Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Photo-Induced Surface Encoding of Gold Nanoparticles

Lukas Stolzer, Alexander S. Quick, Doris Abt, Alexander Welle, Denys Naumenko, Marco Lazzarino, Martin Wegener, Christopher Barner-Kowollik and Ljiljana Fruk**

Materials

Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot xH_2O$, 99.999%, Sigma-Aldrich), 11-mercapto-1-undecanol (MUD, 97%, Sigma-Aldrich), lithium triethylborohydride 1.0 M solution in THF (Super-Hydride, Sigma-Aldrich), *N*,*N*′-dicyclohexylcarbodiimide (DCC, 99%, Sigma-Aldrich), 4-(dimethylamino)pyridine (DMAP, 99%, Sigma-Aldrich), iodine (≥99.5%, Roth), maleimide (99%, Sigma-Aldrich), tetrahydrofuran (THF, ≥99.9%, VWR), dimethylformamide (DMF, ≥99.9%, VWR), methanol (≥99.8%, VWR), and dichloromethane (DCM, ≥99.8%, VWR) were used as received. Synthesis of 4-((2-formyl-3-methylphenoxy)methyl)benzoic acid[1] were performed according to a literature procedure. The glass surface was coated with maleimide groups in a two step approach employing (3-aminopropyl)triethoxysilane (APTES) and 4-maleimidopropanoyl chloride as previously reported.[2]

Methods

The structures of the synthesized compounds were confirmed *via* ^{1}H- and ^{13}C-*NMR spectroscopy* using a Bruker AM 250, Bruker AM 300 or Bruker AM 400 spectrometer at 250 MHz, 300 MHz or 400 MHz for hydrogen nuclei and at 100 MHz for carbon nuclei. Samples were dissolved in $CDCl_3$, DMSO-d^6 or in methanol-d^4. The δ-scale is referenced to tetramethylsilane as the internal standard.

UV- Vis spectra were obtained using VARY 300 Scan UV-Visible Spectrometer (Varian Inc., Germany).

UV-Vis characterization of the immobilized Au NPs was performed on an inverted optical microscope (Axiovert 200, Zeiss) in transmitted mode with a top illumination (HAL 100 illuminator, Zeiss) coupling a microscope with a 750 mm long spectrometer (Shamrock SR-750, Andor Technology plc). First, a sample was mounted on the XY sample holder in order to obtain the confocal laser scanning images. 532 nm (Cobolt Samba, 50 mW) CW laser was used as the source of monochromatic light. A laser beam was reflected by a beamsplitter, directed to the microscope and then focused on the sample by 100× air objective (NA 0.8, EC Epiplan, Zeiss) resulting in a diameter of laser spot on the sample of around 0.5 μm. The reflected light was collected by the same objective and then directed into the spectrometer with a mounted femtowatt photoreceiver (New Focus, 2151, Newport Corp.). The signal from a photoreceiver was transferred to the controller of the atomic force microscope (Nanowizard

II, JPK), which controls the XY piezostage (TAO module, JPK) and allows to scan a sample in the range of 100 μm by 100 μm, recording finally the confocal laser scanning images. The laser power on the sample was controlled by a variable metallic neutral density filter (NDC-50C-4M, Thorlabs) and kept at 0.05 mW to avoid the heating of the structures. After that with a top illumination from a halogen source, the light was directed into a spectrometer, dispersed by a diffractive grating of 600 lines mm^{-1}, and finally analyzed using TE-cooled EMCCD (Newton DU971-UVB, Andor Technology plc). The position of the grating was controlled by Andor SOLIS software and changed automatically to cover a wavelength range of 450-900 nm. The XY sample holder allows move the sample with micrometre precision focusing on the locations of interest, i.e. on the patches (to measure the intensity of transmitted light I) or clean glass surface (to measure the reference intensity I_0). A basic equation to calculate the extinction is A + S + R + T = 1, where A is absorption, S is scattering, A + S = E is extinction, R is reflection, and T is transmission of the light. Neglecting the differences in the light reflection from the surfaces of clean glass and gold patches, the extinction was calculated as E = 1 − T, where $T = I/I_0$ is the measured light transmission through the sample. Thus, a final equation to calculate the extinction is $E = (I_0–I)/(I_0–I_{bg})$, where I_{bg} is the measured dark thermal noise of CCD.

Fast Atom Bombardment Mass Spectrometry (FAB-MS): the mass spectra were measured using Finnigan MAT90 mass spectrometer.

Electrospray Ionization-Mass Spectrometry (ESI-MS) spectra were recorded on an LXQ Scientific spectrometer (ThermoFisher Scientific, East Grinstead, UK) 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 was set to 10 V, 70 V, and 300 °C respectively. The samples were dissolved with a concentration of 0.1 $mg \cdot mL^{-1}$ in a mixture of THF and MeOH (3:2) containing 100 μmol of sodium triflate and infused with a flow of 10 $\mu L \cdot min^{-1}$.

Transmission Electron Microscopy (TEM) images were obtained using a CM200-FEG microscope (Philips) operating at 200 kV. Further TEM imaging, HAADF-STEM was done on the Titan^3 80-300 TEM microscope (FEI) operating at 80 kV. TEM samples were prepared by putting droplets of sample suspension onto a copper TEM grid covered with a thin amorphous carbon film of less than 3 nm nominal thickness. Subsequently the prepared samples were dried in air at atmosphere.

Scanning Electron Microscopy (SEM) images were obtained using a Scanning Electron Microscope (Zeiss FIB 1540 ESB) operating at 2 kV and ESB (Energy Selective Backscattered) detector with a ESB grid voltage of 1.5 kV.

Dynamic light scattering (DLS) was obtained using a Malvern Nano Zeta-Sizer (ZS Nano, Malvern).

Spatially resolved surface encoding of gold nanoparticles was performed using a home-built setup that has been described elsewhere[3] with a repetition rate of 80 MHz and a 700 nm center wavelength.

Time-of flight secondary ion mass spectrometry was performed on a TOF.SIMS5 instrument (ION-TOF GmbH, Münster, Germany. This spectrometer is equipped with a Bi cluster primary ion source and a reflectron type time-of-flight analyzer. UHV base pressure was < 5×0^{-9} mbar. For high mass resolution the Bi source was operated in the "high current bunched" mode providing short Bi_1^+ or Bi_3^+ primary ion pulses at 25 keV energy and a lateral resolution of approx. 4 µm. The short pulse length of 1.1 to 1.3 ns allowed for high mass resolution. The primary ion beam was raster across a 500×500µm field of view on the sample, and 128×128 data points were recorded. Primary ion doses were kept below 10^{11} ions/cm^2 (static SIMS limit). For charge compensation an electron flood gun providing electrons of 21 eV was applied and the secondary ion reflectron tuned accordingly. Spectra were calibrated on the omnipresent C^-, 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. For high lateral resolution imaging the primary ion source was operated in "burst alignment" mode. Here, only nominal mass resolution is obtained but the lateral resolution of the instrument is in the range of 150nm. Therefore, $Au_xS_y^-$ peaks (x = 1 - 5, y = 0 - 2) were used for imaging since these peaks do not show adjacent signals at the same nominal mass (m/z). In case of

bromine imaging this prerequisite was not given (see Fig. S 24, insert). Therefore, bromine imaging (Fig. 4 c) was performed using "bunched" mode operation of the primary ion gun, providing high lateral and high mass resolution. Based on this instrument setting and the very low amount of bromine as compared to gold, overall count rates were much lower for bromine (Fig. 4 c) as compared to gold clusters (Fig. 4b)

Setup for Light-Triggered Reactions in Solution

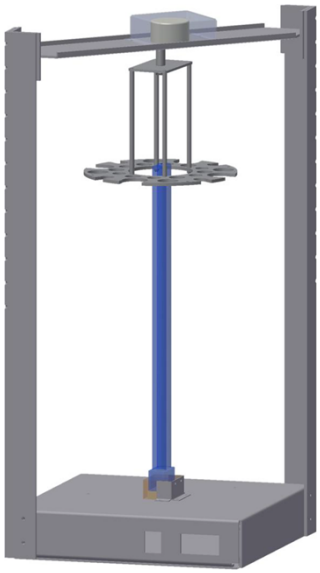


Figure S1. Drawing of the custom-built photoreactor employed in the current study for reactions in solution.

The photoreactions (Fig. 4a and Scheme S2) were performed in a custom-built photoreactor (Fig. S1) consisting of a metal disk which revolves at a distance of 40-50 mm around a compact low-pressure fluorescent lamp with λ_{max} = 320 nm ± 30 nm (36 W, Arimed B6, Cosmedico GmbH, Germany) (Fig. S2).

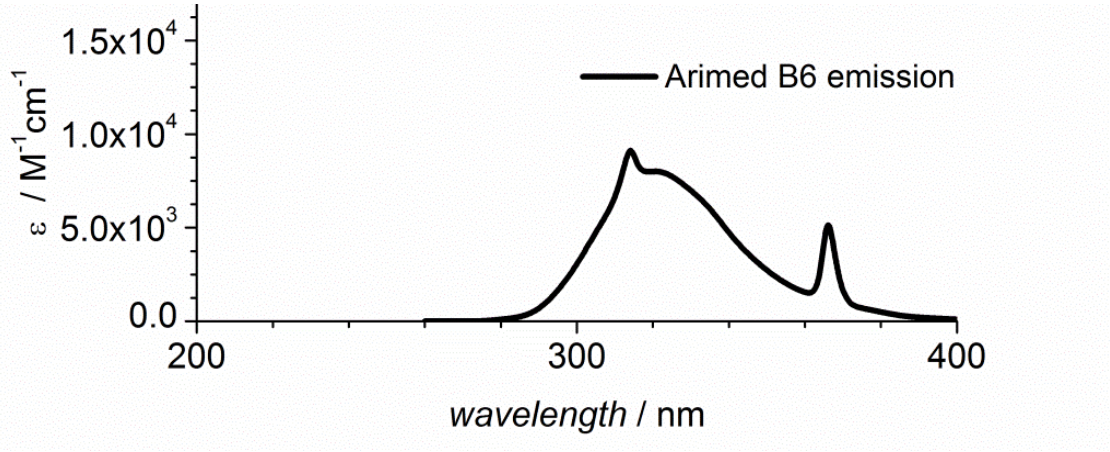


Figure S2. Emission spectrum of the employed compact low-pressure fluorescent lamp (36 W, Arimed B6, λ_{max} = 320 nm).

