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Chemical surface reactions by click chemistry: coumarin dye modification of 11-bromoundecyltrichlorosilane monolayers

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Abstract
The functionalization of surfaces and the ability to tailor their properties with desired physico-chemical functions is an important field of research with a broad spectrum of applications. These applications range from the modification of wetting properties, over the alteration of optical properties, to the fabrication of molecular electronic devices. In each of these fields, it is of specific importance to be able to control the quality of the layers with high precision. The present study demonstrates an approach that utilizes the 1,3-dipolar cycloaddition of terminal acetylenes to prepare triazole-terminated monolayers on different substrates. The characterization of the precursor monolayers, the optimization of the chemical surface reactions as well as the clicking of a fluorescent dye molecule on such azide-terminated monolayers was carried out. A coumarin 343 derivative was utilized to discuss the aspects of the functionalization approach. Based on this approach, a number of potential surface reactions, facilitated via the acetylene-substituted functional molecules, for a broad range of applications is at hand, thus leading to numerous possibilities where surface modifications are concerned. These modifications can be applied on non-structured surfaces of silicon or glass or can be used on structured surfaces. Various possibilities are discussed.

1. Introduction

The functionalization of surfaces by means of self-assembled monolayers is an active area of research that opens versatile possibilities for the tailoring of surface properties in a controllable fashion [1]. Extensive work has been performed on the self-assembly of alkyl thiol and alkyl silane monolayers, that are known to form stable, covalently anchored monomolecular layers on a variety of substrates, e.g. gold, silver, glass or silicon. In particular, the silane chemistry is of interest for practical applications because of the physical and chemical stability of silanes and the technologically relevant substrates, which can be used for surface modification [2]. These alkylsiloxane monolayers are generally prepared by immersing the substrate in a dilute solution of alkyltrichlorosilanes (R-SiCl$_3$), alkyltrimethoxysilanes (R-Si(OMe)$_3$) or alkyltriethoxysilanes (R-Si(OEt)$_3$). With improving patterning techniques, particularly functional alkylsiloxanes have become focal points for current research [3–6]. These compounds are, to a certain extent, commercially available: however, the presence of a second functional group frequently implies the disadvantage of incompatibility and/or interaction of the functional groups and the silane groups used in order to bind to the substrate, thus preventing the formation of a well-defined monolayer.

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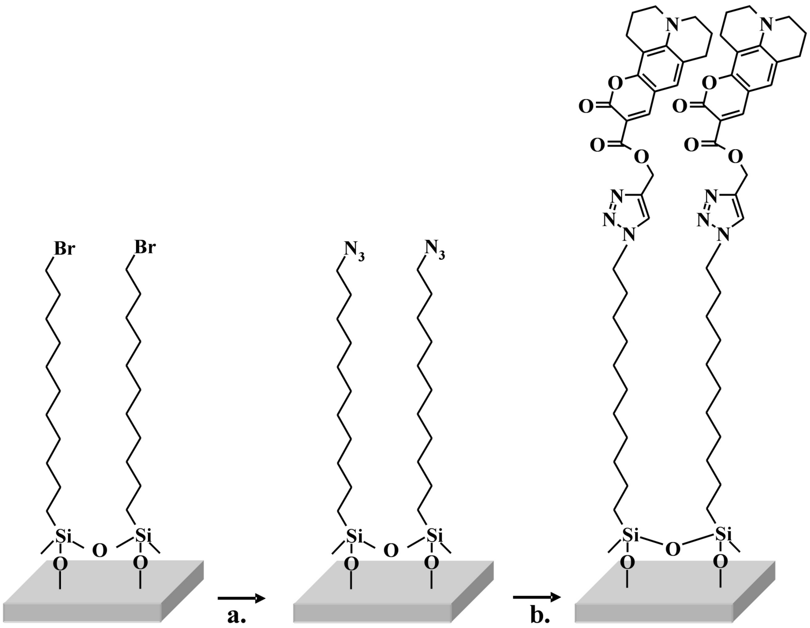

Scheme 1. A schematic representation of the modification sequence of the precursor monolayer. (a) NaN_3, 24 h/room temperature, (b) coumarin dye, $CuSO_4 \times 5H_2O$, sodium ascorbate, 24 h/room temperature.

