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Chemical Surface Modification of Self-Assembled Monolayers by Radical Nitroxide Exchange Reactions

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Abstract: This article describes the application of nitroxide exchange reactions of surface-bound alkoxyamines as a tool for reversible chemical modification of self-assembled monolayers (SAMs). This approach is based on radical chemistry, which allows for introduction of various functional groups and can be used to reversibly introduce functionalities at surfaces. To investigate the scope of this surface chemistry, alkoxyamines with different functionalities were synthesized and were then applied to the immobilization of, for example, dyes, sugars, or biotin. Surface analysis was carried out by contact angle, X-ray photoelectron spectroscopy, and fluorescence microscopy measurements. The results show that this reaction is highly efficient, reversible, and mild and allows for immobilization of various sensitive functional groups. In addition, Langmuir–Blodgett lithography was used to generate structured SAMs. Site-selective immobilization of a fluorescent dye could be achieved by nitroxide exchange reactions.

Keywords: alkoxyamines · monolayers · exchange reactions · radicals · self assembly · surface chemistry

Introduction

Self-assembled monolayers (SAMs) with specific functional groups as head groups are of high interest for many research fields. Surface properties such as wettability, friction, adhesion, or biocompatibility can be tuned as a function of the surface functionalities.[1] Thiols on gold and silanes on silicon have been shown to form stable self-assembled monolayers. A broad variety of standard organic reactions have been conducted at SAMs including alkene oxidations, amino acylations, imine bond formations, alcohol acylations, and epoxide openings with alcohols and amines.[1d,f,g] Other methods for chemical surface modification have been studied, such as electrochemical and photochemical transformations, which allow the in-situ-modulation of SAMs to provide dynamic surfaces.[1c,d,2] Patterning of SAMs is crucial for various applications and can be achieved by different lithographic techniques, for example, photolithograpy, microcontact printing, or scanning-probe lithography.[1f,g]

Recently, we reported the use of thermal radical carboaminoxylations at olefin-terminated SAMs for chemical conjugation of silicon surfaces with different functionalized alkoxyamines.[3] In these processes, the generation of a radical occurs by thermal C–O bond homolysis of a starting alkoxyamine. Subsequent addition of the carbon-centered radical onto the olefin-containing SAM is followed by an irreversible nitroxide-trapping to afford the carboaminoxylation product.[4,5] This approach allows the efficient introduction of various functional groups at SAMs. Importantly, the radical approach is complementary to commonly used ionic-bond-forming reactions at surfaces.

Reversible covalent bond formation has been applied intensively in supramolecular chemistry, yet it is not investigated well in surface chemistry.[6] Reversible radical exchange reactions, which belong to the class of dynamic covalent chemistry, have not been applied at SAMs to date.[7] Thermal nitroxide exchange reactions have already been utilized for the synthesis and functionalization of polymers and polymer brushes.[8] Additionally, these reactions have been applied to the generation of dynamic covalent polymers as well as to the synthesis of dynamic covalent macrocycles.[8d,e,g] Recently, we reported the use of nitroxide exchange reactions for reversible assembly of organic–inorganic hybrid microcrystals.[8n] Herein, we describe the application of radical nitroxide exchange reactions at SAMs as a reversible process to introduce a broad variety of functional groups at silicon surfaces (Scheme 1).

Thermal C–O-bond homolysis in alkoxyamines leads to transient carbon-centered radicals and persistent nitroxides. In these processes, the radicals diffuse out of the solvent cage and, controlled by the persistent radical effect (PRE), undergo selective cross-coupling to reform the alkoxy-

