Supporting Information for

Light-driven reversible surface functionalization with anthracenes: visible light writing and mild UV erasing

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Contents

1 Materials

9-Bromoanthracene (9-BA; Sigma–Aldrich, 94 %), 9-anthracenemethanol (Sigma–Aldrich, 97%), 1,1'-carbonyldiimidazole (CDI; TCI, ≤ 97 %), azobisisobutyronitrile (AIBN; Sigma–Aldrich, ≥ 98 %), benzoic acid (Sigma–Aldrich, 99.5 %), bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$; Sigma–Aldrich, ≥99 %), copper (I) iodide (CuI; Sigma–Aldrich, ≥ 99.5 %), *N,N'*-dicyclohexylcarbodiimide (DCC; Acros, 99 %), dimethylaminopyridine (DMAP; Sigma-Aldrich, 99 %), ethynyltrimethylsilane (Sigma–Aldich, 98 %), *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine (PMDETA; Sigmal–Aldrich 99 %), piperidine (Acros Organics, 99 %), di-phosphorus pentasulfide (P_4S_{10}; Merck Millipore), ammonium chloride (NH_4Cl; Roth, 98 %), potassium bicarbonate (K_2CO_3; Roth, 99 %) sodium sulfate (Na_2SO_4; Roth, 99 %), d-chloroform ($CDCl_3$; Sigma–Aldrich, 99.8 %), dimethylsulfoxide-d_6 (DMSO-d_6; Euriso-Top, 99.8 %), dry *N*,*N*-dimethylformamide (DMF; Acros Organics, extra dry, 99,7 %), dry tetrahydrofurane (THF; Acros Organics, AcrosSeal®, 99.95 %), dry toluene (Acros Organics, extra dry 99.8 %), diethylether (Et_2O; VWR, p.a.), DMF (VWR, p.a.), methanol (MeOH; VWR, p.a.), triethylamine (Roth, p.a.), toluene (VWR, p.a. or Roth), dichloromethane (DCM; VWR, p.a.), cyclohexane (VWR, p.a.), ethyl acetate (VWR, p.a.), acetonitrile (VWR, p.a.), THF (VWR, p.a.), sulfuric acid (H_2SO_4; Roth, 96 %) and hydrogen peroxide (H_2O_2; Roth, 35 %) were used as received.

For the surface reactions, acetone (Fischer, electronis (MOS) grade), MiliQ water, extra dry toluene (Acros), toluene (Alfa Aesar, HPLC grade), dichloromethane (Fischer, synthesis grade), and ethanol (Fischer, laboratory reagent grade) were used as received. The argon stream was filtered through an activated charcoal filter (Supelco 24518).

Copper (II) bromide was treated with glacial acetic acid for reduction to copper (I) bromide, which was stored under inert gas.

2 Methods and Characterization

^1H and ^{13}C NMR spectroscopy was performed on a Bruker Ascend 400 at 400 MHz for hydrogen nuclei and at 101 MHz for carbon nuclei. All samples were dissolved in $CDCl_3$ or DMSO-d_6. The δ-scale is referenced to the respective residual solvent peak.

Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the m/z range of 74-1822 using a premixed standard comprising caffeine, Met-Arg-Phe-Ala acetate (MRFA), and a mixture of fluorinated phosphazenes (Ultramark 1621). A constant spray voltage of 4.6 kV and a dimensionless sweep gas flow rate of 5 were applied. The capillary temperature and the S-lens RF level were set to 320 °C an 62.0, respectively. The samples were dissolved with a concentration of 0.05 $mg\cdot mL^{-1}$ in a mixture of THF and MeOH (3:2) containing 100 µmol sodium trifluoracetate (NaTFA). The samples were infused with a flow of 5 $\mu L\cdot min^{-1}$. Spectra were recorded in the negative mode.

UV-Vis spectra were recorded on an OceanOptics USB4000 spectrometer coupled to an USB-ISS-UV-Vis detecting unit. All spectra were recorded in acetonitrile with a concentration of 0.01 mol/L.

Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories (Varian) PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 mm bead-size guard column (50 × 7.5 mm), one PLgel 5 mm Mixed E column (300 × 7.5 mm), three PLgel 5 mm Mixed C columns (300 × 7.5 mm) and a differential refractive index detector using THF as the eluent at 35 °C with a flow rate of 1 mL min^{-1}. The employed GPC system was calibrated using linear poly(styrene) standards ranging from 476 to $2.5\cdot10^6$ g $mol^{-1}$and linear poly(methyl methacrylate) standards ranging from 700 to $2\cdot10^6$ g mol^{-1}. The resulting molar mass distributions were determined by universal calibration using Mark-Houwink parameters for polystyrene ($K = 14.1\cdot10^{-5}$ *d*L g^{-1}, $\alpha = 0.7$).

X-Ray Photo electron spectroscopy (XPS) measurements were performed using a K-Alpha+ XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK). Data acquisition and processing using the Thermo Avantage software is described elsewhere.[1] All samples were analyzed using a microfocused, monochromated Al K_α X ray source (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) and Scofield sensitivity factors were applied for quantification.[2] All spectra were referenced to the C 1s peak attributed to C-C, C-H at 285.0 eV binding energy controlledby means of the well-known photoelectron peaks of metallic Cu, Ag, and Au, respective

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were performed on a TOF.SIMS5 instrument (ION-TOF GmbH, Münster, Germany). This spectrometer is equipped with a bismuth cluster primary ion source and a reflectron type time-of-flight analyzer. UHV base pressure was < 5×10-9 mbar. For high mass resolution the Bi source was operated in the "high current bunched" mode providing short Bi^{3+} primary ion pulses at 25 keV energy and a lateral resolution of approx. 4 µm. The short pulse length of < 1.3 ns allowed for high mass resolution. Due to the required large fields of view, the stage scan mode was used and individual patches of 500×500 µm^2 were stitched by moving the sample. Each patch consists of 30 scans, rastered in random mode, with 100 pixels/mm^2. Pulsed primary gun target currents were recorded (approx. 0.5 pA @ 10 kHz) and all data were normalized on constant primary ion dose density. Spectra were calibrated on the omnipresent C^-, CH^-, CH^{2-}, C^{2-}, C^{3-}; or on the C^+, CH^+, CH^{2+}, and CH^{3+} peaks. Based on these datasets the chemical assignments for characteristic fragments were determined.

All *light sensitive reactions* were carried out in a yellow light environment. This was achieved by adding wavelength filters to normal neon lamps (Asmetec, T8-ASR-G10, gold, 520 nm).

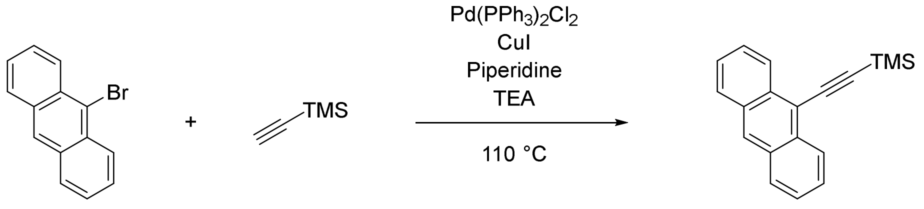
Irradiations were carried out employing either a custom built LED setup consisting of three 3 W LEDs (Avonec Online Handel, λ_{max} = 410 nm) at a distance of 30 mm or a custom built photo reactor equipped with a compact low pressure fluorescent lamp (Cleo PL-L, Philips Deutschland GmbH, λ_{max} = 355 nm) at a distance of 50 mm.

The *emission spectra* of the irradiation setups were recorded with a UV sensor (Opsytec Dr. Gröbel GmbH; Ettlingen, Germany).

3 Experimental Procedures

3.1 Synthetic Protocols

Synthesis of (anthracen-9-ylethynyl)trimethylsilane (**1**)



In a 50 mL flame-dried Schlenk tube equipped with a stirring bar, 9-bromoanthracene (9-BA, 500 mg, 1.95 mmol, 1 eq), CuI (43.4 mg, 0.23 mmol, 0.11 eq), Pd(PPh$_3$)$_2$Cl$_2$ (140 mg, 0.2 mmol, 0.1 eq), and ethynyltrimethylsilane (750 µL, 517 mg, 5.27 mmol, 2.7 eq) were dissolved in piperidine (1.5 mL) and dry TEA (15 mL). The reaction mixture was stirred at 110 °C overnight and subsequently extracted with 50 mL sat. NH$_4$Cl solution. The aqueous phase was extracted with 30 mL cyclohexane three times. The combined organic phases were dried over Na$_2$SO$_4$ and concentrated under vacuum. The raw product was purified by column chromatography (silica gel, cyclohexane + 0.5 vol% toluene, R_f = 0.5) to yield (anthracen-9-ylethynyl)trimethylsilane (**1**) (531 mg, 1.93 mmol, 99 %).

1H NMR (400 MHz, CDCl$_3$) δ / ppm = 8.56 (dq, J = 8.8, 1.1 Hz, 2H), 8.42 (s, 1H), 8.04–7.96 (m, 2H), 7.59 (ddd, J = 8.8, 6.6, 1.3 Hz, 2H), 7.50 (ddd, J = 8.0, 6.6, 1.2 Hz, 2H), 0.43 (s, 9H).