An elegant approach to overcome this problem is the use of functional precursor molecules, that form reasonably well-packed monolayers on a substrate, and to proceed to alter the chemical nature of the terminal monolayer functions by chemical surface reactions after the monolayer is formed. Thereby, protected terminal functional groups, relatively inactive leaving groups or chemical reactions that have a high yield and high selectivity are the focal points of such approaches [7]. However, a serious concern for the successful conversion of the terminal groups is frequently seen in the steric hindrance of the molecules within well-defined monolayers. This can prevent the quantitative conversion of the terminal groups. Other critical issues that have to be taken into account are the required reaction conditions (presence of solvents, high reaction temperatures, etc) that must be compatible with the precursor monolayer.

A class of chemical reactions that is compatible with these requirements is the so-called click chemistry approach. This is a widely used chemical reaction that has, since its introduction in 2001 by Sharpless *et al* [8], found countless applications in fields as broad as polymer chemistry, surface modification, cellulose chemistry, etc [9–20]. In particular, the Huisgen 1,3-dipolar cycloaddition reaction [21] of terminal acetylenes with azides is known as one of the most perfectly working click reactions. This approach was chosen for the present study in order to investigate the requirements for the successful introduction of physico-chemical properties, in particular the fluorescent properties of a coumarin dye [22], on silicon and glass substrates. Special emphasis was placed on preserving the monolayer quality, as the concept certainly provided the possibility of acting as a powerful tool also for micro- and nanofabrication approaches, where a quantitative conversion of the precursor is required due to the relatively small number of reaction sites present in a confined surface area. It should be mentioned, that the coumarin 343 derivative represents only one of a plethora of molecules that can be employed in the click chemistry approach and was chosen here mainly for demonstration purposes. However, fluorescent molecules are an important building block of sensor devices as they provide a convenient means for read-out processes. Therefore, the possibility of using the clicking of fluorescent dye molecules on nanometer-sized structures was screened and additional requirements for future progress were defined.

2. Results and discussion

The essential part of the present investigation was the choice of a suitable, commercially available precursor molecule, which would allow the reproducible and reliable formation of a chemically active monolayer. In particular, 11-bromoundecyltrichlorosilane was found to have suitable properties for forming such monolayers and, moreover, the terminal bromine moiety provided the possibility of serving as a functional group that could be converted into the desired azide functions.

The entire sequence of the modification steps required to functionalize a glass or silicon substrate with the coumarin compound is schematically outlined in scheme 1.

The first step of the functionalization sequence was the formation of a reliable 11-bromoundecyltrichlorosilane monolayer on the substrate. Grazing angle FT-IR spectroscopy of the $–CH_2$ stretching vibrations (figure 1(a), top left) is a powerful tool to analyze the quality of the precursor layer, as the individual positions of the $–CH_2$ vibrations provided information on the quality of the monolayer.

The asymmetric and symmetric vibrations for the 11-bromoundecyltrichlorosilane monolayer on silicon were located at 2926 and 2854 cm^{-1}, respectively. The positions

