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COOH-terminated SAMs on gold fabricated from an azobenzene derivative with a 1,2-dithiolane headgroup

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Abstract

Well-defined and homogeneous, contamination-free self-assembled monolayers (SAMs) were fabricated by the chemisorption of lip-NH-*p*-C₆H₄-N=N-*p*-C₆H₄-COOH (lip = α -lipoyl) onto gold. This adsorbate species is composed of a 1,2-dithiolane-based headgroup, an azobenzene-based (and hence photochromic) spacer unit and a carboxylic acid functional group. The SAM constituents are covalently attached to the substrate by the bidentate thiolate anchor groups and exhibit a strongly tilted binding configuration.

Keywords

Azobenzene; Gold; NEXAFS; Self-assembly; XPS

1. Introduction

Self-assembled monolayers (SAMs) [1] which contain azobenzene-based tailgroups are of great current interest, since these SAMs can exhibit photoswitchable properties [2–3]. The (*E*)-(Z) isomerisation of azobenzene derivatives is a well-known process [4] which has been fully characterised even at the single molecular level [5]. The synthesis of azobenzene derivatives suitable for chemisorption onto solid substrates is a prerequisite for the fabrication of such ‘smart’ surfaces [6]. We have utilised 1,2-dithiolane headgroups in this context and have shown that azobenzene derivatives functionalised with such headgroups based on the natural products α -lipoic acid [3d] and asparagusic acid [3a] are suitable for the fabrication of photoswitchable SAMs on gold. As an extension of this work, we have now fabricated COOH-terminated SAMs of this type. This terminal functionality is suitable, for example, for metal ion binding [7], which can be utilised, inter alia, for the construction of surface-mounted metal-organic frameworks [8]. It was recently demonstrated that the combination of terminal COOH units with a photochromic azobenzene-based unit may give rise to SAMs whose metal ion binding affinity can be photoregulated [7a].

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2. Experimental methods

2.1 Chemical synthesis

2.1.1 General—Synthetic work was routinely performed under an atmosphere of dry nitrogen by using standard Schlenk techniques or a conventional glovebox. Solvents were appropriately dried and purified. $\text{H}_2\text{N}-p\text{-C}_6\text{H}_4\text{-N=N-}p\text{-C}_6\text{H}_4\text{-COOH}$ was prepared from 4-nitrobenzoic acid and 1,4-diaminobenzene by slight modification of a published procedure [9]. All other chemicals were procured from standard commercial sources and used as received. NMR spectra were recorded with a Varian Unity INOVA 500 spectrometer operating at 500.13 MHz for ^1H . ESI mass spectra were obtained with a Finnigan LCQ Deca instrument (ThermoQuest, San José, USA). High-resolution ESI mass spectra were obtained with micrOTOF instrument (Bruker Daltonics, Bremen, Germany) utilising an ApolloTM ion funnel ESI ion source. Mass calibration was performed immediately prior to the measurement with ESI Tune Mix Standard (Agilent, Waldbronn, Germany).

2.1.2 Preparation of $\text{H}_2\text{N}-p\text{-C}_6\text{H}_4\text{-N=N-COOMe}$ [10]—A stirred suspension of $\text{H}_2\text{N}-p\text{-C}_6\text{H}_4\text{-N=N-COOH}$ (4.17 g, 16.4 mmol) in SOCl_2 (30 ml) was refluxed for 1.5 h. Volatile components were removed in vacuo. Methanol (8 ml) and pyridine (24 ml) were added and the mixture was refluxed for 1.5 h. It was subsequently allowed to cool to room temperature. Water (40 ml) was added and the precipitate isolated by centrifugation. The solid was dried on a clay plate. It was subsequently subjected to Soxhlet extraction with diethyl ether. The product crystallised from the concentrated extract. Yield 1.60 g (38%).

^1H NMR (DMSO-d_6): δ = 3.86 (s, 3 H), 6.33, (s, 2 H), 6.68 (“d”, apparent J = 8.8 Hz, 2 H), 7.70 (“d”, apparent J = 8.7 Hz, 2 H), 7.81 (“d”, apparent J = 8.6 Hz, 2 H), 8.07 (“d”, apparent J = 8.6 Hz, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO-d_6): δ = 52.0, 113.4, 121.8, 125.9, 129.5, 130.6, 142.9, 153.8, 155.3, 165.8. MS (ESI+): m/z (%) 256 (100) $[\text{M} + \text{H}]^+$.

