Supporting Information

Polymer Surface Patterning via Diels-Alder Trapping of Photo-Generated Thioaldehydes

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Materials: Dichloromethane and toluene were dried and stored over 4Å molecular sieves. (Phenacylthio)acetic acid was synthesized according to the literature[1] and recrystallized from $CHCl_3$. Cyclopentadiene was prepared by thermal cracking and distillation of dicyclopentadiene (Sigma-Aldrich). All other chemicals were used as supplied by the manufacturers.

Size Exclusion Chromatography-Electrospray Ionization Mass Spectrometry (SEC-ESI-MS): Spectra were recorded on an LXQ mass spectrometer (ThermoFisher Scientific, San Jose, CA) 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 containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage of 6 kV was used and nitrogen at a dimensionless sweep gas flow-rate of 2 (approximately 3 $L \cdot min^{-1}$) and a dimensionless sheath gas flow-rate of 5 (approximately 0.5 $L \cdot min^{-1}$) were applied. The capillary voltage, the tube lens offset voltage and the capillary temperature were set to 10 V, 70 V and 315 °C respectively. The LXQ was coupled to a Series 1200 HPLC-system (Agilent, Santa Clara, CA, USA) consisting of a solvent degasser (G1322A), a binary pump (G1312A), a high-performance autosampler (G1367B), followed by a thermostated column compartment (G1316A). Separation was performed on two mixed bed size exclusion chromatography columns (Polymer Laboratories, Mesopore 250 × 4.6 mm, particle diameter 3 µm) with precolumn (Mesopore 50 × 4.6 mm) operating at 30°C. THF at a flow rate of 0.30 $mL \cdot min^{-1}$ was used as eluent. The mass spectrometer was coupled to the column in parallel to an RI-detector (G1362A with SS420x A/D) in a setup described earlier.[2] 0.27 $mL \cdot min^{-1}$ of the eluent were directed through the RI-detector and 30 $\mu L \cdot min^{-1}$ infused into the electrospray source after postcolumn addition of a 100 µM solution of sodium iodide in methanol at 20 $\mu L \cdot min^{-1}$ by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 20 µL aliquot of a polymer solution with a concentration of 3 $mg \cdot mL^{-1}$ was injected onto the HPLC system.

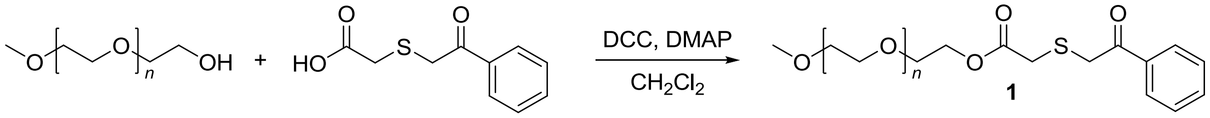
UV/Vis Spectroscopy: UV/Vis spectra were recorded on a Varian Cary 300 Bio spectrophotometer.

^{1}H-NMR Spectroscopy: ^{1}H-NMR spectra were recorded using a Bruker AM 400 spectrometer at 400 MHz for hydrogen nuclei. All samples were dissolved in $CDCl_3$.

XPS (X-ray photoelectron spectroscopy): XPS measurements were performed using a K-Alpha XPS instrument (ThermoFisher Scientific, East Grinstead, UK). Data acquisition and processing using the Thermo Avantage software is described elsewhere.[3] All samples were analyzed using a microfocused, monochromated Al Kα X-ray source (30-400 µm spot size). The K-Alpha charge compensation system was employed during analysis, using electrons of 8 eV energy and low-energy argon ions to prevent any localized charge build-up. The spectra were fitted with one or more Voigt profiles (BE uncertainty: +/- 0.2eV). The analyzer transmission function, Scofield sensitivity factors,[4] and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2M formalism.[5] All spectra were referenced to the C1s peak of hydrocarbon at 285.0 eV binding energy controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au.

ToF-SIMS (time-of-flight secondary ion mass spectrometry): Time-of-flight secondary ion mass spectrometry was performed on a TOF.SIMS 5 instrument from ION.TOF GmbH, Münster, Germany. This instrument is equipped with a Bi cluster liquid metal ion source and a reflectron type time-of-flight analyzer and is operated at $< 5 \times 10^{-9}$ mbar. For spectrometry and imaging short primary ion pulses (<1 ns) of Bi^+ at an energy of 25 keV were applied providing high mass resolution secondary ion spectra with a spot size of about 2 µm (bunched mode). The primary ion beam was rastered over 500 × 500 µm. To obtain larger scan sizes also the sample holder was shifted and images stitched automatically. Images were recorded at 100 pixel/mm. Spectra were calibrated on the omnipresent C^+,CH^+, CH_2^+ peaks. Deviations from the theoretical mass were usually < 10 ppm.

