Angewandte Chemie International Edition

Surface Chemistry **Hot Paper**

International Edition: DOI: 10.1002/anie.201500485
German Edition: DOI: 10.1002/ange.201500485

Macromolecular Surface Design: Photopatterning of Functional Stable Nitrile Oxides**

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Abstract: *The efficient trapping of photogenerated thioaldehydes with functional shelf-stable nitrile oxides in a 1,3-dipolar cycloaddition is a novel and versatile photochemical strategy for polymer end-group functionalization and surface modification under mild and equimolar conditions. The modular ligation in solution was followed in detail by electrospray ionization mass spectrometry (ESI-MS). X-ray photoelectron spectroscopy (XPS) was employed to analyze the functionalized surfaces, whereas time-of-flight secondary-ion mass spectrometry (ToF-SIMS) confirmed the spatial control of the surface functionalization using a micropatterned shadow mask. Polymer brushes were grown from the surface in a spatially confined regime by surface-initiated atom transfer radical polymerization (SI-ATRP) as confirmed by TOF-SIMS, XPS as well as ellipsometry.*

The controlled immobilization of biomolecules, such as proteins and peptides, onto the surface of a solid substrate with a certain size and dimension is of fundamental importance in biotechnology.[1] Microscale surface patterning with polymer brushes has recently attracted increasing attention owing to potential applications in areas such as biosensors,[2] biocompatible materials,[3] and protein immobilization.[4] Surfaces can be functionalized in a spatially controlled fashion by applying photo-induced reactions. In recent years, light-induced modular ligation reactions[5] that provide spatial control over the surface grafting and light-controlled/living radical polymerization techniques have been developed.[6] Several photo-induced reactions, including Diels–Alder,[7,8] thiol–ene,[9] thiol–quinone,[10] and thiol–yne[11] ligations, have been applied to attach functional groups and biomolecules to surfaces and to control patterning. In this line, the photogeneration of cyclooctynes,[12] nitrile imines,[13] oximes,[14] and *o*-naphthoquinone methides,[15] which can be efficiently trapped by dienophiles, has recently been reported by us and others. Furthermore, in 2013, our research group introduced a light-triggered ligation method based on the Diels–Alder reaction of photogenerated thioaldehydes as an efficient method for spatially controlled surface design.[16] The photofragmentation of phenacyl sulfides (i.e., photocaged thioaldehydes) is a mild and efficient method for the preparation of highly reactive thioaldehydes, which can be trapped in situ by dienes, nucleophiles,[17] or in a 1,3-dipolar cycloaddition with nitronate esters.[18,19]

Nitrile oxides are among the most reactive species in organic chemistry and are usually trapped by 1,3-dipolar cycloaddition reactions.[20,21] The cycloaddition between nitrile oxides and alkynes represents a metal-free ligation reaction that has been employed for polymer end-group modifications.[22] However, nitrile oxides are prepared in situ from the oxime precursors owing to their rapid dimerization to furoxans, which strongly limits their applicability in modular ligation strategies. The spontaneous dimerization to furoxans can be prevented by substituents on the aromatic ring that is attached to the nitrile oxide group. However, employing such stable nitrile oxides in cycloadditions to C=C or C≡N multiple bonds for polymer modifications requires elevated temperatures.[23,24] Only one example of a cycloaddition of a thermally generated thioaldehyde with a stable nitrile oxide has been reported to date.[25]

To address these significant barriers, we herein report, for the first time, the catalyst-free 1,3-dipolar cycloaddition of shelf-stable and functional nitrile oxides with photochemically generated thioaldehydes for end-group modifications of linear polymers as well as between small molecules in solution at ambient temperature (Scheme 1). The modular ligation reaction was subsequently adopted for the spatially resolved (dual) surface encoding of functional nitrile oxides. Furthermore, poly(oligoethylene glycol methyl ether methacrylate)

