Supporting information for the article: Structure and Conductance of Aromatic and Aliphatic Dithioacetamide Monolayers on Au(111)


Sony Deutschland GmbH, Materials Science Laboratory, Hedelfinger Strasse 61, 70327 Stuttgart, Germany.

†Laboratory for Micro and Nanotechnology, Paul Scherrer Institut, 5232 Villigen Switzerland.

DFT calculations. The relaxed structures of DMAAB (a) and DMAAcH (b) monolayers on a periodic Au(111) slab are shown in Fig. S1. The average packing density of the dithioacetamide molecules on Au, as determined from XPS data, is only 20% lower than in the ($\sqrt{3} \times \sqrt{3}$)R30° overlayer structure known from alkanethiols on Au(111). Thus, as an approximation, a ($\sqrt{3} \times \sqrt{3}$)R30° overlayer structure was assumed for the calculation. In the relaxed structure (equilibration of the dithioacetamide adsorbates but not of the Au slab), the dithioacetamides are chemisorbed to Au(111) with the sulfur atom located in between a “bridge site” and a “on top site”. The next-neighbor S-Au bond distance is 2.5 Å and the tilt angle of the molecular backbone towards the surface normal is less than 20°. The molecular lengths are $d_{S-S} = 1.3$ nm for DMAAB and $d_{S-S} = 1.26$ nm for DMAAcH. Nevertheless, due to the various possible orientations of the molecule within the unit cell, other equilibrium structures of dithioacetamides on Au
cannot be ruled out. Note that, in contrast to polar interactions (H-bonds), intermolecular dispersion forces (van der Waals forces) are not fully accounted for within the DFT model. This drawback of the model is probably of minor relevance due to the dominant character of H-bond interactions between the dithioacetamides in the monolayer.

A two layer Au(111) slab in a periodic $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell is employed to model the surface. Perpendicularly to the surface, the size of the unit cell is 28 Å. Thus, the vacuum gap thickness between adlayer and the Au layer of the adjacent cell is about 10 Å. DFT calculations are performed in the local density approximation using the VWN LDA functional\(^1\) with a double numerical basis set with polarization functions (DND), as provided by Dmol3.

![Figure S1](image)

**Figure S1.** Relaxed structures of DMAAB (a) and DMAAcH (b) on a periodic Au(111) slab. The coordination of the thiolate to Au is similar in both cases, corresponding to a slightly off-axis bridge site. In the periodic case, the length of the two compounds differs due to the higher flexibility of the DMAAcH compound and due to the effect of intermolecular interactions. In both cases, the orientation of the molecule is almost perpendicular to the surface. The molecular lengths are \(d_{S,S} = 1.3\) nm for DMAAB and \(d_{S,S} = 1.26\) nm for DMAAcH.

Model of a DMAAB domain structure: In Fig. S2, the structure of a hypothetical DMAAB domain inserted in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ octanethiol monolayer on Au(111) is presented. It shows a section along the [11-2] direction of the Au(111) surface. The octanethiol layer was relaxed within a periodic DFT calculation in a $(2\sqrt{3} \times 2\sqrt{3})$ unit cell, using the VWN LDA functional. Subsequently some of the octanethiol molecules were removed, creating a defect with the lateral size corresponding to two adjacent DMAAB molecules. Finally, the DMAAB molecules were relaxed within a COMPASS force-field calculation, while the host layer and the Au slab were kept frozen. As shown in Fig. S2, the physical size of the defect is 13.2 Å. Considering that the shape-broadening due to the STM imaging mechanism (i.e. completely neglecting further broadening due to tip convolution) is about 0.7-1 nm, an effective domain size of at least 20-23 Å is expected from STM images of this structure. Experimental STM profiles showed the presence of bright spots with diameters down to 1.5 nm (see Article), thus allowing the conclusion that these small features might correspond to single DMAAB molecules isolated in the host matrix.

