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Research Article

Single-Molecule Orthogonal Double-Click Chemistry—Inorganic to Organic Nanostructure Transition

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Cite This: *ACS Appl. Mater. Interfaces* 2020, 12, 27737−27744

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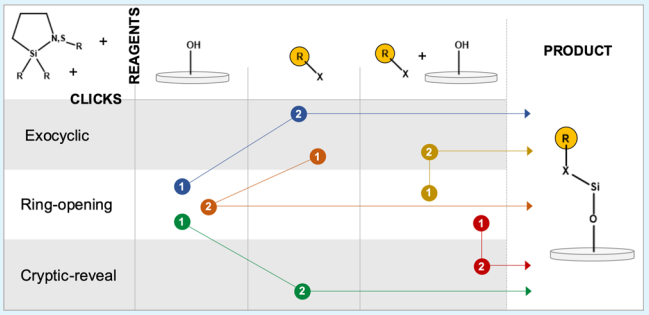
ABSTRACT: Thiasilacyclopentane (TSCP) and azasilacyclopentane (ASCP) heteroatom cyclics have proven capable of rapidly converting hydroxylated surfaces to functionalized surfaces in inorganic click reactions. In this work, we demonstrate that the use of these reagents can be extended to "simultaneous double-clicking" when both inorganic and organic substrates are present at the onset of the reaction. The simultaneous double-click depends on a first ring-opening click with an inorganic substrate that is complete in ∼1 s at 30 °C and results in the reveal of a cryptic mercaptan or secondary amine group, which can then participate in a second click with an organic substrate. TSCPs and ASCPs can take part in tandem double-click reactions in which the organic substrate is added to the reaction mixture after the initial inorganic click reaction is completed. Additionally, ASCPs with exocyclic functionality, specifically *N*-alkenyl-, *N*-aminoalkyl, and *N*-alkynyl-ASCPs, are shown to be options for tandem double-clicking in which functionalization proceeds in two independent steps and the sequence of the double-click reaction can be reversed.



KEYWORDS: *double-click chemistry, heteroatom silacyclopentanes, surface modification, thiol−ene, Huisgen cycloaddition, glass-strengthening, antiproliferative coating*

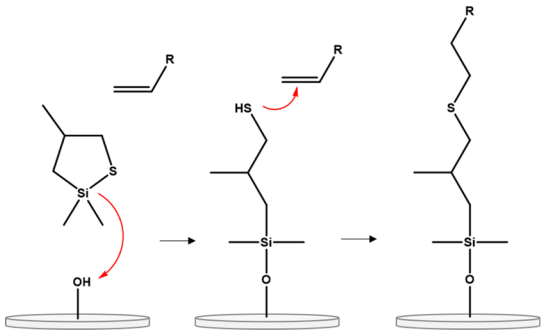
INTRODUCTION

Transitions between nano-featured inorganic surfaces and organic materials found in integrated semiconductor devices, nanocomposites, biofunctional nanoparticles, and microfluidic heterodevices often present challenges. Although such applications rely on inorganic structures for fundamental mechanical, electrical, optical, or other properties, effective overall performance frequently demands efficient direct or mediated interaction between the outer boundary of the inorganic phase and an organic or polymeric material. Biotechnology examples on a nanoscale include silica nanoparticles that present bioactive coronas in therapeutic regimens as well as porous electroluminescent silicon particles in which enzymes and bioactive molecules are payloads sequestered within pores and then released by a biodissolution process. On a macroscale, the surface of an implantable medical device with an *in vivo* environment may need to be passive—either suppressing a response or providing a tissue regeneration scaffold. Similarly, in nanoscale optical applications such as quantum dots, environmental resistance or environmental interaction may be a key required performance property of the shell. On a macroscale, optical fibers employed in communication and sensor applications frequently require both resistance to both environmental factors and stress-induced failure.

The transition from inorganic to organic necessarily takes place in a region, denoted as the interphase, in which there is a steep gradient between the underlying material and the outer boundary. From a material property perspective, the most general requirements for the interphase are durability and near-zero thickness. From a process perspective, interphase formation must occur rapidly and under conditions which do not compromise performance of either the inorganic or the organic phase. These process conditions are consistent with the parameters established by Sharpless for "click" chemistry: high conversion yield, low-temperature reaction, and minimal byproducts.[1] Here, we present single-molecule orthogonal "double-click" chemistry, which enables either a multistep one-pot reaction with all reactants present at the outset, referred to here as a simultaneous double-click reaction, or a step-wise reaction with reactants added in a desired sequence, referred to here as a tandem double-click reaction. An example of a double-click reaction is provided in eq 1. In both cases, a rapid and nearly quantitative functionalization of hydroxylated surfaces is effected by two classes of heteroatom silacyclopentanes, thiasilacyclopentanes (TSCP) and azasilacyclopentanes

Received: March 24, 2020
Accepted: May 4, 2020
Published: May 27, 2020

https://dx.doi.org/10.1021/acsami.0c04018
ACS Appl. Mater. Interfaces 2020, 12, 27737−27744



(1)

(ASCP). Importantly, the reagents in this process can be reacted with inorganic substrates not only in solution and condensed phase but also from the vapor phase without a catalyst, consistent with molecular layer deposition (MLD) techniques favored in semiconductor and heterodevice fabrication.

