethylsiloxy)methylsilane and acryloxypropyltris(trimethylsiloxy)silane was performed using a Varian Oxford AS400 400 MHz spectrometer. The conversion (%) of the epoxy addition at 25 °C and 50 °C was determined by following the disappearance of the glycidyl ether protons at 2.8, 3.2, and 3.7 ppm.The conversion (%) of the Michael addition at 25 °C and 50 °C was determined by following the disappearance of the acrylate protons at 5.8 and 6.4 ppm.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: click chemistry · nanostructures · silanes · surface analysis · surface modification

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