Figure S2. Structure of a hypothetical DMAAB domain inserted in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ octanethiol monolayer on Au(111). A section along the [11-2] direction of the Au(111) surface is shown. The octanethiol layer was relaxed within a periodic DFT calculation, while the inserted DMAAB molecules were placed into defects and relaxed with the COMPASS force field method. The octanethiol vacancy is selected in such a way that 2 DMAAB molecules fit into the defect site. The physical size of the gap bridging the defect is ~13.2 Å.
Growth kinetics of a dithioacetamide SAM. The SAM growth process is studied by monitoring adsorption chemistry and SAM coverage as a function of assembly time in a 1 mM DMAAB solution. Figure S3 shows the evolution of DMAAB coverage with assembly time. The XPS results suggest that the film growth is governed by two processes. In the initial phase, the growth is determined by the interaction of the thiol headgroup with the Au substrate, leading to the formation of a lying down phase. Indeed, the high S 2p(thiolate)/S 2p(total) ratio suggests that part of the molecules bind with both thiolate groups to the substrate. Within the first 10 minutes of SAM growth, the S 2p(thiolate)/Au 4f ratio increases by 15% as a result of the higher density of molecules covalently linked to Au. During the same time, the DMAAB coverage increases by 20%, indicating that part of the molecules bound with both thiolate groups are forced into an upright position by polar interaction forces. Beyond an assembly time of 10 minutes, a long term growth process, associated with a further increase of the S 2p component at 163.5 eV BE takes place. In particular, while the S 2p(thiolate)/Au 4f ratio remains stable, an increase by 27% in the S 2p(total)/Au 4f ratio is observed, joined by an increase of the component related to the presence of thiol sulfur in the SAM (S 2p at 163.5 eV BE).
Figure S3. High resolution XPS S $2p$ core level spectra of a DMAAB SAM at different stages of SAM growth. The contribution from thiolate sulfur (162 eV and 161 eV BE) increases within the first 10 minutes of SAM growth. (b) Between 10 min and 20 h assembly time, only the component associated to free thiol (163.5 eV BE) increases.

Thiol and disulfide S $2p$ components in a dithioacetamide monolayer. Further experiments were performed to separate the contribution from the thiol and the disulfide species in dithioacetamide layers. First, the BE of the thiol sulfur in DMAAB was found by XPS measurements on DMAAB multilayers. The multilayers are obtained by drop casting a saturated DMAAB solution on a Au substrate and evaporation of the solvent. The S $2p$ signal for S-H sulfur is found at 163.5 ± 0.1 eV (Figure S4a). Second, the BE of the disulfide sulfur in DMAAB oligomers is determined by adding iodine (I$_2$) to solution before assembly. Iodine is an oxidation agent that is known to trigger the formation of
oligomers via disulfide bridges. Here, the S 2p signal for S-S sulfur (there might be also a minor contribution from S-H sulfur in this peak) is found at 163.5 ± 0.15 eV (Figure S4b). Since in the two experiments both the S-S and the S-H sulfur S 2p signals are found at the same BE, a distinction of disulfides and thiols is not possible within the experimental accuracy.

**Figure S4:** High resolution XPS S 2p spectra of DMAAB multilayers (a) and of DMAAB SAMs treated with an iodine (I₂) solution (b). In DMAAB multilayers (a), the peak corresponding to thiol sulfur at 163.5 eV is dominant. In DMAAB SAMs prepared from iodine solution, the peak corresponding to disulfide sulfur is found at the same binding energy, i.e. at 163.5 eV.

**Processes during thermal annealing and temperature stability of DMAAB.** We found that an annealing temperature of 80°C is required to observe a ripening of DMAAB domains. Thus, it is assumed that a high activation energy is needed to initiate diffusion of DMAAB molecules or aggregates, since a single DMAAB molecule is hardly removed from a DMAAB island (hydrogen bonds) and probably the DMAAB aggregates have to diffuse along the surface “en bloc”. In turn, alkanethiols diffuse and partially desorb from surface at 80°C, reason for which the substrates are
immersed in alkanethiol solution upon thermal annealing, such that alkanethiol molecules are allowed to refill the vacancies and to form an equilibrated, close packed SAM. XPS analysis is performed after each of the mentioned processing steps, and no significant change in the composition of the SAM is observed, showing that DMAAB is stable under annealing conditions and also towards replacement by alkanethiols. Furthermore, NMR experiments prove that no DMAAB decomposition occurs if the substance is heated for 1 h at 90°C in DMF.