2.1.3 Preparation of lip-NH- $p\text{-C}_6\text{H}_4\text{-N=N-}p\text{-C}_6\text{H}_4\text{-COOMe}$ (1Me)— α -Lipoic acid (0.52 g, 2.5 mmol) and N,N' -dicyclohexylcarbodiimide (DCC) (0.31 g, 1.5 mmol) were dissolved in dichloromethane (15 ml). The solution was stirred for 20 h and subsequently filtered to remove the precipitate (N,N' -dicyclohexylurea). A small amount (ca. 20 mg) of 4-(dimethylamino)pyridine (DMAP) was added to the filtrate. A solution of $\text{H}_2\text{N}-p\text{-C}_6\text{H}_4\text{-N=N-COOMe}$ (0.32 g, 1.25 mmol) in dichloromethane (25 ml) was added dropwise with stirring. Stirring was continued for 3 d, after which time volatile components were removed in vacuo. The crude product was purified by column chromatography on silica gel. Impurities were eluted with dichloromethane-*n*-hexane (1:1). 1Me was subsequently eluted with ethyl acetate. Yield 0.55 g (98%).

^1H NMR (CDCl_3): δ = 1.56 (m, 2 H), 1.75 (m, 4 H), 1.92 (m, 1 H), 2.43 (m, 3 H), 3.10 (m, 1 H), 3.16 (m, 1 H), 3.58 (m, 1 H), 3.94 (s, 3 H), 7.32 (s, 1 H), 7.69 (“d”, apparent J = 8.6 Hz, 2 H), 7.90 (“d”, apparent J = 8.4 Hz, 2 H), 7.93 (“d”, apparent J = 8.8 Hz, 2 H), 8.16 (“d”, apparent J = 8.4 Hz, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 25.0, 28.9, 34.6, 37.7, 38.5, 40.3, 52.4, 56.4, 119.6, 122.5, 124.4, 130.6, 131.5, 141.0, 148.9, 155.2, 166.5, 171.1. MS (ESI−): m/z (%) 442 (100) $[\text{M} - \text{H}]^-$.

2.1.4 Preparation of lip-NH- $p\text{-C}_6\text{H}_4\text{-N=N-}p\text{-C}_6\text{H}_4\text{-COOH}$ (1H)—1Me (0.50 g, 1.1 mmol) was added to a solution of NaOH (45 mg, 1.1 mmol) in ethanol-water (1:1, 100 ml). The suspension was stirred in a closed Schlenk tube at 60 °C for 5 d. It was subsequently allowed to cool to room temperature and filtered. The filtrate was reduced to dryness in vacuo, affording the crude sodium salt 1Na. The salt was dissolved in water (100 ml). The solution was carefully acidified (pH 5) with dilute hydrochloric acid. The mixture was

extracted with diethyl ether (3×50 ml). The combined extracts were reduced to dryness. The crude product was purified by column chromatography on silica gel with ethyl acetate–THF (1:1). Yield 0.12 g (25%).

^1H NMR ($\text{DMSO}-d_6$): δ = 1.42 (m, 2 H), 1.64 (m, 4 H), 1.87 (m, 1 H), 2.39 (m, 3 H), 3.11 (m, 1 H), 3.18 (m, 1 H), 3.63 (m, 1 H), 7.79 (“d”, apparent J = 8.1 Hz, 2 H), 7.83 (“d”, apparent J = 8.3 Hz, 2 H), 7.87 (“d”, apparent J = 8.9 Hz, 2 H), 8.08 (“d”, apparent J = 8.1 Hz, 2 H), 10.42 (s, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$): δ = 24.8, 28.3, 34.2, 36.3, 38.1, 56.2, 119.2, 121.5, 123.7, 130.2, 142.6, 147.4, 152.7, 171.7. HRMS (ESI $^-$): m/z (%) 428.1110093 $[\text{M} - \text{H}]^-$, calcd. for $[\text{C}_{21}\text{H}_{22}\text{N}_3\text{O}_3\text{S}_2]^-$ 428.109709.

2.2 SAM fabrication

The gold substrates for SAM fabrication were prepared by thermal evaporation of 100 nm gold (99.99% purity) onto polished single-crystal silicon (111) wafers (Silicon Sense) primed with a 5 nm Ti layer for adhesion promotion. The resulting films were polycrystalline with a grain size of 20 – 50 nm and predominantly possessed (111) orientation [16]. The films were formed by immersion of freshly prepared 1×1 cm gold substrates in 10 μM solutions of the target compounds in DMSO at room temperature for 24 h. After immersion the samples were sonicated and carefully rinsed with copious amounts of DMSO, blown dry with nitrogen, and kept in plastic containers filled with nitrogen until they were characterised.

