

Click Chemistry in Mesoporous Materials: Functionalization of Porous Silicon Rugate Filters

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In this paper we report the use of the optical properties of porous silicon photonic crystals, combined with the chemical versatility of acetylene-terminated SAMs, to demonstrate the applicability of “click” chemistry to mesoporous materials. Cu(I)-catalyzed alkyne–azide cycloaddition reactions were employed to modify the internal pore surfaces through a two-step hydrosilylation/cycloaddition procedure. A positive outcome of this catalytic process, here performed in a spatially confined environment, was only observed in the presence of a ligand-stabilized Cu(I) species. Detailed characterization using Fourier transform infrared spectroscopy and optical reflectivity measurements demonstrated that the surface acetylenes had reacted in moderate to high yield to afford surfaces exposing chemical functionalities of interest. The porous silicon photonic crystals modified by the two-step strategy, and exposing oligoether moieties, displayed improved resistance toward the nonspecific adsorption of proteins as determined with fluorescently labeled bovine serum albumin. These results demonstrate that “click” immobilization offers a versatile, experimentally simple, and modular approach to produce functionalized porous silicon surfaces for applications as diverse as porous silicon-based sensing devices and implantable biomaterials.

Introduction

Since the introduction of the click chemistry concept in 2001 by Sharpless and colleagues with the definition of the click principles,¹ virtually all areas of modern chemistry, from drug discovery to material science,^{2–5} have seen a large number of reported applications of this sensible and efficient modular synthetic approach. Recent developments of the click chemistry concept include numerous surface science applications.^{6,7} A major reason for this excitement regarding click chemistry in surface science is that Chidsey and co-workers reported near quantitative coupling yields on surfaces using Cu(I)-catalyzed alkyne–azide cycloaddition reactions.^{7–9} This premier example of a click reaction^{10,11} has been successfully used to functionalize gold nanoparticles,¹² single-walled carbon nanotubes,¹³ powdered silica,^{14,15} metal nanoparticles,¹⁶ and flat silicon wafers.¹⁷ While

triazole-containing architectures, as a product of the click cycloaddition of an azide and an alkyne, have been prepared under various solid phase conditions,^{7,8,18,19} and are generally tolerant toward steric congestion of the individual precursors,²⁰ the great majority of the examples of click chemistry on surfaces thus far have been on flat or nanoscale convex surfaces, which minimize steric constraints. Examples of the functionalization of networks or gel materials through click reactions, where access constraint exists and high surfaces are modified, have only recently been reported in literature.^{4,21} In this paper we demonstrate for the first time the successful implementation of click chemistry inside silicon mesoporous materials. In this material, both steric hindrance due to the reaction occurring on a concave surface and access constraints to a high surface area material represent possibly the most demanding of surfaces for click chemistry to occur. The specific limitations these materials place on performing the Huisgen 1,3-dipolar cycloaddition reaction of alkynes and azides are illustrated. Porous silicon (PSi) is the mesoporous material used in this work, as it can be conveniently tailored to prepare optical materials exhibiting a precise pattern of reflected light^{22,23} and is being explored for label-free biosensing applications.^{24–26} We have recently reported an experimentally simple and versatile two-step approach to covalently modify flat silicon(100) surfaces.¹⁷ The methodology involved the modification of hydrogen-