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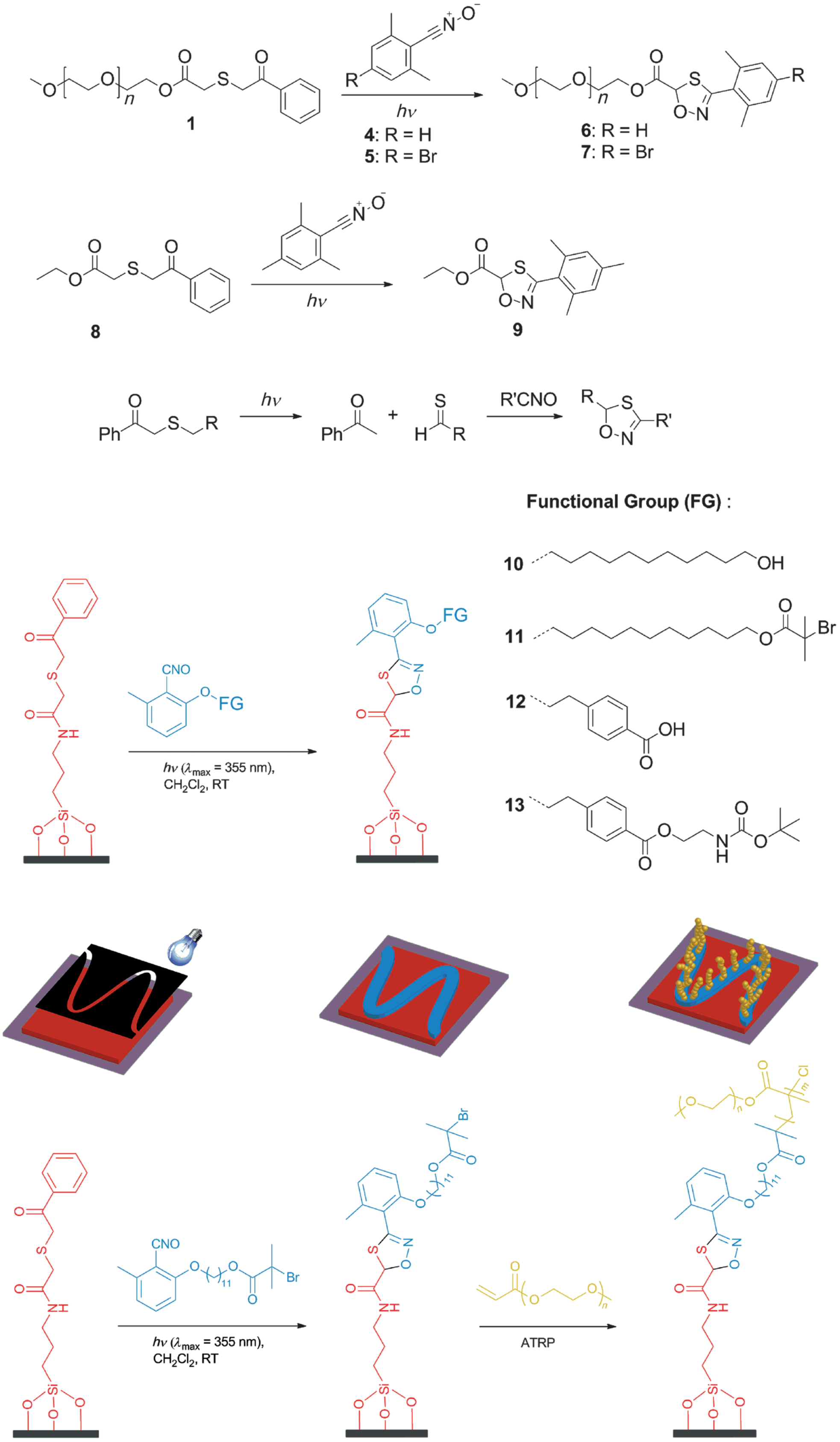
[**] C.B.-K. acknowledges funding from the Karlsruhe Institute of Technology (KIT) in the context of the BioInterfaces program of the Helmholtz association. C.R-E. thanks the Alexander von Humboldt Foundation for financial support through a Humboldt Research Fellowship for Postdoctoral Researchers and the Grant Agency of the Czech Republic (GACR; P20512G118).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201500485.

[poly(MeOEGMA)] brushes were grafted from silicon surfaces by surface-initiated atom-transfer radical polymerization (SI-ATRP)[26] using an ATRP initiator immobilized on the surface by the 1,3-dipolar cycloaddition as depicted in Scheme 1 (bottom).

