Supporting Information for

Spatially Controlled Surface Immobilization of Nucleophiles via Trapping of Photo-Generated Thioaldehydes

Thomas Pauloehrl,^a Alexander Welle,^b Kim K. Oehlenschlaeger,^a and Christopher Barner-Kowollik,^{a,c}*

^a Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe and Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany, <u>christopher.barnerkowollik@kit.edu;</u> Phone: (+49) 721 608 45741, Fax: (+49) 721 608 45740.

^b Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Hermannvon-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

^c Soft Matter Synthesis Laboratory, Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1,76344 Eggenstein-Leopoldshafen, Germany.

Materials

Organic synthesis and surface functionalization performed at the KIT (Karlsruhe)

2-(4-bromophenyl)ethanamine (98 %, Sigma Aldrich), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimid hydrochlorid (EDC hydrochloride, 98 %, Alfa Aesar), 3-(triethoxysilyl)propan-1amine (98 %, Abcr), (4-bromophenyl)methanethiol (98%, Alfa Aesar), 4dimethylaminopyridine (DMAP, 99 %, Abcr), acetone (VWR, Normapur), acetonitrile (AcN, HPLC grade, Acros), dichloromethane (DCM, 99.5 %, VWR for synthesis), diethyl ether (99.9 %, VWR), ethanol (VWR, Normapur), ethyl acetate (Normapur grade, VWR), hydrochloric acid (37 % in water (v/v), reinst, Roth), hydrogen peroxide (35 % v/v in water, Merck), N,N'-dicyclohexylcarbodiimide (DCC, 99 %, Acros), n-hexane (Normapur grade, VWR), N.N-diisopropylethylamine (DIPEA, 99 %, Alfa Aesar), magnesium sulfate (> 99 %, Roth), methanol (chromasolv, Roth), mono-functional amino end-capped poly(ethylen)glycol methyl ether (mPEG-amine, 1000 g•mol⁻¹, Alfa Aesar), octadecan-1-amine (98%, Alfa Aesar), (O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (Alfa Aesar, 99+ %), potassium carbonate (99 %, Merck), potassium hydroxide (> 86 % pellets, Fluka), sodium bicarbonate (> 99 %, Roth), sodium hydroxide (> 99 %, Roth), sulfuric acid (95 %, Roth), tetrahydrofuran (THF, multisolvent, 250 ppm BHT, Scharlau), tetrahydrofuran (VWR, 99.5 %, VWR), and toluene (99.8 %, Acros, extra dry) were used as received. Synthesis of (phenacylthio)acetic acid was synthesized according to a literature procedure (purification by recrystallization from chloroform).^{1,2} The synthesis of 2-((2-oxo-2-phenylethyl)thio)-N-(3-(triethoxysilyl)propyl)acetamide was performed according to a literature procedure.²

Characterization Techniques

Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker Avance III Microbay 400 MHz.

SEC/ESI-MS (Size-Exclusion Chromatography coupled to Electrospray Ionization-Mass Spectrometry) spectra were recorded on a LXQ mass spectrometer (ThermoFisher Scientific) equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray mode. The instrument was calibrated in the m/z range 195-1822 using a standard comprising caffeine, Met-Arg-Phe-Ala acetate (MRFA), and a mixture of fluorinated phosphazenes (Ultramark 1621, all from Aldrich). A constant spray voltage of 4.5 kV and a dimensionless sweep gas flow rate of 2 and a dimensionless sheath gas flow rate of 12 were applied. The capillary voltage, the tube lens offset voltage, and the capillary temperature were set to 60 V, 110 V, and 275 °C, respectively. The LXQ was coupled to a Series 1200 HPLC system (Agilent) that consisted of a solvent degasser (G1322A), a binary pump (G1312A) and a high-performance autosampler (G1367B), followed by a thermostated column compartment (G1316A). Separation was performed on two mixed-bead GPC columns (Polymer Laboratories, Mesopore 250×4.6 mm, particle diameter 3µm) with pre-column (Mesopore 50 \times 4.6 mm) operating at 30 °C. THF at a flow rate of 0.3 mL·min⁻¹ was used as the eluent. The mass spectrometer was coupled to the column in parallel to an RI detector (G1362A with SS420 \times A/D) in a setup described previously.³ A 0.27 mL·min⁻¹ aliquot of the eluent was directed through the RI detector and 30 μ L·min⁻¹ infused into the electrospray source after postcolumn addition of a 0.1 mM solution of sodium iodide in methanol at 20 μ L·min⁻¹ by a micro flow HPLC syringe pump (Teledyne ISCO, Model 100DM). The polymer solutions (20 μ L) with a concentration of ~ 1.0 mg·mL⁻¹ were injected into the HPLC system.