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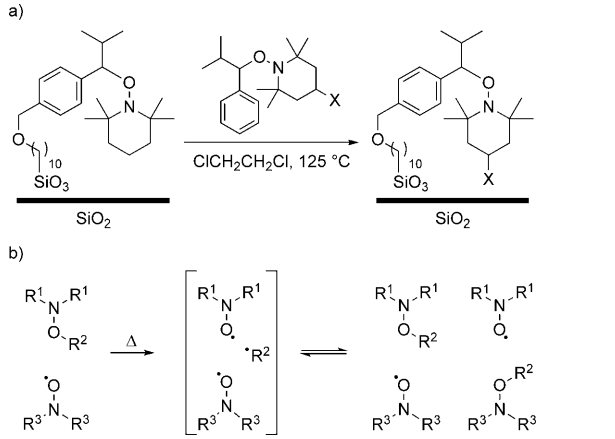
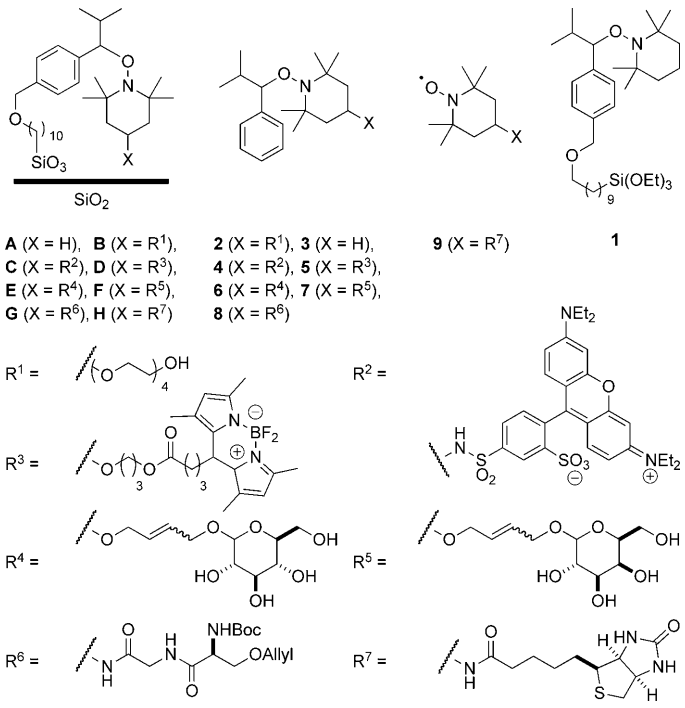


Scheme 1. Surface nitroxide exchange reaction (a) and nitroxide exchange reaction by C–O-bond homolysis of alkoxyamines (b).

amine.[9] Thermolysis in the presence of an additional nitroxide or alkoxyamine leads to crossover of the nitroxide moieties in the alkoxyamines (Scheme 1).

Results and Discussion

The modification of silicon surfaces by nitroxide exchange reactions demands the synthesis of silanes with alkoxyamine head groups for subsequent SAM formation. We synthesized the alkoxyamine **1** with a silane functionality and prepared alkoxyamine-terminated SAMs using oxidized silicon wafers, as previously reported (Scheme 2, wafer **A**).[10] Surface nitroxide exchange reactions were conducted by subjecting these alkoxyamine terminated SAMs to a solution of $ClCH_2CH_2Cl$ containing an additional alkoxyamine, which contained a different nitroxide moiety under heating. Functionalized 2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO) nitroxide derivatives, generated in situ by homolysis of the corresponding soluble alkoxyamines, should undergo nitroxide exchange with the surface-bound alkoxyamines. As the concentration of functionalized nitroxides in solution should be intrinsically much higher compared to the concentration of unfunctionalized TEMPO nitroxide that is liberated from the surface bound alkoxyamine **1**, quantitative nitroxide exchange at the surface should be achieved. For our studies, alkoxyamine and nitroxide conjugates **2**–**9** were prepared (see the Supporting Information) and used in surface nitroxide exchange reactions to generate chemically modified wafers **B**–**H** (Scheme 2). Initial reactions were conducted by placing a wafer of type **A** in a solution of alkoxyamine **2** in $ClCH_2CH_2Cl$ (10 mmol L^{-1}) under an argon atmosphere. The reaction time was systematically varied and analysis of the modified surface was performed by contact angle (CA) measurements. The starting SAM (wafer **A**) showed a CA_{adv} (CA_{adv} = advancing contact angle) of 87±2°. We found that after a reaction time of 1 h, a significant change of the CA was observed (Table 1, entry 2). As expected for a successful reaction with a tetraethyleneglycol (TEG) alkoxyamine, the surface polarity increased.