2.3 SAM characterisation

2.3.1 X-ray photoelectron spectroscopy (XPS)—The XP spectra were acquired with a SSI S-Probe XPS system (Surface Science Instruments, Mountain View, CA) using a monochromatic Al $\text{K}\alpha_{1,2}$ X-ray source ($h\nu$ = 1486.6 eV). The determined SAM composition was an average from three spots on two distinct samples (a total of 6 analysis spots). Molecular environments of the samples were probed by collecting high-resolution (analyser pass energy = 50 eV) spectra from the N 1s, O 1s, C 1s, and S 2p regions at a take-off angle (TOA) of 55°. Here, the photoelectron TOA is defined as the angle between the surface normal and the axis of the analyser lens. Energy scales were calibrated by normalising the Au $4f_{7/2}$ peak to 84.0 eV and a linear background was subtracted for all peak quantifications. The peak areas were normalised by the manufacturer supplied sensitivity factors and surface concentrations were calculated using the Analysis 2000 software. Atomic compositions were calculated from C 1s and Au 4f peak areas obtained from survey (0–1100 eV), detail O 1s (524–544 eV), detail N 1s (390–410 eV), and detail S 2p (155–173 eV) spectra (analyser pass energy = 150 eV).

2.3.2 Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS)—NEXAFS spectra were measured at the National Synchrotron Light Source (NSLS) U7A beamline at Brookhaven National Laboratory, using an elliptically polarised beam with ~85% p -polarization. This beam line uses a monochromator and 600 l/mm grating that provides a full-width at half-maximum (FWHM) resolution of ~0.15 eV at the carbon K -edge (285 eV). The monochromator energy scale was calibrated using the 285.35 eV C 1s $\rightarrow \pi^*$ transition on a graphite transmission grid placed in the path of the X-rays [11]. To eliminate the effect of incident beam intensity fluctuations and monochromator absorption features, nitrogen K -edge NEXAFS spectra were normalised by the signal from a bare dodecanethiol SAM and C K -edge spectra were normalised by the spectrum of a clean gold surface prepared by evaporation of gold in vacuo. Both reference and signal were divided by the beam flux during each respective data acquisition [12]. Partial electron yield was monitored by a detector with the bias voltage maintained at –150 V and –360 V for C K -edge and N K -edge, respectively. Samples were mounted to allow rotation about the vertical

axis to change the angle between the sample surface and the incident X-ray beam. The NEXAFS angle is defined as the angle between the incident X-ray beam and the sample surface.

3. Results and discussion

3.1 Chemical synthesis

The synthesis of the target compound is outlined in Figure 1. α -Lipoic acid anhydride [13], prepared in situ by treatment of α -lipoic acid (lip-OH) with DCC, was reacted with the amino-functionalised azobenzene derivative $\text{H}_2\text{N}-p\text{-C}_6\text{H}_4\text{-N=N-COOMe}$, which had been obtained by reaction of the corresponding acid chloride with methanol in the presence of pyridine (Einhorn acylation). Finally, the resulting amide lip-NH- $p\text{-C}_6\text{H}_4\text{-N=N-}p\text{-C}_6\text{H}_4\text{-COOMe}$ (**1Me**) was subjected to saponification of the methyl ester group under basic conditions (NaOH, aqueous ethanol). Standard workup under mild acidic conditions afforded the target compound lip-NH- $p\text{-C}_6\text{H}_4\text{-N=N-}p\text{-C}_6\text{H}_4\text{-COOH}$ (**1H**) in 25% yield after purification by column chromatography.

3.2 SAM characterisation

3.2.1 XPS—Normalised C 1s, S 2p, N 1s, and O 1s XP spectra of the SAMs are presented in Figure 2, along with the corresponding fits. The S 2p spectra exhibit a single S 2p_{3/2,1/2} doublet. The binding energy (BE) position of the S 2p_{3/2} component (ca. 162.2 eV) is characteristic of thiolate-type sulfur bonded to metal surfaces [14–16]. This proves that during the chemisorption of **1H** on Au the S–S bonds of the 1,2-dithiolane headgroup are cleaved through an oxidative addition mechanism and that two covalent sulfur–gold bonds are subsequently formed [3d,17]. No traces of unbound dithiolane or oxidised sulfur species are visible in the spectrum.