Phenacyl sulfide functionalized poly(ethylene glycol) monomethyl ether (1)



Poly(ethylene glycol) monomethyl ether (2.00 g, 1.00 mmol), 4-dimethylaminopyridine (7.0 mg, 0.6 mmol) and (phenacylthio)acetic acid (631 mg, 3.00 mmol) were dissolved in 10 mL dry CH_2Cl_2. A solution of DCC (619 mg, 3.00 mmol) in 2 mL dry CH_2Cl_2 was added and the reaction mixture stirred overnight at ambient temperature. The solution was filtered and the polymer precipitated in cold diethyl ether to give a white solid.

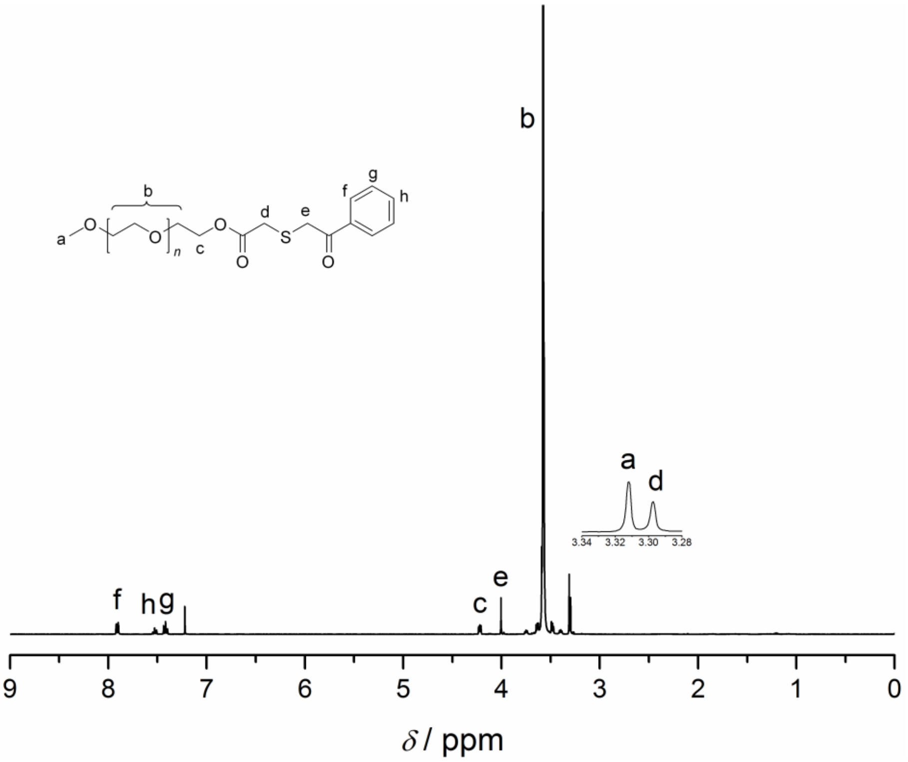


Figure S1 ^{1}H-NMR spectrum of phenacyl sulfide functionalized PEG (**1**).

