

Supporting Information for

Tailoring the Properties of Surface-Immobilized Azobenzenes by Monolayer Dilution and Surface Curvature

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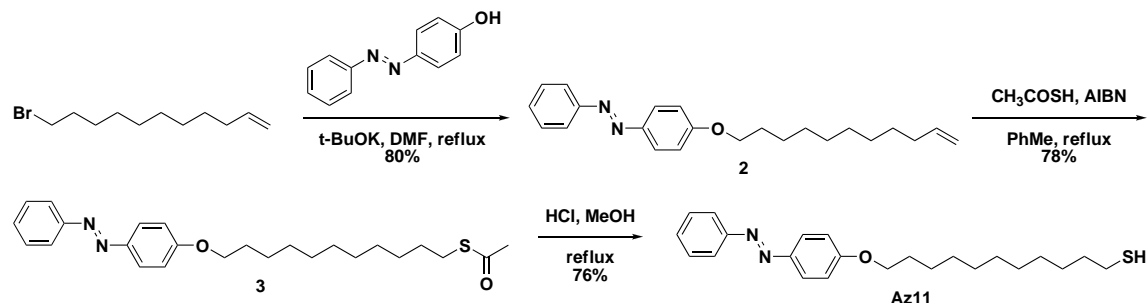
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1 Synthesis

1.1 11-(4-(Phenyldiazenyl)phenoxy)undecane-1-thiol (Az11)[1][2, (SI)]



1-Phenyl-2-(4-(undec-10-en-1-yloxy)phenyl)diazene (**2**).

4-(phenyldiazenyl)phenol (2.100 g; 10.60 mmol) and potassium tert-butoxide (1.247 g; 11.13 mmol) were placed in a dry, two-neck, round-bottom flask equipped with a magnetic stirring bar, a reflux condenser, and a rubber septum. The flask was evacuated and purged with nitrogen, then 25 mL of anhydrous N,N -dimethylformamide (DMF) was added while stirring. As soon as the solids disappeared, 11-bromo-1-undecene (2.44 mL; 2.595 g; 11.13 mmol) was added and the solution was quickly heated, and allowed to reflux for 10 min. Formation of white precipitate was observed, and the color of the solution changed from deep red to bright orange. After 10 min, the heating was discontinued, and the flask was allowed to cool down. The reaction mixture was poured into a separatory funnel containing 100 mL of water, and extracted with four 50 mL portions of hexane. Hexane fractions were combined and dried over magnesium sulfate. Hexane was removed on the rotary evaporator, and the residue was purified by column chromatography (ethyl acetate:hexane 1:20 v/v) to give analytically pure product. Yield = 2.95 g (79.5%).

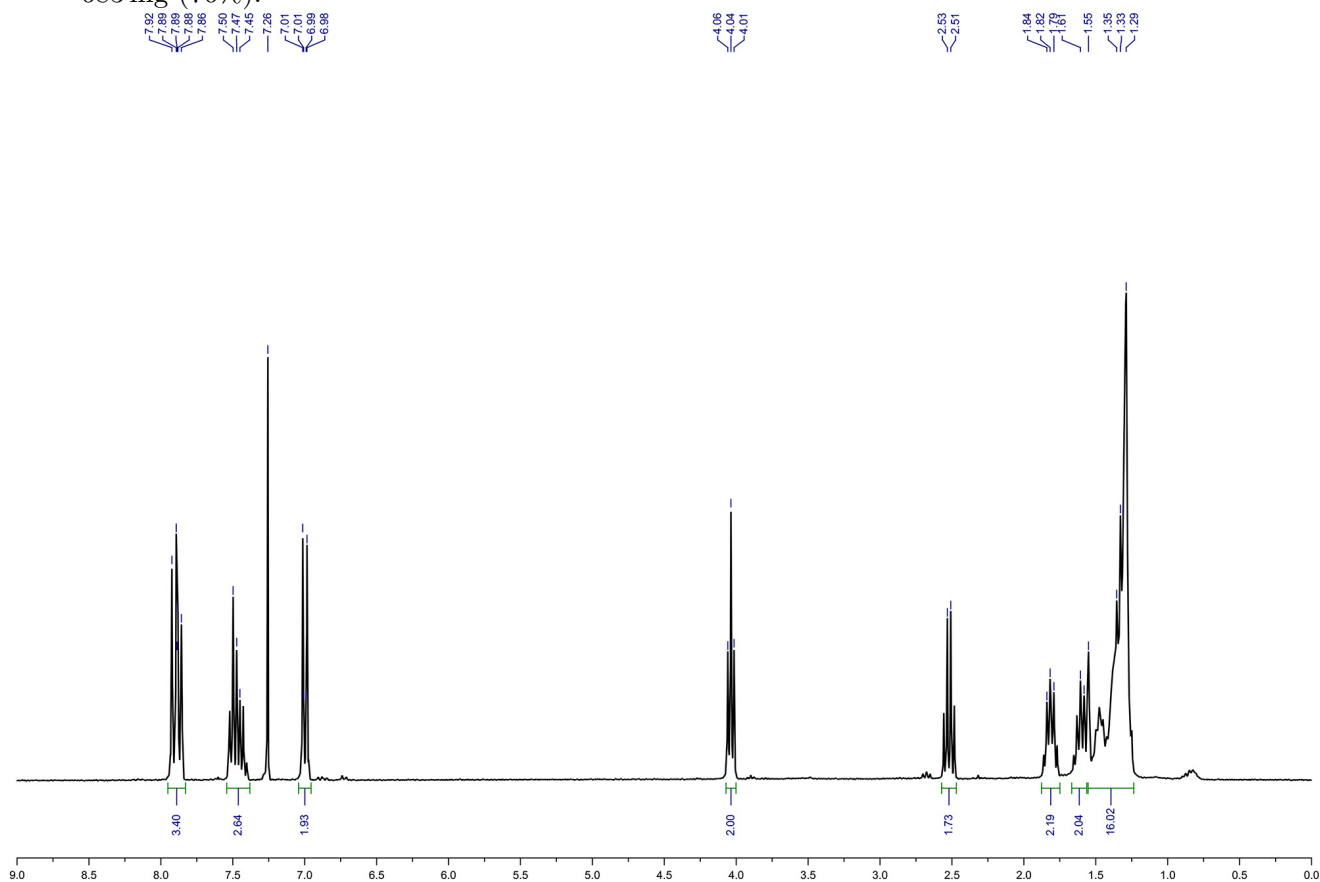
S-(11-(4-(Phenyldiazenyl)phenoxy)undecyl)ethanethioate (**3**).