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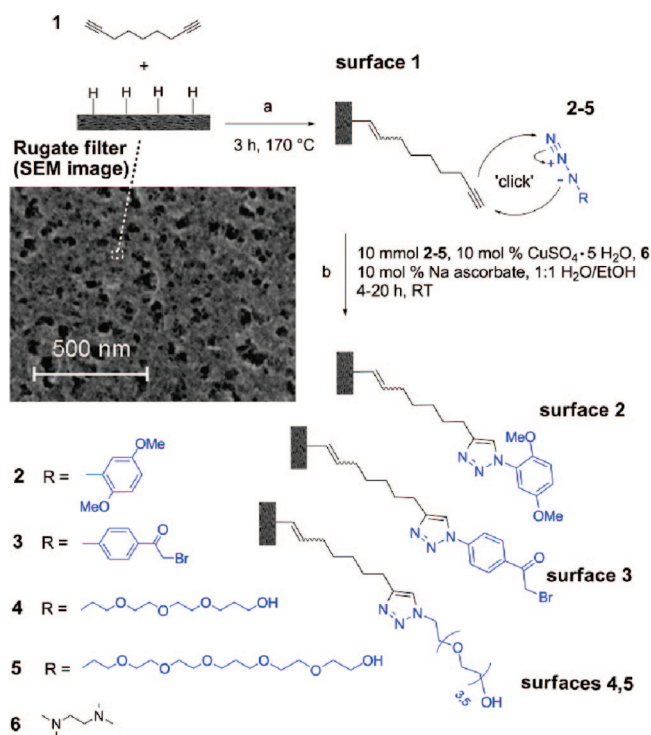
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Scheme 1. Click Chemistry on Acetylenyl PSi Rugate Filters^a

^a The preparation of a monolayer presenting an alkyne functionality (a) was followed by ligand-assisted click reactions with substituted azido species (b) to afford a nanostructured network presenting functionalities of interest. Molecular components are shown colored for clarity.

terminated silicon surfaces via hydrosilylation of a commercially available dialkyne, 1,8-nonadiyne (**1**), followed by the copper-catalyzed click cycloaddition of the distal alkyne with substituted azides to yield surface-bound triazole species (Scheme 1).

Experimental Section

A. Materials. Single-side polished p-type Si(100) wafers were obtained from the Institute of Electronic Materials Technology (ITME, Warsaw, Poland). All chemicals, unless noted otherwise, were of analytical grade and used as received. Solvents for substrate cleaning were redistilled prior to use. Milli-Q water (~18 MΩ cm) was used for preparing solutions, chemical reactions, and surface cleaning. 1,8-Nonadiyne (**1**; Aldrich) of a nominal purity of 98% was redistilled from sodium borohydride (Sigma-Aldrich, 99+%) under reduced pressure (79 °C, 8–9 Torr), collected over molecular sieves (4 Å), and stored under an argon atmosphere prior to use. 4-Azidophenacyl bromide (**3**; 98%) was purchased from Sigma-Aldrich. Dichloromethane and pyridine, used as solvents in chemical reactions, were distilled from calcium hydride and potassium hydroxide, respectively, and stored over molecular sieves (4 Å) prior to use. *N,N*-Dimethylformamide (Fluka, 98+%) was distilled under reduced pressure from calcium hydride. *p*-Toluenesulfonyl chloride (Sigma-Aldrich, 98%) was recrystallized from chloroform (EMD Chemicals, HPLC grade)/hexane (redistilled). Sodium azide (Sigma-Aldrich) was crystallized from water by the addition of ethanol. Albumin-fluorescein isothiocyanate conjugate (FITC-BSA, ≥7 mol FITC/mol albumin) was purchased from Sigma.

B. Purification and Analysis of Synthesized Compounds. Thin-layer chromatography (TLC) was performed on Merck silica gel aluminum sheets (60 F₂₅₄). Merck silica gel (grade 9385, 230–400 mesh) was used for column chromatography. NMR spectra were recorded on a Bruker Avance 300 spectrometer, using the solvent signal (CDCl₃ purchased from Aldrich, passed through basic alumina) as an internal reference. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer, accumulating a minimum of 32 scans and selecting a resolution of 2 cm⁻¹. Arylazide **2** was prepared from 1,4-dimethoxybenzene (a)

in a two-step procedure (Scheme S1, Supporting Information). Azides **4** and **5** were synthesized from tetra(ethylene glycol) (**c**) and hexa(ethylene glycol) (**d**), respectively, via the corresponding monotosylated derivatives **e** and **f** (Scheme S2, Supporting Information).