The key idea of the current study is to confirm the trapping of photogenerated thioaldehydes with stable nitrile oxides and subsequently utilize the reaction for light-triggered surface encoding at ambient temperature. To establish the suitability of the concept, we performed reactions on a model system in solution to assess the reaction kinetics in detail as well as to analyze the reaction products by electrospray ionization mass spectrometry (ESI-MS) and ^{1}H and ^{13}C NMR spectroscopy. For these purposes, polymer **1** was prepared by coupling of commercially available monohydroxy-capped poly(ethylene glycol) methyl ether (mPEG-OH, 2000 g mol^{-1}) with (phenacylthio)acetic acid as previously described.[16] 2,4,6-Trimethylbenzaldehyde oxime (**2**) and 4-bromo-2,6-dimethylbenzaldehyde oxime (**3**) were prepared according to a previously reported procedure.[27]

The oxime moieties were converted into the corresponding stable nitrile oxides in the presence of triethylamine and *N*-bromosuccinimide (NBS; for details of the synthesis and characterization, see the Supporting Information). A 36 W compact fluorescent lamp ($\lambda_{max} = 355$ nm; for the emission spectrum, see the Supporting Information, Figure S36) was employed as the UV source for the photofragmentation of phenacyl sulfide end-capped polymer **1** (see Scheme 1). The latter was irradiated for two hours in



Scheme 1. Top: The photolytic cleavage of phenacyl sulfides yields acetophenone and thioaldehydes, which can be trapped with shelf-stable nitrile oxides. Middle: Surface patterning of silicon wafers: Various functional stable nitrile oxides are patterned employing a 1,3-dipolar cycloaddition reaction by irradiation through a shadow mask, also in a dual fashion. Bottom: The ATRP initiator is subsequently utilized for growing poly(MeOEGMA) on the pattern areas.

the presence of five equivalents of the respective stable nitrile oxide (**4** or **5**) in degassed dichloromethane (DCM). ESI-MS analysis (Figure S7) revealed a full shift towards higher mass-to-charge ratios. Congruent with the complete disappearance of the quasimolecular ion [**1**+Na]$^+$ and the appearance of the cycloaddition products [**6**+Na]$^+$ or [**7**+Na]$^+$, these results demonstrate the successful 1,3-dipolar cycloaddition of the stable nitrile oxide to the photogenerated thioaldehyde at ambient temperature. Integration of the mass spectral abundances after various irradiation times shows that complete conversion was achieved after 30 minutes (Figure 2, bottom). Further inspection of Figure S7 (bottom) confirms the characteristic isotopic pattern of bromine-containing compounds. The experimental and theoretical *m/z* values of all species shown in Figure S7 are presented in the Supporting Information (see Table S1) and are in excellent agreement. The formation of the 1,3-dipolar cycloaddition adduct was also confirmed by ^{1}H NMR spectroscopy (Figure S8), which indicated the disappearance of the proton resonances of the phenacyl group at $\delta = 7.91$, 7.52, and 7.41 ppm and the appearance of the aromatic proton resonance of the mesityl group at $\delta = 6.82$ ppm as well as of the signal of the 1,4,2-oxathiazole ring proton at $\delta = 6.43$ ppm. Moreover, an additional model reaction was performed with stable nitrile oxide **4** and compound **8**. The formation of the 1,4,2-oxathiazole was confirmed by ^{1}H NMR (Figure 1) and ^{13}C NMR spectroscopy (Figure S13), ESI-MS (see the Supporting Information), and FT-IR spectroscopy (Figure S14). Inspection of Figure 1 clearly indicates the generation of the 1,4,2-oxathiazole ring in excellent agreement with the ^{1}H NMR spectrum of polymer **1**. Further inspection of the corresponding ^{13}C NMR spectrum (Figure S13) clearly confirms the disappearance of the resonance of the phenacyl carbonyl carbon atom at $\delta = 194.07$ ppm and the appearance of the carbon resonance of the 1,4,2-oxathiazole ring at $\delta = 86.41$ ppm. Further evidence for the 1,3-dipolar cycloaddition was obtained by FT-IR spectroscopy (Figure S14): The band at 2293 cm^{-1}, which arises from the nitrile oxide, completely disappeared after photoligation.