2 (1.0 g; 2.86 mmol) and 2,2'-azobisisobutyronitrile (AIBN) (141 mg; 0.86 mmol) were placed in a dry, two-neck round-bottom flask equipped with a magnetic stirring bar, a reflux condenser, and a rubber septum. The flask was evacuated and purged with nitrogen, then 20 mL of degassed toluene was added while stirring. 806 μL (871 mg; 11.44 mmol) of thioacetic acid was added, and the solution was heated and allowed to reflux. The course of the reaction was monitored by TLC (silica gel, ethyl acetate-hexane 1:9). After 1 h, the conversion of starting material was complete, and the flask was allowed to cool down to room temperature. The solution was poured into a separatory funnel containing 100 mL of saturated sodium bicarbonate solution in water, and 50 mL toluene. The organic phase was separated, extracted with four 50 mL portions of deionized water, and dried over MgSO_4 . The residue that was obtained after removing the solvent on a rotary evaporator was puri-

fied by column chromatography (ethyl acetate:hexane 1:15 v/v) to give the desired product **3**. Yield = 954 mg (78%).

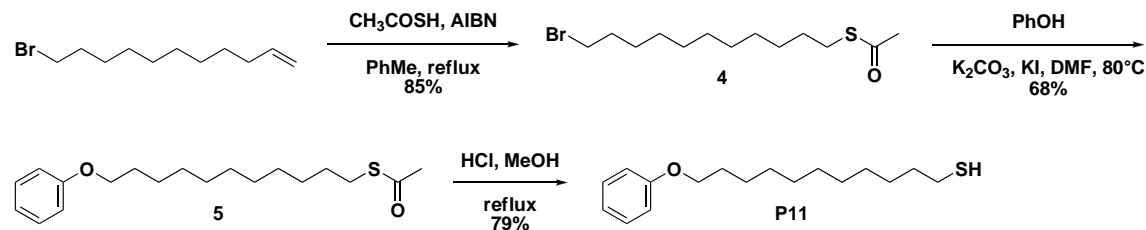
11-(4-(Phenyldiazenyl)phenoxy)undecane-1-thiol (Az11).

3 (999 mg; 2.345 mmol) was placed in a round-bottom flask equipped with a reflux condenser. The flask was purged with nitrogen and 18 mL of degassed methanol, followed by 8.0 mL of 1.25 M methanolic HCl solution were added. The reaction mixture was then heated at a reflux temperature under a blanket of nitrogen. After 2 h, the reaction was discontinued and the red solution was allowed to cool down. Upon reaching room temperature, the product spontaneously precipitated as orange crystals. The crystals were washed with hexane and dried under vacuum. No further purification was required. Yield = 683 mg (76%).