ToF-SIMS (time-of-flight secondary ion mass spectrometry) was performed on a ToF-SIMS instrument (ION-TOF GmbH, Münster, Germany) equipped with a Bi cluster liquid metal primary ion source and a non-linear time of flight analyzer. Samples were rinsed and sonicated in HPLC grade water (Carl Roth) prior to analysis. The Bi source was operated in the "bunched" mode providing Bi_1^+ or Bi_3^+ ion pulses at 25 keV energy and a lateral resolution of approx. 4 µm. The short pulse length allowed for high mass resolution to analyze the complex mass spectra of the immobilized organic layers. Images larger than the maximum deflection range of the primary ion gun of 500×500 µm² were obtained using the manipulator stage scan mode. Negative polarity spectra were calibrated on the C⁻, CH⁻, CH₂⁻ peaks. Positive polarity spectra were calibrated on C⁺, Si⁺ and small hydrocarbon peaks. Primary ion doses were kept below 10¹¹ ions/cm² (static SIMS limit).

UV/Vis spectra were recorded on a Varian Cary 300 Bio spectrophotometer.

Synthesis

Synthesis of N-octadecyl-2-((2-oxo-2-phenylethyl)thio)acetamide



600 mg (2.9 mmol; 1.0 eq.) (phenacylthio)acetic acid, 770 mg (2.9 mmol, 1.0 eq.) octadecan-1-amine and 850 mg (4.40 mmol, 1.5 eq.) EDC hydrochloride were dissolved in 10 mL predried DCM. 100 mg (0.82 mmol, 0.12 eq.) of DMAP was added and the solution was stirred overnight. The reaction mixture was diluted with 30 mL of water and the organic layer was subsequently washed with 2×30 mL of diluted aqueous HCl and 2×30 mL of saturated aqueous NaHCO3. The organic layer was dried over magnesium sulfate. The solvent was removed under reduced pressure and 580 mg (1.3 mmol, 45 %) of N-octadecyl-2-((2-oxo-2phenylethyl)thio)acetamide was obtained as a white solid after recrystallization from ethanol. 1H NMR (CDCl3, 400 MHz, δ) 7.96 (d, J = 7.9 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 6.76 (bs, 1H), 3.95 (s, 2H), 3.29-3.18 (m, 4H), 1.55-1.43 (m, 2H), 1.36-1.14 (m, 28H), 0.88 (t, J = 6.4 Hz, 3H) ppm; 13C NMR (CDCl3, 101 Mhz, δ) 194.31 (m), 168.02 (l), 135.13 (k), 134.02 (j), 129.01 (i), 40.05 (h), 38.31 (g), 36.15 (f), 32.07 (e), 29.9-29.4 (d), 27.07 (c), 22.83 (b), 14.26 (a) ppm.



Figure S1. ESI-MS spectrum of *N*-octadecyl-2-((2-oxo-2-phenylethyl)thio)acetamide.



Figure S2. ¹H-NMR of *N*-octadecyl-2-((2-oxo-2-phenylethyl)thio)acetamide.in CDCl₃. The peak at 1.6 ppm corresponds to water traces in the NMR solvent.



Figure S3. ¹³C-NMR of *N*-octadecyl-2-((2-oxo-2-phenylethyl)thio)acetamide.in CDCl3.

Synthesis of 2-((2-oxo-2-phenylethyl)thio)-N-(3-(triethoxysilyl)propyl)acetamide



The synthesis of phenacyl sulfide (FAS) containing silane 2-((2-oxo-2-phenylethyl)thio)-N-(3-(triethoxysilyl)propyl)-acetamide was performed according to a literature procedure.² ESI-MS: $[\mathbf{M}+\mathrm{Na}]^+ m/z \exp = 436.2$ and m/z theo. $[\mathbf{M}+\mathrm{Na}]^+ = 436.2$ (see Figure S4).