2-Iodo-1,4-dimethoxybenzene (b). Compound **b** was prepared from **a** following literature procedures.²⁷ To a stirred solution of **a** (383 mg, 2.8 mmol) in methanol/water/sulfuric acid (100:20:2) (10 mL), periodic acid (128 mg, 0.56 mmol) and iodine (281 mg, 1.11 mmol) were added. Stirring was continued under argon at 55 °C for 3 h. Upon cooling to room temperature, sodium dithionite was added to the reaction mixture to destroy excess iodine. The crude reaction mixture was then cooled in an ice-bath, the reaction mixture was filtered, and the filtrate was extracted twice with diethyl ether (2 × 25 mL). The combined organic layers were then washed with water (2 × 25 mL) and saturated sodium bicarbonate (2 × 25 mL), then dried (MgSO₄), and the solvent was removed under reduced pressure to leave a pale yellow residue. Silica gel chromatography (dichloromethane/hexane, 2:3) of the crude product afforded 420 mg (56%) of the title compound as a white solid: ¹H NMR (300 MHz, CDCl₃) δ 7.33 (d, *J* = 2.6 Hz, 1H), 6.85 (dd, *J* = 2.6, 8.7 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 3.81 (s, 3H), 3.74 (s, 3H); ¹³C NMR (300 MHz, CDCl₃) δ 154.29, 152.72, 124.88, 114.74, 111.66, 86.09, 57.01, 55.94; IR (neat) 2937, 2832, 1601, 1486, 1435, 1271, 1220, 1049 cm⁻¹.

2-Azido-1,4-dimethoxybenzene (2). Compound **b** was converted to the corresponding aryl azide **2** according to minor modifications of literature procedures.²⁸ A 50 mL pressure tube was loaded with the aryl iodide **b** (528 mg, 2 mmol), sodium azide (156 mg, 2.4 mmol), copper(I) iodide (38 mg, 0.2 mmol), *L*-proline (46 mg, 0.4 mmol), and sodium hydroxide (16 mg, 0.4 mmol). Upon the addition of argon-purged dimethyl sulfoxide (4 mL), the tube was sealed under an argon atmosphere and transferred to an oil bath set to 70 °C. After 24 h, the mixture was allowed to cool to room temperature, was diluted with diethyl ether (10 mL), and then was partitioned between ethyl acetate and saturated sodium chloride. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2 × 15 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude product, obtained as a dark orange oil, was loaded onto a silica gel column and eluted with a dichloromethane/hexane (2:3) mixture to afford 162 mg (45%) of the title compound as a yellow oil: ¹H NMR (300 MHz, CDCl₃) δ 6.82 (d, *J* = 8.7 Hz, 1H), 6.62 (dd, *J* = 3.0, 8.7 Hz, 1H), 6.58 (d, *J* = 3.0 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H); ¹³C NMR (300 MHz, CDCl₃) δ 153.35, 145.43, 128.26, 113.55, 110.27, 106.90, 56.88; 55.90; IR (neat) 2954, 2835, 2119, 1613, 1505, 1220, 1044 cm⁻¹.

11-Azido-3,6,9-trioxaundecan-1-ol (4). To a solution of anhydrous pyridine (4 mL) and anhydrous dichloromethane (20 mL), compound **c** (5 g, 29 mmol) was added. The solution was stirred and cooled to -10 °C under an argon atmosphere. Dropwise, a solution of *p*-toluenesulfonyl chloride (1 g, 5 mmol) in dry dichloromethane (10 mL) was added over an hour period with stirring. The resultant mixture was stirred at room temperature for 20 h (reaction monitored by TLC, dichloromethane/methanol 5:1). The reaction mixture was concentrated under reduced pressure, and the residue was purified using silica gel column chromatography (dichloromethane/methanol 10:1) to afford compound **e** (monotosylated glycol) as a colorless oil (1.24 g, 71%): ¹H NMR (300 MHz, CDCl₃) δ 2.42 (s, 3H), 2.66 (br s, 1H), 3.63 (m, 14H), 4.13 (t, *J* = 5.0 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (300 MHz, CDCl₃) δ 144.74, 132.84, 129.73, 127.82, 72.39, 70.55, 70.48, 70.28, 70.14, 69.16, 68.54, 61.50, 21.5; IR (neat) 1176, 1247, 1292, 1355, 1425, 1597, 1724, 2874, 3457 cm⁻¹.