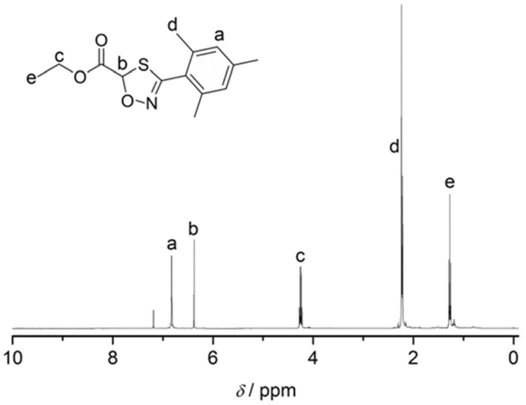


Figure 1. ^{1}H NMR spectrum of ethyl 3-mesityl-1,4,2-oxathiazole-5-carboxylate in CDCl$_3$.

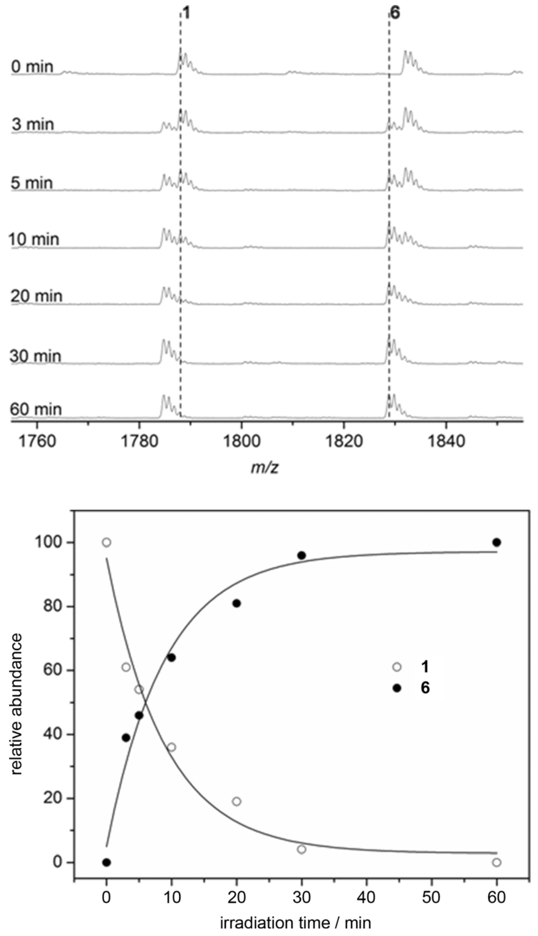


Figure 2. Top: ESI-MS spectra of phenacyl sulfide capped PEG (**1**) before and after irradiation for various periods of time in the presence of stable nitrile oxide **4**. Bottom: Plot of the conversion versus the irradiation time derived by integration of the mass spectral abundances of compounds **1** and **6**.

The kinetic investigation of the photofragmentation of **1** by integration of the mass spectral abundances after predefined irradiation times demonstrated that complete conversion was achieved after irradiation for 30 minutes (Figure 2). To investigate the efficiency of the trapping reaction, solutions of **1** and various equivalents of stable nitrile oxide **4** in DCM were degassed for five minutes and subsequently irradiated for 120 minutes at ambient temperature. The progress of the reactions was monitored by ESI-MS (Figure S9). One equivalent of nitrile oxide was sufficient to achieve close to quantitative conversion, placing the reaction among the most efficient ligation processes.[28]

The model reactions in solution demonstrate that photogenerated thioaldehydes can be efficiently trapped with equimolar amounts of shelf-stable nitrile oxides at ambient temperature. The light-based nature of the conjugation technique prompted us to translate it to the spatially constrained grafting of molecules onto surfaces to obtain molecular patterns. Surface characterization was performed by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary-ion mass spectrometry (ToF-SIMS). Phenacyl sulfide functionalized silicon wafers were prepared by employing a functional silane (see the Supporting Information and Scheme S1). The surfaces were rinsed extensively