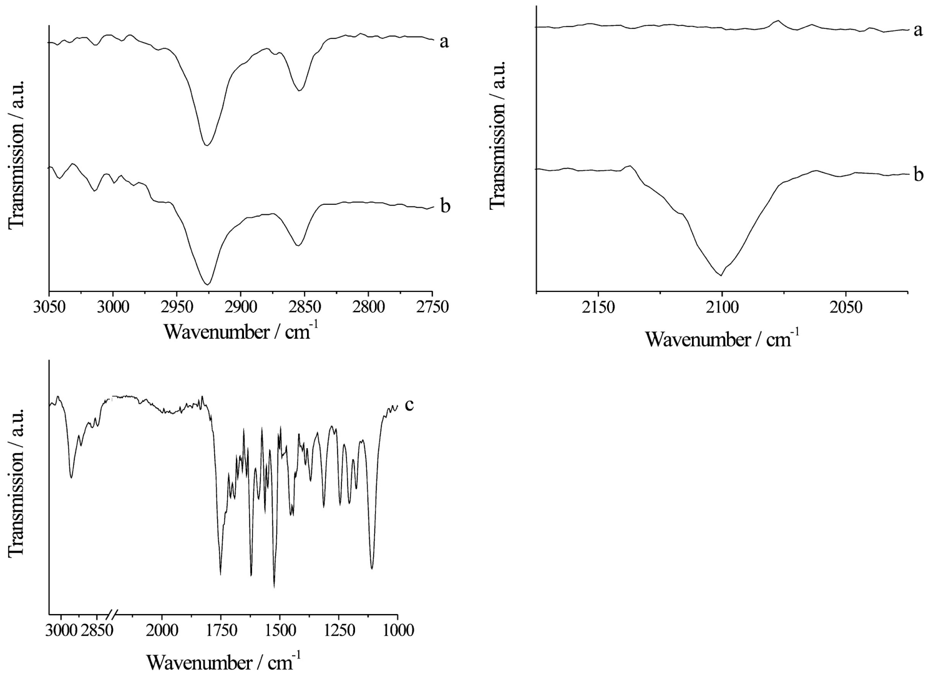

Figure 1. Grazing angle FT-IR spectra of the (a) bromine-, (b) azide- and (c) coumarin-terminated silicon substrates. Top left: spectral region of the –CH_2 stretching vibrations. Top right: spectral region of the azide vibration. Bottom left: spectrum of the characteristic peaks observed for coumarin.

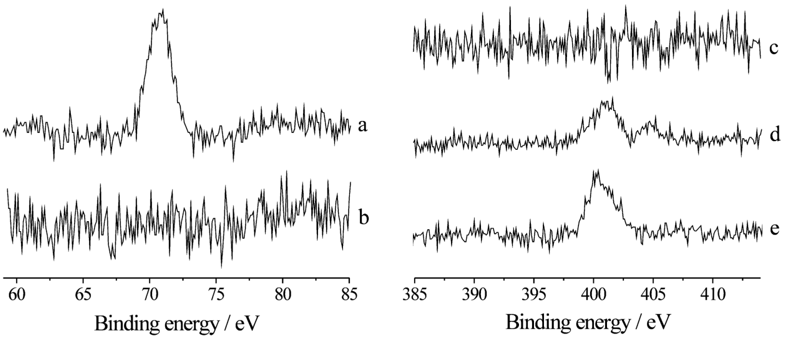

Figure 2. Left: XPS spectra of the Br(3d) region of (a) bromine- and (b) azide-terminated SAM. Right: XPS spectra of the N(1s) region of (c) bromine-, (d) azide-and (e) click-terminated SAM.

of the CH_2 vibrations for the bromine monolayer on glass are at 2926 and 2855 cm^{-1}, indicating that the monolayers have the same quality on both substrates. It has to be mentioned that these values were significantly higher than those of, for instance, a highly ordered *n*-octadecyltrichlorosilane monolayer (i.e. 2917 and 2850 cm^{-1}), which is expected to be densely packed. The main reason for the lower quality of the monolayer was most probably the shorter alkyl chain of the 11-bromoundecyltrichlorosilane precursor molecule, which is the main driving force for the well-ordered packing of the individual molecules within a monolayer. The shorter alkyl chain leads to a less ordered packing of the monolayer due to reduced van der Waals interaction energies between adjacent chains [23]. The relatively bulky character of the bromine function might have contributed as well to the reduced molecular order of such monolayers. However, it was observed that the quality of the monolayer was sufficient and did not degrade within the sequence of the modification steps, as was observed in the spectral region of the –CH_2 vibrations after the conversion of the terminal bromine to azide (figure 1(b), top left). The peaks remained comparable both in position and in their relative intensity, which was an important indication of the maintained properties of the undecyltrichlorosilane precursor. However, the appearance of the characteristic azide peak at 2100 cm^{-1} indicated the successful formation of azide moieties after the first reaction step, since such a peak was not present in the original monolayer (figures 1(a) and (b), top right). However, grazing angle FT-IR could not provide evidence of the quantitative conversion of bromine to azide. Therefore, associated high resolution XPS investigations were performed (figure 2) due to their higher sensitivity. Special emphasis was placed on the investigation of the Br(3d) and N(1s) regions of the spectra in order to quantify the chemical functionalization steps.