Figure S4. ESI-MS spectrum of 2-((2-oxo-2-phenylethyl)thio)-*N*-(3-(triethoxysilyl)propyl)-acetamide.

Synthesis of phenacyl sulfide (FAS) mono-functional amino end-capped poly(ethylen)glycol methyl ether 1

126 mg (0.6 mmol; 4.0 eq.) (phenacylthio)acetic acid, 250 mg (mPEG-amine, 1000 g•mol⁻¹, 0.15 mmol, 1.0 eq.) mono-functional amino end-capped poly(ethylen)glycol methyl ether, and 62 mg (0.30 mmol, 2.0 eq.) DCC were dissolved in 5 mL pre-dried DCM. 7 mg (0.06 mmol, 0.40 eq.) DMAP was added and the solution was stirred overnight. Precipitated urea was filtered off and the solvent was removed under reduced pressure. The polymer **1** was obtained by re-dissolution in DCM by precipitation in cold diethyl ether. To remove the starting material, the solid was suspended in 3 mL de-ionized water and filtered through a 0.45 mm PTFE standard GPC filter (note: this step drastically reduced the yield of the synthetic step, since the polymer is hardly water solvable. The excess of (phenacylthio)acetic acid is S8

however efficiently removed). 22 mg of polymer 1 were obtained by removing the solvent via freeze-drying.

Note: The procedure can also be performed by exchanging the coupling reagent DCC with EDC hydrochloride (3 eq.). After the reaction, the product mixture (dissolved in DCM) is diluted with water and the organic layer is washed with diluted aqueous HCl (2×10 mL) and saturated aqueous NaHCO₃ (2×10 mL).



Figure S5. ESI-MS spectrum of PEG-model system 1.

Irradiation Methods and Experiments

Irradiation methods

The samples to be irradiated were placed on a metallic disk revolving around a compact lowpressure fluorescent lamp (Philips CLEO Compact PL-L, $\lambda_{max} = 355$ nm), the emission spectrum is included in Figure S6) at a distance of 40–50 mm in a custom-built photoreactor (Figure S7).



Figure S6. a) Emission spectrum of the employed compact low-pressure fluorescent lamp (36W, Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, dotted line) and absorption spectrum of the phenacyl sulfide (FAS) containing *N*-octadecyl-2-((2-oxo-2-phenylethyl)thio)acetamide (0.021 mol·L⁻¹, solid line). b) Experimental determination of the extinction coefficient of the FAS moiety at $\lambda_{max} = 335$ nm (dotted line, 350 L·mol⁻¹·cm⁻¹) and at the emission maximum of

the employed lamp ($\lambda = 355$ nm, solid line, 200 L·mol⁻¹·cm⁻¹). The quantum yield for the fragmentation of phenacyl sulfides lies between 0.2-0.4 (depending on their structure).⁴



Figure S7. Drawing of the custom-built photoreactor employed in the current study.





Irradiation experiments in solution

Overall concept for light-triggered modifications of 1



Scheme S1. Overall photo-triggered strategy for the attachment of amines (A), hydroxylamines (B) and thiolates (C) to phenacyl sulfide model system 1.



Figure S9. Full ESI-MS single charged spectra of a phenacyl sulfide (FAS) end-capped polymer 1 and after irradiation for 1 hour with nucleophiles (2 molar eq.). The reaction with 2-(4-bromophenyl)ethanamine yields imine 2 and the thioamide fragment 2' (note the characteristic isoptopic pattern of the bromine species), whereas quantitative formation of 3 observed for the in-situ photoconjugation was one-pot with O-(2,3,4,5,6pentafluorobenzyl)hydroxylamine hydrochloride. Disulfide 4 formed by treatment with (4bromophenyl)-methanethiol and N.N-diisopropylethylamine (DIPEA) (note the characteristic isoptopic pattern of the bromine species, hydrogen peroxide was added directly before measurement to reverse the partially formation of thiols from disulfide reduction)

Photo-triggered reaction of 1 with 2-(4-bromophenyl)ethanamine

A solution of 0.5 mg (4.2 µmol, 1.0 eq.) of **1** and 0.17 mg (8.4 µmol, 2.0 eq.) 2-(4bromophenyl)ethanamine in 2 mL of dichloromethane (prepared from stock solutions) was added into a headspace vial, which was crimped air-tight using SBR seals with PTFE inner liner. The solution was deoxygenated by purging with nitrogen for 3 min. The flask was subsequently irradiated for 1 hour by revolving around a compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, the emission spectrum is included in Figure S6) at a distance of 40–50 mm in a custom-built photoreactor (see Figure S7). After irradiation, the solvent was removed under reduced pressure and the sample was subjected to SEC-MS analysis (see Figure S9).