The C 1s spectrum consist of three distinct features, one at 285 eV corresponding to the CH₂ alkyl chain and aromatic carbon backbone and two high energy shoulders at 286.8 eV and 288.9 eV. The latter features can be assigned to an N–C species and the two C=O units [18], respectively. The N 1s spectrum of the SAM exhibit a single component at 400.1 eV related to the azo unit. A peak related to the NH group in the spacer unit (expected near 399.2 eV) is not resolvable under the experimental conditions used to acquire the N 1s spectrum. The O 1s spectrum consists of two components found at 533.7 eV and 531.9 eV. These BEs can be assigned to the C–O and C=O groups, respectively [18].

XPS was also used to determine the elemental compositions of the SAM. Pertinent data are collected in Table 1. The surface composition showed the presence of carbon, nitrogen, sulfur, oxygen, and gold (from the underlying substrate). Omitting the Au contribution (Table 1), some significant differences between the theoretical and experimental compositions become clear: The atomic percentages of S and N are lower than expected. These lower percentages can be explained by attenuation of the sulfur and nitrogen signals due to inelastic scattering from the long hydrocarbon overlayer. On the other hand, the somewhat higher oxygen content is a result of the position of the COOH groups at the ω -terminus of the molecules. These results allow the conclusion that a relatively ordered monolayer was formed.

Apart from the composition analysis, the effective film thickness could be determined on the basis of the intensities of the C 1s and the Au 4f emissions [19]. The thickness values were derived from the $I_{\text{C1s}}/I_{\text{Au4f}}$ intensity ratios using previously reported attenuation lengths [20]. Following this procedure, we have obtained a thickness values of 13.1 Å. This value is rather low compared with an expected thickness for a monolayer of untilted (vertically oriented, upright) molecules of 23.1 Å (estimated from the structure of the precursor

molecules) indicating that the chemisorbed molecules assume a strongly tilted binding configuration. We note that in the case of the closely related lip-NH-*p*-C₆H₄-N=N-Ph a film thickness of 18.4 Å was obtained, consistent with the tilt angle of ca. 30° determined by NEXAFS spectroscopy [3d].

In summary, the XPS data allow the conclusion that **1H** forms well-defined and homogeneous, contamination-free SAMs on gold, whose constituents are covalently attached to the substrate by the bidentate thiolate anchor groups.

3.2.2 NEXAFS spectroscopy—Additional valuable information concerning the identity, chemical integrity and morphology of the SAMs is provided by NEXAFS spectroscopy. This technique provides insight into the electronic structure of the films by sampling unoccupied molecular orbitals [12]. In addition, it can probe structural parameters of the film such as molecular alignment using the linear dichroism of X-ray absorption. By measuring the dependence of the absorption resonance intensities on the orientation of the electric field vector of the synchrotron X-ray beam with respect to the orientation of the respective molecular orbital. This effect can be conveniently monitored by recording spectra at normal and glancing incidence angles. Spectra collected at the so-called magic angle of X-ray incidence (55°) are not affected by structural parameters and are only representative of the electronic structure of the surface [12]. These spectra can thus provide information about the chemical identity of surface species.

C *K*-edge spectra acquired at X-ray incidence angles of 70°, 55°, and 20° are presented in Figure 3, along with the difference between the 70° and 20° spectra. All spectra in Figure 3 exhibit an absorption edge related to the excitation of the C 1s electrons into the continuum states and the characteristic absorption resonances. The spectra are dominated by the pronounced π_1^* resonance of phenyl ring near 285.2 eV, which is accompanied by a weak low energy shoulder at around 284.6 eV. We note that we have observed this shoulder, which is not present in spectra of related biphenyl terminated SAMs, for a variety of azobenzene-containing films [3d,f]. It might be related to the C–N bonds at the phenyl rings or caused by excitonic effects similar to what has been observed for polyacenes [21],¹¹ anthracenes [22],¹² and other highly conjugated systems [12]. The spectra also exhibit a weak Rydberg resonance (R^*) near 287.1 eV, a π^* resonance assigned to the terminal carboxylic acid C=O unit at 288.2 eV, and several broad σ^* resonances at higher photon energies. The above assignments were made in accordance with the literature [12,22–26]. The spectra exhibit a pronounced linear dichroism, which is additionally highlighted by the respective 70° – 20° difference curve. This is a clear signature of orientational order. However, the negative sign of the observed difference peaks for the π^* resonances imply an inclined orientation of the molecular constituents in the SAM.

N *K*-edge NEXAFS spectra acquired at X-ray incidence angles of 70°, 55°, and 20° are shown in Figure 4, along with the respective 70° – 20° curves. They are dominated by a distinct π^* resonance at 398.3 eV related to the central N=N unit of the azobenzene moiety. This feature is accompanied by several weak π^* features in the 400–405 eV range and several broad σ^* resonances at higher photon energies [27–30]. In agreement with the C *K*-edge data, the N *K*-edge spectra of the SAM exhibit a significant negative linear dichroism for the π^* resonance related to the azo unit. This supports our previous statement that the chemisorbed molecules are tilted in the monolayer film.