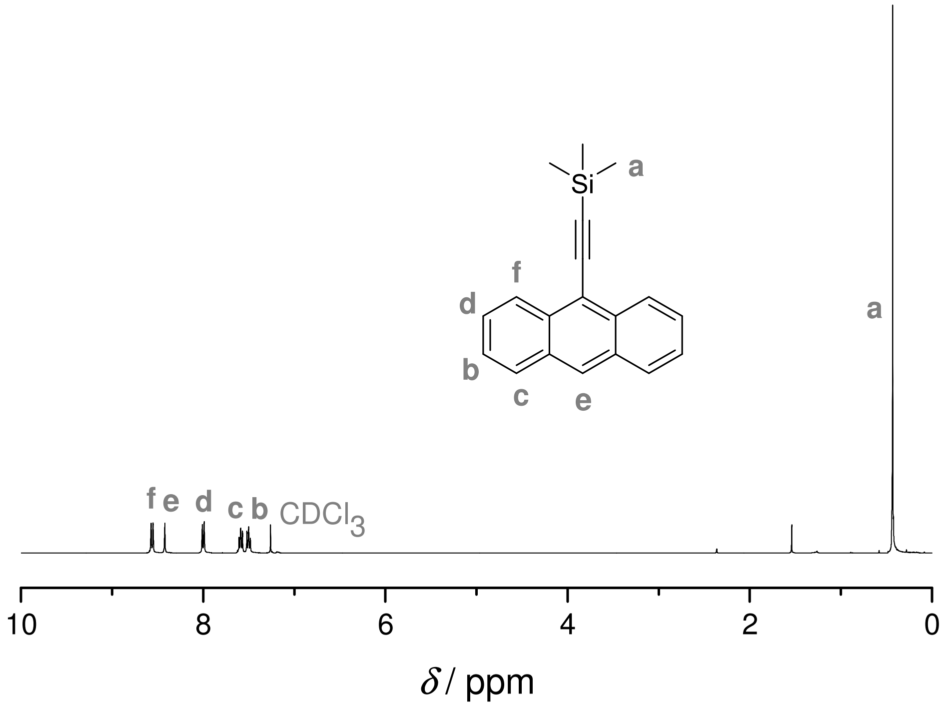
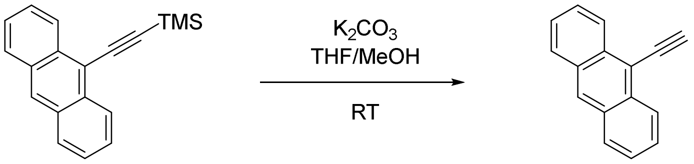


Figure S1. ^{1}H NMR spectrum of 2-anthracen-9-ylethynyl(trimethyl)silane.

Synthesis of 9-ethynylanthracene (**2**)



(Anthracen-9-ylethynyl)trimethylsilane (**1**) (400 mg, 1.46 mmol, 1 eq) and K_2CO_3 (1.41 g, 10.2 mmol, 7 eq) were dissolved in a mixture of 40 mL MeOH/THF (1/1 v/v) and stirred overnight at ambient temperature. The reaction solution was poured into a mixture of 40 mL dist. H_2O/ Et_2O. The organic phase was washed with 30 mL dist. H_2O three times, dried with Na_2SO_4, and concentrated under vacuum. The raw product was filtered through a short column of silica gel (cyclohexane + 0.5 vol% toluene) to yield 9-ethynylanthracene (**2**) (270 mg, 1.33 mmol, 91 %), which was directly used in the next synthesis due to solubility issues upon storage.

^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm = 8.59 (dq, *J* = 8.8, 1.0 Hz, 2H), 8.46 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.60 (ddd, *J* = 8.7, 6.6, 1.3 Hz, 2H), 7.51 (ddd, *J* = 8.0, 6.6, 1.3 Hz, 2H), 3.99 (s, 1H).

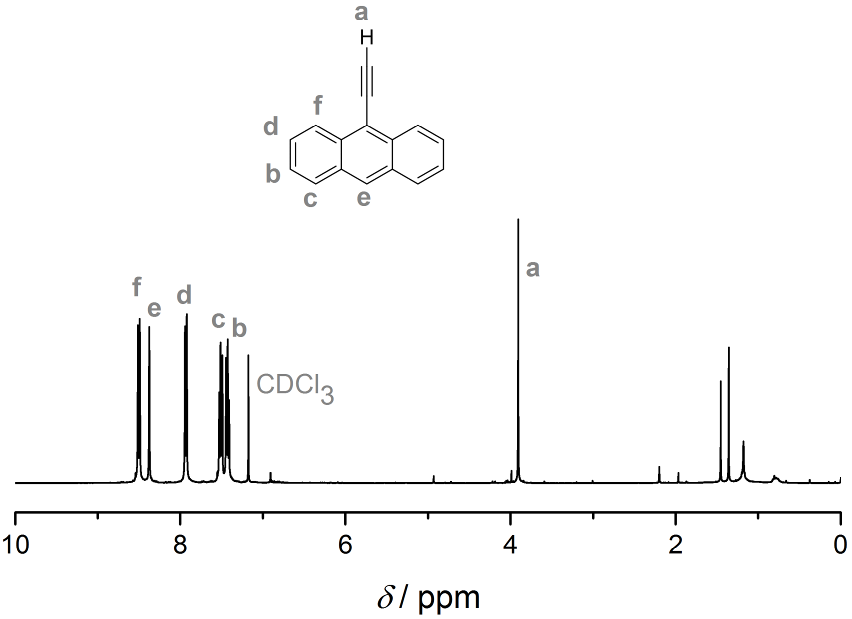


Figure S2. ^{1}H NMR spectrum of 9-ethynylanthracene.

Synthesis of 4-azidobenzoic acid (**3**)

4-Aminobenzoic acid (1.37 g, 10 mmol, 1 eq) was suspended in 22 mL dist. H_2O/conc. HCl (1/1 v/v) and cooled in an ice bath at 0 °C. Sodium nitrite ($NaNO_2$, 0.79 g, 11.5 mmol, 1.15 eq) was dissolved in dist. H_2O (8 mL), the solution was cooled to 0 °C and subsequently added dropwise to the 4-amidobenzoic acid. Subsequently, the mixture was stirred for 20 min in an ice bath. Sodium azide (NaN_3, 0.72 g, 11 mmol, 1.1 eq) was dissolved in dist. H_2O (8 mL) and also cooled to 0 °C. The solution was added dropwise to the cooled reaction mixture, which was then stirred for another hour. The white precipitate was filtered off, subsequently washed with ice cooled dist. H_2O, and dried under vacuum to yield 4-azidobenzoic acid (**3**) (1.40 g, 8.6 mmol, 86 %)

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ / ppm = 7.98–7.93 (m, 2H), 7.24–7.19 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ / ppm = 166.6, 143.9, 131.2, 127.3, 119.2.

ESI-MS: *m/z* calculated for $C_7H_5O_2N_3$ [M-H]$^-$ 162.0309, found 162,0299.

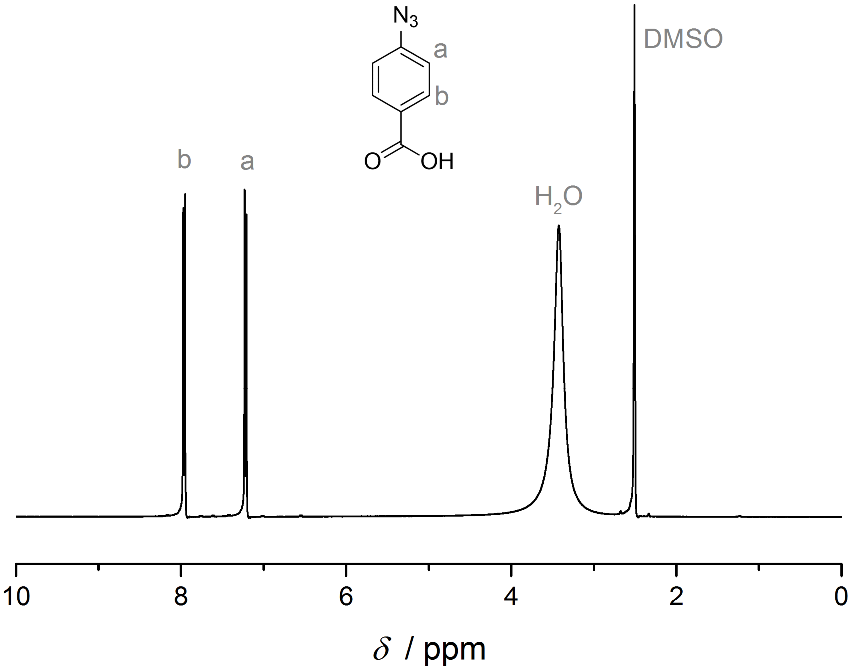


Figure S3. ^{1}H NMR spectrum of 4-azidobenzoic acid.

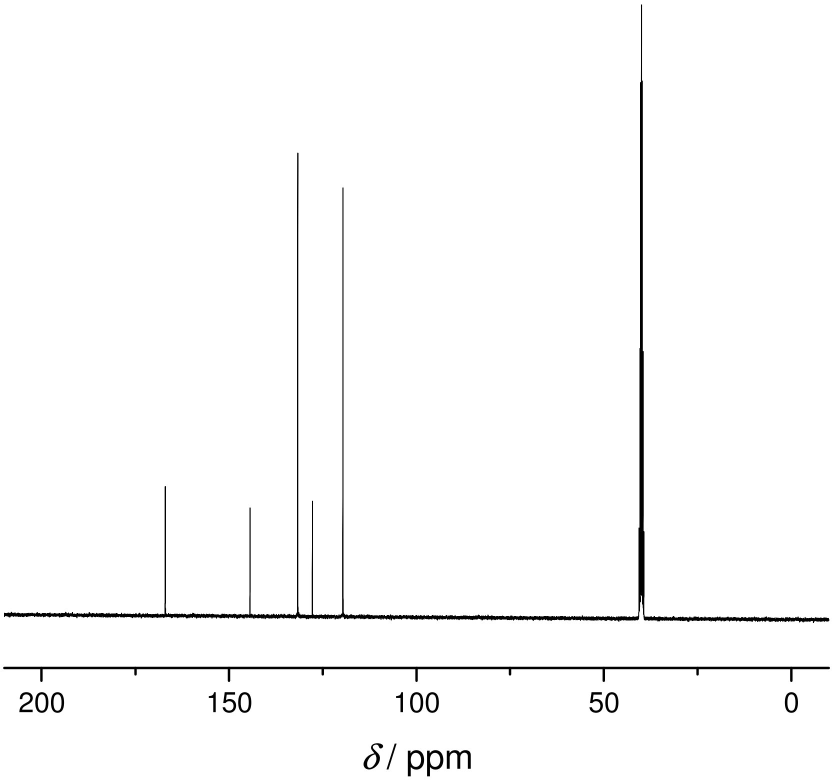
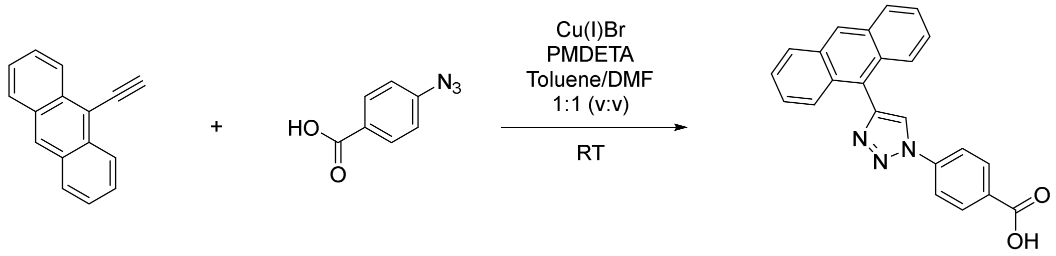