**STM topography of a DMAAB SAM.** A characteristic overlayer structure is observed in STM images of a DMAAB monolayer, consisting of 3-4 nm sized bumps separated by depressions. The measured height profile is presented in Figure S5, showing an average modulation of 0.25 nm in the topography of the monolayer. It is attributed to differences in the molecular orientation of the DMAAB molecules as a result of an inhomogeneous growth of DMAAB aggregates on Au(111). A possible reconstruction of the Au(111) surface due to DMAAB adsorption is unlikely, since terrace edges are clearly visible and not much affected by the monolayer growth (not shown here).

![STM image](image-url)

**Figure S5:** STM image (50nm x 30 nm) of a DMAAB monolayer on Au(111). A section along the scan direction, averaged over 15 scan lines, is shown at the bottom. The average STM height difference between the islands and the depressed areas is ~ 0.25 nm. The STM height is measured at the position of the two red arrows.
Determination of dithioacetamide coverage by contact angle goniometry. A series of co-assembled, DMAAB/dodecanethiol monolayers with different DMAAB/dodecanethiol concentration ratios in solution is measured by STM, XPS and contact angle goniometry in parallel (See “Mixed SAMs by co-assembly” in the results section). Contact angle measurements with a water droplet are performed with a KSV CAM 100. From the contact angles on DMAAB and dodecanethiol SAMs, the two separate contributions are determined. Then the contact angle $\theta_{\text{eff}}$ for the mixed, two component SAM is measured. Coverages for the mixed SAMs are obtained using the Cassie equation

$$\cos \theta_{\text{eff}} = \varphi_A \cos \theta_A + \varphi_B \cos \theta_B$$

that relates the contact angle $\theta_{\text{eff}}$ of a multi-component surface to the contact angles $\theta_A$ and $\theta_B$ of surfaces covered with the single components A and B. From this equation, we obtain the relative coverages $\varphi_A$ and $\varphi_B$ using the relationship

$$\varphi_A = 1 - \varphi_B$$

Figure S6 shows a plot for the DMAAB coverage determined via the Cassie-equation. Comparison to the XPS data presented in Figure 4 shows a good agreement and demonstrates that this method is a valid alternative for a qualitative coverage determination. The mismatch at a DMAAB concentration higher than 30% (compared to XPS data) could be related to differences in the SAM structure.

Figure S6. DMAAB coverage as determined from contact angle goniometry.
Formation of DMAAcH rod-like domains. Structures that are attributed to DMAAcH rod-like domains are observed in mixed DMAAcH/octanethiol monolayers (Figure S7). The monolayers are prepared by immersing the crystalline Au(111) substrates in a equimolar DMAAcH/octanethiol mixed solution (1 mM) for 24 h at RT. Finally, the monolayers are thermally annealed in the assembly solution at 95°C for 1 h. This allows phase segregation of DMAAcH and dodecanethiol. The rods have a length of ~ 6 nm and a width of ~ 2 nm. The molecular structure of a few of these rods could be resolved as seen in the STM scan in Fig. S7 (right image), showing the formation of a double row of stacked aliphatic DMAAcH molecules.

Figure S7. STM scans of mixed DMAAcH/octanethiol monolayers. The monolayers are obtained upon assembly at RT and subsequent thermal annealing of the samples in a 1:1 DMAAB/dodecanethiol solution at ca. 95°C for 1 h. (a) The orientation of the rods follows the surface lattice orientation of Au(111), i.e. the relative orientation of the rods correspond to multiples of 60°. (b) The inset shows a high resolution image of a rod, consisting of two rows of DMAAcH molecules. The scans are recorded at a bias voltage of $U_{\text{Gap}} = 400$ mV and a tunneling current of $I_{\text{tunn}} = 2$ pA.