To a solution of the monotosylated glycol **e** (0.989 g, 2.84 mmol) in *N,N*-dimethylformamide (10 mL) and water (7 mL), sodium azide (2.94 g, 45 mmol) was added in one portion. The resultant suspension was warmed to 60 °C in an oil bath and stirred overnight. The

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mixture was concentrated under reduced pressure and the resulting residue was suspended in 80 mL of ethyl acetate. The suspension produced was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified using silica-gel chromatography (ether) to give the substituted azide **4** as a colorless oil (0.373 g, 60%): $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 3.07 (br s, 1H), 3.36 (t, $J = 4.9$ Hz, 2H), 3.57 (t, $J = 4.9$ Hz, 2H), 3.66 (m, 12H); $^{13}\text{C NMR}$ (300 MHz, CDCl_3) δ 72.41, 70.53, 70.51, 70.42, 70.18, 69.87, 61.54, 50.55; IR (neat) 1120, 1286, 2096, 2870, 3437 cm^{-1} .

17-Azido-3,6,9,12,15-pentaoxaheptadecan-1-ol (5). Compound **5** was prepared from **d** as described for the azide **4**. The tosylated precursor 17-hydroxy-3,6,9,12,15-pentaoxaheptadecyl 4-methylbenzenesulfonate (**f**) was obtained as a colorless oil (48%): $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.41 (s, 3H), 3.56 (m, 22H), 4.12 (t, $J = 4.5$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 2H), 7.77 (d, $J = 8.3$ Hz, 2H); $^{13}\text{C NMR}$ (300 MHz, CDCl_3) δ 144.67, 132.94, 129.71, 127.84, 72.38, 70.61, 70.56, 70.49, 70.41, 70.37, 70.14, 69.17, 68.55, 61.53, 21.5; IR (neat) 852, 859, 850, 1112, 1248, 1300, 1348, 1452, 2109, 2870, 3465. Nucleophilic displacement of the tosyl group with sodium azide as discussed for the azide **4** yielded the desired product **5** as a colorless oil (54% yield): $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 3.32 (m, 2H, $-\text{CH}_2\text{N}_3$), 3.66 (m, 22H); $^{13}\text{C NMR}$ (300 MHz, CDCl_3) δ 72.39, 70.51, 70.46, 70.42, 70.19, 69.86, 61.52, 50.54; IR (neat) 1124, 1292, 2098, 2875, 3440 cm^{-1} .

C. Surface Modification. PSi rugate filters for characterization by FTIR and reflectance spectroscopy were prepared with an average pore size of ~ 11 nm from p-type Si(100) wafers with a nominal resistivity of 0.07 Ω cm, whereas PSi rugate filters for the protein adsorption assays were fabricated with an average pore size of ~ 50 nm from p-type Si(100) with a nominal resistivity of 0.005 Ω cm. Wafers were anodized in 25% hydrofluoric acid (HF) in ethanol with a sinusoidally varying current density with apodization. The etching profile included refractive index matching layers at the air-PSi and PSi-Si interfaces.²³ Freshly etched filters were transferred, taking extra care to completely exclude air from the reaction vessel, to a degassed sample of **1**. The sample was kept under a stream of argon while the reaction vessel was immersed in a oil bath set to 170 $^\circ\text{C}$ for 3 h. The flask was then opened to the atmosphere, and the functionalized surface sample rinsed consecutively with copious amounts chloroform, ethyl acetate, and then ethanol, before being either analyzed or further reacted with substituted azide species. In a typical click procedure, to a reaction vial containing the alkyne-functionalized PSi surface were added (i) the azido compound (**2–5**, 10 mM, EtOH/ H_2O 1:1), (ii) copper(II) sulfate pentahydrate (1 mol % relative to the azide compound), (iii) sodium ascorbate (25 mol % relative to the azide compound), and (iv) 1 mol % (relative to the azide) of the amino compound **6**.