Figure S4. ^{13}C NMR spectrum of 4-azidobenzoic acid (**3**).

Synthesis of 4-(4-(anthracen-9-yl)-1*H*-1,2,3-triazol-1-yl)benzoic acid (**4**)



In a 25 mL flame-dried Schlenk tube 4-azido benzoic acid (**3**, 228 mg, 1.40 mmol, 1 eq), 9-ethynylanthracene (**2**, 283 mg, 1.40 mmol, 1 eq), and PMDETA (453 µL, 376 mg, 2.17 mmol, 1.55 eq) were mixed in dry toluene/DMF (1/1 v/v, 8 mL) and the tube was purged with argon for 30 min. 301 mg Cu(I)Br (2.10 mmol, 1.5 eq) were added under an argon atmosphere and the content was stirred overnight at ambient temperature. The reaction mixture was diluted with 20 mL DCM and subsequently extracted with 30 mL sat. NH_4Cl solution three times. The organic layer was dried with Na_2SO_4 and concentrated under vacuum to yield 4-(4-(anthracen-9-yl)-1*H*-1,2,3-triazol-1-yl)benzoic acid (**4**, 351 mg, 0.93 mmol, 67 %).

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 13.29 (s, 1H), 9.37 (s, 1H), 8.80 (s, 1H), 8.23 (dt, *J* = 17.0, 8.6 Hz, 6H), 7.95 (s, 2H), 7.55 (dddd, *J* = 24.0, 8.1, 6.5, 1.3 Hz, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ / ppm = 166.5, 162.3, 143.7, 139.7, 131.1, 130.8, 130.6, 128.5, 128.3, 126.5, 125.8, 125.5, 124.4, 124.1, 119.9.

ESI-MS: *m/z* calculated for $C_{23}H_{15}O_2N_3$ $[M-H]^-$ 364.1092, found 364.1097.

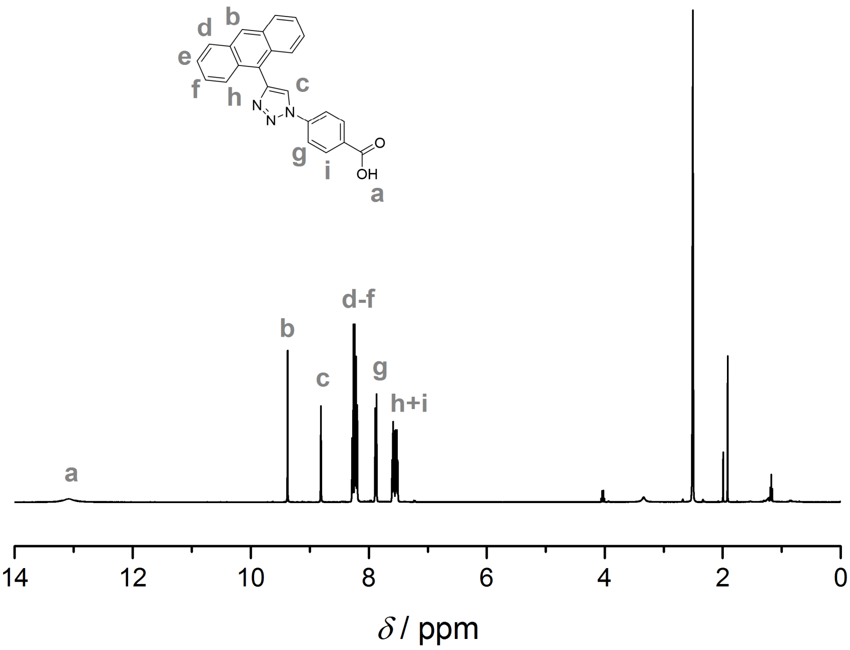
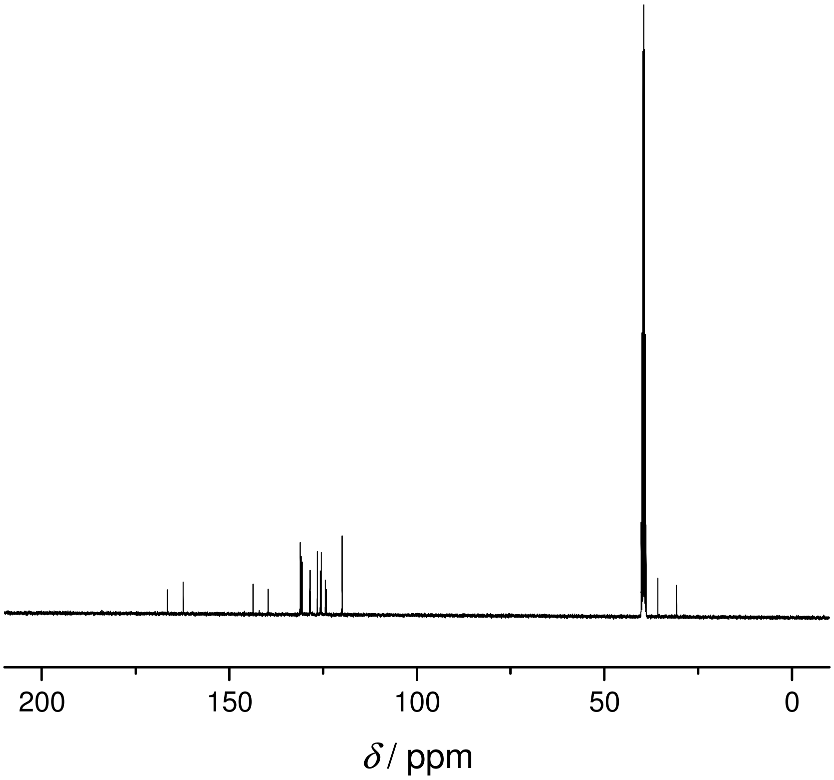
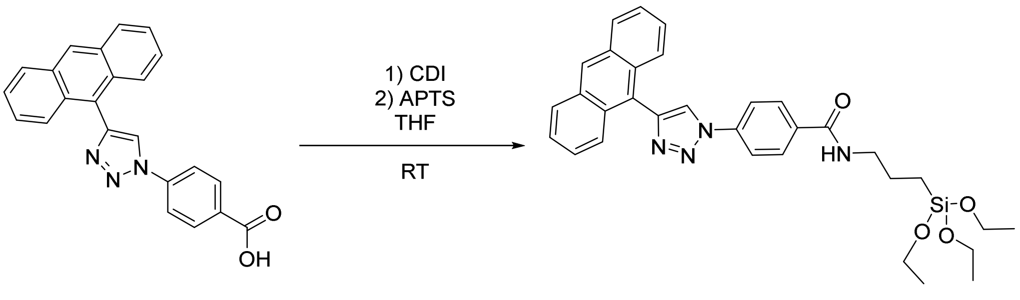


Figure S5. ^{1}H NMR spectrum of 4-(4-(anthracen-9-yl)-1*H*-1,2,3-triazol-1-yl)benzoic acid (**4**).



FigureS6. ^{13}C NMR spectrum of 4-(4-(anthracen-9-yl)-1*H*-1,2,3-triazol-1-yl)benzoic acid (**4**).

Synthesis of 4-(4-(anthracen-9-yl)-1*H*-1,2,3-triazol-1-yl)-*N*-(3-(triethoxysilyl)propyl)benzamide (**5**)



In a flame-dried 25 mL Schlenk tube 4-(4-(anthracen-9-yl)-1*H*-1,2,3-triazol-1-yl)benzoic acid (**4**) (180 mg, 0.47 mmol, 1 eq) and CDI (76.9 mg, 0.47 mmol, 1 eq) were dissolved in dry THF (5 mL) and stirred at ambient temperature for 3 h. Subsequently, APTES (110 µL, 105 mg, 0.47 mmol, 1 eq) was added and the reaction mixture was stirred overnight at ambient temperature. The crude reaction mixture was concentrated under vacuum and purified by column chromatography (silica gel, cyclohexane/ ethyl acetate 3:4, R_f = 0.58) to yield 4-(4-(anthracen-9-yl)-1*H*-1,2,3-triazol-1-yl)-*N*-(3-(triethoxysilyl)propyl)benzamide (202 mg, 0.36 mmol, 76 %).