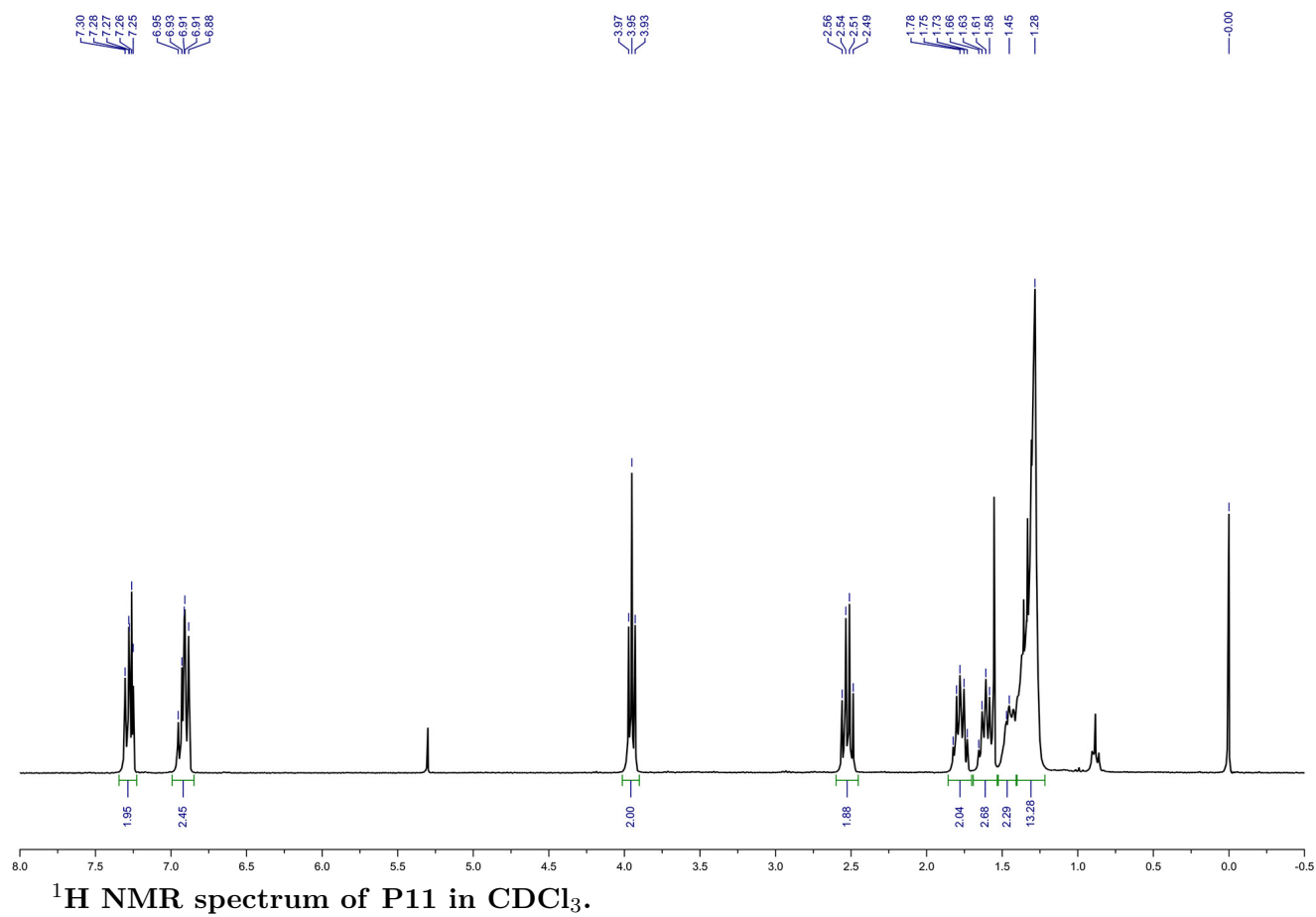
^1H NMR spectrum of Az11 in CDCl_3 .

1.2 11-Phenoxyundecane-1-thiol (P11)[3]



S-(11-Bromoundecyl)ethanethioate (4). A round-bottom flask was charged with toluene (70 mL) and purged with nitrogen for 1 h under stirring. 11-bromo-1-undecene (1.41 mL, 4.49 g, 6.4 mmol) was added under a nitrogen atmosphere, followed by thioacetic acid (2.61 mL, 2.78 g, 36.5 mmol) and 2,2'-azobisisobutyronitrile (AIBN) (9.65 mL, 0.2 M solution in toluene). The reaction mixture was refluxed for 3 h under nitrogen and then cooled down to room temperature. The mixture was washed several times with a saturated NaHCO_3 solution in water, followed by washing with water. The toluene phase was dried with MgSO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of hexane and dichloromethane (4:1, v/v) as an eluent to afford the pure product **4** (1.69 g, 85%) as colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 3.40 (t, 2H, $J = 6.8$ Hz), 2.86 (t, 2H, $J = 7.3$ Hz), 2.32 (s, 3H), 1.89–1.80 (m, 2H), 1.60–1.51 (m, 2H), 1.44–1.27 (m, 14H).

11-Phenoxyundecane-1-thiol (P11). To a stirred solution of phenol (190 mg, 2 mmol) in DMF (8 mL) was added K_2CO_3 (1.34 g, 9.7 mmol) at room temperature under a nitrogen atmosphere. After 10 min, compound **4** (495 mg, 1.6 mmol) and catalytic amount of KI (20 mg) were added. The resulting mixture was heated at 80° for 6 h and then cooled down to room temperature. The reaction mixture was diluted with 130 mL of water and the product was extracted several times with diethyl ether. Combined organic layers were washed with saturated K_2CO_3 solution in water followed by water and dried with anhydrous MgSO_4 . The organic phase was evaporated under reduced pressure to afford crude S-11-phenoxyundecyl ethanethioate **5** (350 mg, 68%) as a dense oil. A solution of **5** (322 mg, 1 mmol) in methanol (30 mL) was then refluxed with conc. HCl in water (1 mL) for 4 h under a nitrogen atmosphere. The reaction mixture was diluted with 100 mL of water and the pH of the solution was adjusted to 7 by diluting with dilute aqueous NaOH. The product was extracted several times with dichloromethane and combined organic layers were dried with MgSO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of hexane and dichloromethane (v/v 90:10) as an eluent to afford the pure product **P11** (227 mg, 79%) as a colorless dense oil. ^1H NMR (300 MHz, CDCl_3): δ 7.31–7.24 (m, 2H), 6.95–6.88 (m, 3H), 3.95 (t, 2H, $J = 6.6$ Hz), 2.56–2.49 (m, 2H), 1.82–1.73 (m, 2H), 1.65–1.58 (m, 2H), 1.47–1.28 (m, 15H).



2 Sample Preparation

2.1 Preparation of planar Az11/C12 SAMs

The solvent used for all stock and incubation solutions for Az11/C12 SAMs was methanol of HPLC grade.

Az11 Stock Solutions. Methanolic solutions of Az11 were prepared by sonication and warming to 40°C. Prepared stock solutions were stored in the fridge for up to four weeks, and warmed to room temperature before opening the flask. Typically, a small amount of a disperse solid residue could be observed. We assume this residue is the corresponding disulfide, as more of it precipitates when kept at room temperature for more than one day. The suspensions were filtered through 0.2 µm PTFE-membrane syringe filters. The purity of the filtrate was checked by ultrahigh-performance liquid chromatography. The filtrate was used as stock solution. Due to the unknown amount of residue filtered off, the concentration of this stock solution had to be determined photometrically, as described below. The concentrations were typically ≈ 0.4 mM.