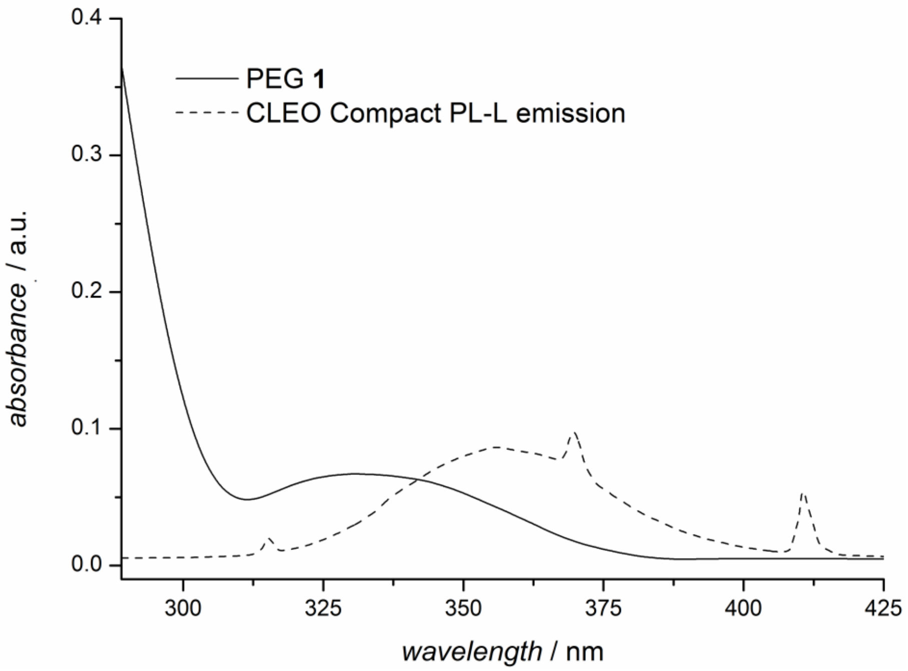


Figure S2 UV-Vis spectrum of phenacyl sulfide functionalized PEG **1** together with the emission spectrum of the employed compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L).

Photo-reactions with small molecule dienes

Phenacyl sulfide functionalized PEG **1** (10 mg, 5 μmol) and the diene (7.5 μmol) were dissolved in 1mL dry CH_2Cl_2 in a headspace vial (Pyrex, dia. 20 mm) which was crimped airtight using styrene/butadiene rubber seals with PTFE inner liner. The solution was deoxygenated by purging with nitrogen for 5 min. The flask was irradiated by revolving around a 36 W compact low-pressure fluorescent lamp (Philips CLEO Compact PL-L, λ_{max} = 355 nm) at a distance of 40-50 mm in a custom built photo reactor (see Figure S 7 for a drawing). After a preset time interval irradiation was stopped and the solvent removed under a stream of nitrogen. The residue was redissolved in THF and analyzed by SEC/ESI-MS.

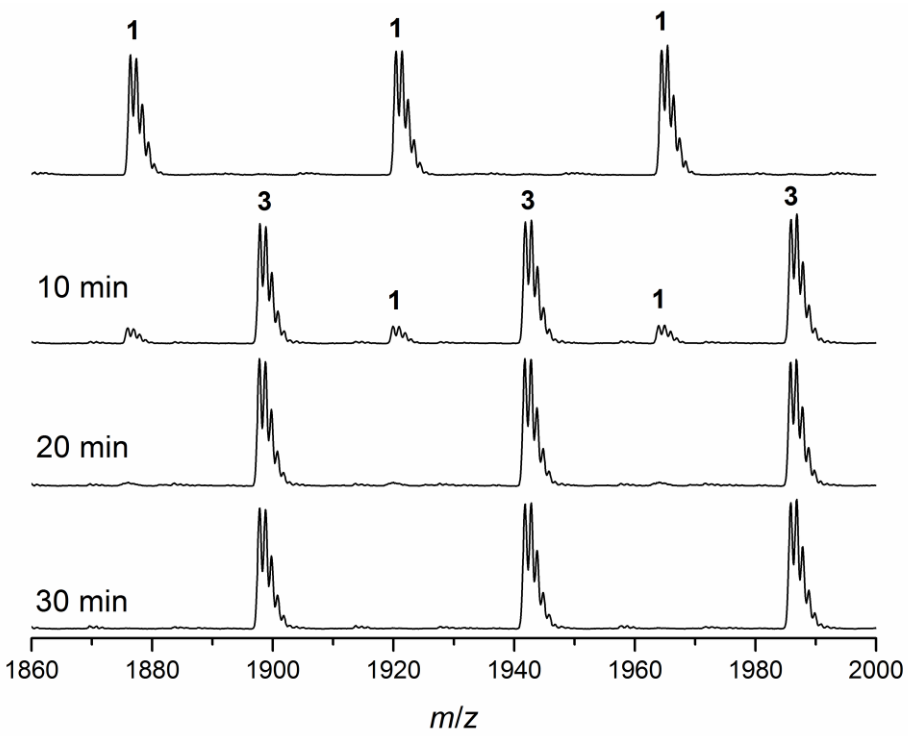
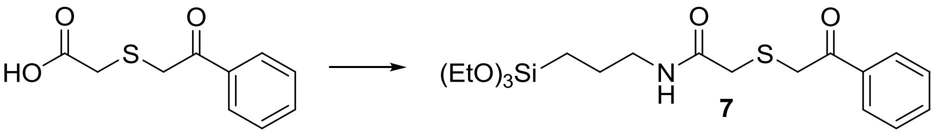


Figure S3 ESI-MS spectra of phenacyl sulfide capped PEG (**1**) before and after irradiation with *trans,trans*-2,4-hexadien-1-ol for different time intervals.