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 9.34 (s, 1H), 8.80 (s, 1H), 8.67 (t, *J* = 5.6 Hz, 1H), 8.24–8.18 (m, 4H), 8.16–8.11 (m, 2H), 7.87 (dq, *J* = 8.7, 1.0 Hz, 2H), 7.61–7.49 (m, 4H), 3.77 (q, *J* = 7.0 Hz, 6H), 3.31–3.26 (m, 2H), 1.68–1.58 (m, 2H), 1.16 (t, *J* = 7.0 Hz, 9H), 0.67–0.60 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ / ppm = 164.9, 143.6, 138.4, 134.5, 130.83, 130.6, 128.9, 128.5, 128.3, 126.5, 125.8, 125.5, 124.3, 124.2, 119.7, 57.7, 42.2, 22.7, 18.2, 7.5.

ESI-MS *m/z* calculated for $C_{32}H_{36}O_4N_4Si$ $[M+Cl]^-$ 603.2200, found 603.2204.

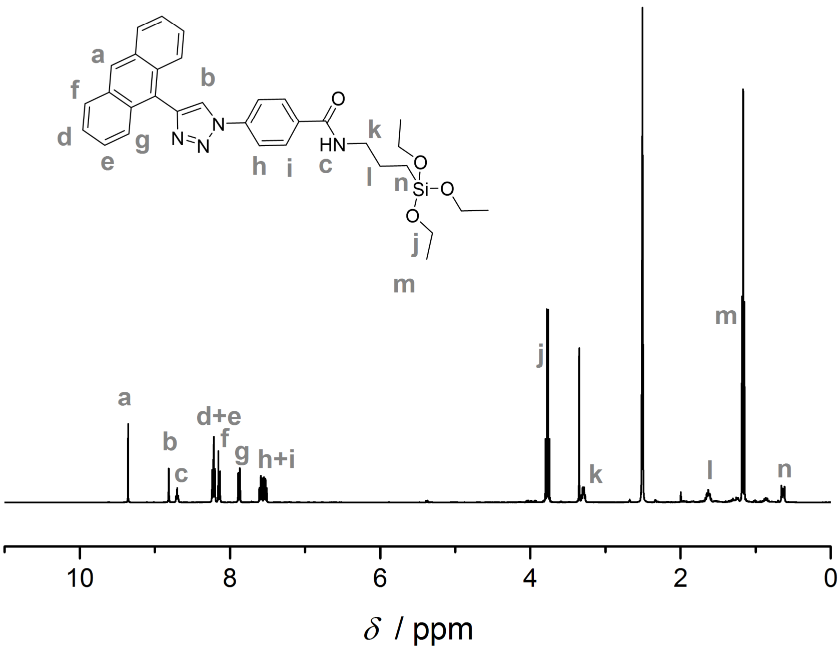


Figure S7. ^{1}H NMR spectrum of 4-(4-(anthracen-9-yl)-1*H*-1,2,3-triazol-1-yl)-*N*-(3-(triethoxysilyl)propyl)benzamide.

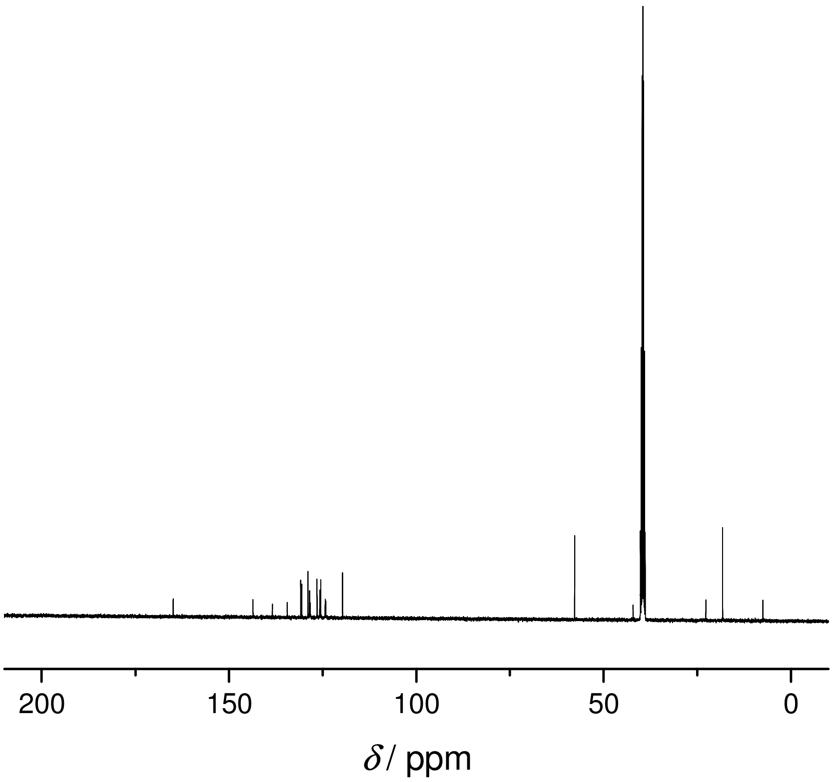


Figure S8. ^{13}C NMR spectrum of 4-(4-(anthracen-9-yl)-1*H*-1,2,3-triazol-1-yl)-*N*-(3-(triethoxysilyl)propyl)benzamide (**5**).

Synthesis of anthracen-9-ylmethyl benzodithioate (**6**)[3]

Benzoic acid (1.22 g, 10 mmol, 1 eq), 9-anthracene methanol (2.08 g, 10 mmol, 1 eq), P_4S_{10} (2.22 g, 5 mmol, 0.5 eq) were dissolved in toluene (40 mL) in a 100 mL three neck round flask. The solution was stirred at ambient temperature under an argon atmosphere for 1 h and subsequently heated to 110 °C for 24 h. The reaction solution was filtered after cooling and the filtrate was washed with dist. H_2O. The organic layer was dried with Na_2SO_4. The solvent was then removed by evaporation and the crude product was purified by column chromatography (silica gel, petroleum ether/benzene 10:1, $R_f = 0.39$) to yield anthracen-9-ylmethyl benzodithioate (**6**) (2.86 g, 8.3 mmol, 83 %) as red crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm = 7.2–8.4 (m, 14H), 4.47 (s, 2H).

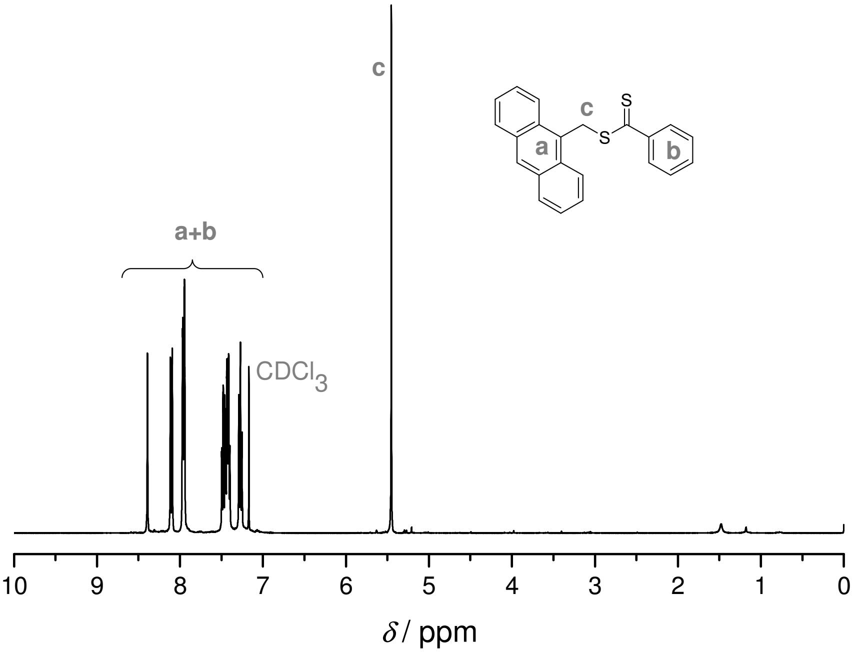


Figure S9. ^{1}H NMR spectrum of anthracen-9-ylmethyl benzodithioate.

Synthesis of anthracene functionalized polystyrene (**P1**)

In a Schlenk tube, anthracen-9-ylmethyl benzodithioate (**6**) (40 mg, 0.116 mmol) and AIBN (3.8 mg, 0.023 mmol) were dissolved in styrene (5.3 mL, 4.82 g, 46.3 mmol). The solution was deoxygenated by percolating with nitrogen for 10 min. The polymerization reaction was performed at 60 °C under nitrogen atmosphere. After 24 h, the reaction was quenched by cooling in an ice bath and the solution was precipitated in methanol. The polymer was obtained by filtration and dried under vacuum. Conversion of styrene was determined gravimetrically and the molar mass was determined by GPC (PS calibration).

$M_{n,GPC} = 8400$ g mol^{-1}, $Đ = 1.03$

Conversion 12%

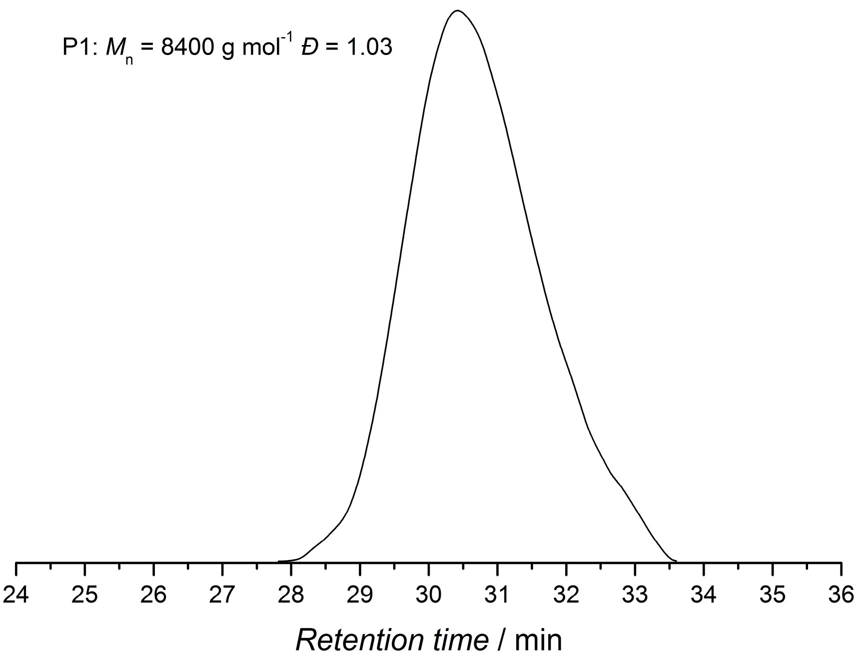


Figure S10. GPC chromatogram of anthracene functionalized polystyrene (**P1**).