Synthetic Procedures

Synthesis of Mercaptoundecanol-capped Gold Nanoparticles (Au-MUD)

Gold nanoparticles were prepared by using the synthesis procedure of Raula et al.[4] $HAuCl_4$ (354 mg, *n*(Au)) 0.93 mmol) was dissolved in dry THF (10 mL) and stirred for 15 min. MUD (184 mg, 0.90 mmol) was added gradually to the mixture under constant stirring. Subsequently, the mixture was stirred for a further 30 min until the color of the mixture changed from brown to orange. Reduction was carried out at ambient temperature slowly adding Super-Hydride (6 mL) to the reaction mixture under fast stirring rate. In the beginning of the addition of the reductant, the solution changed to a black suspension. Thereby, the temperature of the mixture slightly increased. The stirring was continued until the temperature of the mixture decreased to ambient temperature after ca. 1 h. Purification of the gold nanoparticles was conducted by centrifugation (13200 rpm) in an ethanol/THF mixture.

Synthesis of Photoenol-modified Gold Nanoparticles (Au-MUD-PE)

MPC-MUD (155 mg), which contained 28.4 µmol of ligands, DCC (3.53 mg, 17.1 µmol), and 4-DMAP (0.17 mg, 1.39 µmol) were dissolved in 1.3 mL of DMF and flushed with dry nitrogen for 15 min. 4-((2-Formyl-3-methylphenoxy)methyl)benzoic acid (1.58 mg, 5.85 µmol) dissolved in 1.3 mL of DMF was added dropwise to the mixture with stirring at ambient temperature. Subsequently, the temperature of the reaction mixture was raised to 30 °C, and kept at that temperature for 48 h. The purification of the product was accomplished

by using a 2000 kDa dialysis bag in water. In the course of the exchange of DMF and water in the dialysis tube, the Au NPs precipitated. The success of the purification was ascertained by ^{1}H-NMR. ^{1}H-NMR (250 MHz, CD_3OD) δ / ppm: 0.8-1.8 (m, 360H, CH_2), 2.53 (s, 3H, CH_3), 3.57 (br, 2H, CH_2), 5.26 (s, 2H, CH_2), 6.86 (d, *J* = 8.1 Hz, 1H, C*H*), 7.06 (d, *J* = 8.2 Hz, 1H, C*H*), 7.42 (t, *J* = 8.1 Hz, 1H, C*H*), 7.53 (d, *J* = 8.1 Hz, 2H, C*H*), 7.59 (d, *J* = 8.4 Hz, 2H, C*H*), 10.64 (s, 1H, C*H*O).

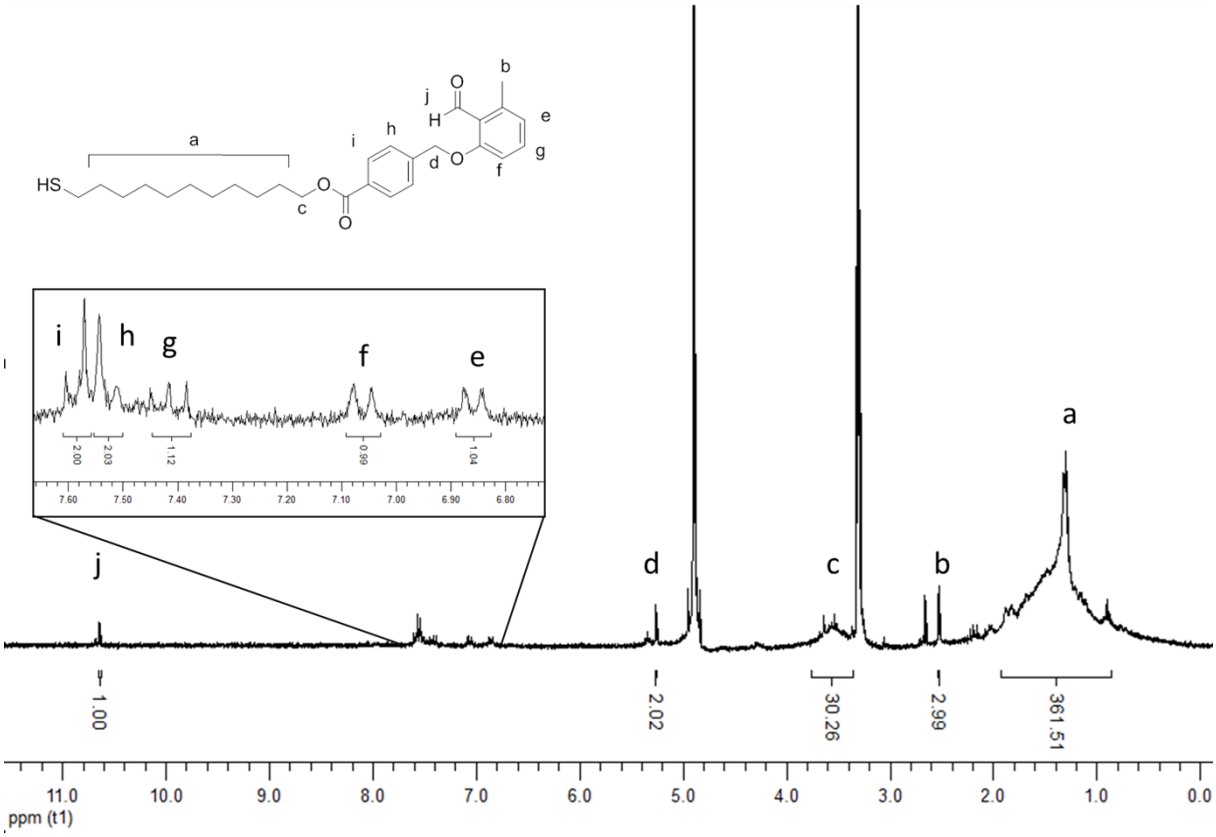
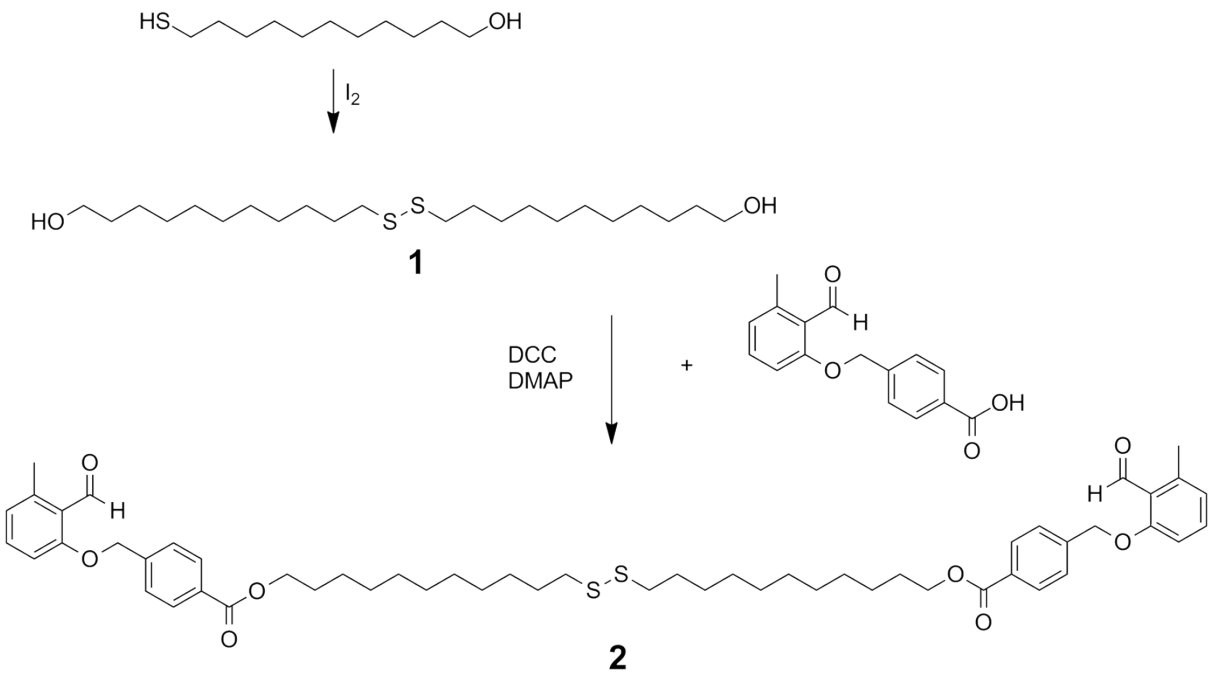


Figure S3. ^{1}H-NMR spectrum of photoenol precursor modified **Au-MUD-PE** in CD_3OD at 250 MHz.

Synthesis of photoenol disulfide linker 2



Scheme S1. Synthesis of photoenol disulphide linker **2**.

Synthesis of 11-Hydroxyundecyldisulfide 1

11-Hydroxyundecylsulfide was prepared via the synthesis procedure of Friederici *et al.*[5] A methanol solution (80 mL) containing 11-mercapto-1-undecanol (1.002 g, 4.90 mmol) was titrated by 1 M iodine methanol solution until the solution turned light yellow. Then the reaction was quenched with sodium bisulfite. The reaction mixture was evaporated to dryness under reduced pressure at ambient temperature and the product, 11-hydroxyundecyldisulfide **1**, was extracted in CH_2Cl_2 as a white solid (900 mg, 90%).