Click chemistry currently plays a significant role in advanced functional soft material development by providing the ability to effectively generate new structures, frequently in conjunction with high-throughput screening.[2] This same approach is highly desirable in heterodevice structures, as laid out in the Heterogeneous Integration Roadmap (HIR), which suggests new structures such as self-reporting sensors and biomaterials for "brain" energy level switching, among others.[3] Yet, heterodevices, and particularly silicon-based ones, present a greater challenge because inorganic and organic structures fundamentally require two different kinds of high-yield clicks. Additionally, extra process steps such as prefunctionalization are discouraged in high-volume manufacture of devices, so the click reagent must be sufficient to drive the chemistry by itself.

TSCP and ASCP heteroatom cyclics have proven capable of rapidly converting hydroxylated surfaces to functionalized surfaces in inorganic click reactions.[4,5] Single-click reactions have been shown using this concept.[6,7] In this work, we demonstrate that the use of these reagents can be extended to "simultaneous double-clicking" when both inorganic and organic substrates are present at the onset of the reaction. The simultaneous double-click depends on a first click with an inorganic substrate, which results in the reveal of a cryptic mercaptan or secondary amine group, which can then participate in a second click with an appropriate organic substrate. TSCPs and ASCPs can also take part in tandem double-click reactions in which the organic substrate is added to the reaction mixture after the initial inorganic click reaction is completed. Additionally, we demonstrate that ASCPs with exocyclic functionality—specifically *N*-alkenyl−, *N*-aminoalkyl, and *N*-alkynyl-ASCPs—are options for tandem double-clicking in which functionalization proceeds in two independent steps and the sequence of the double-click reaction can be reversed.

While there have been previous reports of double-click chemistry, these have been limited to repeating the same click twice: for example, sequential double-click for graft polymers or simultaneously performing two clicks on two sites with the same chemistry.[8,9] While a nonorthogonal thiol−ene double-click, comprising self-cross-linked nanolayer deposition in tandem with interfacial cross-linking, has also been reported, no discrimination was made between the self-reaction of bifunctional allylmercaptan and polyisoprene.[10] Inorganic substrates are not amenable to standard click chemistry. For example, while Deng *et al.* overcoat an inorganic substrate with functionalized paracyclophanes that provide an orthogonal double-click of sorts, the initial deposition reaction creates a thin layer that in reality constitutes a barrier to the substrate rather than a basis for functional interconnect bonding.[11]

RESULTS AND DISCUSSION

Overview of Heteroatom Silacyclopentanes. The general structure of the heteroatom silacyclopentane allows design flexibility in order to meet the requirements of specific reactivity. Table 1 provides a list of exemplary structures, including both previously reported and new compounds that satisfy the parameters for orthogonal double-click chemistry.[4,5,12] Vapor pressure data are also included, as volatility parameters are important considerations for MLD.

Click Chemistry. The double-click presented here (Figure 1) is a combination of two of the following clicks performed by a single heteroatom silacyclopentane reagent. The single clicks can briefly described as:

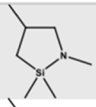
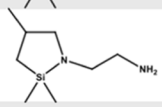
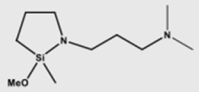
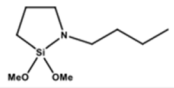
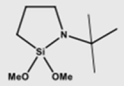
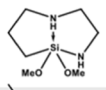
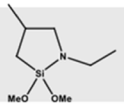
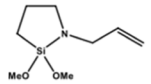
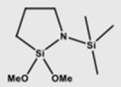
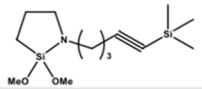
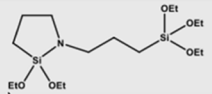
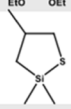
- A Ring-opening click with hydroxyl-containing substrates, with the concomitant reveal of a cryptic mercaptan group or a secondary amine group
- B Cryptic amine-reveal click: protic-amine (epoxy, isocyanate)
- C Cryptic mercaptan-reveal click: thiol−ene/yne
- D Exocyclic click: azide-yne or alkene (Huisgen or thiol−ene/yne) for organic substrates

Ring-Opening Click Reaction (How Quick Is the Click?). The ring-opening click reaction occurs primarily because of the thermodynamic advantage of forming a silicon−oxygen bond in preference to a silicon−nitrogen or a silicon−sulfur bond and secondarily because of the relief of ring-strain of the heteroatom silacyclopentanes. The speed of the ring-opening reaction is greater than the speed of both uncatalyzed azide-yne (Huisgen) or non-photoactivated thiol−ene reactions. Uncatalyzed azide−yne reactions show measurable conversions in approximately 4 h at room temperature but typically proceed to maximum yield in ∼24 h at room temperature.[13] Catalyzed reactions at elevated temperatures require minutes to hours to obtain the maximum yield.[14] Nguyen et al. have reported "ultrafast" reaction times for thiol−ene reactions, noting a cure after 2 min of exposure times,[15] while a prior report for photoactivated thiol−ene of poly(mercapto-functional)siloxane cross-linking of vinylsiloxane resins indicated time scales of ∼2 min.[16] Earlier studies of pulsed solution exposure of ASCPs showed virtually complete reactions of fumed silica with a surface area of 200 m^2/g in ∼15 s.[12] Vapor phase studies with ASCPs under MLD conditions proceeded even more rapidly: for example, thermal oxide silicon wafers were shown to achieve saturation in approximately 0.1 s.[17]