Scheme 2. Chemically modified silicon surfaces **A**–**H** and molecular structures of surface bound alkoxyamine **1**, alkoxyamines **2**–**8** and nitroxide **9** used in nitroxide exchange reactions.

Table 1. Radical nitroxide exchange reaction using wafer **A** and alkoxyamine **2** in $ClCH_2CH_2Cl$ at 125 °C.

Entry	*t* [h]	CA_{adv} [°][a]	CA_{rec} [°][b]	O[c] [%]	N[c] [%]	C[c] [%]	Si[c] [%]	C–C/C–O
1	0	87±2	68±2	21.8	0.6	19.7	57.8	7:1
2	1	64±1	45±1	24.2	–	26.1	49.7	5:1
3	5	64±1	44±1	24.6	–	22.9	52.5	4:1
4	10	66±2	45±1	24.5	–	23.5	52.0	4:1
5	20	63±4	44±2	24.5	–	23.8	51.7	3:1
6[d]	20	92±3	38±2	25.9	0.1	22.9	55.0	5:1

[a] CA_{adv} = advancing contact angle; [b] CA_{rec} = receding contact angle. [c] Photoelectron spectroscopy (XPS). [d] Wafer **B** (resulting from entry 4) and alkoxyamine **3** were used in the nitroxide exchange reaction.

Analysis of the CA after 5 h, 10 h and 20 h did not indicate any further change (Table 1, entries 3–5). Since the CA is not sensitive enough to properly evaluate the success of the surface nitroxide exchange reaction, we used X-ray photoelectron spectroscopy (XPS) to obtain more detailed information on the reaction progress. In particular, we used high resolution XPS C 1 s signals to determine the C–C/C–O bond relations before and after surface modification. Unfortunately, it was impossible to relate the amount of carbon and nitrogen by using XPS, due to the large error (see the Supporting Information). XPS revealed a C–C/C–O bond ratio of 7:1 (calculated C–C/C–O-bond ratio: 9:1, see the Supporting Information) for the starting SAM **A** (Table 1, entry 1).

In contrast to the CA measurements, in which no change was detected by extending reaction time from 1 h to 20 h, the C–C/C–O-bond ratio measured by XPS changed from 5:1 after 1 h to 3:1 after 20 h. A further extension of the reaction time did not lead to any significant change of the C–C/C–O bond ratio. This value agrees well with the calculated ratio of a fully exchanged wafer (Table 1, entry 5). All following experiments were therefore conducted for 20 h. The nice feature of our approach is the dynamic character of the nitroxide exchange reaction. To document reversibility we subjected wafer **B** to a large excess of **3** under the optimized conditions (Table 1, entry 6). The values of the XPS- and CA measurements are in qualitative agreement to those of wafer **A**. This indicates that the reversible nitroxide exchange reactions can be applied to switch surface properties, for example, from hydrophobic (**A**) to hydrophilic (**B**) and back to hydrophobic (**A**).

To investigate the scope of the nitroxide exchange reaction at surfaces we synthesized alkoxyamines **4** and **5** attached to fluorescent dyes (see the Supporting Information). We used wafers containing a 300 nm oxide layer to prevent fluorescence quenching for the formation of **A** and exposed them to alkoxyamine **4** under the optimized reaction conditions. The success of the reaction was readily confirmed by fluorescence microscopy, after extensive washing of the modified wafer with CH_2Cl_2 and water to remove the physiadsorbed dye (Figure 1). Using alkoxyamine **5** under identical conditions we also observed fluorescence at the silicon surfaces, which provides further support for the success of the reaction. Furthermore, we analyzed the resulting surfaces by using XPS, which revealed a significant change of surface composition (see the Supporting Information).