Synthesis of disulfanediylbis(undecane-11,1-diyl) bis(4-((2-formyl-3-methylphenoxy) methyl)benzoate) 2

To a solution of 11-hydroxyundecyldisulfide (0.253 g, 0.62 mmol) in 40 mL CH_2Cl_2, 4-((2-formyl-3-methylphenoxy)methyl)benzoic acid (0.335 g, 1.23 mmol), DCC (0.277 g, 1.34 mmol) and DMAP (0.014 g, 0.11 mmol) were successively added. The resulting mixture was allowed to stir overnight at ambient temperature under argon. After the reaction was finished, the white solid was removed by filtration, solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica using a mixed eluent (cyclohexane:ethyl acetate, 5:1), obtaining **2** as a yellow solid (251 mg, 56%). ^{1}H-NMR (400

MHz, $CDCl_3$) δ / ppm: 1.18-1.38 (m, 28H, CH_2), 1.59 (qi, *J* = 7.3 Hz, 4H, CH_2), 1.69 (qi, *J* = 7.3 Hz, 4H, CH_2), 2.51 (s, 6H, CH_3), 2.60 (t, *J* = 7.3 Hz, 4H, CH_2), 4.24 (t, *J* = 6.7 Hz, 4H, CH_2), 5.14 (s, 4H, CH_2), 6.76 (d, *J* = 7.4 Hz, 2H, C*H*), 6.78 (d, *J* = 8.2 Hz, 2H, C*H*), 7.28 (t, *J* = 8.0 Hz, 2H, C*H*), 7.42 (d, *J* = 8.2 Hz, 4H, C*H*), 7.99 (d, *J* = 8.3 Hz, 4H, C*H*), 10.68 (s, 2H, C*H*O). ^{13}C-NMR (100 MHz, $CDCl_3$) δ / ppm: 21.52 (*C*H_3), 26.05 (*C*H_2), 28.63 (*C*H_2), 29.27 (*C*H_2), 39.17 (*C*H_2), 65.26 (*C*H_2), 69.93 (*C*H_2), 110.31 (C_{Ar}), 123.66 (C_{Ar}), 124.69 (C_{Ar}), 127.07 (C_{Ar}), 129.68 (C_{Ar}), 134.42 (C_{Ar}), 141.22 (C_{Ar}), 142.30 (C_{Ar}), 161.92 (C_{Ar}), 166.28 (O*C*O), 192.00 (*C*HO) . HR-MS: (FAB) *m/z* calculated for $C_{54}H_{70}S_2O_8$, 910.4512; found, 910.4514.

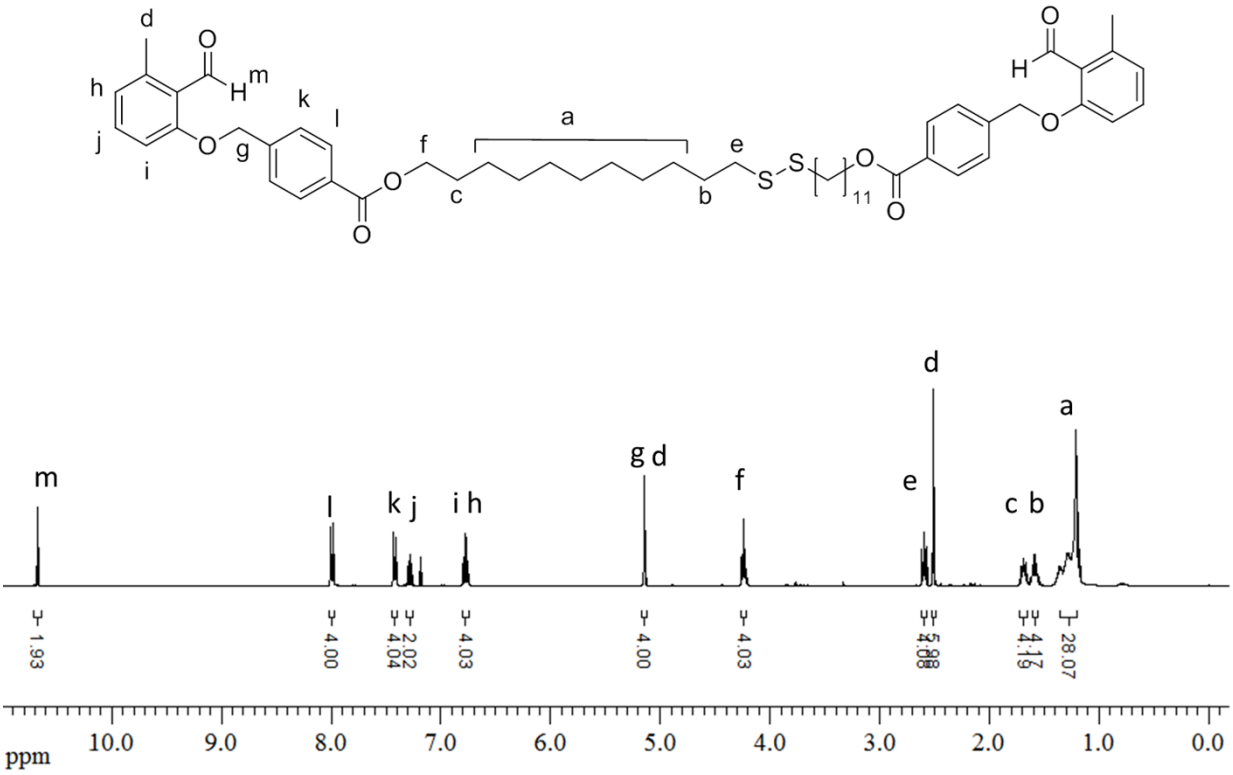


Figure S4. ^{1}H-NMR spectrum of the photoenol disulphide linker **2** in $CDCl_3$ at 400 MHz.

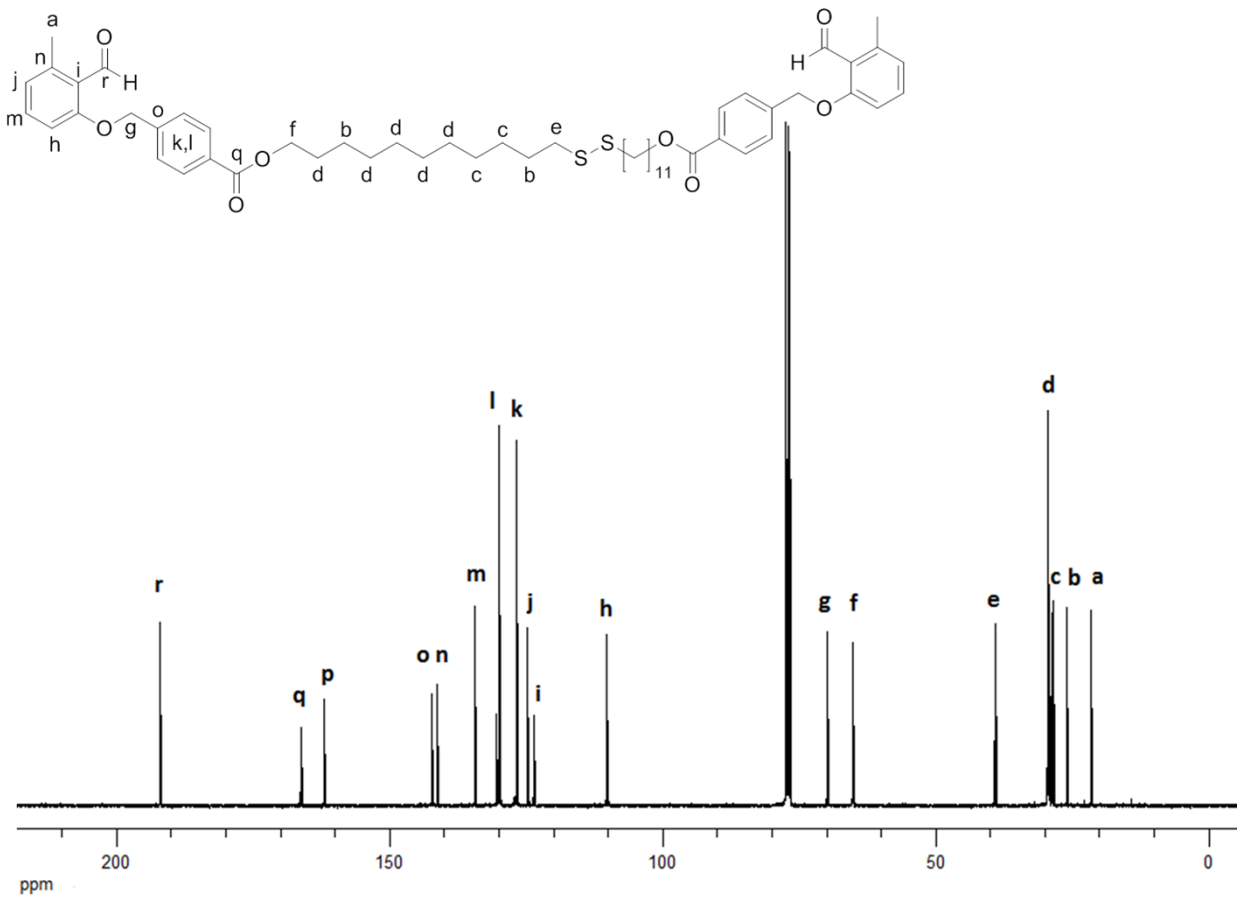


Figure S5. ^{13}C-NMR spectrum of the photoenol disulphide linker **2** in $CDCl_3$ at 100 MHz.