D. Surface Characterization. Transmission-mode FTIR spectra for p-type Si(100) wafers (0.07 Ω cm) were recorded in air on a Thermo Nicolet Avatar 370 FT-IR spectrometer relative to unmodified Si(100), selecting a 4 cm^{-1} resolution and accumulating a minimum of 128 scans. Optical reflectivity spectra were measured at normal incidence using a J/Y SPEK 1681 spectrometer and a silicon detector.²³ Nonspecific adsorption of fluorescein isothiocyanate-labeled bovine serum albumin (FITC-BSA) on the functionalized PSi samples, relative to the alkyne-terminated surface **1**, was evaluated for surfaces **4** and **5**, according to the procedure described by Clare and co-workers.²⁹ Briefly, samples were wetted with ethanol and then exposed for a 1 h period to a labeled-protein solution (0.1% FITC-BSA, 0.1 M NaHCO_3 , pH 8.3). The samples were subsequently rinsed with copious amounts of Milli-Q water, and then incubated with the elution buffer (0.3 M NaCl, 20 mM Na_2HPO_4 , 2 mM EDTA, 1% Triton X-100, 1% β -mercaptoethanol, pH 7.4.) for a 16 h period. Fluorescence intensities ascribed to the labeled-protein eluted from the surface were measured on a Perkin-Elmer LS 50B spectrofluorometer using a 490 ± 10 nm excitation source and recording fluorescence at 520 ± 10 nm. Samples were prepared in quadruplicate, and for each sample a minimum of three repeated fluorescence measurements were obtained. The 95% confidence limit of the mean

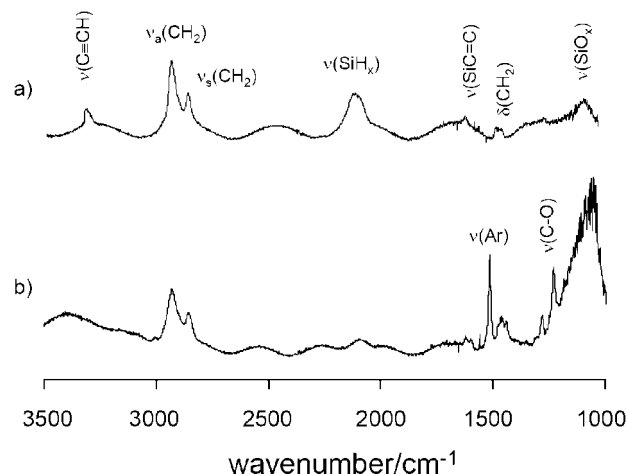


Figure 1. Transmission-mode FTIR spectrograph of acetylenyl PSi rugate filters prior (a) and upon (b) ligand-assisted click reactions with substituted azide **2** to yield corresponding surface-bound triazole species (surface **2**).