We also performed an exchange reaction on wafer **A** with the rhodamine conjugate **4** at room temperature to confirm that immobilization of the fluorescent dye is caused by thermal nitroxide exchange reaction and not as a result of physiadsorption. In fact, in that case we did not observe any fluorescence at the surface after careful washing of the wafer (see the Supporting Information).

A further important issue was if the surface nitroxide exchange reactions could be applied to prestructured SAMs. For the spatially controlled attachment of alkoxyamine **1** to a silicon wafer we applied Langmuir–Blodgett (LB) lithography. It was shown that mixed monolayers of L-α-dipalmitoyl-phosphatidylcholin (DPPC) and dyes can be transferred by the LB technique onto a surface in regular stripes with sub-micrometer lateral dimension.[11] As reported, regular stripes of covalently on-wafer-bound alkoxyamine **1** can be obtained by LB-transfer of a mixed monolayer of DPPC and **1** with subsequent covalent attachment of **1** by trans-silyletherification and removal of the structure-determining non-covalently-bound DPPC (wafer **I**, Scheme 3).[10a]

Pleasingly, we observed site-selective immobilization of rhodamine at the prestructured SAM (wafer **J**) by treatment of **I** with alkoxyamine **4** at 125 °C for 20 h. Success of the exchange process was readily confirmed by fluorescence microscopy (see Figure 1 and the Supporting Information)

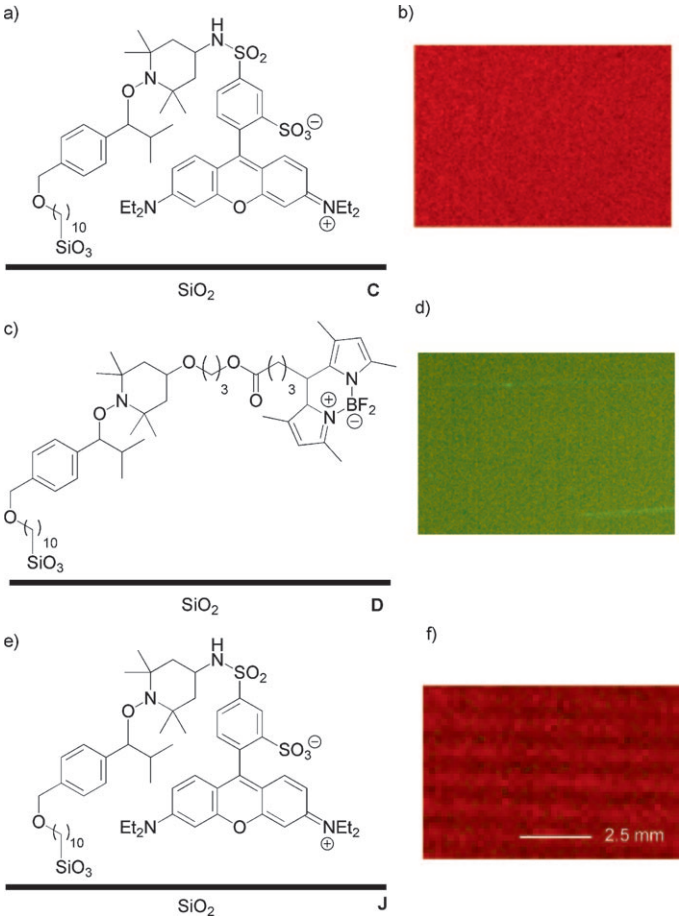
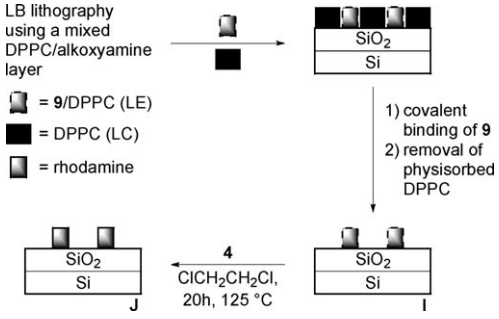


Figure 1. Structure of rhodamine (a), bodipy (c) and site-selective with rhodamine (e) modified silicon surfaces. Fluorescence images of rhodamine (b), bodipy (d) and site-selective rhodamine (f) modified SAMs.