Table S1 Theoretical and measured *m*/*z* ratios ([M+Na]$^+$) of phenacyl sulfide functionalized PEG (**1**) and the Diels-Alder adducts with different dienes (see Figure 1 of the main text). The values refer to the first peak of the isotopic pattern.

Structure	Formula	m/z^{theo}	m/z^{meas}	$\Delta m/z$
1	$[C_{81}H_{152}O_{38}SNa]^+$	1787.96	1788.17	0.21
2	$[C_{81}H_{158}O_{38}SNa]^+$	1794.01	1794.08	0.07
3	$[C_{81}H_{158}O_{39}SNa]^+$	1810.00	1810.00	0.00
4	$[C_{81}H_{156}O_{38}SNa]^+$	1791.99	1791.92	0.07
5	$[C_{80}H_{155}O_{38}SNa]^+$	1777.97	1777.92	0.05
6	$[C_{79}H_{152}O_{39}SNa]^+$	1779.95	1779.75	0.20

Phenacyl sulfide functionalized silane (7)



1.00 g (4.76 mmol) (phenacylthio)acetic acid was dissolved in 20 mL dry THF. 730 µL of triethylamine were subsequently added. The solution was purged with nitrogen for 5 min, 619 mg (5.71 mmol) ethyl chloroformate were added at 0 °C and stirred at 0 °C for 4 h. 1.05 g

(4.76 mmol) 3-(triethoxysilyl)propan-1-amine were added dropwise at 0 °C and the reaction mixture was stirred over night at ambient temperature. The solution was filtered and the solvent was removed under reduced pressure. Ethyl acetate was added and the organic layer was washed with water, saturated $NaHCO_3$ solution and brine. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, ethyl acetate/ hexane 1:1). 451 mg (1.09 mmol; 23%) of silane **7** were obtained as a slightly yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 7.93–7.86 (m, 2H), 7.57–7.52 (m, 1H), 7.45–7.40 (m, 2H), 3.90 (s, 2H), 3.74 (q, ^3J = 7.0 Hz, 6H), 3.23–3.15 (m, 2H), 3.17 (s, 2H), 1.62–1.52 (m, 2H), 1.15 (t, ^3J = 7.0 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ/ppm = 194.28 (C), 135.18 (C), 133.96 (CH), 128.98 (CH), 128.80 (CH), 58.58 (CH_2), 42.42 (CH_2), 38.30(CH_2), 36.08 (CH_2), 23.04 (CH_2), 18.43(CH_3), 7.89 (CH_2). ESI-MS: m/z = 436.25 ([M+Na]$^+$, m/z^{theo} = 436.16).