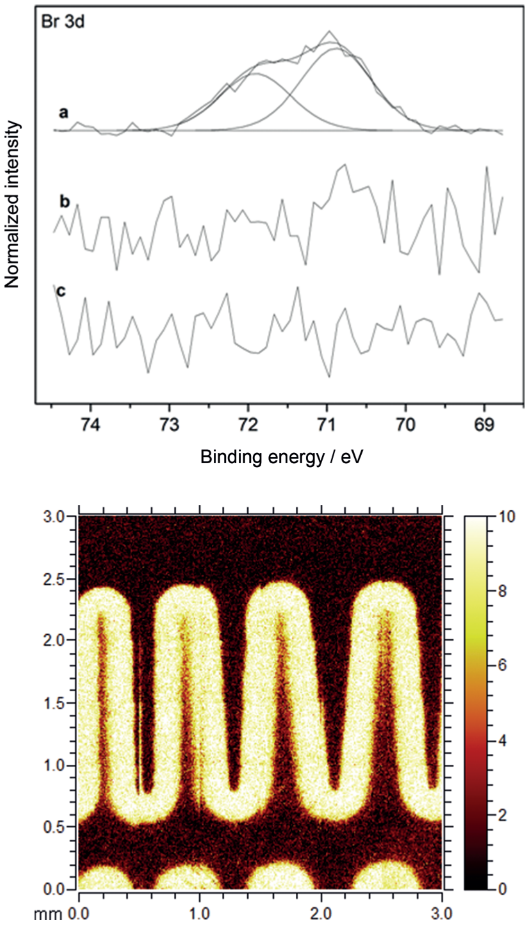


Figure 3. Top: Comparison of the Br 3d XPS spectra of a phenacyl sulfide functionalized silicon wafer after irradiation in a) a solution containing the bromine-functionalized stable nitrile oxide **5**, b) pure DCM, or c) a solution of 4-bromotoluene. Bottom: TOF-SIMS image of a silicon wafer patterned with **5** detected through its Br isotopes.

with fresh solvents (see the Supporting Information) and sonicated to remove any physisorbed material from the surface. To graft stable nitrile oxide **5** to the surface, a silicon wafer was placed in a quartz flask containing a solution of the bromine-functionalized stable nitrile oxide **5** in DCM and irradiated with a suitable light source (36 W, $\lambda_{max} = 355$ nm) for one hour while the reaction flask revolved around the lamp. XPS was employed to confirm the functionalization of the silicon wafers. The Br 3d spectrum of the surface after irradiation in the presence of the bromine-functionalized nitrile oxide displayed a pronounced bromine signal at a binding energy of 70.8 eV[29] indicating the successful surface attachment of the bromine-functionalized nitrile oxide (Figure 3 a). XPS spectra after irradiation without a stable nitrile oxide as a control experiment are shown in Figure 3 b and c. Importantly, no bromine was detected by XPS when the phenacyl sulfide functionalized surface was irradiated in pure DCM (Figure 3 b) or in the presence of 4-bromotoluene (Figure 3 c), indicating that the bromine signal observed in the XPS spectrum is exclusively associated with the covalent attachment of the nitrile oxide.

Whereas XPS can provide information on the binding situation in the irradiated areas of the substrate, ToF-SIMS imaging enables the spatially resolved analysis of molecular patterns on solid substrates. In contrast to traditional fluorescence imaging, ToF-SIMS data provide detailed information on the chemical composition, which is essential for the analysis of non-fluorescent molecules. For instance, brominated compounds with their inherent isotopic pattern can be unambiguously detected by ToF-SIMS. Therefore, bromine-containing stable nitrile oxide **5** was utilized in the current study as a molecular marker to spatially map the locally constrained surface grafting. Photopatterning was achieved by irradiation of silicon wafers that had been functionalized with photocaged thioaldehydes and immersed in a solution of **5** utilizing a shadow mask (see Figure S16 and Scheme S1). The ToF-SIMS image in Figure 3 (bottom) clearly reveals that Br^- secondary ions can only be found in the irradiated area. Therefore, the ToF-SIMS experiments confirmed that the spatially controlled surface patterning of stable nitrile oxides is possible.