Scheme 3. Formation of patterned alkoxyamine SAMs (LC = liquid condensed phase, LE = liquid expanded phase) and nitroxide exchange reaction at LB prestructured SAMs with surface-bound alkoxyamine **1** and soluble alkoxyamine **4**.

It is important to note that our nitroxide exchange reaction is based on radical chemistry that tolerates many functional groups. Moreover, radical chemistry is orthogonal to ionic chemistry. The introduction of sensitive functionalities, for example, unprotected alcohols, should be possible by this methodology because the surface nitroxide exchange reaction can be conducted under neutral conditions. In con-

trast to ionic reactions, no protecting group strategies are required applying our approach. For this purpose, we investigated the immobilization of unprotected sugar conjugates **6** and **7** using surface nitroxide exchange reactions.

The success of the surface reaction was followed by CA measurements and XPS studies (Table 2). The immobilization of sugar conjugates **6** and **7** caused a significant decrease of the CA (wafer **E** and **F**; Table 2, Figure 2), and also a significant increase of the C–O content at the surface as measured by high resolution XPS C 1 s (Figure 2). The C–C/C–O bond ratio detected by XPS changed from 7:1 (wafer **A**) to 1:1 (wafer **E** and **F**) after 20 h, which is a much higher value than theoretically expected for a quantitative exchange reaction. Due to the fact that the C–O bonds of the sugar moiety are at the top of the SAM they are therefore close to the analyzed interface. Signals of bonds at the interface appear in XPS generally stronger, due to a higher mean free path of the corresponding electrons.[12]

Table 2. Radical nitroxide exchange reaction using wafer **A** and bioconjugates **6**, **7**, **8**, and **9** (wafers **E**, **F**, **G**, and **H**) in $ClCH_2CH_2Cl$ at 125 °C.

Wafer	CA_{adv} [°][a]	CA_{rec} [°][a]	O [%]	N [%]	C [%]	Si [%]	C–C/C–O
A	87±2	68±2	21.8	0.6	19.7	57.8	7:1
E	40±3	<10	27.3	0.9	42.3	28.3	1:1
F	42±4	<10	30.0	0.8	35.6	30.3	1:1
G	73±2	34±1	29.3	0.6	16.3	53.1	5:1
H	68±4	34±1	27.5	0.6	20.5	49.8	5:1

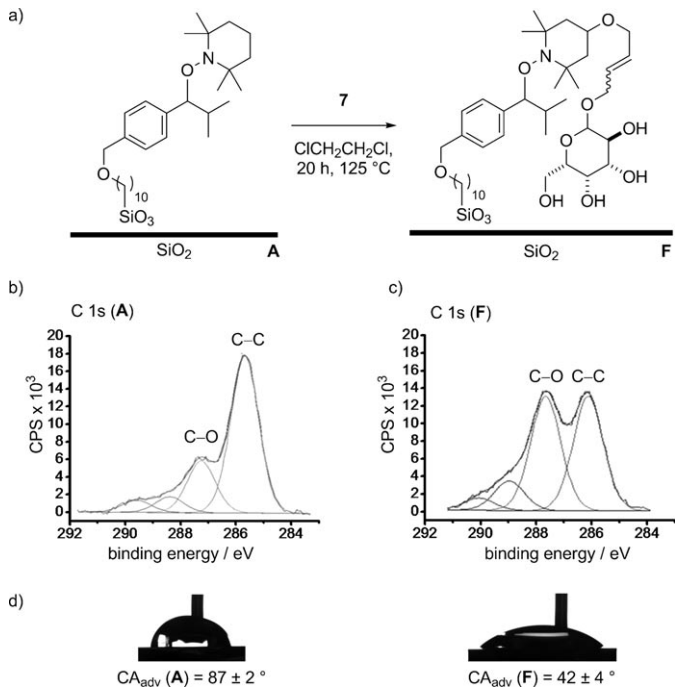


Figure 2. Surface reaction scheme for the immobilization of sugar conjugate **7** (a), high resolution XPS C 1 s before (b) and after (c) surface reaction. Water droplet on a hydrophobic (**A**) and hydrophilic (**F**) surface (d).