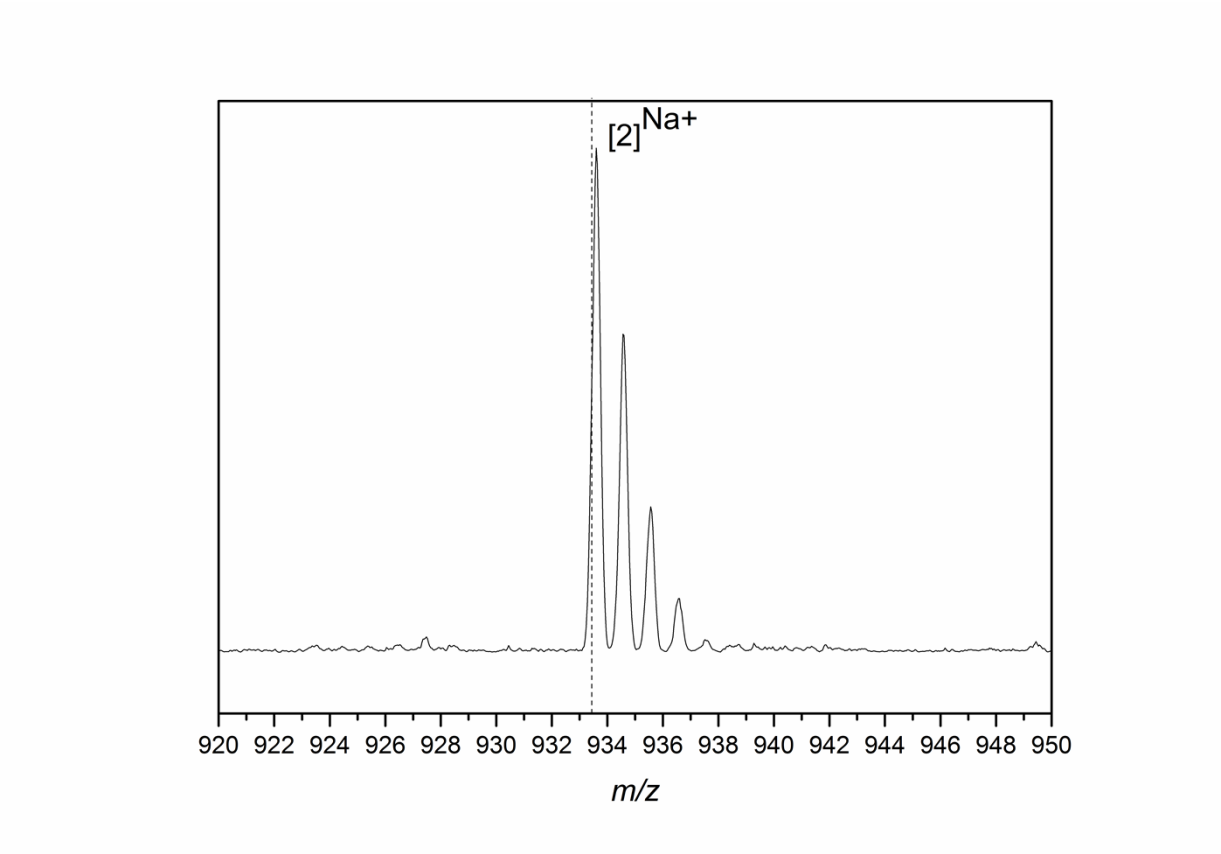
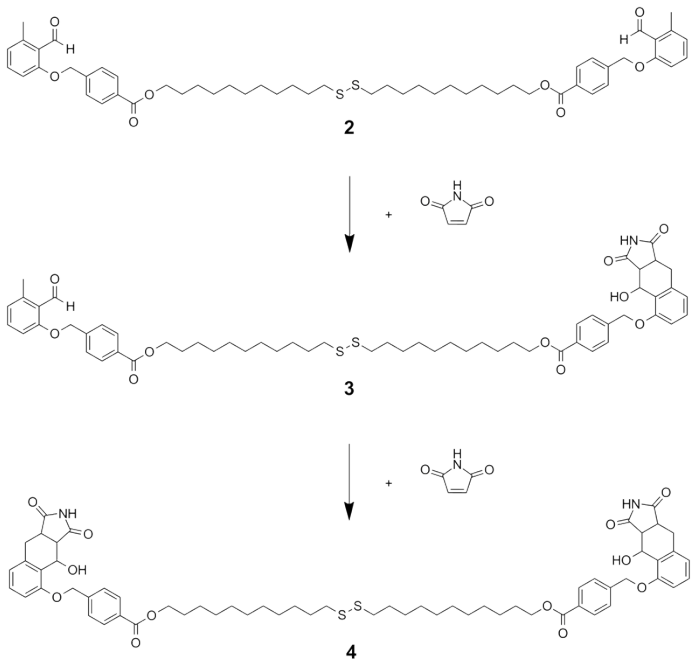


Figure S6. Zoom into the ESI-MS spectrum of the photoenol disulphide linker **2**. The label indicates the theoretical mass of photoenol disulphide linker **2** ionized with Na^+ (stemming from added NaTFA).

Kinetic Study of the Light-Triggered Reaction of 2 and Maleimide

0.40 mg (0.439 µmol; 1 eq) of **2** and 0.85 mg (8.78 µmol; 20 eq) were dissolved in 1.6 mL dry DMF and aliquoted in 4 different headspace vials (200 µL in each one, Pyrex, diameter 20 mm), which were crimped air-tight using SBR seals with PTFE inner liner. The solution was deoxygenated by purging with nitrogen for 10 min. The vials were subsequently irradiated for 0 min, 5 min, 15 min, 45 min by revolving around a compact low-pressure fluorescent lamp (Arimed B6, Cosmedico GmbH, Stuttgart, Germany) emitting at 320 nm (± 30 nm, 36 W, the emission spectrum of the employed compact low-pressure fluorescent lamp is included in Fig. S1) at a distance of 40-50 mm in a custom-built photoreactor (Fig. S2). The solvents were evaporated under vacuum after the reaction, THF/methanol 3:2 (0.5 mL) was added in each vial and the four solutions were analyzed *via* ESI-MS.



Scheme S2. Kinetic study of the model reaction between photoenol disulphide linker **2** and maleimide employing photoreactor and Arimed B6 UV lamp. The photoreaction initially generates mono-functionalized intermediate **3** and subsequently the di-functionalized product **4**.

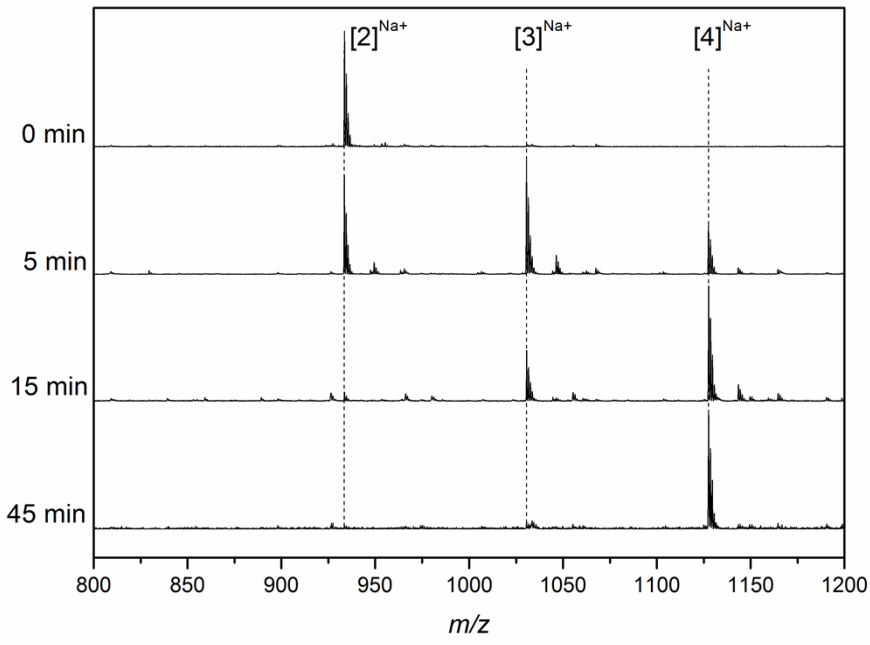


Figure S7. ESI-MS spectrum of the photoreaction between photoenol disulphide linker **2** and maleimide after 0, 5, 15, and 45 min, respectively.

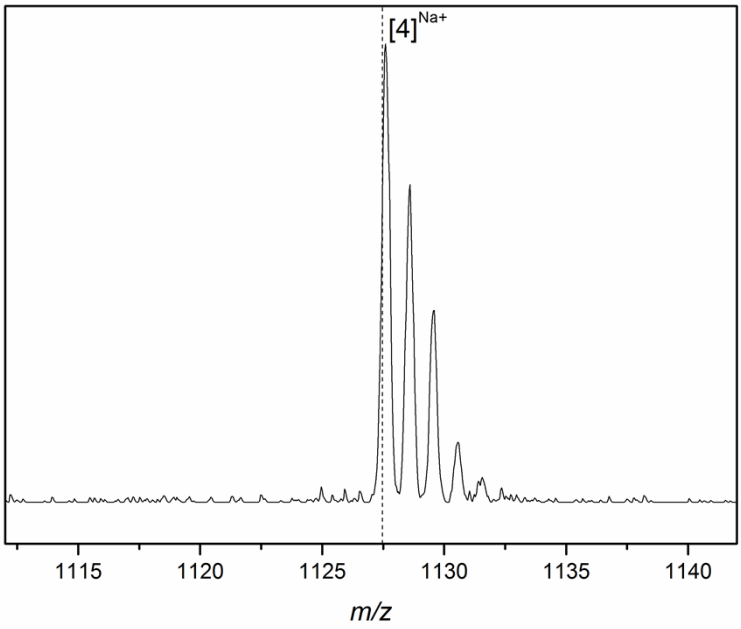


Figure S8. Zoom into the ESI-MS spectrum of the photoreaction between photoenol disulphide linker **2** and maleimide after 45 min irradiation. The label indicates the theoretical mass of photoadduct **4** ionized with Na^+ (stemming from added NaTFA).