Photo-triggered reaction of mPEG-amine with *N*-octadecyl-2-((2-oxo-2-phenylethyl)thio)acetamide



A solution of 0.5 mg (1000 g·mol⁻¹, 0.50 µmol, 1.0 eq.) mPEG-amine and 2.3 mg (5.0 µmol, 10.0 eq.) *N*-octadecyl-2-((2-oxo-2-phenylethyl)thio)acetamide in 1 mL of dichloromethane was added into a headspace vial, which was crimped air-tight using SBR seals with PTFE inner liner. The solution was deoxygenated by purging with nitrogen for 3 min. The flask was subsequently irradiated for 3 hours by revolving around a compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, the emission spectrum is included in Figure S6) at a distance of 40–50 mm in a custom-built photoreactor (see Figure S7). After irradiation, the solvent was removed under reduced pressure and the sample was subjected to SEC-MS analysis (see Figure S10).



Figure S10. Photo-triggered reaction of **1** with 10 eq. of *N*-octadecyl-2-((2-oxo-2-phenylethyl)thio)acetamide. This experiment utilizes an excess of phenacylsulfide, not of the respective amine. As a result, the corresponding thioamide fragment was obtained as the main product (higher sulfur concentration).

Photo-triggered reaction of 1 with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride

A solution of 0.5 mg (0.42 µmol, 1.0 eq.) of **1** and 0.21 mg (0.84 µmol, 2.0 eq.) O-(2,3,4,5,6pentafluorobenzyl)hydroxylamine hydrochloride in 2 mL of acetonitrile (prepared from stock solutions) was added into a headspace vial, which was crimped air-tight using SBR seals with PTFE inner liner. The solution was deoxygenated by purging with nitrogen for 3 min. The flask was subsequently irradiated for 1 hour by revolving around a compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, the emission spectrum is included in Figure S6) at a distance of 40–50 mm in a custom-built photoreactor (see Figure S7). After irradiation, the solvent was removed under reduced pressure and the sample was subjected to SEC-MS analysis SEC-MS (see Figure S9).

Photo-triggered reaction of 1 with (4-bromophenyl)-methanethiol

A solution of 0.5 mg (0.42 µmol, 1.0 eq.) of 1, 0.17 mg (0.84 µmol, 2.0 eq.) (4-bromophenyl)methanethiol and 0.13 mg (1.0 µmol, 2.4 eq.) DIPEA in 2 mL of dichloromethane (prepared from stock solutions) was added into a headspace vial, which was crimped air-tight using SBR seals with PTFE inner liner. The solution was deoxygenated by purging with nitrogen for 3 min. The flask was subsequently irradiated for 1 hour by revolving around a compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, the emission spectrum is included in Figure S6) at a distance of 40–50 mm in a custom-built photoreactor (see Figure S7). After irradiation, the solvent was removed under reduced pressure, 50 µL of hydrogen peroxide was added to reverse disulfide reduction and the sample was subjected to SEC-MS analysis SEC-MS (see Figure S9).

NMR study for the photo-triggered reaction of *N*-octadecyl-2-((2-oxo-2-phenylethyl)thio)acetamide with octadecan-1-amine.

30.0 mg (0.065 mmol, 1.0 eq.) *N*-octadecyl-2-((2-oxo-2-phenylethyl)thio)acetamide and 21.0 mg (0.078 mmol, 1.2 eq.) octadecan-1-amine were dissolved in 4 mL predried DCM and added into a headspace vial, which was crimped air-tight using SBR seals with PTFE inner liner. The solution was deoxygenated by purging with nitrogen for 3 min. The flask was subsequently irradiated for 1 hour by revolving around a compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, the emission spectrum is included in

Figure S6) at a distance of 40–50 mm in a custom-built photoreactor (see Figure S7). After irradiation, the solvent was removed under reduced pressure, 5 mL ethanol was added and the suspension was filtered. The solvent was removed under reduced pressure and the reaction product was analyzed via ¹H NMR (see Figure S11).