We were also interested in the immobilization of other biologically important functionalities. Along this line, we were able to immobilize a hydrophobic dipeptide using alkoxyamine **8**, as confirmed by CA measurements and XPS. The CA changed from 87±2 to 73±2° and the high resolution XPS C 1 s revealed an increase of the C–O bond content (wafer **G**; Table 2) at the surface. We also generated biotinylated surfaces using the nitroxide exchange reaction. However, in that case we had to use the free nitroxide **9** instead of the corresponding alkoxyamine, due to decomposition of the alkoxyamine during surface reaction. The measurement of the CA and analysis by XPS indicate the success of the surface reaction (wafer **H**; Table 2). This experiment shows that nitroxide exchange reactions can be conducted either with soluble alkoxyamines or directly with the corresponding free nitroxides, which was even superior to alkoxyamines in the latter case.

Biotinylated surfaces are of high interest as they can be used for the immobilization of streptavidin and, more generally, for the generation of protein biochips. To this end, we treated wafer **H** with a fluorescent-dye-tagged streptavidin (Oyster-488 conjugate) and observed successful protein immobilization as analyzed by fluorescence microscopy (see the Supporting Information). The control experiment on the unmodified surface revealed no protein binding after careful washing.

Another point of interest was the proper quantification of the surface nitroxide exchange reactions, since CA and XPS does not allow for a highly accurate determination of the reaction yield. To this end, we prepared SAMs using alkoxyamine **10** based on a fluorinated nitroxide **11**. The resulting wafer **K** contains fluorine atoms and was verified by XPS (1.6 At%, Figure 3). Wafer **K** was treated with TEMPO under optimized conditions and the resulting monolayer was again, after careful washing, analyzed by XPS. In fact, even fluorine, which is readily detected by XPS, could not be identified anymore at the surface. Wafer **A** was reacted with nitroxide **11** under the optimized conditions as a control experiment.[13] In that case, fluorine was again detected by XPS at the surface (1.5 At%, see the Supporting Information). Therefore, we conclude that, at least for that particular reaction, a highly efficient nitroxide exchange at the surface occurred. Since we used similar conditions for all other exchange reactions, we assume that these processes generally occur with high efficiency at the surface (Figure 3).

Conclusion

We have reported the first application of nitroxide exchange reactions at SAMs. Due to its reversible character, functionalities can be removed and new functionalities can be introduced in the same operation. One important advantage of this approach is that nitroxide exchange reactions can be conducted under neutral conditions. They are orthogonal to ionic reactions and various functional groups are tolerated. However, reaction temperatures are still relatively high, so