Table S1. Experimental and theoretical *m/z* values for the labelled peaks of Fig. S6, Fig. S7 and Fig. S8.

m/z_{exp}	assignment	formula	m/z_{theo}	$\Delta m/z$
933.44	$[2]^{Na+}$	$[C_{54}H_{70}S_2O_8Na]^+$	933.60	0.16
1030.64	$[3]^{Na+}$	$[C_{58}H_{73}NS_2O_{10}Na]^+$	1030.46	0.18
1127.64	$[4]^{Na+}$	$[C_{62}H_{76}N_2S_2O_{12}Na]^+$	1127.47	0.17

UV-Vis Spectroscopy

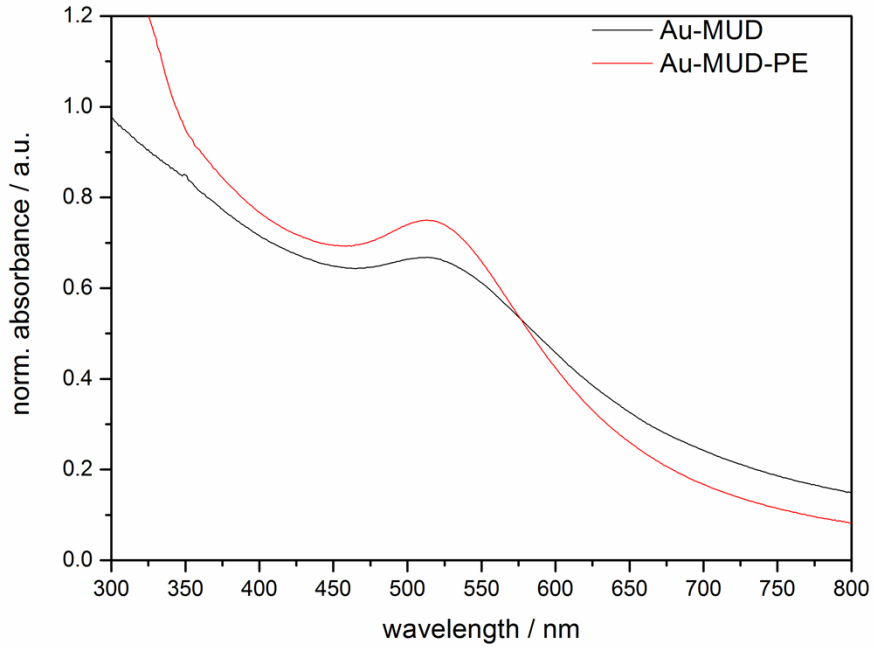


Figure S9. UV-Vis spectrum of mercaptoundecanol-capped Au NPs (**Au-MUD**) and photoenol precursor modified Au-MUD NPs (**Au-MUD-PE**).

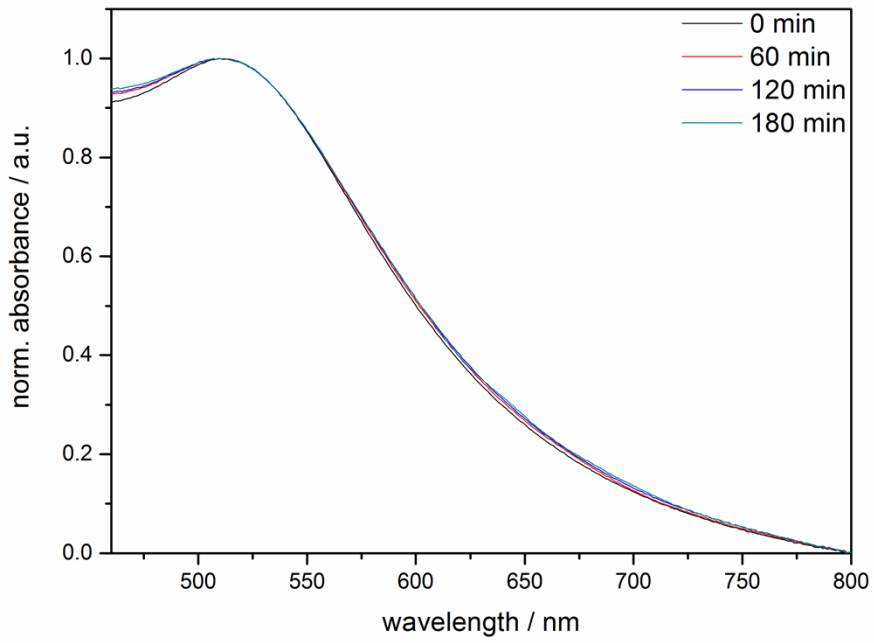


Figure S10. UV-Vis measurement of **Au-MUD-PE** after irradiation for 0, 60, 120, and 180 min employing an Arimed B6 UV lamp.

FT-IR Spectroscopy

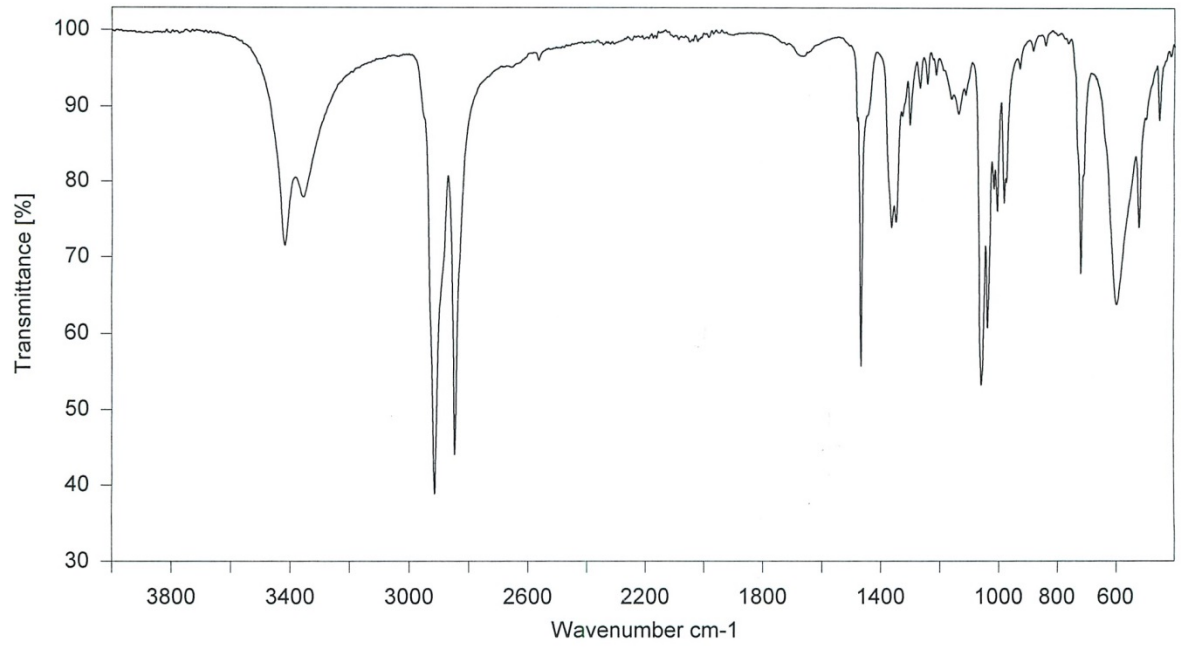


Figure S11. FT-IR spectrum of mercaptoundecanol.

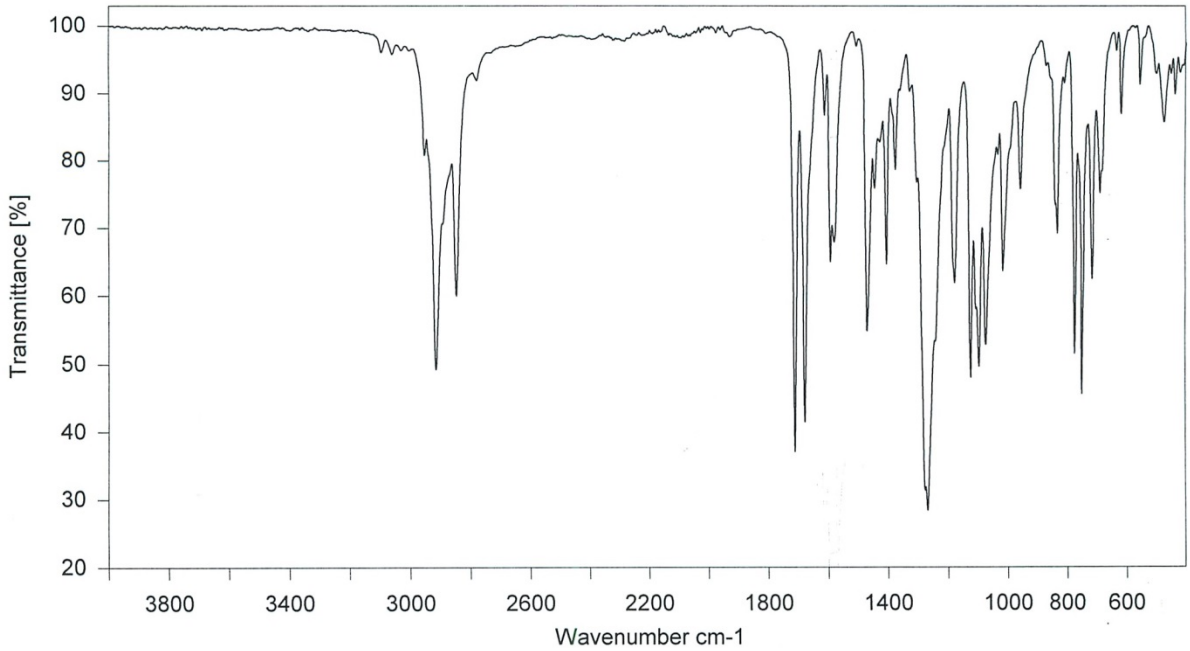


Figure S12. FT-IR spectrum of photoenol disulphide linker **2**.