Our own studies showed similar deposition rates for both ASCPs and TSCPs. Both copper (PVD-copper-coated silicon) and silicon ⟨100⟩ substrates with native oxides were separately exposed to *N*-methyl-dimethyl-ASCP and dimethyl-TSCP at 30 °C at <1.0 Torr under pulse conditions in a Picosun deposition tool (Figure 2). As ellipsometrically modeled, immediate changes to the thickness of the organic layer were observed, followed by a plateau indicative of self-limiting monolayer formation on the scale of several seconds. The majority of deposition occurred in the first 0.1 s, and saturation occurred in 1−2 s under typical ALD tool conditions, as determined by both water contact angle and in situ ellipsometry. Initially untreated copper substrates were observed to have relatively high contact angles, whereas untreated silicon substrates with native oxides

https://dx.doi.org/10.1021/acsami.0c04018
ACS Appl. Mater. Interfaces 2020, 12, 27737−27744

Table 1. ASCPs and Thiasilacylopentanes for Orthogonal Double-Click Chemistry[a]

#	Structure	Name	Vapor Pressure (Torr @ °C)	Clicks				Monolayer stabilization	%Yield[method]
				Ring-opening	Cryptic amine-reveal	Cryptic mercaptan-reveal	Exocyclic	Hydrolytic condensation	
1		N-methyl-dimethyl-ASCP	760 / 137°	✓	✓				92.4[a]
2		N-aminoethyl-dimethyl-ASCP	22 / 54-55°	✓	✓		✓		55.0[a]
3		N-dimethylaminopropyl-methyl, methoxy-ASCP	0.5 / 65-67°	✓	✓			✓	57.2[b]
4		N-n-butyl-dimethoxy-ASCP	3 / 63-71°	✓	✓			✓	61.0[b]
5		N-t-butyl-dimethoxy-ASCP	3 / 58-60°	✓	✓			✓	49.6[b]
6		N-aminoethyl-dimethoxy-ASCP	2.5 / 71-73°	✓	✓		✓	✓	55.0[b]
7		N-ethyl-dimethoxy-ASCP	25 / 95°	✓	✓			✓	43.8[c]
8		N-allyl-dimethoxy-ASCP	3 / 52-54°	✓	✓		✓	✓	33.4[b]
9		N-trimethylsilyl-dimethoxy-ASCP	0.5 / 40.2°	✓	✓			✓	30.4[c]
10		N-(trimethylsilyl)pentynyl-dimethoxy-ASCP	0.2 / 95-97°	✓	✓		✓	✓	16.0[b]
11		N-triethoxysilylpropyl-diethoxy-ASCP	1 / 136-138°	✓	✓			✓	74.0[b]
12		Dimethyl-TSCP	35 / 75-80°	✓		✓			50.1[f]
13		Dimethoxy-TSCP	7 / 57-58°	✓		✓		✓	30.4[e]
14		Diethoxy-TSCP	75 / 136-139°	✓		✓		✓	38.8[d]

[a]Synthetic methods a: rxn of chlorosilane w/amine; b: catalyzed equilibrium ring-closure of aminoalkylalkoxysilane; c: catalyzed equilibrium ring-closure of aminoalkylalkoxysilane with HMDS acceptor; d: catalyzed equilibrium ring-closure of mercaptoalkylalkoxysilane with HMDS acceptor; e: catalyzed equilibrium ring-closure of mercaptoalkylalkoxysilane; f: rxn of chlorosilane with Na_2S (experimental details provided in the Supporting Information section).

had relatively low contact angles. The water contact angles of copper and silicon substrates approached convergence when subjected to exposure with the same reagents. Silicon ⟨100⟩ wafers could be successfully coated with *N*-methyl-dimethyl-ASCP at substrate temperatures as high as 300 °C with no observable effect on the required deposition time and only a slight impact on the contact angle (Figure 3).

Cryptic-Reveal Clicks. A cryptic-mercaptan reveal click is illustrated in eq 1. TSCPs rely on the reveal of a cryptic mercaptan functionality by an inorganic click ring-opening reaction with a hydroxyl-containing substrate, which is followed by a thiol−ene reaction with an unsaturated (olefinic) species. It is important to note that the reaction with the hydroxylic substrate occurs first regardless of the presence of an olefin. If the