Table 1. Assignments of the FTIR Bands for Derivatized PSi Rugate Filters Samples^a

assignment	surface 1 (cm^{-1})	surface 2 (cm^{-1})	surface 3 (cm^{-1})	surface 4 (cm^{-1})
$\nu(\text{C}\equiv\text{CH})$	3309	n.o.	3310	n.o.
$\nu_a(\text{CH}_2)$	2929	2930	2928	2926
$\nu_s(\text{CH}_2)$	2858	2860	2857	2857
$\nu(\text{SiH})^b$	2100	2100	2100	2100
$\nu(\text{C}=\text{O})$			1693	
$\nu(\text{Ar})$		1625	1600	
$\nu(\text{SiC}=\text{C})^c$	1598	n.o.	n.o.	n.o.
$\nu(\text{Ar})$		1510	1505	
$\delta(\text{CH}_2)$	1457	1460 ^d	1460 ^d	1464
$\nu(\text{C}-\text{O})$		1230		
$\nu(\text{SiO})^e$	1050	1050	1050	1050

^a (n.o. = not observed). ^b Broad peak assigned to Si-H, stretches ($x = 1, 2, 3$). ^c Indicative of a monosilylated surficial olefin. ^d Broadened $\delta(\text{CH}_2)$ bending mode of increased intensity (relative to the corresponding band observed for surface **1**) as a result of a contribution of a ring mode to the same band. ^e Peak assigned to the Si-O-Si asymmetric stretching vibration greatly varied in intensity between samples (Figure S1), presumably as a result of differences in the water and/or oxygen content in the reaction chamber.

was calculated as $t_{n-1}s/n^{1/2}$, where $t_{n-1} = 4.3$, s is the standard deviation, and n is the number of repeat measurements. Fluorescence intensities were normalized to those observed for the surface **1**.

Results and Discussion

The thermally induced hydrosilylation reaction of the anhydrous diacetylene species **1** on freshly etched PSi surfaces produced surface **1**, as determined using FTIR spectroscopy. Figure 1a and Figure S1 (Supporting Information) show typical transmission-mode FTIR spectra of the prepared acetylene-decorated nanostructured PSi. The peak assignments are summarized in Table 1. According to the presence of $\nu(\text{C}\equiv\text{CH})$, $\nu(\text{CH}_2)$ and $\nu(\text{SiC}=\text{C})$ modes, the formation of an alkyne-terminated monolayer via alkenyl substitution at the hydrogen-terminated silicon surface is suggested, as depicted in Scheme 1, for the thermal, uncatalyzed reaction of **1** with PSi.

The presence of the alkenyl substitution at the proximal end of the molecule is the subject of some debate. Bateman and co-workers suggested that, for the thermal reaction of 1-alkynes on PSi, the formation of monolayers occurred with complete reduction of the alkyne functionality to alkane.³⁰ Conversely, results in our hands for the hydrosilylation of the diacetylene species **1** are consistent with a Si-alkenyl-functionalized PSi surface, thus suggesting a partial reduction of the alkyne function

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involved in the grafting event, as proposed by Zuilhof and co-workers.³¹ Antisymmetric and symmetric methylene stretching vibrations appear near 2929 and 2858 cm^{-1} , respectively, with spectral positions shifted to lower wavenumbers compared with the corresponding signals observed for the neat diacetylene species **1**.³² Such shifts are indicative of a well-formed monolayer, as they are interpreted as the transition from a liquid-disordered state to a solid-crystalline state due to an increase in the order and density of the alkyl chains in the monolayer compared to the neat liquid.

Initial attempts to "click" any of the species **2–4** onto the acetylenyl terminated PSi surface using a Cu(I) catalyst, however, proved unsuccessful. Evidence for this statement arises from transmission-mode FTIR spectra of PSi samples after exposure of surface 1 to the substituted azide species **2–4** in the presence of Cu(I) under conditions such that a click reaction might occur to give surfaces 2, 3, and 4, respectively (Figures S2, S3, and S4, Supporting Information). Spectroscopic data showed that the intended functionalization did not proceed to any appreciable extent, despite our previous observations on flat silicon surfaces where high coupling yields were observed.¹⁷ Employment of 1 mol % of the ligand (*N,N,N',N'*-tetramethylethane-1,2-diamine (**6**)) in the reaction mixture to stabilize the Cu(I) catalyst however, remarkably resulted in near quantitative azide–alkyne cycloaddition reaction as described below. The four representative substituted azides **2–5** used in the click step, were chosen to impart a range of physical and spectroscopic properties to the modified PSi substrate. Compounds **2** and **3** were selected as convenient candidates for the cycloaddition reaction, primarily for spectroscopic purposes with the presence of carbonyl groups, aromatic rings, and methoxy substituents, in the intended triazole product (surfaces 2 and 3), introducing clear spectral features in the recorded FTIR spectra (Figure 1b and Figure S5, Supporting Information). The oligoether (OEO) portions exposed on surface 4 and on surface 5 were chosen for their applicability to using PSi in biosensing, as these molecules impart resistance toward unwanted nonspecific protein adsorption.^{33,34}