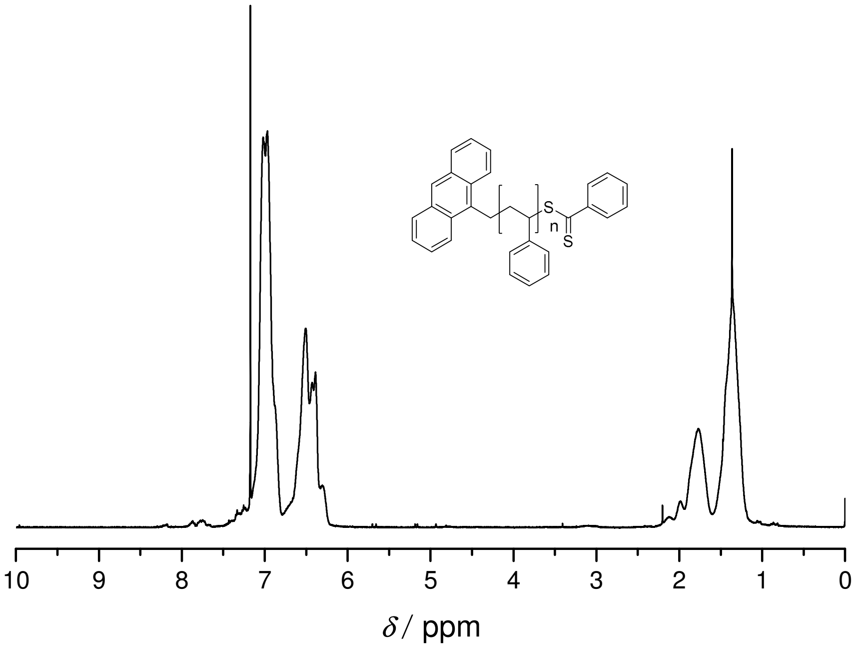


Figure S11. ^{1}H NMR spectrum of anthracene functionalized polystyrene (**P1**).

Synthesis of 9-anthrylmethyl 2-bromo-2-methyl propanoate (**7**)[4]

9-Anthracene methanol (1 g, 4.8 mmol, 1 eq) and triethylamine (0.98 mL, 0.72 g, 7 mmol, 1.45 eq) were dissolved in 20 mL dry THF. The solution was cooled in an ice bath and a solution of 0.87 mL 2-bromoisobutyryl bromide (1.62 g, 7 mmol, 1.45 eq) in 10 mL of dry THF was added dropwise under nitrogen atmosphere. The ice bath was removed and the reaction was stirred at room temperature overnight. The precipitate was filtered off and the solvent was evaporated. The raw product was dissolved in dichloromethane, subsequently washed with $NaHCO_3$ solution, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the yellow oil was recrystallized from hexane to yield 9-anthrylmethyl 2-bromo-2-methyl propanoate (1.49 g, 4.18 mmol, 87%) as light yellow crystals.

^{1}H NMR (400 mHz, $CDCl_3$) δ / ppm = 7.4–8.4 (m, 9H), 6.20 (s, 2H), 1.80 (s, 6H).

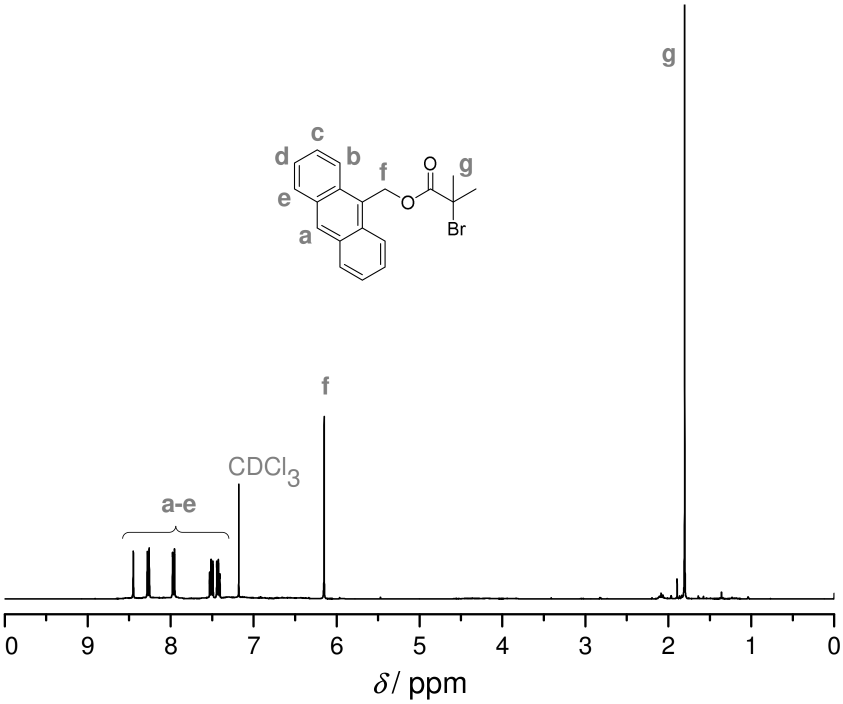


Figure S12. ^{1}H NMR spectrum of 9-anthrylmethyl 2-bromo-2-methyl propanoate (**7**).

Synthesis of anthracene functionalized poly(*n*-butyl acrylate) (**P2**)

In a Schlenk tube, 9-anthrylmethyl 2-bromo-2-methyl propanoate (**7**, 78 mg, 0.219 mmol), PMDETA (46 µL, 38.2 mg, 0.291 mmol) and Cu(I)Br (31.3 mg, 0.219 mmol) were dissolved in *n*-butylacrylate (6.27 mL, 5.61 g, 43.7 mmol) and deoxygenated by three freeze-pump-thaw cycles. The polymerization reaction was performed at 110°C under nitrogen atmosphere. After 30 min the reaction was quenched by cooling in an ice bath and the solution was precipitated in a methanol/water mixture. The polymer was then dissolved in THF and purified by passing through a short alumina column. The polymer was dried under vacuum. Conversion of *n*-butyl acrylate was determined by ^{1}H NMR and the molar mass was determined by GPC (PMMA calibration).

$M_{n,GPC}$ = 8200 g mol^{-1}, $Đ$ = 1.26

Conversion 17%

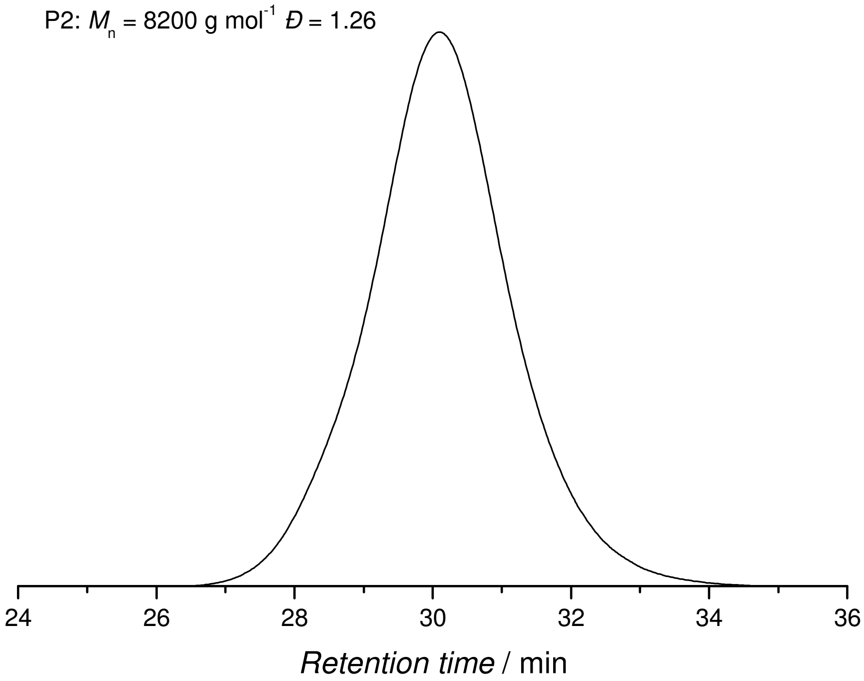


Figure S13. GPC chromatogram of anthracene functionalized poly(*n*-butyl acrylate) (**P2**).