Photometric Determination of Az11. Stock solutions were diluted to a nominal concentration of 0.03 mM and the absorbance in the main band at $\lambda_{\text{max}} = 347$ nm was compared to the absorption coefficient $\epsilon_{\text{max}} = (27.3 \pm 0.3) \times 10^3 \text{ cm}^2 \text{ mmol}^{-1}$ of Az6 (6-4-[phenyldiazenyl]phenoxyhexane-1-thiol) in methanol, a compound with the same chromophore that dissolves completely and shows an absorbance spectrum indistinguishable from the one of Az11. The absorption coefficient of Az6 was determined from ≈ 0.03 mM solutions prepared by adding the appropriate amount of methanol by weight to weighed samples dried over P_4O_{10} in vacuum for 24 h.

All UV/Vis measurements performed were done using disposable UV cells, semi-micro, Brand GmbH & Co. KG, Germany, Cat. No. 759150.

Solubility of Az11. The solubility of Az11 in methanol is low and it is easily underestimated due to the presence of the insoluble residue, most likely disulfide. We determined a solubility of (0.54 ± 0.02) mM in the following way: Az11 was repeatedly added to the solution and the resulting suspension filtered until the absorbance of the filtrate remained constant.

C12 Stock Solutions. 1 mM stock solutions of 1-dodecanethiol (C12) were prepared by diluting the liquid compound in 2 steps, assuming a density of 0.845 g cm^{-3} [4]. The stock solutions were stored in a fridge and warmed to room temperature before re-opening the flask.

2.2 Synthesis and Functionalization of Gold Nanoparticles

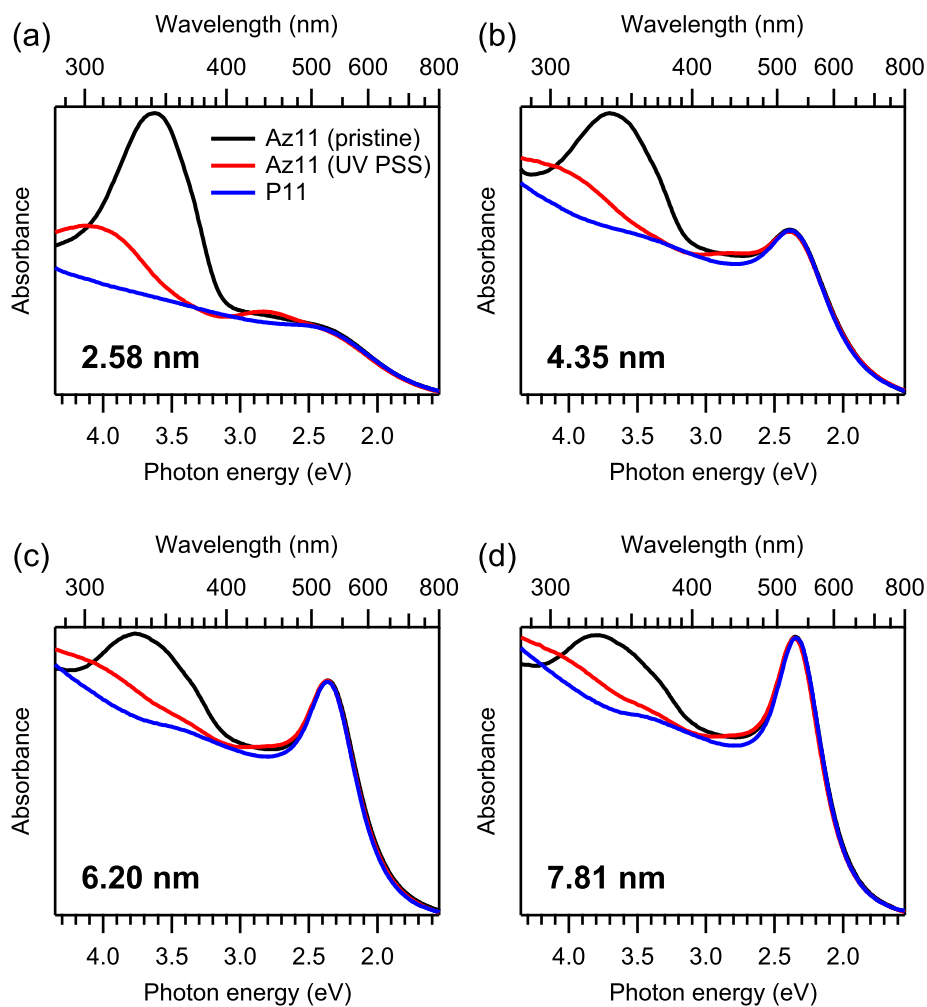
Synthesis of (2.58 ± 0.45 nm) Gold Nanoparticles. Didodecyldimethylammonium bromide (DDAB) stock solution was first prepared by dissolving DDAB (833 mg, 1.80 mmol) in toluene (18 mL) (with sonication). $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (50 mg, 125 μmol) and dodecylamine (DDA) (450 mg, 2.43 mmol) were added to 12.5 mL of the stock solution and the solution was sonicated until the solids dissolved completely. Gold(III) was then reduced by fast addition of tetrabutylammonium bromide (TBAB) (125 mg, 486 μmol) in DDAB stock solution (5 mL) under vigorous stirring.