Attenuations of the FTIR peaks centered at 3309 cm^{-1} , ascribed to the $\nu(\text{C}\equiv\text{CH})$ mode, were used as a convenient analytical tool to monitor the "click" reaction. The attachment of **2** on the acetylenyl substrate will serve as an example of the reported functionalization strategy. After a 15 h cycloaddition reaction of surface 1 with the azido species **2**, a very significant attenuation of the acetylenic stretch was evident in the recorded FTIR spectra (Figure 1b, surface 2). Even though only semiquantitative considerations can be drawn from analysis of an FTIR spectrograph,⁷ the lack of a resolved acetylenic stretch upon the click derivatization suggests a high yield for the immobilization of solution phase azide species onto the ethynyl-modified porous network, which is analogous to our observations of flat silicon surfaces.¹⁷ Similar results were observed for compounds **3–5** (Figures S5, S6 and S7, Supporting Information). The appearance of an $\nu(\text{C–O})$ at 1230 cm^{-1} , further supports the chemical derivatization of the base monolayer to afford surface 2. The vinyl group stretching mode absorption (silylated olefin at $\sim 1598 \text{ cm}^{-1}$), evident for the acetylenyl substrate, overlapped with the

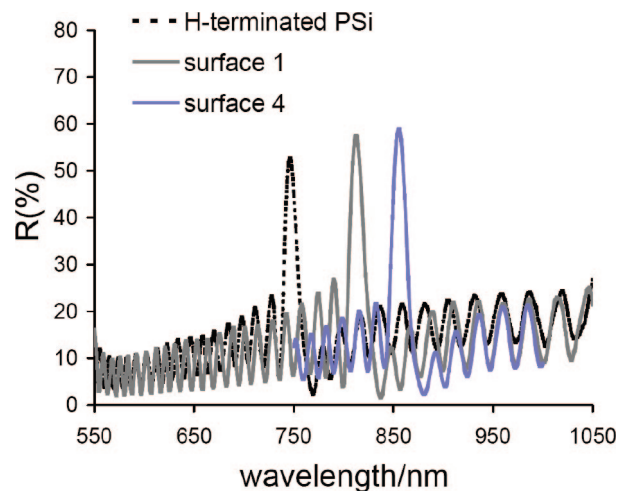


Figure 2. Optical shifts in the high reflectivity band for PSi rugate filters modified through a two-step acetylenylation/click procedure.

various $\nu(\text{C}=\text{C})$ aromatic modes introduced upon the click step and could not be resolved in the observed spectra.

The above results raise the question as to why the ligand stabilization is so important for successful "click" reactions in mesoporous materials. Previous solution phase reports consistently showed increased rates of triazole formation in the presence of an amine base under oxo and aqueous conditions,^{18,35} and we have shown this for surface click reactions,¹⁷ but the click reaction between an azide and an alkyne has always been shown to proceed even in the absence of a stabilizing ligand for the Cu(I) catalyst. The enhanced rate of reaction in the presence of the ligand has been attributed to the stabilization of the Cu(I) oxidation state, which undergoes a facile disproportionation in water,³⁶ and aids in the formation of the copper–acetylide intermediate.¹¹ Here we hypothesize that the necessity to perform click reactions under ligand-assisted conditions may be a direct consequence of the reported copper-binding ability of soft ligands such as 1,4-disubstituted 1,2,3-triazoles.^{35,37} A sufficiently high density of triazole moieties, initially formed at the pore entrance, might act in a very similar fashion to a polytriazole system³⁵ and complex the Cu(I). The complexation of the Cu(I) would prevent its further ingress into the PSi structure, and hence little or no click reaction will occur within the PSi structure.