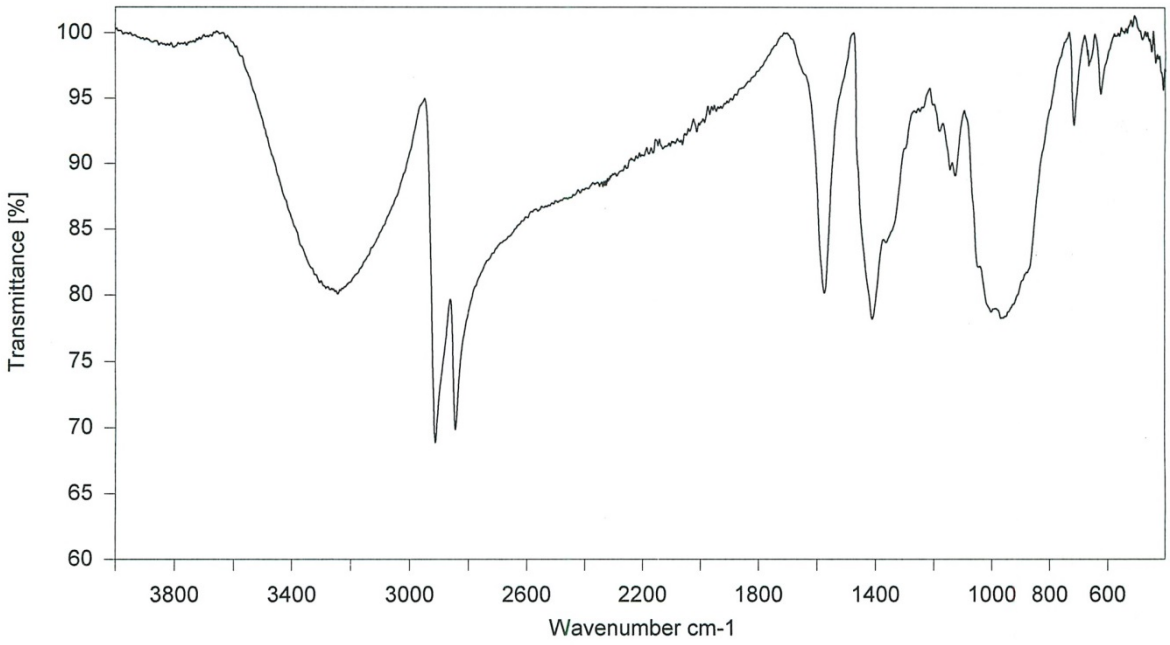


Figure S13. FT-IR spectrum of mercaptoundecanol-capped Au NPs (**Au-MUD**).

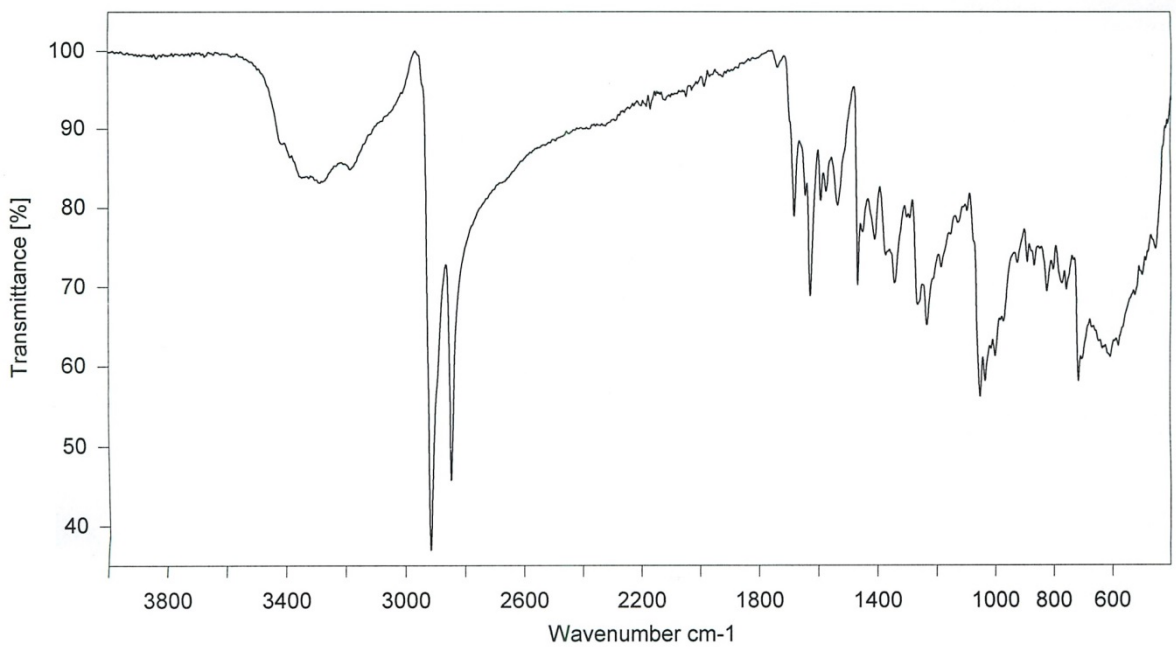


Figure S14. FT-IR spectrum of photoenol-modified Au NPs (**Au-MUD-PE**),

TEM Imaging

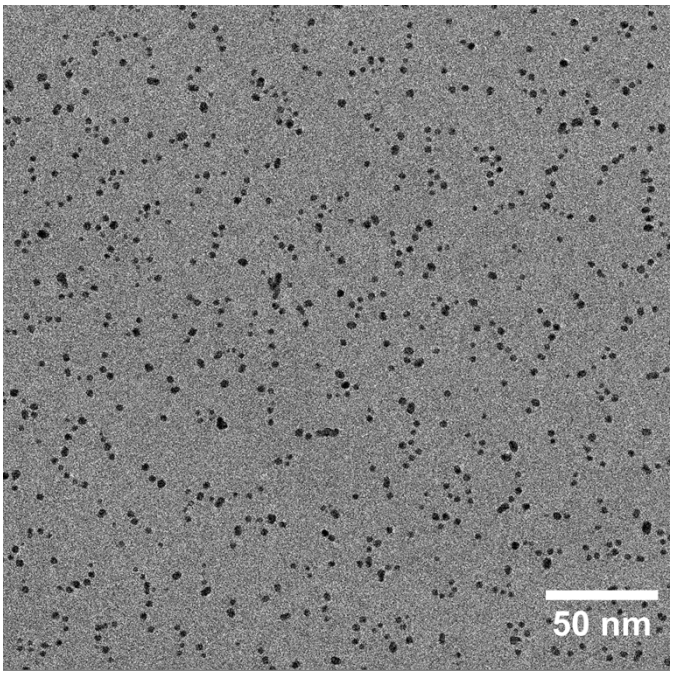


Figure S15. TEM image of mercaptoundecanol-capped Au NPs (**Au-MUD**).

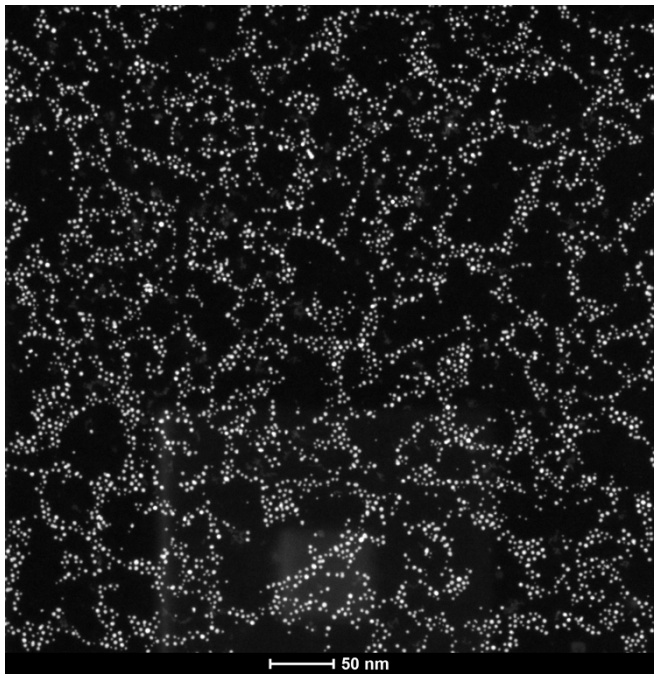


Figure S16. Scanning transmission electron microscopy **(**STEM) image of **Au-MUD-PE**.