General Procedure for Obtaining Gold Nanoparticles by Seeded Growth. As-prepared 2.58 nm gold nanoparticles were aged for 24 hours and used as seeds. A growth solution was prepared by sequentially dissolving 808 mg DDAB, 1496 mg DDA, and 162 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 40.4 mL of toluene. 2.0 mL of the aged seed solution was then added to a given volume of the growth solution. Finally, gold (III) was reduced by dropwise addition of a given volume of a reducing solution obtained by dissolving 106 μL of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in 16.2 mL toluene containing 748 mg of DDAB. Slow addition of the reducing solution was important for the preparation of highly monodisperse nanoparticles (we dispensed ≈ 7 μL droplets from a micropipette at a rate of 1 drop per second). For (4.35 ± 0.41) nm Au nanoparticles, 5.46 mL of the growth solution and 2.47 mL of the reducing solution were used. For (6.20 ± 0.47) nm Au nanoparticles, 18.34 mL of the growth solution and 8.36 mL of the reducing solution were used. For (7.81 ± 0.96) nm Au nanoparticles, 41.72 mL of the growth solution and 18.98 mL of the reducing solution were used. The same method was successfully used to prepare larger nanoparticles by modifying the volume ratio of the seed to the growth solution; these larger particles, however, could not be redissolved after functionalization with thiols.

Functionalization of Gold Nanoparticles. 2.58 nm Au nanoparticles were functionalized 30 min after the injection of TBAB, without purification. A ten-fold excess of thiol^a(Az11 or P11) was used for surface modification. The colloidal solution was left on a shaker for 24 h. Larger nanoparticles were first quenched with one volume of methanol and the mixture was left undisturbed (with occasional stirring) for two hours. The resulting black precipitate was collected by decantation and redissolved in the initial amount of toluene. A ten-fold excess of thiol was added and the solutions were left on a shaker for 6 h. Functionalized particles were purified by the addition of one volume of methanol followed by centrifugation. The supernatants were discarded and the remaining solids were washed several times with pure methanol, dried with a stream of nitrogen and redissolved in pure toluene. We verified by transmission electron microscopy that the functionalization procedure did not affect the size and size distribution of the nanoparticles.

^aThe number of binding sites on the surface of NPs was calculated assuming that a single thiolate ligand occupies a surface area of 0.217 nm² [1].

3 UV/Vis Spectra of Curved SAMs

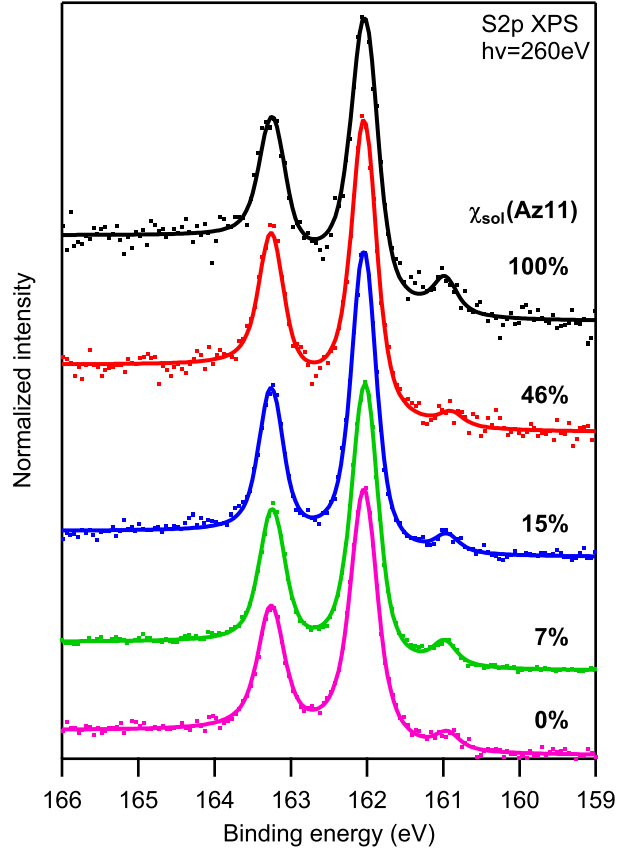


Additional plots of UV/Vis spectra of Az11 SAMs on NPs in the pristine state and in the 365 nm (UV) photostationary state (PSS); in comparison with P11 SAMs on NPs, normalized to the plasmon resonance peak at ≈ 2.4 eV (520 nm). We verified that the UV/Vis spectra of P11-functionalized NPs were not affected by light.

4 X-ray Photoelectron Spectroscopy (XPS)

4.1 S2p XPS

We recorded S2p XP spectra on planar SAMs prepared from mixed solutions of Az11 and C12 with varying mole fraction $\chi_{\text{sol}}(\text{Az11})$. The spectra shown below were recorded at the Bessy II synchrotron facility of the Helmholtz-Zentrum-Berlin.