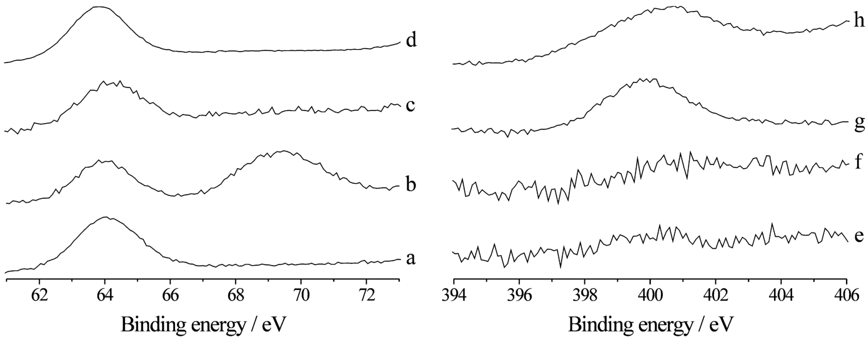

Figure 3. Left: XPS spectra of the Br(3d) region of (a) unmodified glass, (b) bromine-, (c) azide-and (d) click-terminated SAM on glass. Right: XPS spectra of the N(1s) region of (e) unmodified glass, (f) bromine-, (g) azide-and (h) click-terminated SAM on glass.

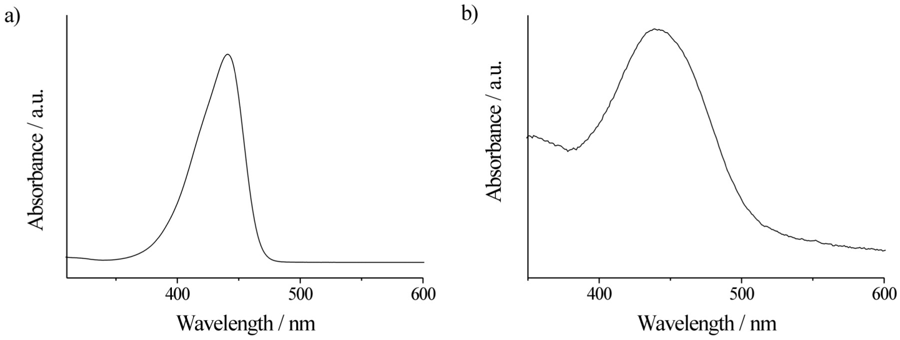

Figure 4. UV/vis spectra of (a) the coumarin dye in solution, (b) the clicked coumarin dye on glass.

The XPS spectrum of the bromine-terminated precursor monolayer (figure 2(a)) revealed a strong peak at 71 eV, which was assigned to the Br(3d) signal, and thus proved the presence of bromine in the precursor layer. However, after the conversion of bromine into azide, this peak disappeared completely (figure 2(b)), indicating the substitution of the bromine functions of the monolayer. A complete loss of the precursor layer could be ruled out due to the presence of the –CH_2 vibrations in the respective FT-IR measurement (figure 1(b), top left). The substitution reaction of bromine with sodium azide resulted in the observation of a signal in the N(1s) region of the XPS spectrum. Careful analysis showed the presence of a split peak with maxima at 401 and 405 eV (figure 2(d)), in a region which did not show any signal for the 11-bromoundecyltrichlorosilane precursor monolayer (figure 2(c)). This peak splitting indicated the presence of two nitrogen species present in the azide-terminated monolayer, and reflected the differently charged nitrogen atoms in the azide group [13, 24]. Moreover, the complete disappearance of the bromine peak that was observed on the 11-bromoundecyltrichlorosilane precursor layer (figure 2(b)) suggested the complete conversion of the bromine functions to azide ($>95\%$).

Such functionalized azide-terminated monolayers now represented a substrate that could be employed in 1,3-dipolar cycloaddition reactions, if reacted with terminal acetylene-substituted molecules. To demonstrate this possibility, the fluorescent coumarin 343 was functionalized with an acetylene moiety in a straightforward, one-step synthesis approach with propargyl alcohol following a protocol previously reported in the literature [19]. These test molecules, which provided characteristic spectra in FT-IR investigations, could be clicked on the azide-terminated monolayer in the presence of a copper(I) catalyst. Substrates were sonicated in ethanol for several hours prior to characterization in order to avoid the presence of unspecifically bound coumarin on the surface. The corresponding FT-IR spectrum is depicted in figure 1(c) (bottom left). Only a very weak peak of an asymmetric azide vibration at 2093 cm^{-1} was observed: however the peak intensity was significantly diminished and thus a high yield of the 1,2,3-triazole was assumed. The reason for the small vibration might be associated with remaining azide moieties within the system, which were not functionalized due to the relatively bulky structure of the coumarin compound itself. Besides this, characteristic peaks from the coumarin compound could be identified (C=O: 1754 cm^{-1}; aromatic system and ring vibrations: 1623, 1524, 1449 cm^{-1}). Additional evidence of the 1,2,3-triazole formation on the azide-terminated monolayer was derived from additional XPS investigations of the N(1s) spectral region, which displayed only a single peak at 400 eV, thus confirming the conversion of the azide functions (figure 2(e)).