In the subsequent step, it was mandatory to determine the tolerance of the photo-induced 1,3-dipolar cycloaddition with respect to various functional groups attached to the nitrile oxides to assess its scope for the covalent immobilization of various functionalities on solid substrates in a spatially resolved fashion. Thus, the hydroxy-functionalized stable nitrile oxide **10**, carboxy-functionalized stable nitrile oxide **12**, and a functional stable nitrile oxide **13** with a protected amine were also prepared (see Scheme 1 for their structures) and characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and ESI-MS. Details of the preparation of these nitrile oxides can be found in the Supporting Information. Photopatterning of each functional species was achieved by irradiation of three different silicon wafers that had been functionalized with photocaged thioaldehydes and immersed in a solution containing functional stable nitrile oxide **10**, **12**, or **13** utilizing a shadow mask. The success of the 1,3-dipolar cycloaddition reactions was unambiguously confirmed by ToF-SIMS characterization (Figure 4). Characteristic mass fragments of the hydroxy-functionalized stable nitrile oxide **10** (CH_2OH^+, Figure 4 a), the carboxy-functionalized stable nitrile oxide **12** ($COOH^-$, Figure 4 b), and functional stable nitrile oxide **13** with a protected amine (CON^-, Figure 4 c) can only be found in the irradiated area, thus confirming that the incorporation of the functional groups in the meander pattern accurately corresponds to the areas irradiated through the shadow mask. Furthermore, the characteristic mass fragments of $C_8H_7NO^-$ and CSN^- are part of the newly formed 1,4,2-oxathiazole ring, which can only be found in the irradiated region (Figure S35), thus additionally confirming the formation of the heterocyclic ring. In a further step, we also confirmed the possibility of immobilizing species that contain an ATRP initiator. Polymer brushes with controlled thickness and well-defined composition and architecture can be grafted under mild conditions from surfaces containing immobilized initiators for surface-initiated atom transfer radical polymerization (SI-ATRP, see below). For this purpose, a new stable nitrile oxide functionalized with an ATRP initiator, namely **11**, was prepared and immobilized onto the silicon surface by the phototriggered