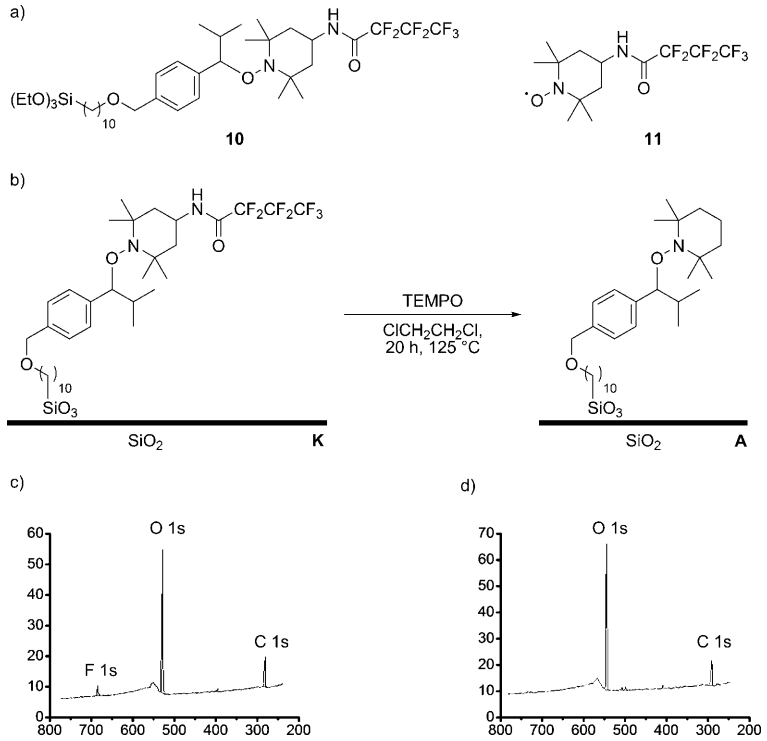


Figure 3. Molecular structure of alkoxyamine **10** and nitroxide **11** (a) and surface reaction Scheme for nitroxide exchange reaction (b) XPS analysis of **K** (c) and **A** (d).

decreasing the reaction temperature remains a future task.[8n,14] Moreover, it is possible to apply this reaction to prestructured SAMs for site-selective immobilization of interesting functionalities. We believe that nitroxide exchange reactions are very well suited for reversible modification of surfaces with a broad variety of substrates. As we have demonstrated, the immobilization of various biologically interesting moieties is possible by this method.

Experimental Section

General: The experimental procedure for the preparation of alkoxyamine **1** and **10** and the preparation of alkoxyamine and nitroxide conjugates **2**–**9** and **11** are described within the Supporting Information. XPS spectra and all detailed data of the surface characterization are also part of the Supporting Information. XPS was performed on a type ESCALAB 250 from Thermo VG Scientific. Monochromatic Al K X-rays were used (15 kV, 150 W, 500 μm). If necessary charge compensation was done using a Flood-Gun (e^- Energy≈6 eV/0.05 mA current). Spectra were measured using pass energy of 80 eV for survey spectra and 30 eV for core level spectra. A magnetic lens was used to increase the signal to noise ratio. Dynamic contact angles were determined on Krüss DSA 100 using Krüss DSA 2 software and epifluorescence microscopy images were measured with an Olympus Reflected Fluorescence System CKX41 microscope equipped with excitation and emission filters and a color Kappa Opto-Electronics camera. Silicon wafers were received from Wacker Siltronic AG and were cleaned by ultrasonication in solvents of increasing polarity (pentane, CH_2Cl_2, acetone, methanol, ultrapure water) for 5 min (wafer with an 300 nm oxide layer were used with alkoxyamine **4**, **5** and nitroxide **9**). The clean surfaces were oxidized with freshly prepared piranha solution (conc. H_2SO_4/H_2O_2 (aq., 30%) = 7:3) for 45 min. The surfaces were rinsed again with ultrapure water and blown dry with argon.

General procedure: The oxidized wafers were placed into a sealed tube and solutions of **1** or **10** were added (1.5 mL, 10 mmol in absolute toluene). The mixture was allowed to stand at 60 °C for three days. The surfaces were rinsed with CH_2Cl_2 followed by soxhlet extraction for at least 14 h in CH_2Cl_2. The surface nitroxide exchange reaction was conducted with alkoxyamines **2**–**8**, TEMPO, or nitroxide **9** and **11** in $ClCH_2CH_2Cl$ (1.5 mL, 10 mmol L^{-1}). The reaction mixture was degassed with argon for 5 min and alkoxyamine-functionalized wafers were added to the solution. The reaction mixture was additionally degassed for 5 min with argon. The sealed tube was allowed to stand at 125 °C for 20 h (in the case of alkoxyamine **2** the reaction time was varied from 1, 5, 10 and 20 h). The wafers were then carefully washed with CH_2Cl_2 and cleaned by ultrasonication and continuous extraction with CH_2Cl_2 for at least 14 h. The wafers were then dried in an argon flow and analyzed by contact angle measurements, XPS or when possible by fluorescence microscopy.

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