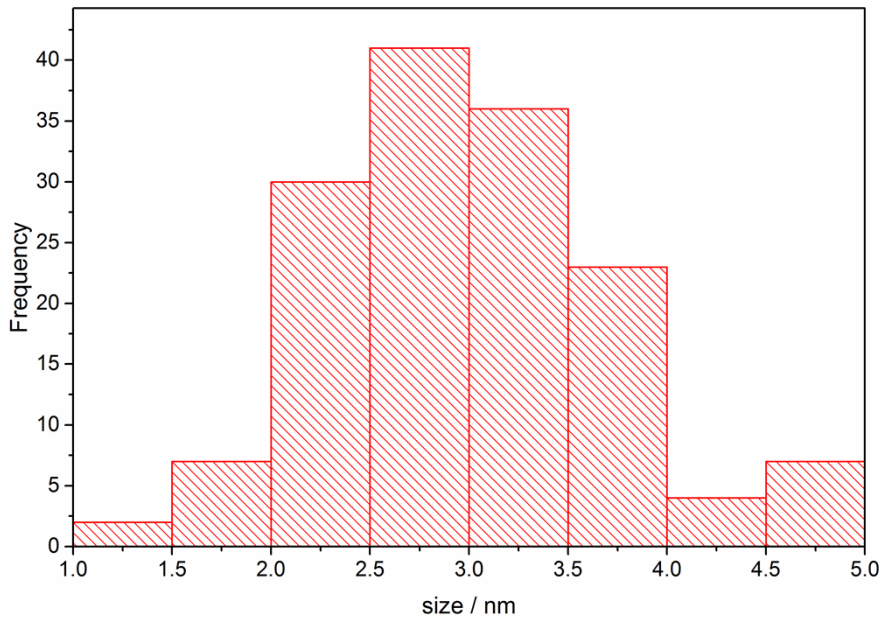


Figure S17. Size distribution of **Au-MUD-PE** (counting 150 NPs in high resolution transmission electron microscopy (HRTEM) images).

Table S2. Characterization of **Au-MUD-PE**.

	diameter
HRTEM	3.02 nm
DLS	5.43 nm

Calculation for Photoenol Linkers per Au NP

Gold nanoparticles were prepared by using the synthesis procedure of Raula *et al*.[4] These authors also determined the amount of MUD ligands by thermogravimetric analysis, resulting in 235 ligands/Au NP (diameter = 3.20 nm). As we observed slightly smaller Au NPs in the range of 3.02, one can estimate the ratio of ligand/Au NP by considering the smaller surface area:

$$\frac{\pi d^2}{\pi d^2} = \frac{\pi 3.02^2}{\pi 3.20^2} \approx 0.89$$

Multiplication of the number of ligands results in the number of ligands for the Au NPs with 3.02 nm in diameter:

$0.89 \cdot 235 = 209$

Based on the NMR analysis (Fig. S1), we assigned that H^a corresponded to 18 H with an integration area of approximately 360, implying 1 of 20 MUD linkers or 5% were modified with photoenol moiety per MUD ligand affording approximately 10 photoenol linkers per Au NP.

Spatially Resolved Immobilization of Au NP

A droplet of suspension containing Au-MUD-PE in DMF (approximately 40 μM) was placed onto the surface of a maleimide containing glass substrate. The reaction sample was subsequently positioned into the DLW setup. All samples were produced using a scanning speed of 100 μm/s.

For squares: each pattern was scanned five times in succession at the corresponding laser power (dimension: 20 μm × 20 μm). The distance of each scanning line was 200 nm. Five squares were patterned for each sample. Each square was patterned using a different laser power (0.2 mW, 0.4 mW, 0.6 mW, 0.8 mW and 4 mW). This exact procedure was also used for all control experiments. For the control experiments, either the Au NPs, the glass substrate or both the Au NPs and the glass substrate were not functional (meaning Au NPs did not contain photoenol units and/or glass substrates did not contain maleimides).

For the large KIT logo (Figure S23): The pattern was scanned once, the distance of each scanning line was 100 nm (dimension: approximately 60 μm × 30 μm). The corresponding laser power was 3.2 mW. After patterning, each sample was immersed into DMF for 20 min. Then, the sample was shortly immersed into acetone and water, and subsequently dried under a flow of nitrogen.

For the small KIT logo: The pattern was scanned once, the distance of each scanning line was 200 nm (dimension: approximately 30 μm × 15 μm). The corresponding laser power was 1.6 mW.

After patterning, each sample was immersed into DMF for 20 min. Then, the sample was shortly immersed into acetone and water, subsequently and dried under flow of nitrogen.

Spatially Resolved Surface Encoding

Fabricated Au NP patterns were immersed into 1 mM solution of 2-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl 2-bromo-2-methylpropanoate in DMF (145 μg mL^{-1}). Patterning was conducted by irradiation for 15 min using a compact low-pressure fluorescent lamp (Arimed B6, Cosmedico GmbH, Stuttgart, Germany) emitting at 320 nm (± 30 nm, 36 W, the emission spectrum of the employed compact low-pressure fluorescent lamp is included in Fig. S2) at a

distance of 40-50 mm in a custom-built photoreactor (Fig. S1). Sample development was performed by immersing the sample into DMF (30 mL, 20 min) and subsequent rinsing with acetone (5 mL) and distilled water (5 mL).

Microscopic Imaging

Bright field images are shown below.

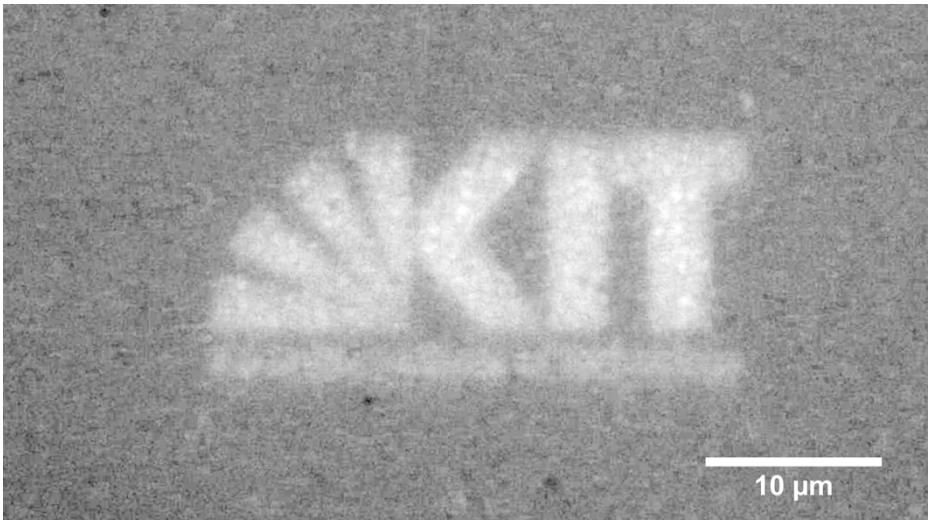


Figure S18. Direct laser writing with **Au-MUD-PE** onto a maleimide coated glass surface to fabricate the KIT logo with a total footprint of approximately 30 µm × 15 µm.

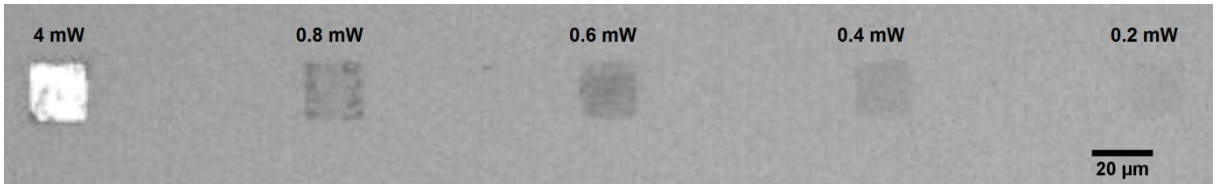


Figure S19. Direct laser writing with **Au-MUD-PE** (functional) on maleimide coated glass surface (functional) using different power rates (from 4 mW to 0.2 mW).

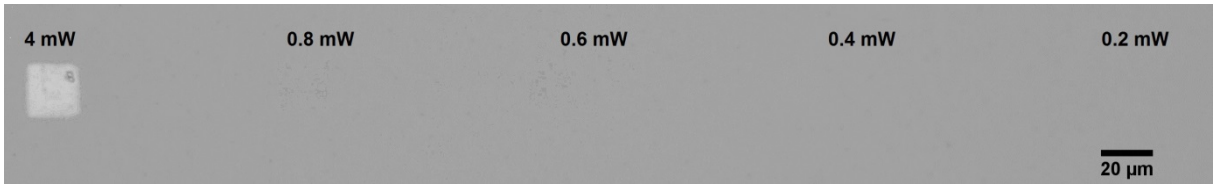


Figure S20. Control experiment. Direct laser writing with **Au-MUD-PE** (functional) on bare glass surface (non-functional) using different power rates (from 4 mW to 0.2 mW).

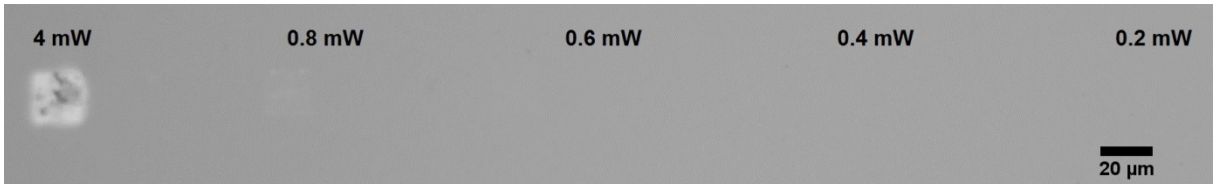


Figure S21. Control experiment. Direct laser writing with **Au-MUD** (non-functional) on maleimide coated glass surface (functional) using different power rates (from 4 mW to 0.2 mW).

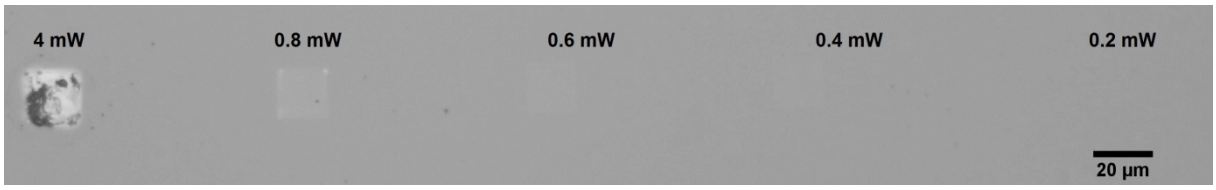


Figure S22. Control experiment. Direct laser writing with **Au-MUD** (non-functional) on bare glass surface (non-functional) using different power rates (from 4 mW to 0.2 mW).