Due to the optical fluorescent properties, an equivalent cycle of modification and reaction steps was performed on transparent glass substrates, which allowed the additional optical characterization of the substrates. XPS investigations and UV/vis measurements were performed to follow the chemical transformation of the substrates and the respective results can be seen in figures 3 and 4.

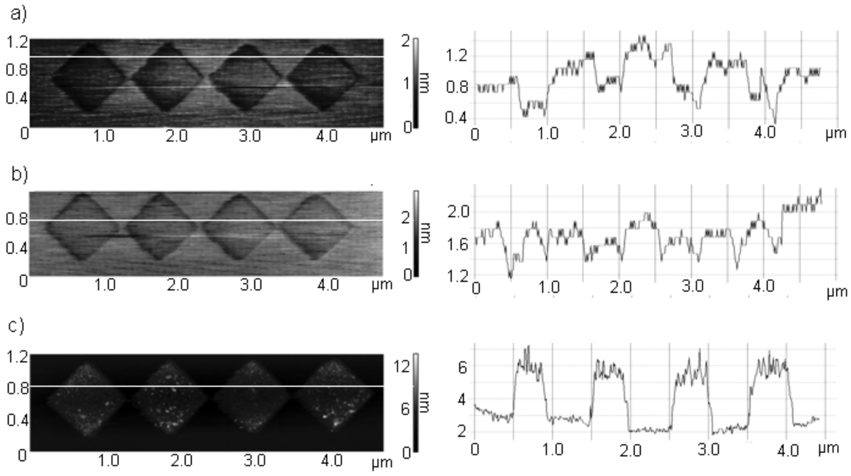

Figure 5. Topographical investigation of electro-oxidatively oxidized OTS monolayers. (a) Topographic structure and line profile of four inscribed square structures scanned in contact mode (scan direction: left to right). (b) The same structures scanned under reversed scan direction. (c) Tapping mode investigation of the same structures after performing the site-selective assembly of a 11-bromoundecyltrichlorosilane monolayer.

(This figure is in colour only in the electronic version)

These investigations confirmed the results obtained on the functionalization carried out on silicon substrates. However, a closer look at the nitrogen region of the azide-terminated glass (figure 3(g)) substrate shows a single peak compared to a split peak of the azide moiety on silicon. This observation is most likely related to a faster degradation of the monolayer on glass because the extensive charging increases the decomposition of the azide which results in the presence of a single peak in the obtained area. An additional peak was observed in the XPS spectra at 64 eV, next to the Br(3d) signal, which originated from sodium additives within the glass substrates. Additional UV/vis spectroscopy was performed on such substrates and the respective spectral data was compared to the absorption spectrum of the dye in solution (figure 4(a)). Figure 4(b) shows the UV/vis spectrum of the surface after excessive cleaning in ethanol. An absorption maximum was observed at 441 nm as compared to 442 nm for the dye in solution. The small redshift that was observed was most probably caused by the difference in polarity of the dye molecules' environment within the monolayer, thus providing more evidence for the successful 1,3-dipolar cycloaddition of the dye onto the azide-terminated monolayer scaffold.