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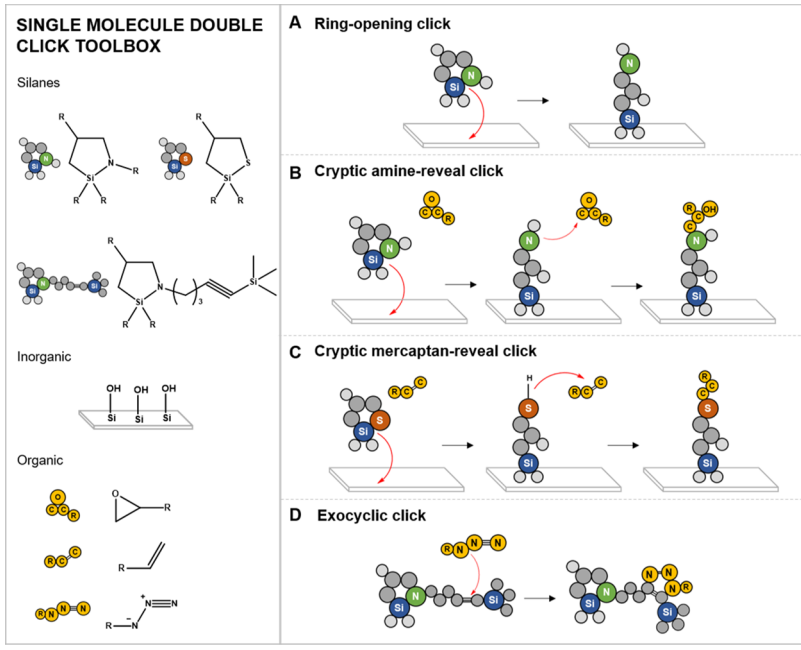


Figure 1. Single-molecule double-click toolbox.

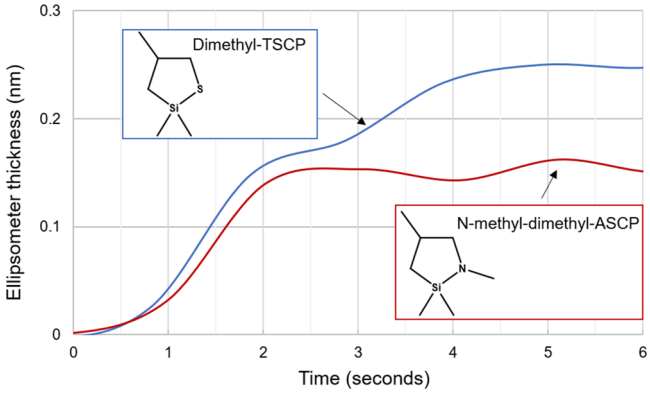
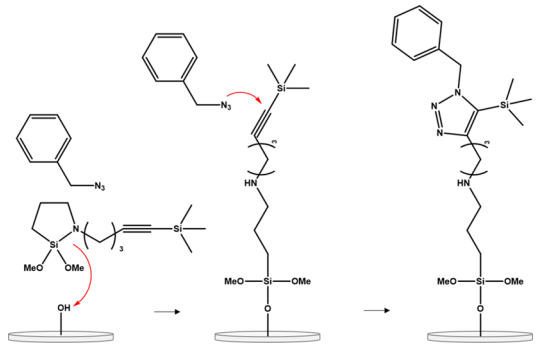


Figure 2. Ellipsometric thickness of silacyclopentane-deposited films. Native oxide on Si ⟨100⟩ at 30 °C.

cryptic-reveal click takes place in a photoactivated environment with the olefin present, both reactions appear to be completed simultaneously in less than a few seconds.

Similarly, the ring-opening reaction of the cyclic *N*-alkynyl azasilanes and unsaturated *N*-alkylsilanes is rapid, with the secondary amine functionality capable of performing a cryptic-amine-reveal click. The cryptic-amine-reveal click can react at moderate timescales with epoxy and isocyanate groups.[18]

Exocyclic Click. Equation 2 shows the ring-opening first click for an alkynyl-substituted ASCP. The reaction with the



(2)

hydroxylated substrate is the first click. The acetylene-substituted ASCP can then undergo a second linear (ring-opened) click: in this case, an azide-yne (Huisgen) organic click reaction succeeds the inorganic click reaction.

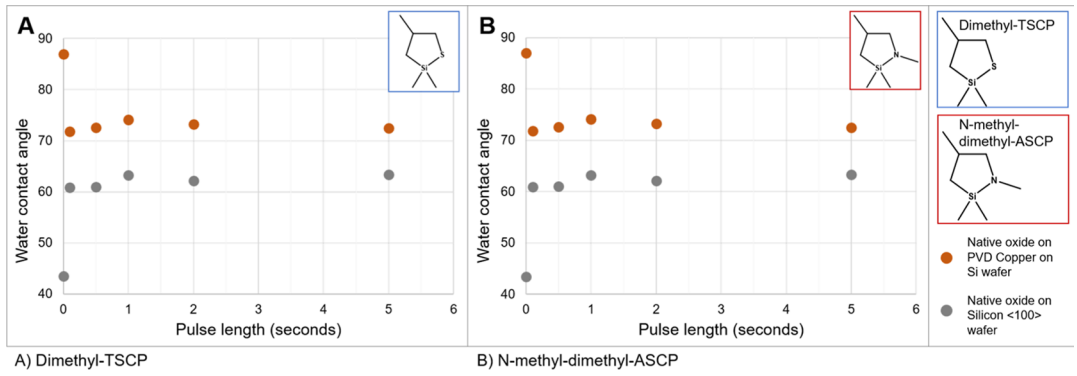
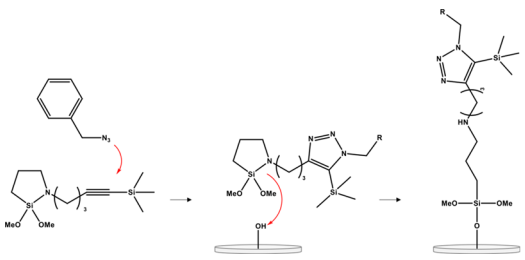


Figure 3. Static water contact angle of silacyclopentane-deposited films.

https://dx.doi.org/10.1021/acsami.0c04018
ACS Appl. Mater. Interfaces 2020, 12, 27737−27744

As shown in eq 3, an exocyclic first click azide-yne (Huisgen) reaction precedes the ring-opening second click; an alkenyl-substituted ASCP can similarly undergo a thiol−ene reaction.