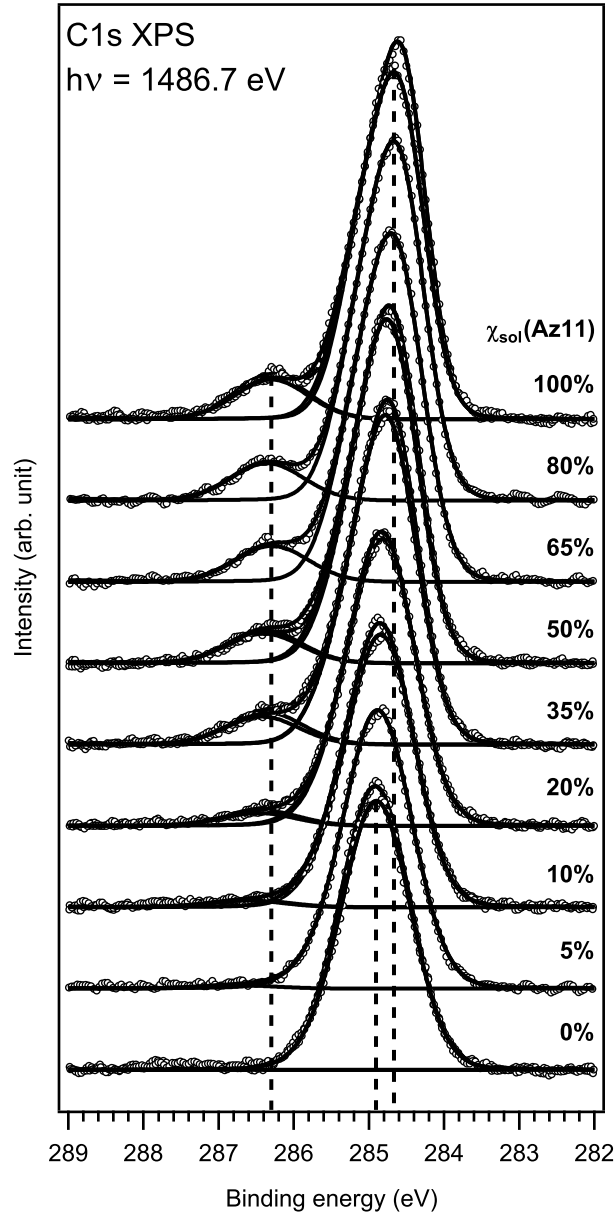


The spectra were fitted using doublets of Voigt line profiles and a Shirley background [5]. The main doublet, $2p_{3/2}$ at a binding energy of 162 eV, is assigned to bound thiol [6, 7]. In addition we find a doublet with a $2p_{3/2}$ binding energy of 161 eV, which is commonly assigned to atomic sulfur [6–10]. Its intensity is well below 10% of the total peak area. There was no indication for further peaks, in particular unbound thiol [6] ($2p_{3/2}$ at 164 eV).

For the samples examined with the lab-based XPS setup, contributions of $2p_{3/2}$ at 161 eV and 164 eV were below the S2p detection limit of 10% of the total peak area.

4.2 C1s XPS

C1s XP spectra were recorded with the lab-based XPS setup on planar Az11/C12 SAMs for different mole fractions $\chi_{\text{sol}}(\text{Az11})$ in the adsorption solution:

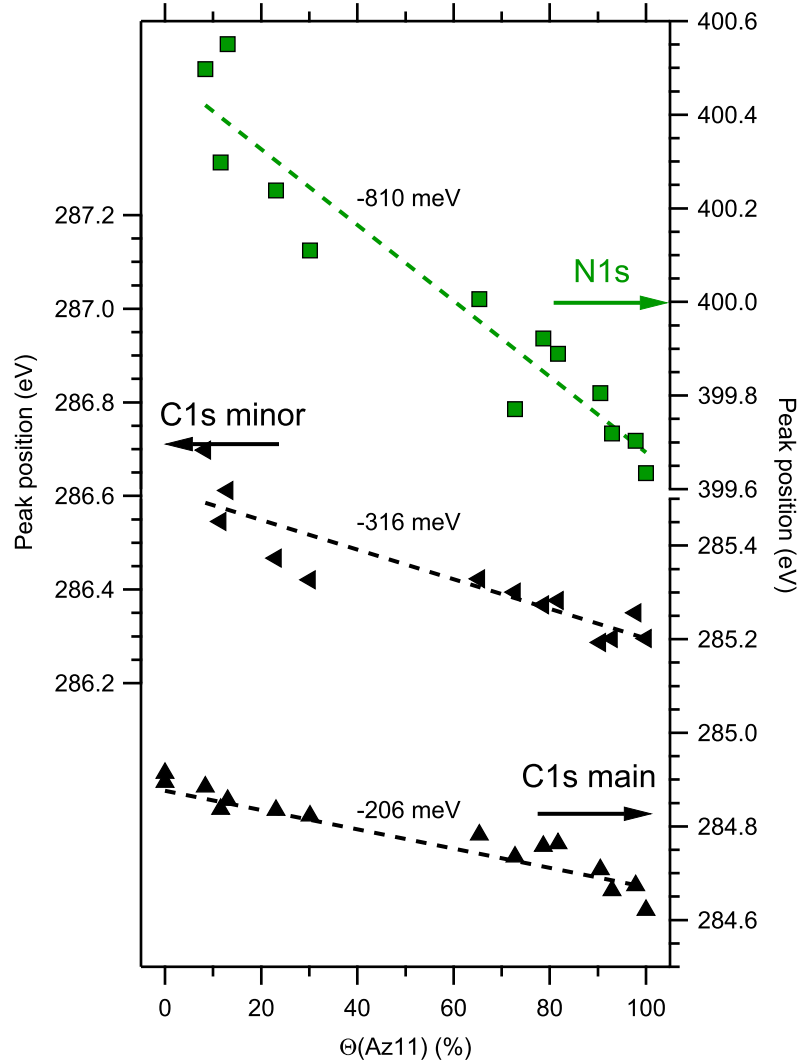


In case of the pure C12 SAM (lowermost spectrum), only one peak is observed at ≈ 284.9 eV. For samples from solutions with increasing $\chi_{\text{sol}}(\text{Az11})$ this main peak shifts to

lower binding energies, while an additional peak at higher binding energies (≈ 286.3 eV) emerges. The main peak contains contributions from aromatic and aliphatic carbon atoms. The high-energy component is assigned to carbon bound to nitrogen and oxygen.