Figure S11. ¹H-NMR spectra of (*E*)-*N*-octadecyl-2-(octadecylimino)acetamide (top) and the reaction product containing a mixture of *N*-octadecyl-2-(octadecylamino)-2-thioxoacetamide and (*E*)-*N*-octadecyl-2-(octadecylimino)acetamide (bottom) in CDCl₃. Note: Due to the high intensity of the peak corresponding to protons b, the signal was cut off at the top of the figure.

Kinetic investigations in solution

In order to gain more detailed insights into the photoreaction sequence, a kinetic investigation for the photofragmentation of **1** was performed by integration of mass spectral abundances of **1** (*m/z*: 1214.0 - 1218.0) and **3** (*m/z*: 1228.5 - 1232.5) after predefined irradiation times. In detail, eight separate solutions with 0.5 mg (0.42 µmol, 1.0 eq.) of **1** and 0.21 mg (0.84 µmol, 2.0 eq.) O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride in 2 mL of acetonitrile (prepared from stock solutions) were prepared and added into eight headspace vials, which were crimped air-tight using SBR seals with PTFE inner liner. The solutions were deoxygenated by purging with nitrogen for 3 min. The flasks were subsequently irradiated for 0 min, 1 min, 2.5 min, 5 min, 10 min, 20 min, 40 min, and 60 min, respectively, by revolving around a compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, the emission spectrum is included in Figure S6) at a distance of 40–50 mm in a custombuilt photoreactor (see Figure S7). After irradiation, the solvent was removed under reduced pressure (vacuum was applied for approximately 20 min) and each sample was subjected to ESI-MS analysis (see Figure S12).



Figure S12. Kinetic investigation of the photofragmentation of **1** by integration of the mass spectral abundances of **1** (m/z: 1214.0 - 1218.0) and **3** (m/z: 1228.5 - 1232.5) after predefined irradiation times. As can be expected, the cleavage of acetophenone was found to follow a first-order kinetic model ($k = 0.28 \text{ s}^{-1}$).

Discussion

The complete disappearance of the quasimolecular ion $[1+Na]^+$ demonstrates that full photofragmentation was achieved after less than 20 min irradiation time. The corresponding first-order plot is depicted in Figure S12 and the rate coefficient was determined to be close to 0.28 s⁻¹. Since we could only detect the nucleophilic addition adducts stemming from reactions with photogenerated thioaldehyde species 1' during mass spectrometric analysis, yet not the thioaldehyde itself, it can be concluded that the nucleophilic addition to the thioaldehyde is not a rate determining step in the overall reaction sequence (see Scheme S2). However, the release of hydrogen sulfide (3' to 3) is the other relevant rate determining step. We observed, for instance, that the product mixture (procedure see above, 30 minutes irradiation time) without previously applying a vacuum contains 3' as the main and 3 as the minor product (see Figure S13). To conclude, the vacuum applied to remove the solvent shifted the equilibrium towards 3. Finally, it is important to note that for surface related immobilizations no influence on the grafting density is to be expected on a surface, regardless if the linkage is based on the one in 3 or the one in 3'.



Scheme S2. A more detailed reaction scheme for the photo-triggered reaction of **1** with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride.



Figure S13. Photo-triggered reaction of **1** with 2.0 eq. O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride in 2 mL of acetonitrile and after 30 minutes of irradiation. The product was directly analyzed without removing the solvent or applying a vacuum.