(3)

The azide-yne reaction of alkynyl substituted cyclic azasilane with azide has not been previously reported. However, our investigation demonstrates that this exocyclic click reaction forming the triazole adduct of ASCP proceeds cleanly at a temperature range of 80−100 °C without the addition of a catalyst and that a 1:2 molar ratio of *N*-(trimethylsilyl)pentynyl-dimethoxy-ASCP to benzyl azide affords the most satisfactory result. ^{1}H NMR shows that an >90% yield can be obtained in about 16 h (Figure 4). GC/MS confirms that the ASCP ring is preserved under these anhydrous conditions, while no ring-opening reaction is observed.

The triazole adduct of the ASCPs undergoes a near-quantitative click with hydroxylated substrates, as exemplified by the reaction of the benzyltriazole ASCP adduct with fumed silica. DRIFT spectra (Figure 5) confirm the click-conversion of surface hydroxyl groups, consistent with earlier reports.[12]

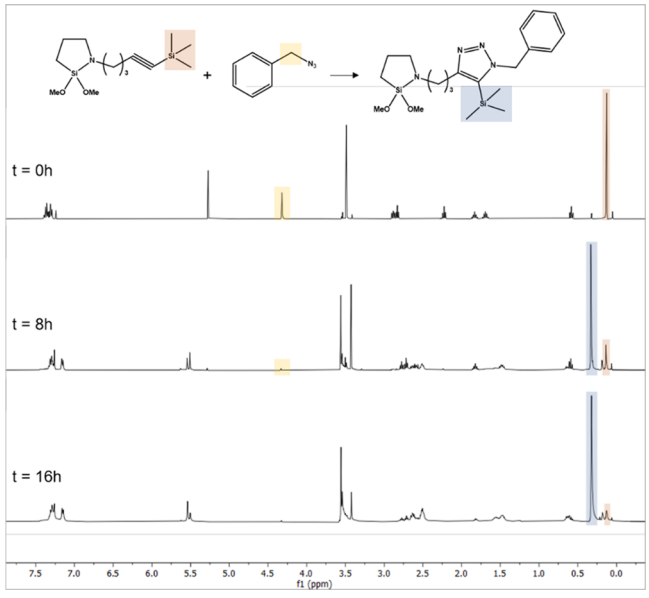


Figure 4. Azide-yne exocyclic click as a function of time. * NMR shows the formation of a triazole ring and preservation of the ASCP ring structure. The relevant NMR peaks that demonstrate the formation of a benzyltriazole ASCP via an azide-yne exocyclic click have been labeled. After heating the reaction mixture of *N*-(trimethylsilyl)pentynyl-dimethoxy-ASCP and benzyl azide for 16 h at 100 °C, >90% of the methylene peak of the benzyl azide starting material disappears (yellow) and >90% of the trimethylsilyl proton peak of the ASCP shifts from 0.13 ppm (orange) to 0.32 ppm (blue). This confirms the formation of a benzyltriazole adduct from a exocyclic click pathway. The NMR spectra show no evidence of ring-opening of the ASCP, which provides the opportunity for performing a second click (ring opening) with a hydroxyl-containing substrate.

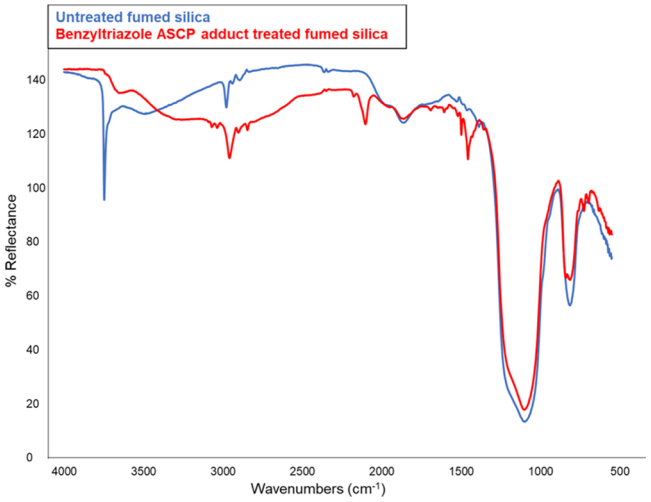


Figure 5. DRIFT spectra of postexocyclic ring-opening with surface hydroxyls. Untreated amorphous fumed silica (blue) shows a strong hydroxyl peak at 3750 cm^{-1}. After exposure to a 0.5 wt % solution of postexocyclic click benzyltriazole ASCP in anhydrous dichloromethane for 1 min, the 3750 cm^{-1} fumed silica peak quantitatively disappears (red), confirming a ring-opening surface modification click.