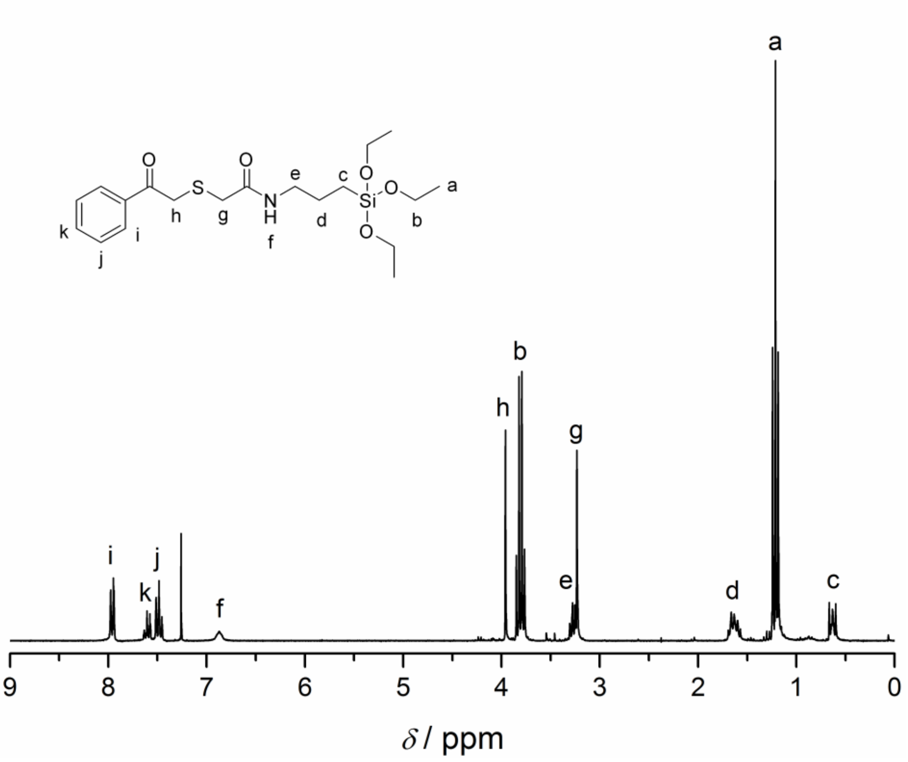


Figure S4 ^{1}H-NMR spectrum of phenacylsulfide functional silane **7** in $CDCl_3$.

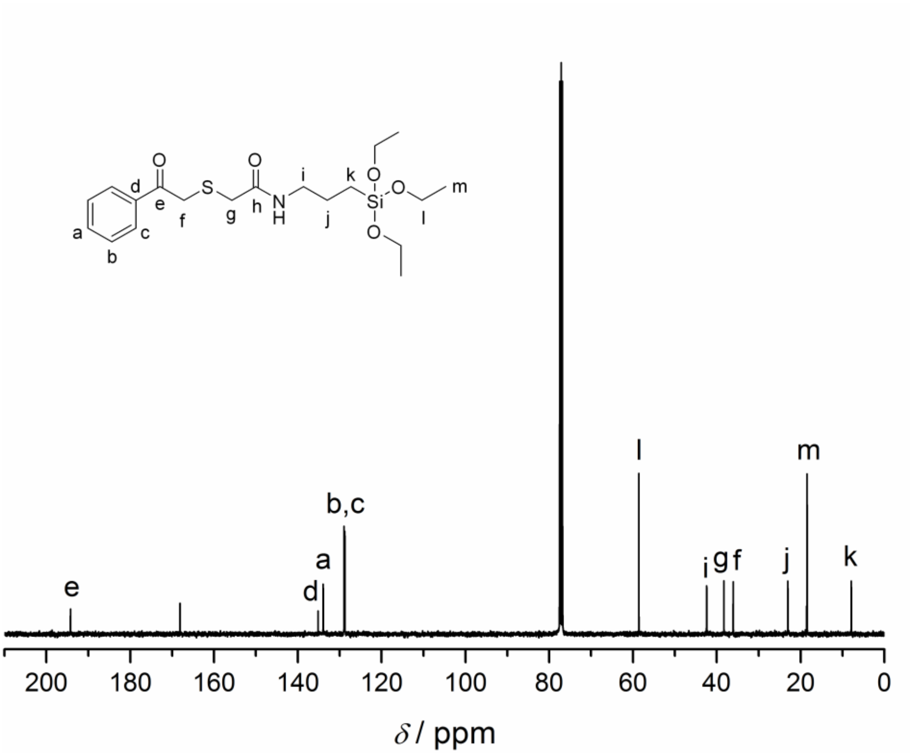


Figure S5 ^{13}C-NMR spectrum of phenacylsulfide functional silane **7** in $CDCl_3$.