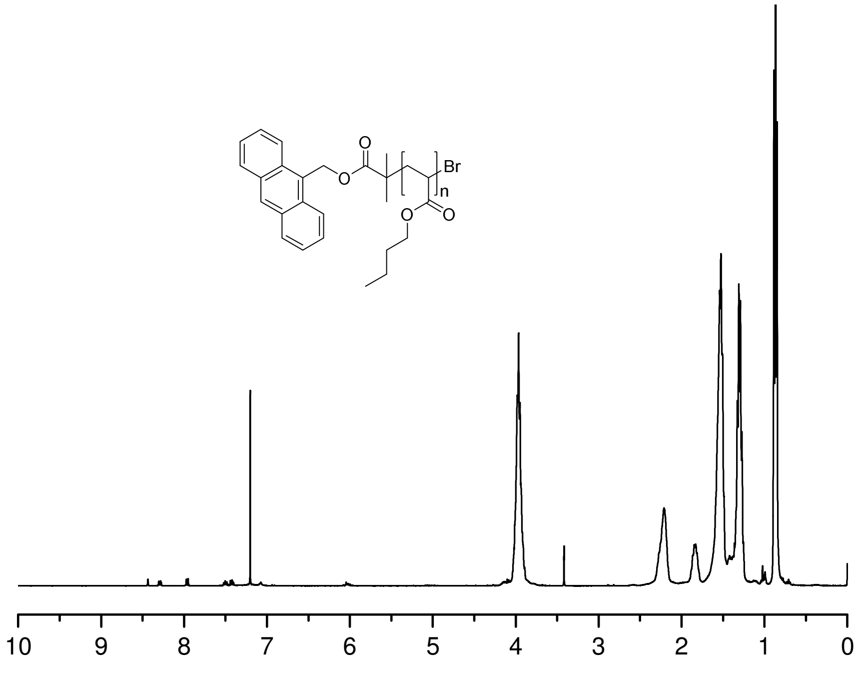


Figure S14. ^{1}H NMR spectrum of anthracene functionalized poly(*n*-butylacrylate) (**P2**).

3.2 Surface Encodings

Silanization Protocol

Silicon wafers were separately placed in 5 mL vials, 3 mL Piranha solution (H_2O_2/H_2SO_4 1/2, v/v) were added and the solution was heated at 80 °C for approx. 60 min. The wafers were rinsed with an excess of water, acetone and DCM and dried under a stream of argon. The activated/cleaned wafers were placed into headspace vials (Pyrex, diameter 20 mm), which were crimped airtight using styrene/butadiene rubber seals with PTFE inner liner. Anthracene silane (**5**) was dissolved in extra-dry toluene (2 mg mL^{-1}) and percolated with argon for 5 min. To each substrate, 2 mL of the silane solution were added. The samples were heated in an oven at 50 °C overnight and were subsequently rinsed with an excess of toluene, DCM, acetone, MilliQ water, acetone and DCM and dried under an argon stream.

Surface patterning (Writing step)

For light induced surface patterning, the silanized silicon wafers were placed in a custom made surface holder and covered with a dotted shadow mask (Figure S1a). The sample holder was placed in a headspace vial (Pyrex, diameter 20 mm) and a solution of the respective anthracene functionalized molecule or polymer in dry MeCN or DCM (1 mg per mL for small molecules, 2 mg per mL for polymers) was added. The vial was crimped airtight using styrene/butadiene rubber seals with PTFE inner liner. The solution war percolated with argon for 5 min and subsequently irradiated at 410 nm with a custom made LED setup (Figure S1b, refer to Scheme S12 for the emission spectrum) for 4 h. Subsequently, the silicon wafer was removed from the sample holder and successively rinsed with MeCN, acetone, toluene and DCM and dried under an argon stream.

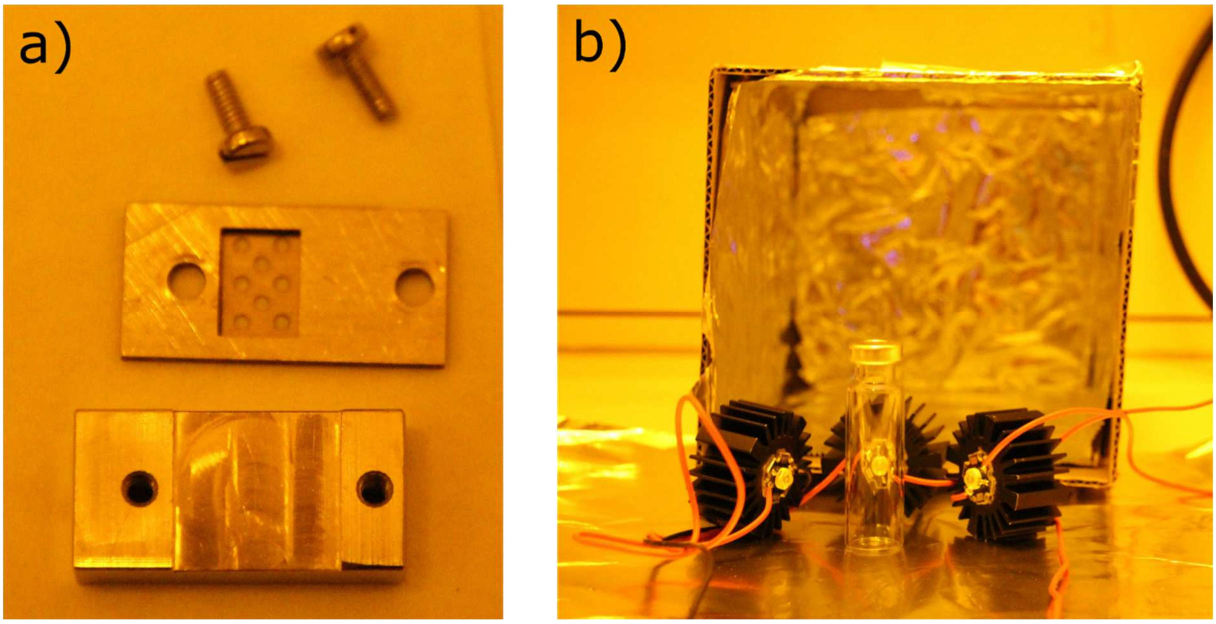
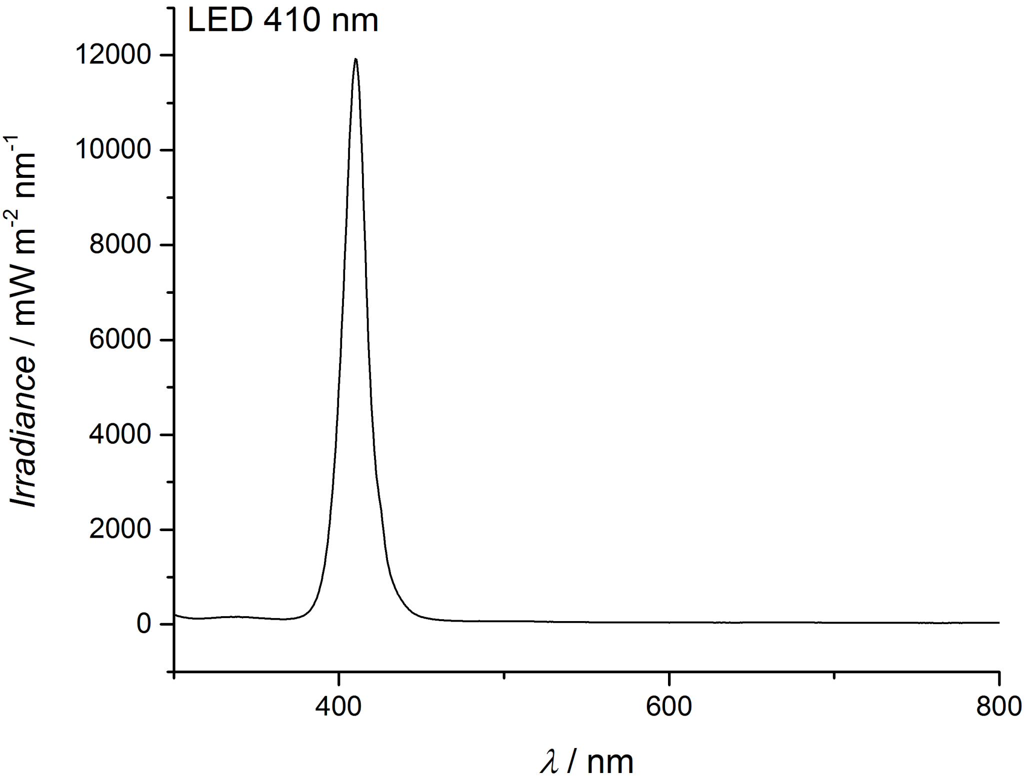


Figure S15. a) Picture of the employed sample holder and dotted shadow mask; b) Picture of the employed custom built LED setup.



Scheme S16. Emission spectrum and intensity of the employed LED setup.

Surface erasing (removal of the pattern)

For light-induced erasing, the patterned silicon wafer was placed in a headspace vial (Pyrex, diameter 20 mm) and 5 mL of pure, dry MeCN or DCM was added. The vial was crimped airtight using styrene/butadiene rubber seals with PTFE inner liner and the solvent was percolated with argon for 5 min. Subsequently, the sample was irradiated in a custom built photoreactor (Figure S2) employing a Philips PL-L lamp (emission spectrum see Scheme S13) for 24 h. After 24 h irradiation time, the MeCN was exchanged for fresh solvent and the sample was irradiated for another 24 h to complete the erasing process.

Figure S17. Picture of the employed custom built photoreactor equipped with the Philips PL-L lamp.