4.3 Shift of XPS peaks

The figure shows the XPS peak position for different core levels versus Az11 coverage Θ :



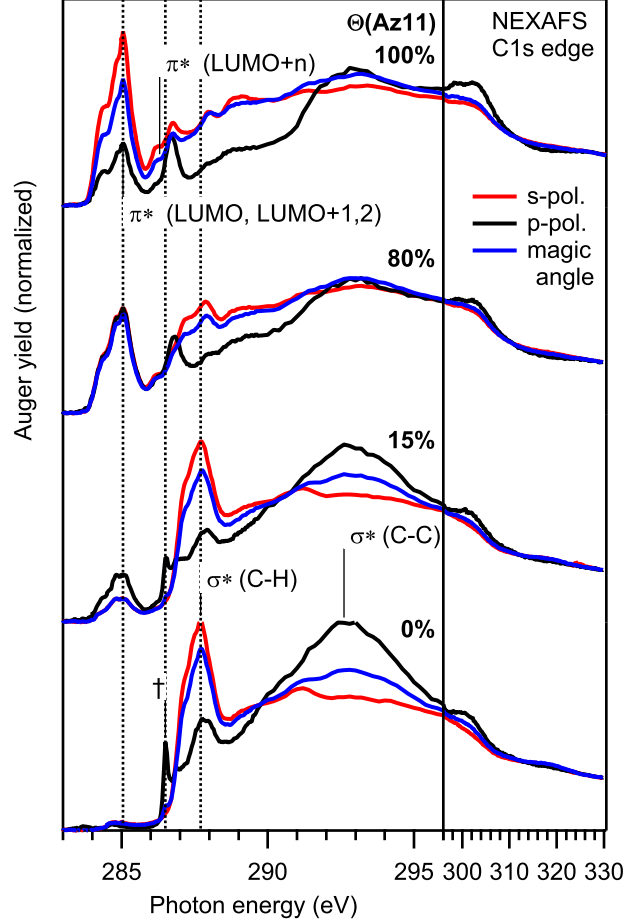
The strongest shift is observed for the N1s peak of the diazo-bridge, the shifts of the C1s main peak and the satellite (C1s minor) are smaller. Dashed lines have been added as guide to the eye. Numbers indicate the (linear) decrease of binding energy from 0 to 100% Az11 coverage.

Note: The shift of the O1s peak is even smaller (not shown) and, as expected, the S2p core level shows a constant binding energy (see 4.1).

5 Near-Edge X-Ray Absorption Fine Structure Spectroscopy (NEXAFS)

5.1 C1s Spectra

We performed C1s NEXAFS spectroscopy on planar SAMs of varying Az11 coverage Θ :



The prominent peaks at 287.8 eV and 293.0 eV are commonly interpreted as σ^* (C-H) and σ^* (C-C) resonances, respectively [10, 11]. The sharp feature (\dagger) at 286.7 eV, visible in the p-polarized spectra of low- Θ -SAMs, is believed to originate from an excitation into a delocalized state at the SAM-vacuum interface [12].

For SAMs containing Az11, the first absorption structures already appear at photon energies of 284 to 286 eV. They are assigned to transitions into LUMO, LUMO+1 and LUMO+2 of the aromatic rings, which have the same symmetry [13]. The polarization dependence of these NEXAFS transitions allows us to determine the average orientation of the phenyl rings.

5.2 Determination of Orientation

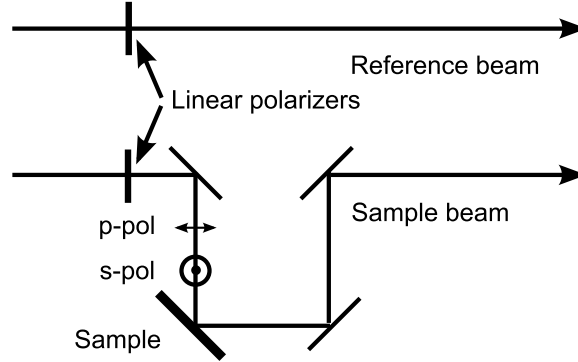
The determination of the molecular orientation on a surface by polarization-dependent NEXAFS has been developed by the group of Stöhr [14, 15]. Applying this to our measurement geometry [13, 16], we obtain an expression for the NEXAFS intensity I , which allows us to determine the angle α between the normal of the molecular plane and the surface normal:

$$I(\beta; \alpha, P, \theta) = C \left[P \left(\sin^2 \alpha \left(1 - 3 \cos^2 \beta \cos^2 \theta \right) + 2 \cos^2 \beta \cos^2 \theta \right) + (1 - P) \left(\sin^2 \alpha \left(1 - 3 \sin^2 \beta \cos^2 \theta \right) + 2 \sin^2 \beta \cos^2 \theta \right) \right], \quad (1)$$

with β being the angle of polarization^b, $P = 0.96$ being the degree of polarization of the X-ray beam, C being a proportionality constant, and $\theta = 20^\circ$ being the fixed angle of the incident X-ray beam relative to the surface plane. This equation can be fitted to the measured intensities of the π^* resonances as a function of the polarization angle β in order to obtain the angle α .

^bThe angle β lies between 90° (s-polarized), and 0° (p-polarized). The magic angle β_{magic} is 52.1° for our measurement geometry.

6 Differential Reflectance (DR) Spectroscopy



The DR spectroscopy setup consists of a Perkin Elmer Lambda 850 spectrometer with a homebuilt reflection unit. The monochromatized beam is split into two beams, reference beam and sample beam and both pass a linear polarizer. The sample beam is guided across three aluminium mirrors and the sample; the intensity of sample and reference beam are alternately measured on the same detector.