Scanning Electron Microscope Imaging

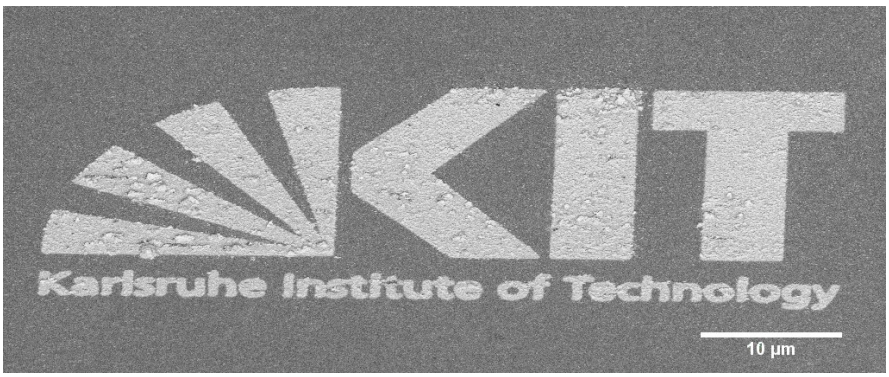


Figure S23. SEM image of KIT logo by DLW of **Au-MUD-PE** with a total footprint of approximately 60 µm × 30 µm (sample was tilted by 54°). Small amount of aggregation is observable.

Localized Surface Plasmon Resonance (LSPR)

Table S3. Maximum LSPR of squares written with different laser powers.

laser power	λ_{max}
0.2 mW	542 nm
0.4 mW	544 nm
0.6 mW	567 nm
0.8 mW	651 nm
4.0 mW	620 nm

Secondary Ion Mass Spectrometry

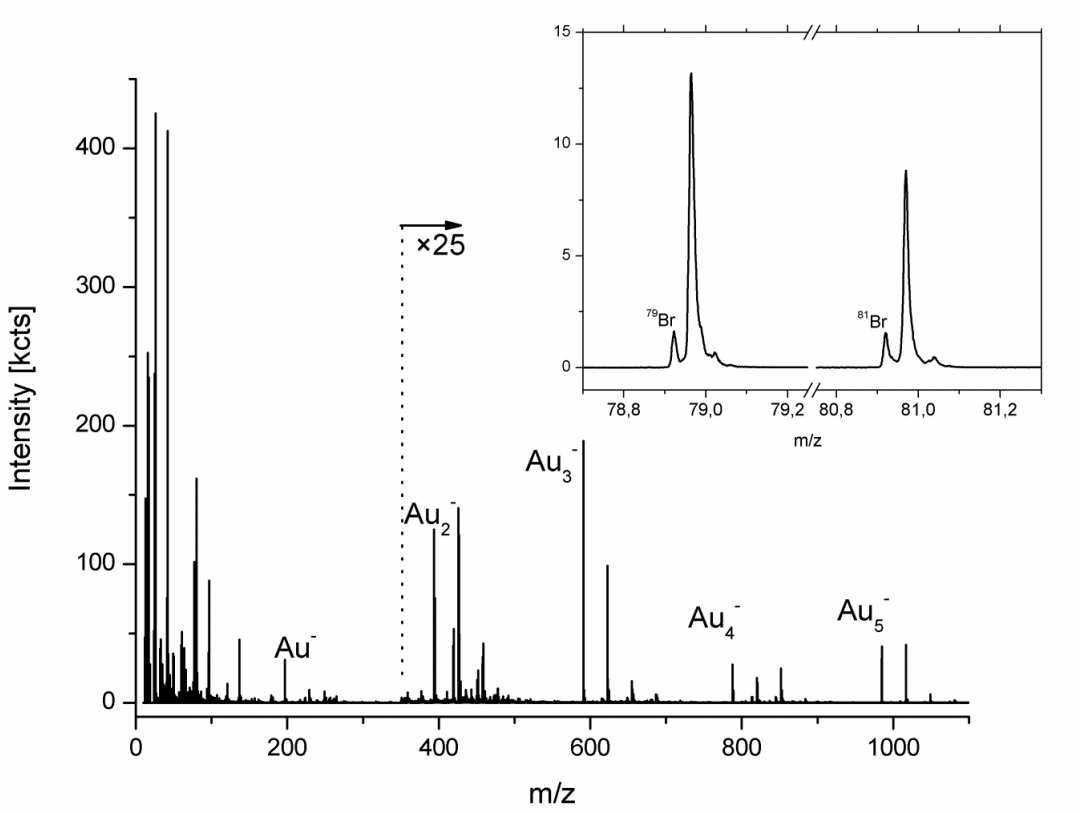


Figure S24. Negative polarity Secondary Ion Mass Spectrum (SIMS), high mass resolution, of immobilized thiolated gold NPs reacted with brominated maleimide according to Fig. 4a obtained from a 1000×500 µm scan area with 16 individual DLW pattern as shown in Fig. S19. Insert: Zoom in on bromine peaks.

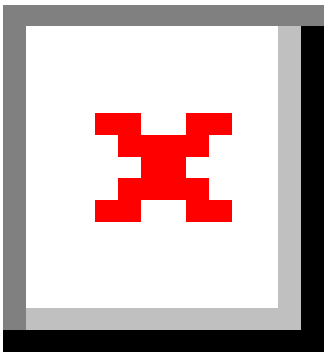
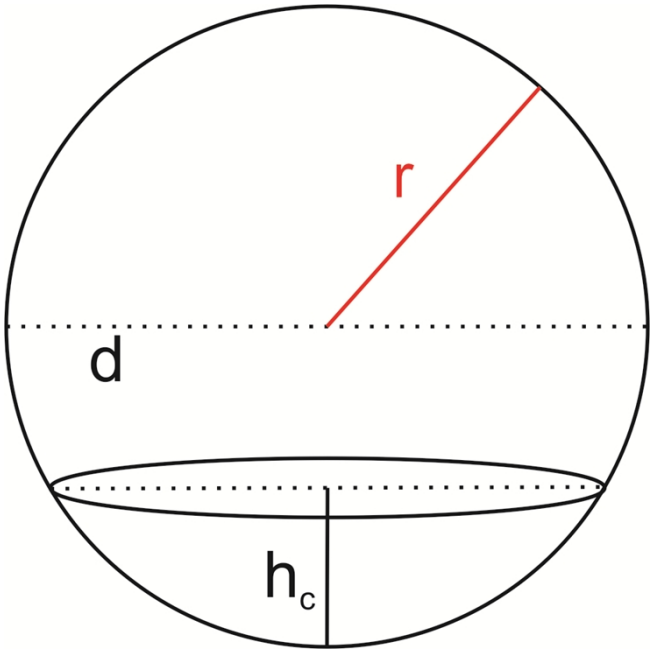


Figure S25. Intensity profile of $Au_xS_y^-$ signals across the DLW patterned KIT logo shown in Fig. 4b demonstrates defined boundaries between immobilized and non immobilized areas of 0.8 µm based on the (84/16) definition.

Hemispherical Cap Area of a Sphere



d : diameter

r: radius

h_c: cap height

A_c: cap area

$A_c = 2 \cdot \pi \cdot r \cdot h_c$

$A_c = 2 \cdot \pi \cdot 1.51\ nm \cdot 0.28\ nm = 2.66\ nm^2$

Figure S26. Schematic drawing of spherical Au NPs.

$$\frac{contact\ area}{total\ area} = \frac{2.66\ nm^2}{28.65\ nm^2} = 0.093$$

10 ligands · 0.093 = 0.93

0.93 photoenol molecules are located on the contact area and enable the photoreaction with the maleimide onto the glass surface. According to literature,[6] the ligands contributing to the light-induced Diels-Alder reaction are those located at the contact area. As we consider spherical Au NPs, the contact area is defined as the hemispherical cap area A_c. The hemispherical area A_c can be calculated with the above mentioned formula with the cap height h_c, which is similar to the diameter of a gold atom (0.28 nm), resulted in A_c = 2.66 nm^2. Assuming that the 10 photoenol ligands are evenly distributed, we expect by division by the total NP area that 0.93 ligands are located at the contact area indicating only a single covalent bond between the Au NP and the glass surface is formed during encoding.

References

[1] T. Pauloehrl, G. Delaittre, V. Winkler, A. Welle, M. Bruns, H. G. Borner, A. M. Greiner, M. Bastmeyer, C. Barner-Kowollik, *Angew. Chem. Int. Ed.,* 2012, **51**, 1071.

[2] B. Yameen, C. Rodriguez-Emmenegger, C. M. Preuss, O. Pop-Georgievski, E. Verveniotis, V. Trouillet, B. Rezek, C. Barner-Kowollik, *Chem. Commun.*, 2013, **49**, 8623.

[3] A. S. Quick, H. Rothfuss, A. Welle, B. Richter, J. Fischer, M. Wegener, C. Barner-Kowollik, *Adv. Funct. Mater.*, 2014, **24**, 3571.

[4] J. Raula, J. Shan, M. Nuopponen, A. Niskanen, H. Jiang, E. I. Kauppinen, H. Tenhu, *Langmuir*, 2003, **19**, 3499.

[5] M. Friederici, I. Angurell, M. Seco, O. Rossell, J. Llorca, *Dalton Trans.*, 2011, **40**, 7934.

[6] I. Rianasari, M. P. de Jong, J. Huskens, W. G. van der Wiel, *Int. J. Mol. Sci.*, 2013, **14**, 3705.