A more quantitative analysis of the NEXAFS spectra was performed to determine the average tilt angles of the SAM constituents. The tilt angles of the π^* orbitals with respect to the surface normal were analysed using the most prominent π^* resonances at the C and N *K*-edge. The intensities of these resonances as a function of the X-ray incidence angle Θ are

evaluated using published procedures for a vector-type orbital [12]. The transition dipole moments (TDMs) of the respective π^* orbitals are oriented perpendicular to the ring plane and to the azo unit. The average tilt angles of the π^* orbitals related to the phenylene and azo moieties have been determined to be $\sim 47^\circ \pm 5^\circ$ and $\sim 41^\circ \pm 3^\circ$, respectively. The values for these moieties are indistinguishable within experimental error and suggest that the phenylene rings are essentially coplanar in the SAM and that the orientation of the π^* -orbitals in the azo unit and the phenylene ring are approximately parallel to each other. The observation of such a coplanar geometry is in line with earlier results for azobenzene-based SAMs on gold [3d]. The determined angles are close to the “magic angle” of NEXAFS spectroscopy (55°) at which a uniformly tilted layer can not be distinguished from a loosely packed and disordered film.[12] However, the possibility of a mostly disordered film is not likely here, since we observed a significant linear dichroism in the spectra (the obtained angles are still $\sim 10^\circ$ away from the magic angle) and the XPS data verify the packing density is consistent with our NEXAFS analysis (see below).

Based on the π^* -orbital tilt angles just described, the average molecular tilt angle in the SAM can in principle be estimated [12]. However, for this analysis not only the tilt but also the twist of the molecules must be taken into account [30,31]. Assumptions about the twist angle are not straightforward to make because small changes to the spacer composition and the terminal groups reportedly have a major impact on the twist angle of azobenzene-based units in SAMs [32]. Since no literature data on the tilt angle of COOH substituted azobenzene derivatives in SAMs or 3D crystals are available, we will not take the molecular twist into account. Such an estimate, omitting the twist, yields a tilt angle of $\sim 44^\circ$, based on an average of the phenyl and azo π^* -orbital orientation. This result represents a lower limit of the molecular tilt angle. Using the obtained orientation and the length of the precursor molecules (23.1 Å) we can estimate the thickness of the SAM to be ~ 16.3 Å, which is in good agreement with the thickness value of 13.1 Å based on the XPS data.

4. Conclusion

Thin films were prepared by the chemisorption of lip-NH-*p*-C₆H₄-N=N-*p*-C₆H₄-COOH (1H) on gold. This adsorbate species is composed of a 1,2-dithiolane-based headgroup, an azobenzene-based (and hence photochromic) spacer unit and a carboxylic acid functional group. Film characterisation was performed by XPS and NEXAFS spectroscopy, which proved the formation of well-defined and homogeneous, contamination-free self-assembled monolayers. The SAM constituents are covalently attached to the substrate by the bidentate thiolate anchor groups and exhibit a strongly tilted binding configuration.

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Fig. 1.
Synthesis of the target compound **1H**.

Fig. 2.

C 1s, S 2p, N 1s and O 1s XP spectra (open circles) of SAMs prepared from **1H** along with the corresponding fits (solid lines). Note that whereas C 1s, N 1s, and O 1s emissions are singlets, S 2p emission is a doublet comprised of two components with a definite spin–orbit splitting and branching ratio.

Fig. 3.
C K-edge NEXAFS spectra of SAMs prepared from **1H** acquired at X-ray incidence angles of 70°, 55°, and 20°. The bottom curves represent the difference between the 70° and 20° spectra. The dotted lines correspond to zero.

Fig. 4. N *K*-edge NEXAFS spectra of SAMs prepared from **1H** acquired at X-ray incidence angles of 70°, 55°, and 20°. The bottom curves represent the difference between the 70° and 20° spectra. The dotted lines correspond to zero.

Table 1

Summary of elemental SAM composition (%) as determined by XPS.

	Au	C	O	N	S
Calcd. comp.	0	72.4	10.3	10.3	6.9
Exp. determined comp. ^a	34.0±0.4	48.6±1.8	9.2±0.4	5.2±0.6	3.0±0.8
Exp. determined comp. without Au	0	73.7±2.6	14.0±0.9	7.8±1.7	4.6±1.2

^a Average experimental composition from two distinct samples (three spots per sample).