Theoretical and experimental values for ESI-MS measurements

$m/z_{\rm expt}$	ion assignment	formula	$m/z_{\rm theor}$	$\Delta m/z$
1302.7	$1_{(n=24)} + Na^+$	$\left[C_{59}H_{109}NNaO_{26}S ight]^{+}$	1302.7	0.0
1303.7	$2_{(n=23)} + Na^+$	$[C_{57}H_{105}BrN_2NaO_{24}]^+$	1303.6	0.1
1291.7	$2'_{(n=22)} + Na^+$	$[C_{55}H_{101}BrN_2NaO_{23}S]^+$	1291.6	0.1
1317.7	$3_{(n=23)} + Na^+$	$\left[C_{56}H_{99}F_5N_2NaO_{25}\right]^+$	1317.6	0.1
1307.4	$3'_{(n=22)} + Na^+$	$\left[C_{54}H_{97}F_5N_2NaO_{24}S\right]^+$	1307.6	0.2
1296.5	$4_{(n=22)} + Na^+$	$[C_{54}H_{100}BrNNaO_{23}S_2]^+$	1296.5	0.0
1317.9	$5_{(n=20)} + Na^+$	$\left[C_{63}H_{126}N_{2}NaO_{22}S\right]^{+}$	1317.8	0.1
1285.9	$5'_{(n=20)} + Na^+$	$\left[C_{63}H_{126}N_2NaO_{22}\right]^+$	1285.9	0.0

Table S1. Experimental and theoretical m/z values for the isotopic distribution of Figure 1(see also Figure S9, Figure S10, and Figure S13) in the m/z range between 1280 and 1325.

Surface Modifications

Preparation of Si-Surface before irradiation

Cleaning and preactivation of the silicon wafers

All Si wafers were cleaned three successive times by ultrasonication for 10 min in acetone, chloroform, ethanol, and finally dried under a nitrogen stream. Preactivation of the surfaces was achieved by separately placing them in small glass vials containing acidic piranha solution (sulfuric acid 95 % / aqueous hydrogen peroxide 35 % 3:1 v/v) for 60 min at 100 °C on a shaker. *Caution: piranha solution is an extremely strong oxidant and should be handled very carefully!* The Si wafers were subsequently washed und ultrasonicated in distilled water for 10 minutes and dried under a nitrogen stream.

Silanization of Si wafers with FAS-containing silane

Preactivated substrates were placed separately in small glass vials containing a solution of 2.0 mg (4.8 μ mol) FAS-containing silane dissolved in 0.5 mL of anhydrous toluene. They were subsequently heated to 50 °C for 2 hours on a shaker (300 rpm) and held overnight at RT. The wafers were subsequently ultrasonicated for 2 minutes in 10 mL of dry toluene and for 2 minutes in 10 mL DCM to remove any physisorbed silane.

Spatially controlled photoactivation of Si-Surfaces

Spatially controlled surface modification with 2-(4-bromophenyl)ethanamine

A mask (see Figures S8) was placed onto a FAS-functionalized Si wafer. The latter was placed into a headspace vial, which was crimped air-tight using SBR seals with PTFE inner liner. A solution of 10 mg (0.05 mmol) 2-(4-bromophenyl)ethanamine in 4 mL of dichloromethane was added and deoxygenated by purging with nitrogen for 3 min. The flask was subsequently irradiated for 1 hour by revolving around a compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, the emission spectrum is

included in Figure S6) at a distance of 40–50 mm in a custom-built photoreactor (see Figure S7). After irradiation, the mask was removed. The wafer was subsequently rinsed and sonicated in dichloromethane for 3 minutes and in acetone for 3 minutes to remove any possibly physisorbed material. The wafer was finally dried under a nitrogen stream and afterwards, a ToF-SIMS analysis was performed (see Figure S14).

Spatially controlled surface modification with mPEG-amine

A mask (see Figures S8) was placed onto a FAS-functionalized Si wafer. The latter was placed into a headspace vial, which was crimped air-tight using SBR seals with PTFE inner liner. A solution of 10 mg (1000 g·mol⁻¹, 0.01 mmol) mPEG-amine in 4 mL of dichloromethane was added and deoxygenated by purging with nitrogen for 3 min. The flask was subsequently irradiated for 1 hour by revolving around a compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, the emission spectrum is included in Figure S6) at a distance of 40–50 mm in a custom-built photoreactor (see Figure S7). After irradiation, the mask was removed. The wafer was subsequently rinsed and sonicated in dichloromethane for 3 minutes and in acetone for 3 minutes to remove any possibly physisorbed material. The wafer was finally dried under a nitrogen stream and afterwards, a ToF-SIMS analysis was performed (see Figure S15).