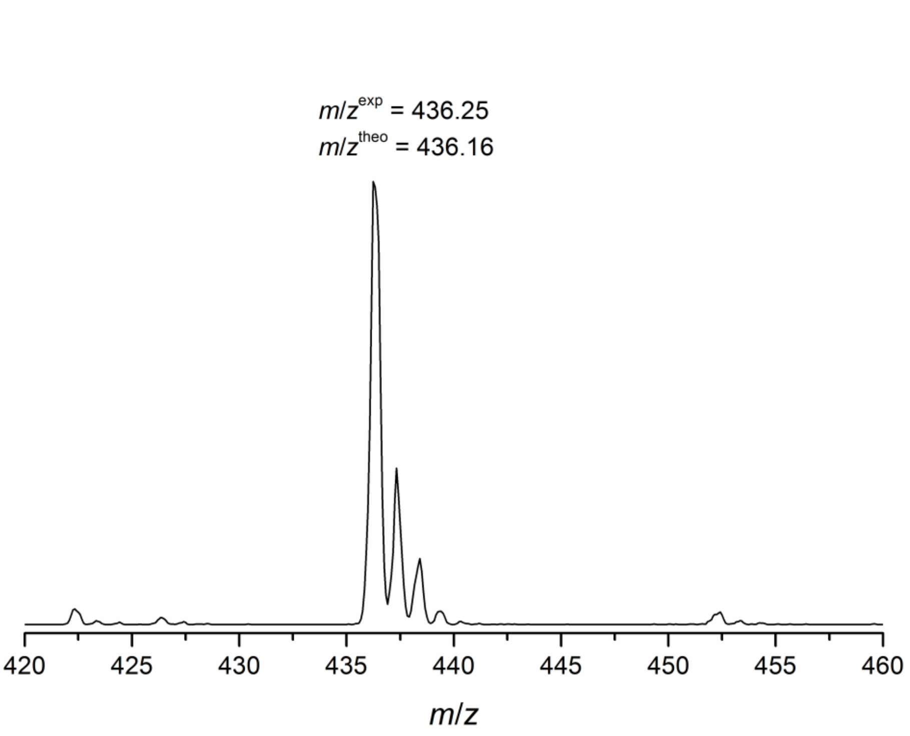


Figure S6 ESI-MS spectrum of phenacylsulfide functional silane **7**.

Surface Modifications

Cleaning and preactivation of silicon wafers

All Si wafers and glass substrates were cleaned three times by ultrasonification for 15 min in chloroform, acetone, and ethanol. Preactivation of the surfaces was achieved by placing them in glass vials containing acidic piranha solution (sulfuric acid 95 % aqueous hydrogen peroxide 35 % 3:1 v/v) for 60 min at 100 °C. The wafers were subsequently rinsed with deinoized water and dried under a stream of nitrogen. Caution: piranha solution is an extremely strong oxidant and should be handled with care!

Silanization of Si wafers with phenacyl sulfide functionalized silane 7

Preactivated substrates were placed separately in small glass vials containing a solution of phenacyl sulfide functionalized silane 7 (10 mg, 22.1 μmol) dissolved in anhydrous toluene (2 mL). They were subsequently heated to 50 °C for 2 h without stirring. The solution was brought to ambient temperature and the wafers were left immersed for another 12 h. The wafers were subsequently ultrasonicated in dry toluene (10 mL, 10 min), acetone (10 mL, 5 min), and finally dichloromethane (10 mL, 5 min) to remove any physisorbed silane and subsequently dried under a stream of nitrogen.

Polymer surface patterning with PEG-Cp

In a headspace vial (Pyrex, diameter 20 mm), PEG-Cp (20 mg, 10 μmol) was dissolved in CH_2Cl_2 (3 mL). A mask (see Figures 3) was placed onto an phenacyl sulfide functionalized Si wafer. The latter was placed into the headspace vial, which was crimped air-tight using SBR seals with PTFE inner liner. The solution was deoxygenated by purging with nitrogen for 10 min. The flasks were subsequently irradiated for 2 h in the photoreactor. After irradiation, the mask was removed. The wafer was subsequently rinsed with CH_2Cl_2 and sonicated 3 times for 5 min in CH_2Cl_2 to remove any physisorbed material. The wafer was finally dried under a stream of nitrogen.

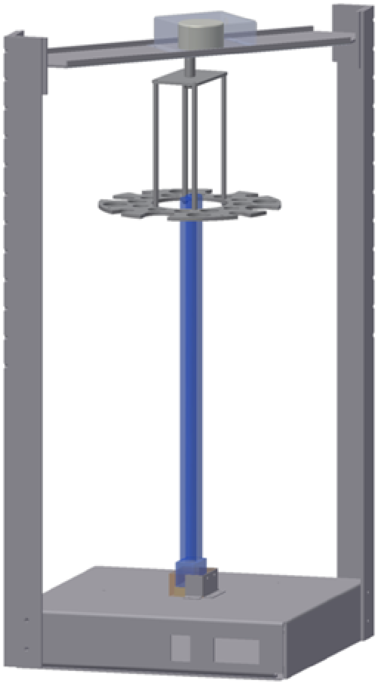


Figure S7 Drawing of the custom-built photoreactor employed in the current study.

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(3) Parry, K. L.; Shard, A. G.; Short, R. D.; White, R. G.; Whittle, J. D.; Wright, A. *Surf. Interface Anal.* **2006**, *38*, 1497.

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(5) Tanuma, S.; Powell, C. J.; Penn, D. R. *Surf. Interface Anal.* **1994**, *21*, 165.