The quality of the acetylene functionalized rugate filter, with regard to the integrity of the photonic crystal properties, was assessed by monitoring the high reflectivity resonance (here indicated as *R*) of the reflectivity spectra.²³ An observed $\sim 66 \text{ nm}$ red-shift in the high reflectivity resonance position (Figure 2), upon the hydrosilylation of the diyne **1**, is consistent with an increase in the composite refractive index of the porous substrate, as air is being replaced by organic material, further supporting a positive outcome of the intended chemical modification.³³ Next, the cycloaddition reaction to form surface 3 yielded a 43 nm shift for the high reflectivity peak, in good agreement with a modification of the base monolayer to give a progressively narrower pore structure upon introduction of **3** moieties.³³

Finally, turning to the application of click chemistry for biosensing interfaces, the antifouling properties of surfaces 4 and 5 were assessed by determining the extent of nonspecific

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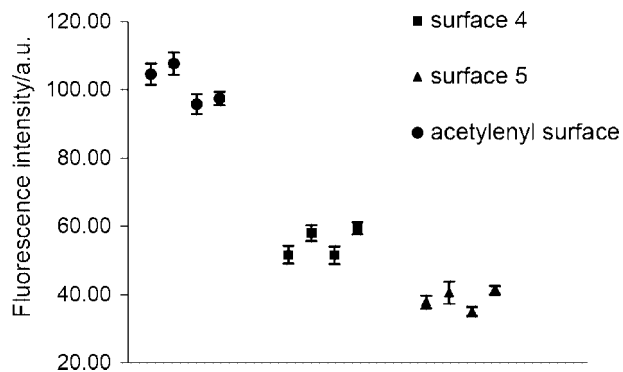


Figure 3. Spectroscopic evaluation of FITC-BSA nonspecifically adsorbed on acetylenyl, tetra-, and hexa(ethylene oxide)-functionalized PSi surfaces (surfaces 1, 4, and 5, respectively). Samples were prepared in quadruplicate, and for each sample a minimum of three repeated fluorescence measurements were obtained.

adsorption of FITC-BSA²⁹ on the click-functionalized PSi samples, relative to the alkyne-terminated surface 1. Both PSi surfaces containing distal OEO functionalities reduced nonspecific adsorption of BSA by ca. 50% (Figure 3) relative to the unmodified acetylenyl surface (surface 1). The hexa(ethylene oxide) interface (surface 5) performed slightly better than the shorter tetra(ethylene oxide) (surface 4) as observed previously.³³

Conclusions

In conclusion, a versatile and experimentally straightforward two-step acetylenylation/click procedure is shown to be a viable

and efficient strategy to impart chemical functionalities of interest to a nanostructured, high surface area, mesoporous architecture. Numerous control experiments indicated how Cu(I) complexation is essential when this cycloaddition event is carried out in a (particularly) sterically congested environment such as a PSi network, while, in contrast, only minor improvements to the coupling efficiencies are seen for analogous reactions on flat silicon surfaces.¹⁷ The outcome of the above-mentioned solid-state cycloaddition reactions were assessed using infrared spectroscopy and the optical properties of the chemically modified material evaluated monitoring the high reflectivity peak, with large red-shifts accompanying both modification steps. The virtues of the reported surface chemistry protocol, associated with the antifouling properties of OEO-modified surfaces may be of significance where functionalized mesoporous materials are pursued for biosensing applications.

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Supporting Information Available: Additional FTIR spectrographs and synthetic schemes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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