The absorbance, A , is defined as

$$A = -\lg\left(\frac{I}{I_0}\right), \quad (2)$$

where I_0 is the initial light intensity and I the intensity after the sample. In our case I is the intensity in the sample beam after passing the three mirrors and the sample. Thus, I can be written as

$$I = I_0 \cdot 3 \cdot R_{\text{Mirror}} \cdot R_{\text{Sample}}, \quad (3)$$

using R as reflectivity. Thus, we obtain

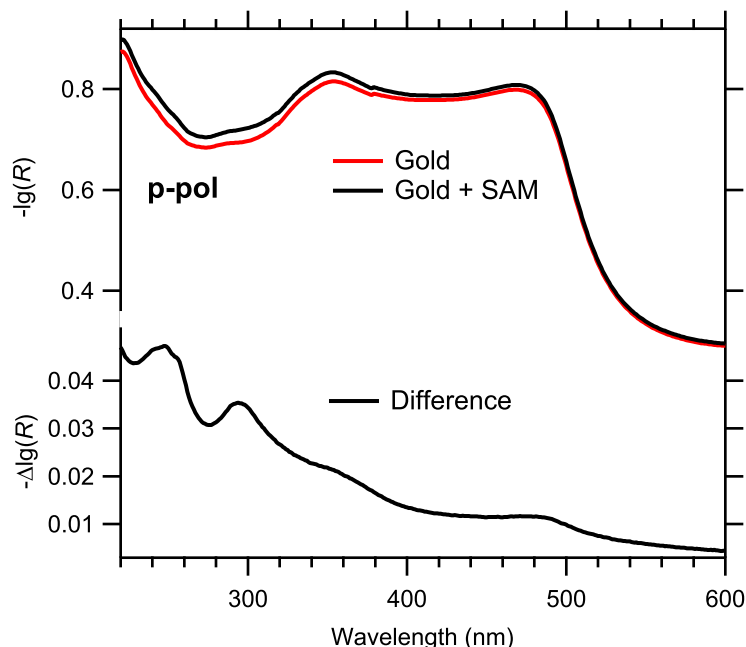
$$A = -\lg(3 \cdot R_{\text{Mirror}} \cdot R_{\text{Sample}}). \quad (4)$$

Using R as reflectivity of the gold sample with SAM and R_0 as the reflectivity of the bare gold sample, we can define the absorbance difference ΔA :

$$\begin{aligned} \Delta A &= -(\lg(3 \cdot R_{\text{Mirror}} \cdot R) - \lg(3 \cdot R_{\text{Mirror}} \cdot R_0)) \\ &= -(\lg(R) - \lg(R_0)) \\ &\equiv -\Delta \lg(R) \end{aligned}$$

In this expression the reflectivity of the mirrors cancels out and the quantity $-\Delta \lg(R)$ reflects the change of reflectivity of the gold layer due to the formation of the SAM on the surface.

As an example we show spectra of a gold spectrum and a 100% Az11 SAM, measured with p-polarized light, and the difference spectrum:



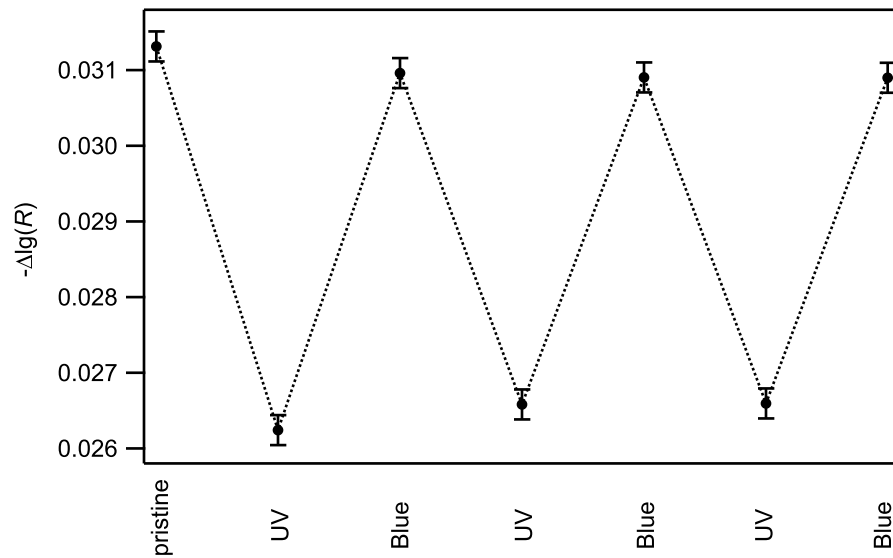
This signal change is so small that even subtle differences between different gold substrate pieces of the same batch play a role, i.e., DR spectra are only meaningful when obtained for the very same sample before and after SAM formation.

Thus, two requirements need to be fulfilled to measure DR spectra of planar SAMs: First, a sample holder, which allows for exact reproducibility of sample position, is required. Second, one needs to exclude time-dependent intensity variations of the spectrometer lamp by using a double-beam spectrometer, because then only intensity ratios of the two beams play a role.

The current setup is improved in two aspects compared to the setup used for earlier work [13]: The sample position is more readily reproducible and polarization-dependent measurements are now possible.

7 Several Photoswitching Cycles in SAMs

Three photoisomerization cycles on a SAM with $\Theta(\text{Az11}) = 83\%$:



Datapoints shown are extracted from p-polarized DR spectra at the S_2 band maximum (4.13 eV, 300 nm), recorded for the pristine SAM and the photostationary states.

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