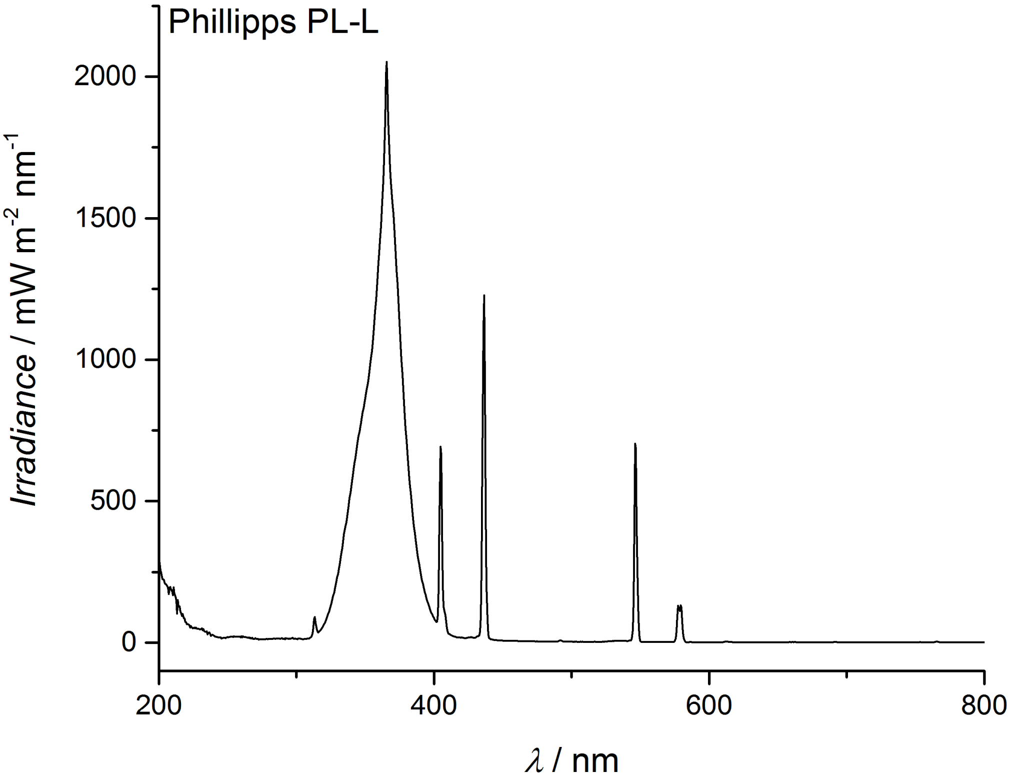


Figure S18. Emission spectrum and intensity of the employed Philipps PL-L lamp.

4 XPS Measurement

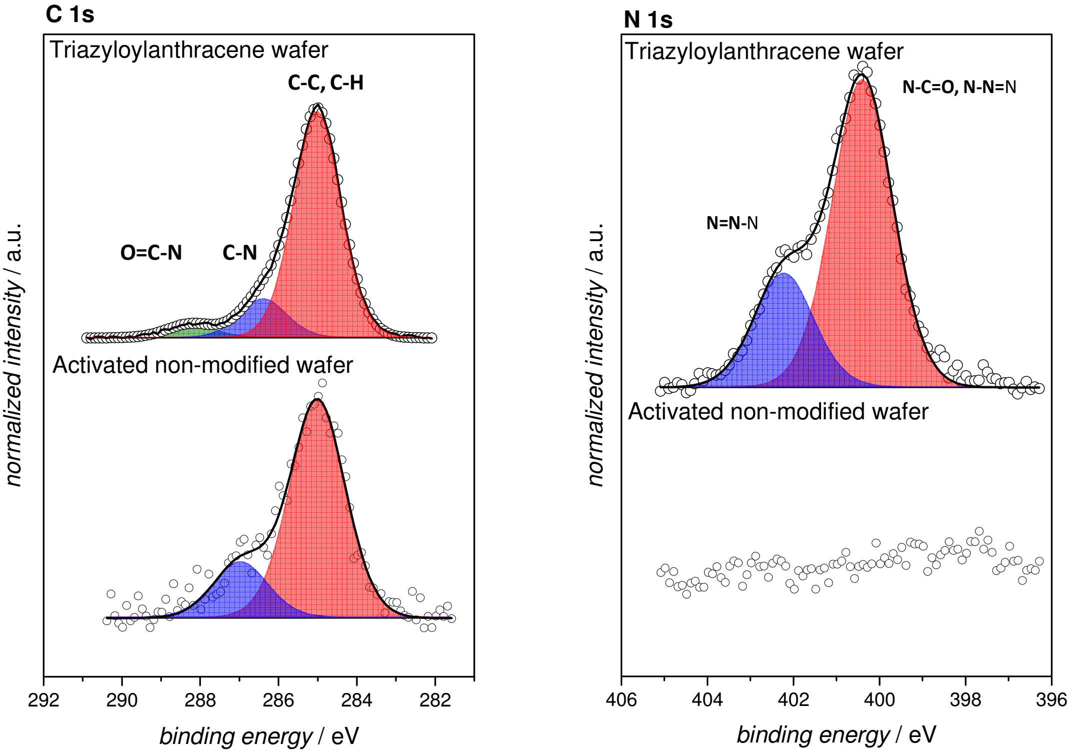


Figure S19. XPS analysis of an activated non-modified wafer versus a silanized wafer treated with anthracene silane (**5**). Deconvolutions of C1s and N1s signals are depicted. In the C1s signal a clear increase of the overall carbonyl content on the wafer is observed (from 2.8 at% to 25.1 at%). Additionally, peaks corresponding to O=C-N and C-N are detected. On the silanized wafer, a clear N1s signal can be detected that was non-existent on the activated non-modified wafer. Additionally, the N1s signal evidences a typical peak pattern for triazole rings.

5 ToF-SIMS Measurements

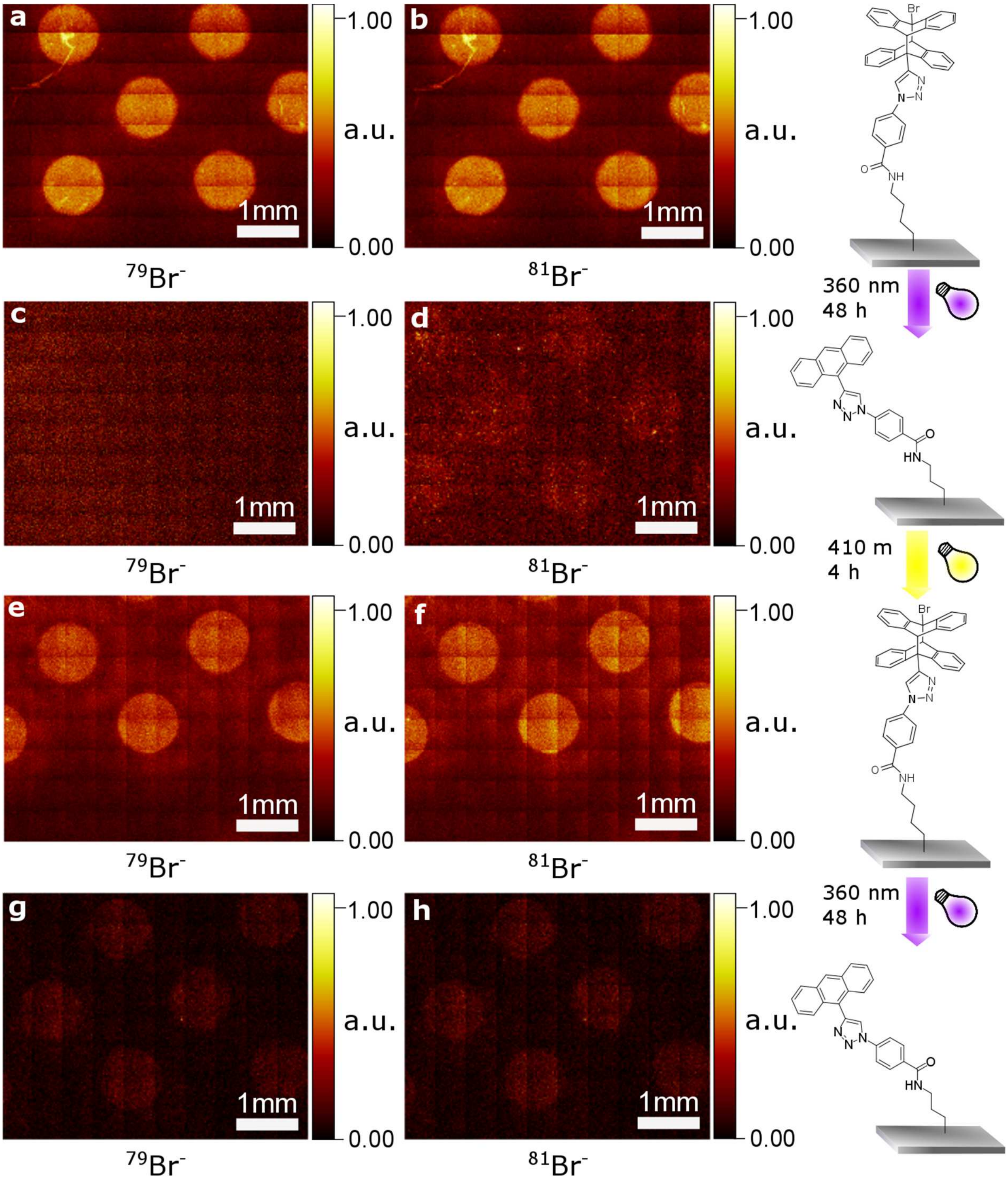


Figure S20. Single fragment ToF-SIMS ion maps of bromine ions for the writing and erasing of 9-BA patterns obtained after irradiation of a silicon wafer: a) + b) visible light (410 nm) for 4 h in the presence of 9-BA (1 mg/mL in DCM); c) + d) mild UV light (360 nm, 48 h, DCM); e) + f) same as a) + b); g) + h) same as c) + d).