Orthogonality. ASCP and TSCP are single-molecule double-click reagents possessing both temporal and spatial orthogonality, thereby providing options for order and selectivity toward a broad range of inorganic and organic substrates (Figure 6). In this discussion, "spatial orthogonality" is defined as selectivity between a solid inorganic substrate and a liquid or vapor-phase organic compound. Note also that, although the orthogonality between hydroxylic inorganic substrates and organic substrates with a specific reactivity to the exocyclic or revealed functionality of the click reagent is demonstrated, hydroxyl-containing organics such as alcohols are an important exception to this orthogonal behavior. Alcohols react rapidly with both ASCPs and TSCPs at reaction rates approaching those of reactions with inorganic surface hydroxyl groups. Other protic species such as mercaptans and secondary amines, on the other hand, react at relatively slow rates, and, for practical purposes, spatial orthogonality is maintained in their presence.

Temporal orthogonality is provided by the flexibility of the sequence of click reactions, the reveal of cryptic functionality, and the relative reaction rate of the ring-opening click versus other click reactions. While there is variability depending on the particular reagent and/or solvent selected, the relative speeds of the click reactions at room temperature are as follows: hydroxylic/ring-opening (<1 s) > photolytic thiol−ene/yne (seconds) > thiol−ene/yne (minutes) ≫ azide-yne (hours). This is an important consideration for the time-order of orthogonality when all reactants are present at the onset of the reaction. While not conclusive at this time, as it was not considered within the scope of these studies, preliminary results indicate that a ring-opening click always precedes an exocyclic click if both organic and inorganic reactants are present. In the absence of the inorganic substrate, the exocyclic reaction takes place exclusively in an aprotic environment. In a nonhydroxylic protic environment with, for example, secondary amines

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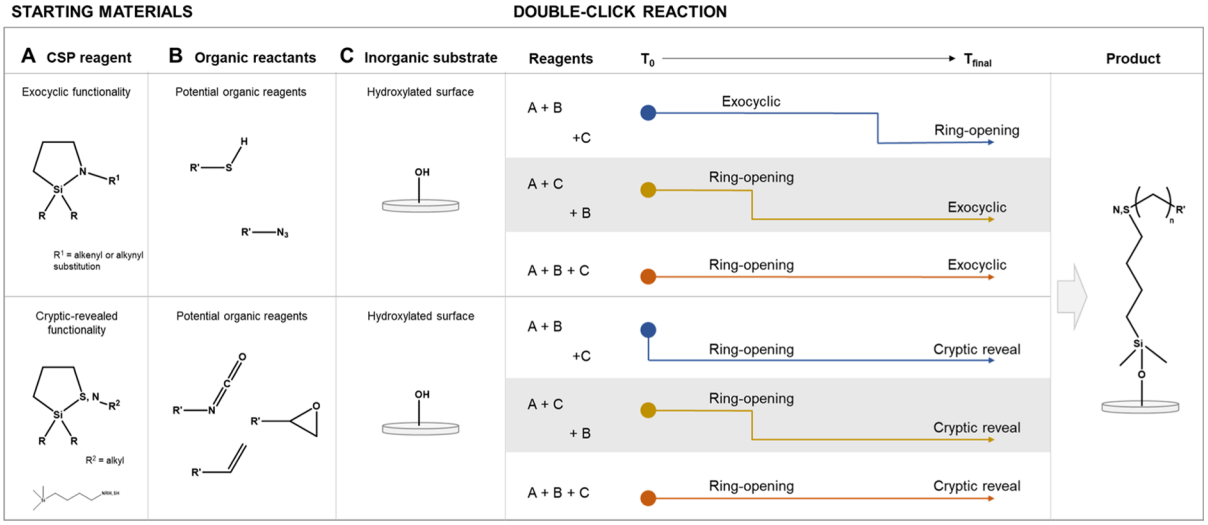


Figure 6. Orthogonality of double-click reactions.