The preparation of nanostructured surfaces is an important goal in the field of nanotechnology [25, 26]. As building blocks for the fabrication of these structures, self-assembled monolayers have been proposed. This research target can be addressed by the introduced reaction mechanism, as click chemistry provides a large variety of possible functionalizations of such structures. A critical issue in this context is certainly the local availability of bromo species in nanoconfined areas. Possible structuring approaches include dip-pen lithography, soft-lithography or electro-oxidative lithography. The latter approach uses chemically inert monolayers of n-octadecyltrichlorosilane (OTS) that can be locally functionalized by means of an electrically conductive SFM tip. The tip gives rise to a local initiation of an electrochemical oxidation of surface-terminated methyl groups to carboxylic acid functionalities or a site-selective degradation of the monolayer [27, 28]. These surface structures can be used directly [29, 30] or be employed to guide the site-selective assembly of trichlorosilane overlayers [5, 31]. This approach provides a straightforward means for using the introduced functionalization concept of click chemistry on structured surface areas.

In figure 5 the fabrication of such patterns is demonstrated. Directly after the pattern inscription no significant topographical change of the OTS monolayer is observed. The small corrugation introduced by the patterning of the four square structures is an artifact of the friction forces, introduced by the oxidation of the methyl groups to hydrophilic carboxylic acid functions and depends on the scan direction. As the contrast inverts upon change of the scan direction (figure 5(b)) it could be previously demonstrated that the contrast is an artifact of the scanning on top of the hydrophilic surface areas [32]. A significant increase of the inscribed structures is observed after the additional self-assembly of the 11-bromoundecyltrichlorosilane precursor layer. These well-defined overlayers provide the desired bromo function onto the structures that are potentially interesting for the transfer of the above introduced click chemistry modification approach. However, such substrates are not well suited for the investigation of nano-optical effects of laterally defined dye structures due to the opaqueness of the silicon substrate. Therefore, the structuring approach has to be transferred onto transparent substrates. This approach has been recently investigated and further research will focus on the extension of the patterning approach onto transparent substrates that additionally will provide the required conductivity in order to initiate an electrochemically driven structuring of the substrate. These investigations are being addressed within current research projects so as to make full use of the powerful modification scheme provided by click chemistry.

3. Conclusions

This proof of concept study demonstrated the ability of 11-bromoundecyltrichlorosilane to form a suitable precursor monolayer, which can be used to introduce tailor-made surface functionalities by means of chemical surface reactions. It was shown that such layers were stable enough to withstand the experimental conditions required for their functionalization with azide functions and further wet chemical processing to obtain the 1,3-dipolar cycloaddition of a fluorescent model compound, i.e. a coumarin 343 derivative. The modification sequence was investigated by FT-IR, XPS and UV/vis spectroscopies and the results displayed the successful attachment of the coumarin dye to the modified silicon and glass substrates. The conversion of the bromine moieties into azide units could be determined and the attachment of the coumarin dye was observed with a high yield. XPS and grazing angle FT-IR suggest a quantitative conversion (>95%). These results encourage further use of this reaction mechanism for the functionalization of micro- and nanopatterned structures. A dense packing of the molecular precursors is essential, especially for devices constructed with nanometer precision. Moreover, starting the introduced approach from a well-ordered, variable precursor unit is advantageous and click chemistry can provide a powerful tool for the functionalization of such structures.

4. Experimental details

11-Bromoundecyltrichlorosilane, *n*-octadecyltrichlorosilane (OTS), coumarin 343, 1-[3-dimethylaminopropyl]-3-ethyl carbodiimide HCl (EDC × HCl), 4-(dimethylamino)-pyridine (DMAP), $MgSO_4$, copper sulfate pentahydrate, bicyclohexane (BCH), propargyl alcohol, sodium azide, sodium ascorbate, sodium hydrogen carbonate, DMF, CH_2Cl_2, ether, ethanol, chloroform, toluene and SiO_2 were commercially available from various suppliers. Bicyclohexane was distilled over sodium before use. The other reagents were used without further purification. Double-sided polished p-type silicon wafers (100) were obtained from UniversityWafer and glass substrates were obtained from PGO. The substrates were treated on both sides for 30 min in a UV/ozone chamber before use.

Bromine-terminated monolayers were prepared by immersing the wafer in a solution of 11-bromo-undecyltrichlorosilane (5 μl) in BCH (5 ml) for 5 min followed by cleaning through Soxhlet extraction in hot chloroform for 2 h. Finally, the monolayers were rinsed with chloroform and dried in a stream of air.

OTS-terminated monolayers were prepared by immersing the wafer two times in a solution of *n*-octadecyltrichlorosilane (5 μl) in BCH (5 ml) for 5 min followed by ultrasonicating in toluene for 5 min. Finally, the monolayers were rinsed with toluene and dried in a stream of air.