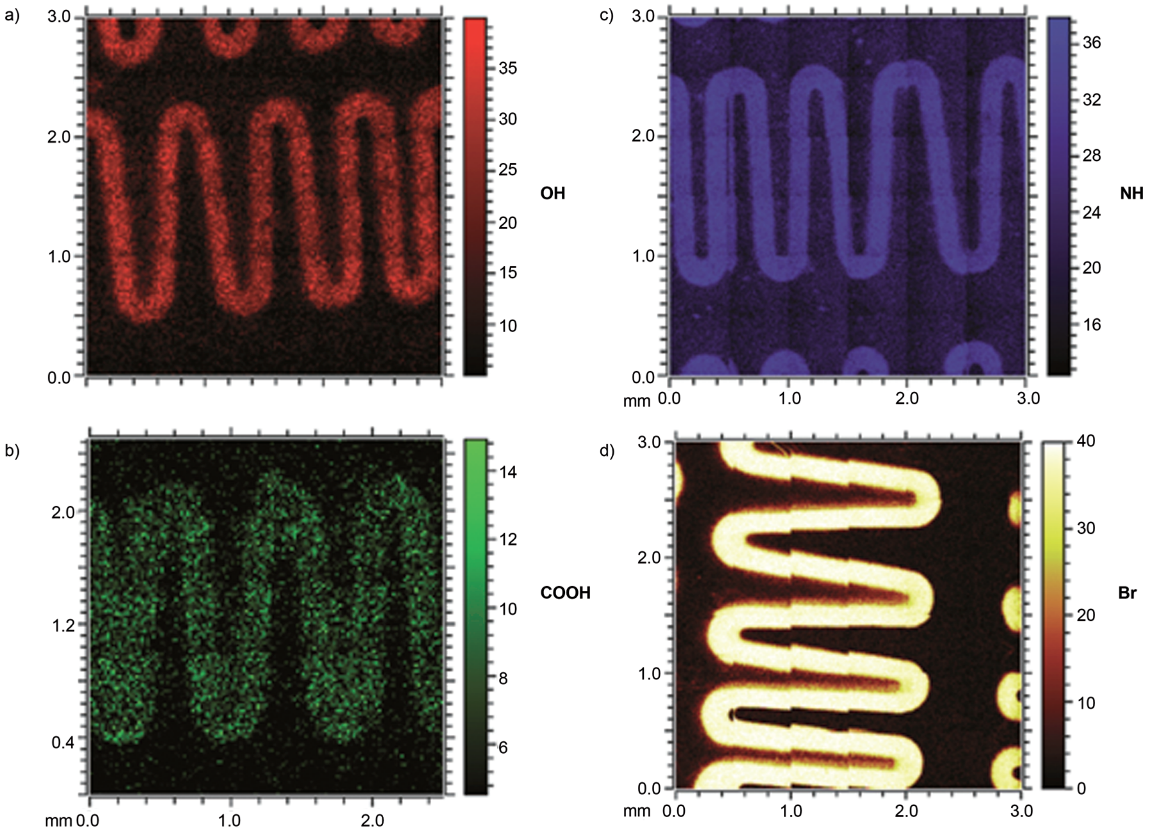


Figure 4. TOF-SIMS images of a silicon wafer patterned with a) hydroxy-functionalized stable nitrile oxide **10** (detected through the CH_2OH^+ fragment), b) carboxy-functionalized stable nitrile oxide **12** (detected through the $COOH^-$ fragment), c) functional stable nitrile oxide **13** with a protected amine (detected through the CON^- fragment), and d) a stable nitrile oxide functionalized with an ATRP initiator (**11**, detected through the Br isotopes).

1,3-dipolar cycloaddition as depicted in Schemes 1 (bottom) and S2. Details of the preparation of this stable nitrile oxide can be found in the Supporting Information. The success of the 1,3-dipolar cycloaddition reaction was unambiguously confirmed by ToF-SIMS characterization (Figure 4d). Mass fragments characteristic for bromine-containing species were solely detected in the irradiated areas.

The power of the light-induced 1,3-dipolar cycloaddition reaction for the spatially resolved encoding of functional nitrile oxides was further investigated in a dual patterning experiment. Initially, the stable nitrile oxide **13** with a protected amine was patterned onto the photocaged silicon surface. After irradiation, the surface was subjected to a typical washing procedure (see the Supporting Information), and the same silicon surface was turned by 90° and repositioned into the sample holder with the photomask. Subsequently, the silicon surface was irradiated in the presence of bromine-functionalized stable nitrile oxide **11**. In Figure 5, ToF-SIMS images of the overlay of the CNO^- and Br^- fragments are depicted. The image unambiguously confirms the ability of the photofunctional system to pattern two functional groups onto the same silicon surface. Nitrile oxide **13** was continuously patterned on the surface during the first irradiation, whereas **11** was discretely patterned on the silicon surface in the second irradiation step. The results indicate that there are no more photoactive phenacyl sulfides in the irradiated areas on the silicon surface after the first irradiation, thus confirming the highly efficient nature of the 1,3-dipolar cycloaddition on the surface. Importantly, the observation of the fragments discussed above corroborates that after the first irradiation, the photocaged thioaldehyde groups are still intact in the non-irradiated areas as they can

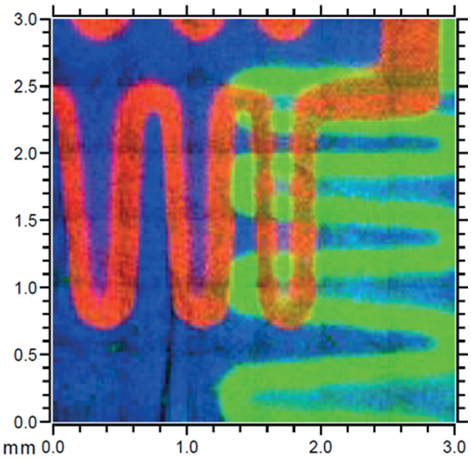


Figure 5. TOF-SIMS images of a silicon wafer patterned with both **13** and **11** (detected through the CON^- and Br^- fragments) on the same surface.

be activated in a subsequent step to enable additional functionalization.

To exemplify the power of the novel ligation technique, we polymerized poly(MeOEGMA) brushes by SI-ATRP from initiator-functionalized (**11**) surfaces (experimental details can be found in the Supporting Information). A photopatterned surface was generated for ToF-SIMS imaging, whereas surface functionalization without a shadow mask was used for XPS and ellipsometry analysis. After ten hours of polymerization, 15 nm thick brushes had been generated as determined by ellipsometry on dry samples. XPS analysis of the brushes grown from the entire surface (Figure 6, top) confirmed the successful polymerization. Compared with the surface carrying the ATRP initiator (Figure 6b), the C 1s spectrum of the polymer brushes shows a strong increase in the peak assigned to the C–O bonds at 286.4 eV,[30] which is due to the oligo(ethylene glycol) (OEG) side chains of the brush, and a decrease in the signal corresponding to the C–C bonds at 285.0 eV (Figure 6a), which results from the poly(MeOEGMA) growth. A clear signal at 289.0 eV, which was attributed to the O–C=O[30] moieties present in poly(MeOEGMA), could also be observed. As a control experiment, a silicon wafer only carrying the phenacyl sulfides was subjected to the same polymerization conditions. When no ATRP initiator has been immobilized on the surface, no polymer growth from the surface can be detected by XPS (Figure 6c). Importantly, the grafting kinetics were followed by measuring the dry thickness of the polymer after various time intervals by ellipsometry.[31] As confirmed by the linear increase in thickness with time, the SI-ATRP of poly(MeOEGMA) brushes proceeded in a well-controlled fashion (Figure S37).