Spatially controlled surface modification with (4-bromophenyl)methanethiol

A mask (see Figures S8) was placed onto a FAS-functionalized Si wafer. The latter was placed into a headspace vial, which was crimped air-tight using SBR seals with PTFE inner liner. A solution of 10 mg (0.05 mmol) (4-bromophenyl)-methanethiol) in 4 mL of dichloromethane and 7.75 mg (0.06 mmol) DIPEA was added and deoxygenated by purging with nitrogen for 3 min. The flask was subsequently irradiated for 1 hour by revolving around a compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, the

emission spectrum is included in Figure S6) at a distance of 40–50 mm in a custom-built photoreactor (see Figure S7). After irradiation, the mask was removed. The wafer was subsequently rinsed and sonicated in acetonitrile for 3 minutes and in acetone for 3 minutes to remove any possibly physisorbed material. The wafer was finally dried under a nitrogen stream and afterwards, a ToF-SIMS analysis was performed (see Figure S16).

Spatially controlled surface modification with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride

A mask (see Figures S8) was placed onto a FAS-functionalized Si wafer. The latter was placed into a headspace vial, which was crimped air-tight using SBR seals with PTFE inner liner. A solution of 10 mg (0.04 mmol) O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride in 4 mL of acetonitrile was added and deoxygenated by purging with nitrogen for 3 min. The flask was subsequently irradiated for 1 hour by revolving around a compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, the emission spectrum is included in Figure S6) at a distance of 40–50 mm in a custom-built photoreactor (see Figure S7). After irradiation, the mask was removed. The wafer was subsequently rinsed and sonicated in acetonitrile for 3 minutes and in acetone for 3 minutes to remove any possibly physisorbed material. The wafer was finally dried under a nitrogen stream and afterwards, a ToF-SIMS analysis was performed (see Figure S17).

Surface Characterization via ToF-SIMS



Reaction with 2-(4-bromophenyl)ethanamine

Figure S14. ToF-SIMS images of silicon wafers patterned with 2-(4-bromophenyl)ethanamine



Reaction with mPEG-amine

Figure S15. ToF-SIMS images of silicon wafers patterned with mono-functional amino endcapped poly(ethylen)glycol methyl ether (mPEG-amine).



Reaction with (4-bromophenyl)methanethiol

Figure S16. ToF-SIMS images of silicon wafers patterned with (4-bromophenyl)methanethiol.

Reaction with 0-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride



Figure S17. ToF-SIMS composition analysis of fluorine and C6F5- species of silicon wafers patterned with O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride in degased acetonitrile

Spatially controlled photoactivation of a glass slide

A mask (see Figures S8) was placed onto a FAS-functionalized glass microscope slide (the preparation was performed in analogy to the FAS-functionalization of Si-wafers). The latter was placed into a headspace vial, which was crimped air-tight using SBR seals with PTFE inner liner. A solution of 10 mg (0.05 mmol) 2-(4-bromophenyl)ethanamine in 4 mL of dichloromethane was added and deoxygenated by purging with nitrogen for 3 min. The flask was subsequently irradiated for 1 hour by revolving around a compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L: $\lambda_{max} = 355$ nm, the emission spectrum is included in Figure S6) at a distance of 40–50 mm in a custom-built photoreactor (see Figure S7). After irradiation, the mask was removed. The wafer was subsequently rinsed and sonicated in dichloromethane for 3 minutes and in acetone for 3 minutes to remove any

possibly physisorbed material. The glass slide was finally dried under a nitrogen stream and afterwards, a ToF-SIMS analysis was performed (see Figure S18).

Note: The employed mask holder is best suited for the masked irradiation of Si-wafers and not so much for the very thin glass microscope slides. This might explain poorer quality of the ToF-SIMS image in Figure S18 if compared to Figure S14.



Figure S18. ToF-SIMS image (Br⁻ content analysis) of a glass microscope slide patterned with 2-(4-bromophenyl)-ethanamine.

References

- (1) Vedejs, E.; Eberlein, T. H.; Wilde, R. G. J. Org. Chem. 1988, 53, 2220.
- (2) Glassner, M.; Oehlenschlaeger, K. K.; Welle, A.; Bruns, M.; Barner-Kowollik, C. *Chem. Commun.* **2013**, *49*, 633.
- (3) Gruendling, T.; Guilhaus, M.; Barner-Kowollik, C. Anal. Chem. 2008, 80, 6915.
- (4) Wagner, P. J. and Lindstrom M. J., J. Am. Chem. Soc. 1987, 109, 3062.