Nanostructured substrates were immersed in a solution of 11-bromoundecyltrichlorosilane (5 μl) in BCH (5 ml) for 5 min followed by ultrasonicating in chloroform for 5 min. Finally, the monolayers were rinsed with chloroform and dried in a stream of air.

10-Oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]antracene-9-caboxylic acid prop-2-ynyl ester, coumarin 343 (0.25 g, 0.876 mmol), propargyl alcohol (0.25 ml, 4.38 mmol) and EDC × HCl (0.5 g, 2.63 mmol) were dissolved in CH_2Cl_2 (33 ml). DMAP (0.01 g, 0.08 mmol) was added, and stirring was carried out overnight at room temperature. The resulting orange solution was washed with 33 ml of saturated aqueous $NaHCO_3$ and 17 ml of water. The aqueous layer was extracted with CH_2Cl_2 (2 × 17 ml). The organic layers were combined and dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure to yield an orange residue that was purified by flash chromatography (SiO_2, Et_2O as eluent).

^1H NMR (400 MHz, $CHCl_3$, 298 K): $\delta = 1.93$–2.00 (m, 4H, $2CH_2$), 2.49 (t, 1H, $^4J = 2.4$ Hz, $C{\equiv}CH$), 2.74–2.77 (m, 2H, CH_2), 2.85–2.89 (m, 2H, CH_2), 3.31–3.36 (m, 4H, CH_2N), 4.88–4.89 (d, 2H, $^4J = 2.8$ Hz, OCH_2), 6.94 (s, 1H, CH_{vinyl}), 8.37 (s, 1H, CH_{aryl}).

UV/vis (CH_2Cl_2): $\lambda_{max}/nm = 229, 266, 298, 442$.

Bromine-terminated silica and glass substrates were immersed in a saturated solution of sodium azide in DMF for 24 h at room temperature. The substrates were then rinsed with DMF, sonicated 3 min in ethanol and 3 min in water, and dried in a stream of air. Cycloaddition reactions were carried out by immersing the azide-functionalized substrate for 24 h in a solution of 10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo[de]anthracene-9-carboxylic acid prop-2-ynyl ester (5 mg, 0.015 mmol) dissolved in 10 ml ethanol at room temperature. $CuSO_4 \times 5\ H_2O$ (0.19 mg, 7.73×10^{-4} mmol, 5 mol%) and sodium ascorbate (0.31 mg, 1.55×10^{-3} mmol, 10 mol%), each dissolved in 1 ml of water, were added as catalysts. Subsequently, the substrates were sonicated in ethanol for 3 min and dried in a stream of air.

FT-IR measurements were performed on a Tensor 37 RT from Bruker with a grazing angle set-up. Spectra were recorded at 4 cm^{-1} resolution using 500 scans and a clean silicon substrate as reference.

^1H NMR was carried out on a Varian Mercury spectrometer at 400 MHz at 25 °C. Chemical shifts were given in ppm downfield from TMS.

UV/vis spectra were recorded on a Perkin-Elmer Lambda-45 spectrometer and a Perkin-Elmer Lambda-900 spectrophotometer. The modified coumarin dye was measured in CH_2Cl_2 ($c = 10^{-5}$ M, 1 cm cuvette).

XPS measurements were carried out on a VG Escalab MKII spectrometer, equipped with a dual Al/Mg Kα x-ray source and a hemispherical analyzer with a five channeltron detector. Spectra were obtained using a magnesium anode (Mg Kalpha = 1253.6 eV) operating at 480 W and a constant pass energy of 20 eV with a background pressure of 2×10^{-9} mbar. Spectra were referenced to the Si(2p) peak at 103.3 eV of the native SiO_2 layer on the substrate [33].

The chemically active surface patterns were inscribed on an *n*-octadecyltrichlorosilane monolayer self-assembled on silicon with a NT-MDT NTEGRA scanning force microscope. Voltage pulses of −10 V with respect to a grounded substrate were locally applied via a conductive, platinum-coated SFM tip (μ-Mash, CSC 35). The typical pulse duration was 20 ms per writing dot. Images and patterning were performed on the basis of a 512 × 512 pixel image.

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