The brush-patterned surfaces were characterized by ToF-SIMS (Figure 6, bottom). Characteristic mass fragments of oligo(ethylene glycol) (CH_3O^-, CHO_2^-, and $C_2H_2O_2^-$) can only be found in the irradiated area, thus confirming the growth of poly(MeOEGMA) in the meander pattern corresponding accurately to the shadow mask.

In summary, we have demonstrated that photogenerated thioaldehydes can be efficiently trapped with readily accessible shelf-stable nitrile oxides at ambient temperature. The introduced method allows the functionalization of polymers by 1,3-dipolar cycloadditions of nitrile oxides under mild conditions, that is, at ambient temperature in the absence of any additives and, importantly, in equimolar ratios, for the first time. We confirmed that the spatially controlled surface patterning of various functional nitrile oxides, such as variants with hydroxy, bromine, carboxy, or protected-amine substituents, can be realized—also in a dual co-grafting fashion—employing surface-attached phenacyl sulfides. The potential of the strategy was further demonstrated by the immobilization of an ATRP initiator and subsequent growth of poly(MeOEGMA) brushes exclusively in the previously irradiated area. The living behavior of the SI-ATRP was confirmed by ellipsometry. We envisage that considering its efficiency, equimolarity, and mild conditions, this strategy will find applications in various fields, for example, for the immobilization of biomolecules or the photolithography of conducting polymers.

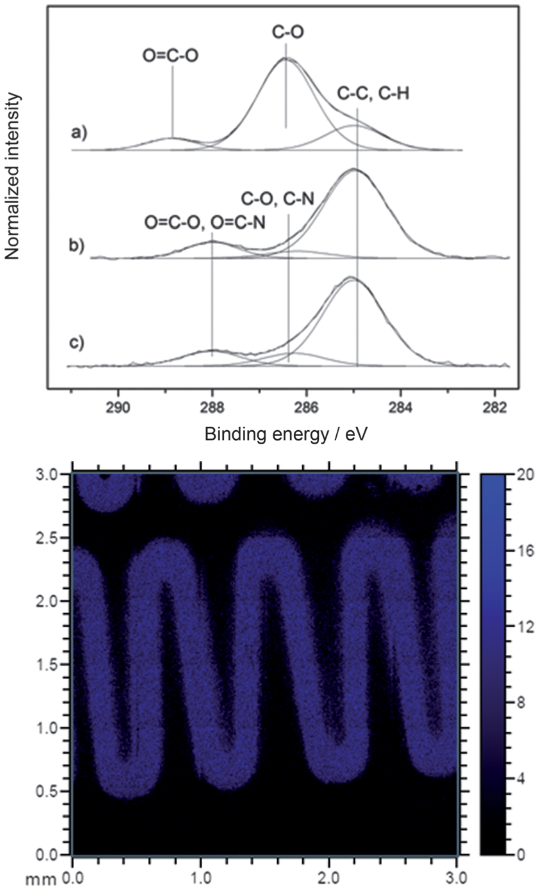


Figure 6. Top: XPS characterization and comparison of the C 1s spectra of a) the surface after SI-ATRP of MeOEGMA, and b) the ATRP initiator surface; c) control experiment. Bottom: TOF-SIMS overlay image constructed from the images of several intense PEG fragments (CH_3O^-, CHO_2^-, and $C_2H_2O_2^-$).

Keywords: modular ligation · nitrogen heterocycles · polymerization · stable nitrile oxides · surface analysis

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 5777–5783
Angew. Chem. **2015**, *127*, 5869–5875

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Received: January 18, 2015