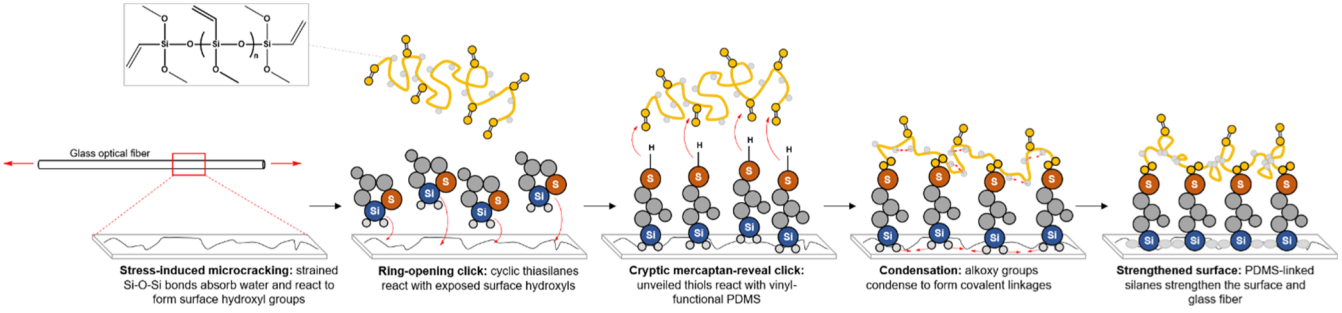
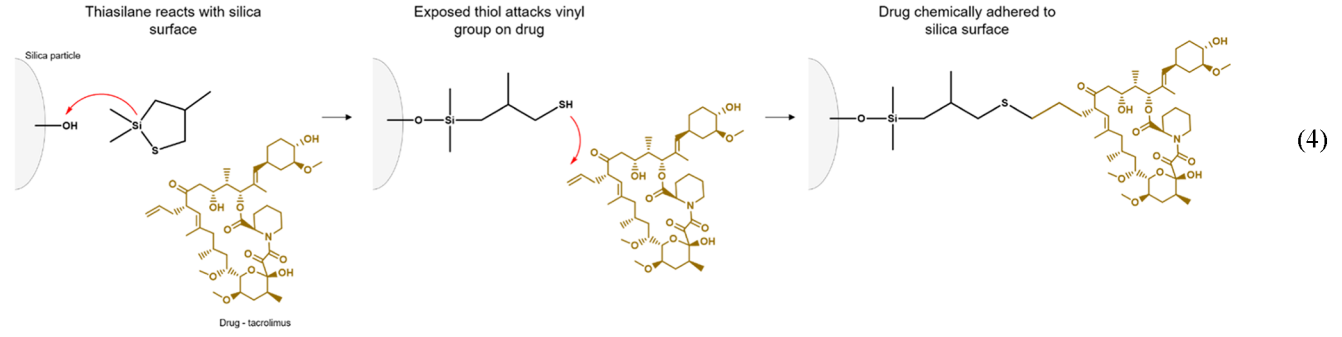


Figure 7. Reduction of stress-induced surface microcracking of vitreous surfaces.



(4)

Figure 8. Formation of an antiproliferative layer of tacrolimus on a silica surface.

present, the relatively slow ring-opening reaction with protic species—which at room temperature progresses over hours (as opposed to seconds)—allows potential competitive reactions. The ring-opening reaction will occur first when hydroxylic substrates are present. Recognizing this, reaction conditions and click reagents can be readily selected to achieve simultaneous or tandem double-click chemistry.

Demonstrations of Orthogonal Double-Click Chemistry. The versatility of orthogonal double-click chemistry is exemplified by the use of TSCP in biofunctional nanoparticles and composite applications. "Tandem double-click" chemistry is shown for hydroxylated silica surfaces representative of those utilized in nanoparticles to deliver biochemical or enzymatic payloads. The first tandem click modifies the silica surface, while the second click binds an immunosuppressant to the presenting surface of the nanoparticle. In the example of the "simultaneous double-click" chemistry presented in Figure 7, the reveal of the cryptic functionality suppresses the propagation of surface microcracks, resulting in glass strengthening and enabling a thiol−ene cross-linking reaction of an optical cladding coating.

Bio-Organic Molecular Anchoring. Sharpless provided early demonstrations of click chemistry with ethynylestradiol.[19] We chose a similarly unsaturated biologically active molecule for our demonstration, but one with relevance to the *in vivo* behavior of the inorganic substrate. Specifically, we demonstrate orthogonal double-click chemistry, in which the "tandem double-click" of dimethyl-TSCP provides an antiproliferative layer on a silica particle of the topical calcineurin inhibitor agent, tacrolimus.[20] Immune-triggered foreign body response is of concern for a wide range of implantable devices that rely on the structural

https://dx.doi.org/10.1021/acsami.0c04018
ACS Appl. Mater. Interfaces 2020, 12, 27737−27744

properties of metals and ceramics, including pace-makers, stents, infusion ports, and drug-delivery systems, among others.[21] The surface modification of silica with tacrolimus serves as a model for the kind of hydroxylated porous silicon drug and enzyme payload delivery reported by Sailor.[6] A reduced physiological response is desirable in this case as well as more generally for the coupling of a bioactive molecule to an inorganic substrate to form a bioactive corona. There is no time requirement for the second click reaction in this example, but tandem double-click chemistry satisfies the requirements for nano-structured materials: it is high-yield, rapid, and imparts little or no contribution to the physical dimensions of the nanoparticle.

Precipitated chromatographic grade silica (200−500 μm) was dried at 150 °C and returned to room temperature under inert atmosphere. Dimethyl-TSCP (2.1 g) in dichloromethane was then added to 30 g of silica and allowed to react with agitation for 1 h. NMR and DRIFT analysis of the silica powder indicated successful surface treatment, and TGA in air confirmed nearly quantitative cryptic click functionalization of the silica. The silica functionalization was followed by a molar equivalent addition of tacrolimus compared to the mercaptan groups, and the silica was then immediately exposed to UV radiation (Uvitron 400R, 240 W/m^2 at the reactor wall) in dichloromethane for 1 h, during which time the mixture was agitated. The ring-opening click with the silica gel and the cryptic-reveal click with tacrolimus are depicted in Figure 8. Under the same conditions, the NMR spectrum of a control solution consisting of mercaptopropyltrimethoxysilane and tacrolimus showed almost complete disappearance of peaks around 1.15 ppm, which represents the −SH proton. The weight gain of the treated silica was determined by TGA to be 10.6%, which represented successful binding of tacrolimus to silica at a 23% loading efficiency. Because of the opacity of the silica, relatively long UV exposure times were required to achieve a reaction.