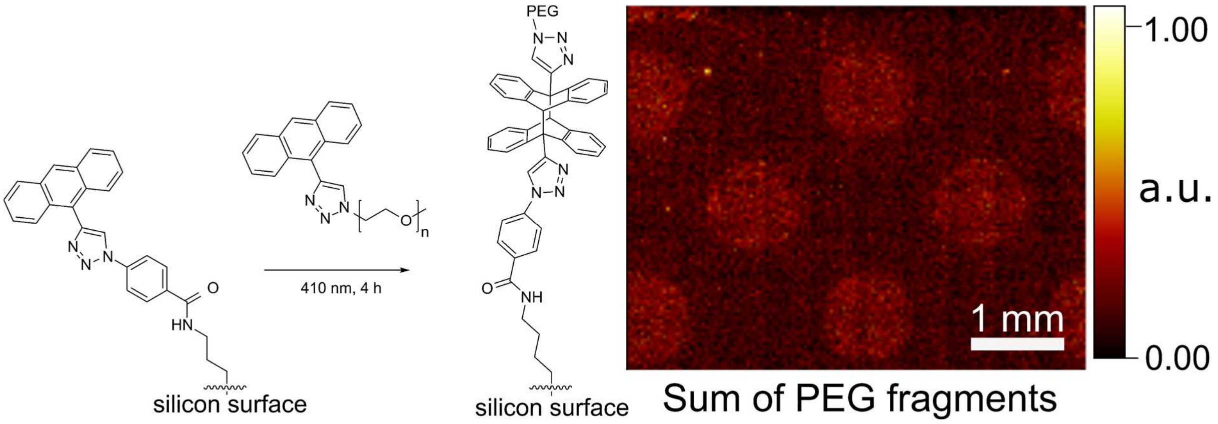


Figure S21. Reaction sequence and ToF-SIMS analysis of the photoreaction between a triazyloylanthracene surface and a triazyloylanthracene end capped PEG chain at 410 nm.

The cross reactivity of the electron rich anthracene was tested with triazyloylanthracene end capped poly(ethylene glycol) (PEG) and irradiating the triazyloylanthracene surface in the presence of the PEG derivative at 410 nm for 4 h through a doted shadow mask (2 mg/mL in DCM, see Figure S21). The ToF-SIMS analysis revealed only a very weak, barely visible dot pattern consisting of PEG characteristic fragments. It is therefore assumed that a self-dimerization of the triazyloylanthracenes on the surface is negligible due to the unfavorable electronic structures of the reaction partners.

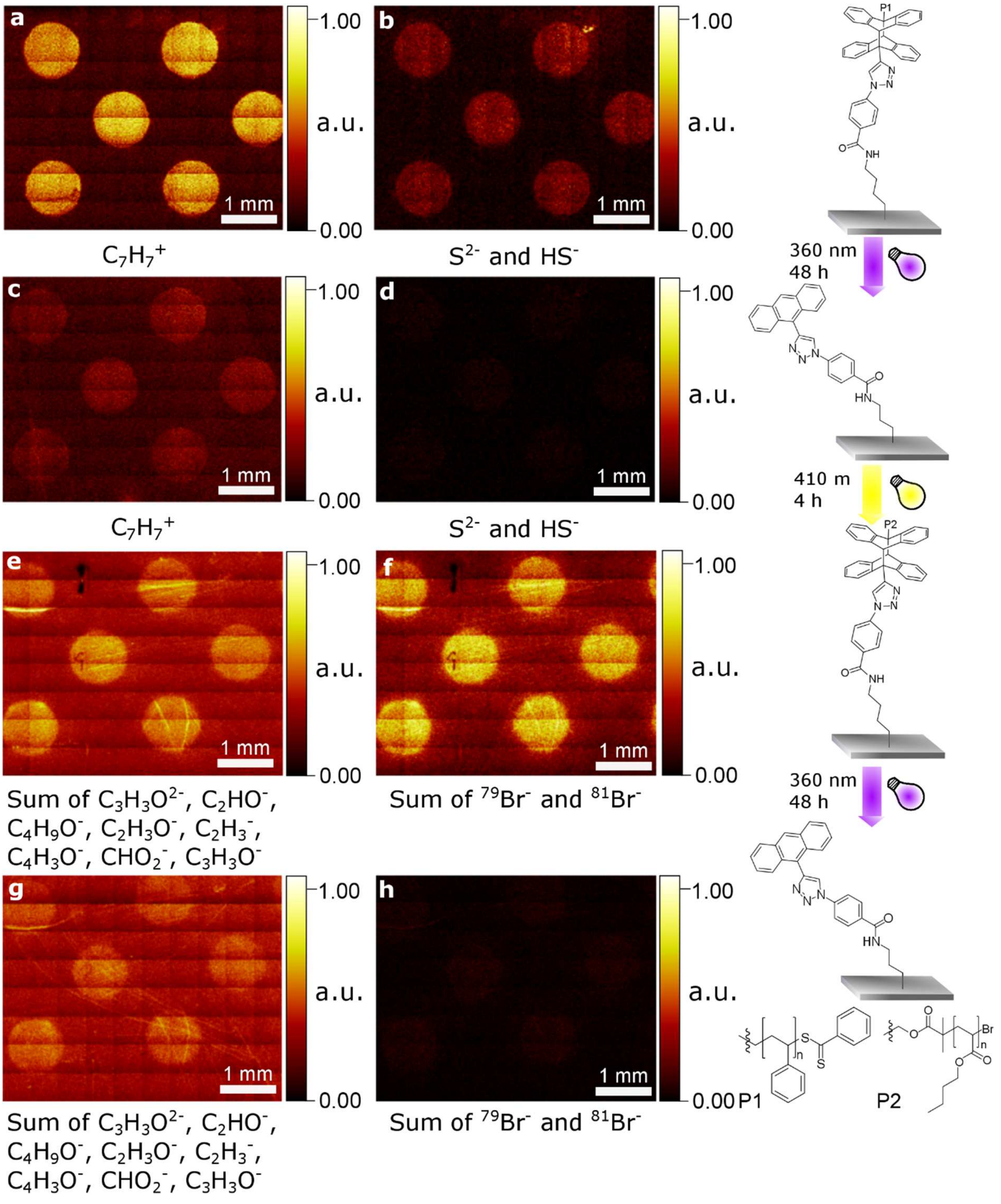
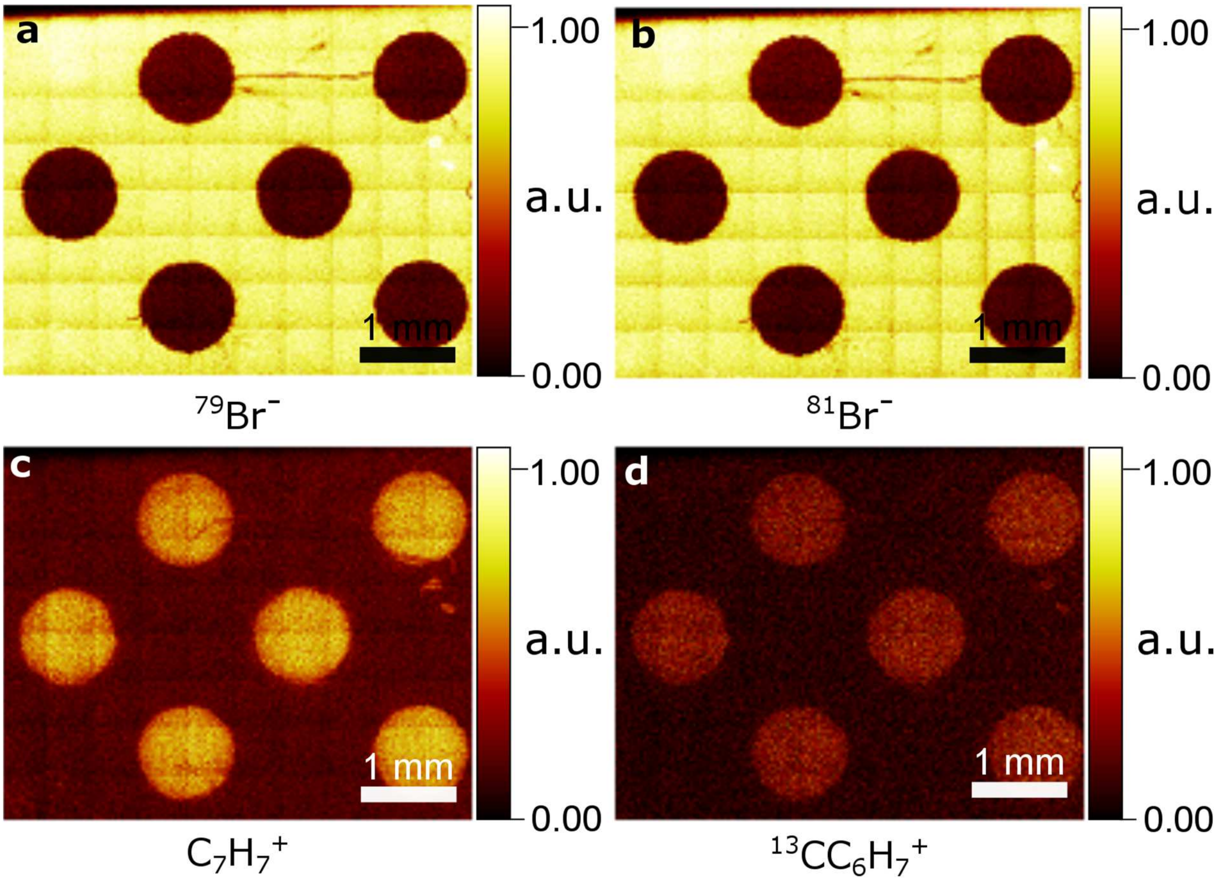


Figure S22. Detailed ToF-SIMS ion maps for the writing and erasing of two polymer patterns obtained after irradiation of a silicon wafer: a) + b) visible light (410 nm) for 4 h in the presence of **P1** (2 mg/mL in DCM); c) + d) mild UV light (360 nm, 48 h, MeCN); e) + f) visible light (410 nm) for 4 h in the presence of anthracene **P2** (2 mg/mL in MeCN); g) + h) mild UV light (360 nm, 48 h, MeCN).



$^{79}Br^{-}$ $^{81}Br^{-}$

$C_7H_7^{+}$ $^{13}CC_6H_7^{+}$

Figure S23. Single fragment ToF-SIMS ion maps obtained after dual functionalization of a silicon wafer with 9-BA (no mask, 410 nm, 4 h), a) + b) erasing a dot pattern (360 nm, 48 h) and c) + d) back-filling the dots with **P1** (410 nm, 4 h).

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