Click-Driven Polymer Cure. The moisture-induced stress-corrosion attack of silica optical fibers is a significant problem associated with the drawing process and results in the long-term loss of reliability.[22,23] Griffith's crack propagation occurs at rapid velocities, depending on the type and geometry of the silica at 10^{-10} to 10^{-6} m/s.[24] Most stress-induced surface microcracking occurs within a few minutes of drawing the optical fiber, when the temperature drops from ∼1650 °C to ambient temperature in the presence of atmospheric water and is gathered by a capstan. While coatings are applied to the fiber immediately after draw and before gathering, they do little to reduce stress-induced surface microcracking.

Stress-induced surface microcracking occurs when strained silicon−oxygen−silicon (Si−O−Si) bonds adsorb water and then react to form hydroxyl groups on the surface. The hydroxyl groups then adsorb more water via hydrogen bond interactions, creating further stress. A passivation of the bare hydroxyl groups by a reaction rapid enough to precede the adsorption of water would therefore be anticipated to reduce microcrack propagation. However, such a reaction must necessarily occur at timescales (<0.5 s) acceptable for optical fiber production. While surface modification with click functionality has been reported earlier for both optical fiber sensors[25] and glass surfaces,[26] the time scales for the initial surface modification are far too slow to be consistent with optical fiber manufacture.

To demonstrate the application of "simultaneous double-click chemistry", a combination of dimethoxy-TSCP and vinylmethoxysiloxane oligomer (Figure 6) was used, as their optical and thermal properties match glass cladding requirements. In this approach, dimethoxy-TSCP is used to consume surface hydroxyls as they are formed, so that the stress-induced silanols are passivated before they can adsorb water or participate in crack propagation. The hydroxyl-initiated ring-opening of the TSCP and cryptic mercaptan reveal is extremely rapid, occurring in less than 0.5 s, more typically on the order of <0.3 s. This timescale is important, as the reaction speed must be consistent with that of radcure process lines. After the cryptic mercaptan is revealed and exposed to an irradiation source in combination with the vinylmethoxysiloxane oligomer, the mercaptan adds to the vinyl group in the liquid polymer to form a nonflowable resin in a second click reaction. This second click is also on a time scale consistent with the drawing process of optical fibers. In a final, slower step, atmospheric moisture opens the unreacted TSCP rings, revealing additional mercaptan groups. Further cross-linking occurs by thiol−ene and hydrolytically induced condensation of the alkoxy substitution of the dimethoxy-TSCP and oligomeric components, resulting in a cured resin that provides mechanical protection. The utility of "simultaneous double-click chemistry," then, lies in the fact that the timescale of the two reactions is sufficiently rapid to disallow secondary and interfering reactions. In this case, advantage is taken of the monolayer stabilization capability of the dimethoxy-TSCP structure.

In order to quantify the effect of "simultaneous double-click chemistry" on glass strengthening and optical cladding coating, borosilicate glass slides were coated with a mixture of dimethoxy-TSCP and oligomeric vinylmethoxysiloxane (Dp = 3−8), where there was a slight excess of vinyl groups compared to cryptic mercaptan groups. The glass slides were then exposed to UV radiation and evaluated for failure under deflection. In one example, glass slides were moisture-conditioned prior to the demonstration in order to accelerate the formation and propagation of surface microcracking. The apparent increase in the strength associated with inhibition of microcrack propagation was in the range of 50−60%, as shown in Table 2.

Table 2. Effect of TSCP-Vinylsiloxane Cladding Resin on Stress-Induced Glass Failure

glass treatment	deflection @ failure (%)	yield stress (mPa)
Control	0.021	79
TSCP-poly(vinylmethoxy)siloxane mixture	0.034	127
TSCP-poly(vinylmethoxy)siloxane mixture (moisture conditioned)	0.032	117

CONCLUSIONS

Cyclic azasilanes have been demonstrated to be highly effective reagents for the modification of hydroxyl-containing surfaces, particularly inorganic surfaces associated with nanoparticles, mesoporous materials, and substrates employed in the fabrication of microelectronic and optoelectronic devices. The reaction of cyclic azasilanes and cyclic thiasilanes proceeds at room temperature in both vapor- or condensed-phase without coreagents or byproducts and provides a unique pathway to orthogonal double-click reactions with organic species. The high conversion efficiency of such reactions offers a convenient and versatile route to functionalizing surfaces. In the fabrication of surface "nanoscale" features, aza- and thia-silacyclopentanes not only effect a self-limiting functionalization of surface hydroxyl groups in high yield and at low temperatures but do so on a

https://dx.doi.org/10.1021/acsami.0c04018
ACS Appl. Mater. Interfaces 2020, 12, 27737−27744

timescale consistent with processing techniques such as MLD, spin-on deposition, and other high-speed fabrication technologies. Further, the amine, alkenyl, alkynyl, and mercapto functionality provides a reactive starting point for a progressive series of reactions that proceed to an operational device or particle.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c04018.

Details of materials, instrumental, synthetic ASCP/TSCP methods, vapor phase ASCP experimental, tacrolimus thiol−ene reaction conditions, and characterization (PDF)

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Notes

The authors declare no competing financial interest.

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