

Au Adatoms in Self-Assembly of Benzenethiol on the Au(111) Surface

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Self-assembly of organosulfur molecules on gold is widely used to construct functional surfaces.¹ The true structure of the anchor bond between self-assembled alkanethiol molecules and the gold surface has begun to be revealed in a recent series of publications reporting the involvement of reactive Au adatoms in the formation of this bond.^{2–4} So far Au adatom bonding has been observed in the 2D and 3D monolayers of alkanethiol molecules on Au(111). It is therefore necessary to extend these studies to the case of arenethiols, which are important candidate molecules for molecular electronics^{5–7} and other applications of organosulfur self-assembled monolayers (SAMs).^{1–8} The bonding and self-assembly of arenethiols is expected to be different from those of alkanethiols due to the steric and chemical differences in the organic residues of the corresponding molecules.⁸ For example, the binding energy of the phenylthiolate (PhS) species on the unreconstructed Au(111) is ~ 0.5 eV smaller than that of methylthiolate (CH₃S).⁹

We have used scanning tunneling microscopy (STM) at low temperature to show that gold adatoms are indeed involved in the self-assembly of phenylthiolate at low coverages. Phenylthiolate species, formed by thermal dissociation of benzenethiol on Au(111) at 300 K, form surface complexes involving two PhS species and one Au adatom (PhS–Au–SPh). The complexes further coalesce due to hydrogen bonding. The presence of Au adatoms in the PhS dimer complex was deduced from the stability of the complexes in the tunneling junction as well as the analysis of the lifting of the herringbone reconstruction that accompanies phenylthiolate self-assembly.

Undissociated benzenethiol molecules (deposited on Au(111) at $T < 70$ K) are imaged by STM as dumbbells (fwhm of the STM profile along the length of the molecule is 0.95 nm) with two lobes of slightly different apparent size and height (Figure 1a). The apparent height of the large lobe is ~ 0.12 nm. First-principles calculations predict PhSH adsorption with the SH group above a lattice Au atom and the phenyl ring nearly parallel to the surface.¹¹ A voltage pulse of > 2.7 V from the STM tip dissociates the S–H bond of the PhSH molecule, producing the PhS species. This reaction is similar to the electron-induced dissociation of CH₃SH and CH₃SSCH₃ on Au(111) at 5 K,¹⁰ where the CH₃S species is produced. The STM images of both CH₃S and PhS have a large lobe and a small tail with a dark halo (not shown). The lobe corresponds to the methyl group in CH₃S and the phenyl group in PhS, while the tail is produced by the sulfur atom which is bonded to the Au–Au bridge site.

We next studied thermally activated dissociation of PhSH molecules. Following benzenethiol adsorption at $T < 70$ K, the Au(111) surface was heated to 300 K to dissociate benzenethiol molecules and produce PhS. As seen in Figure 2a, most of the dissociation products are found

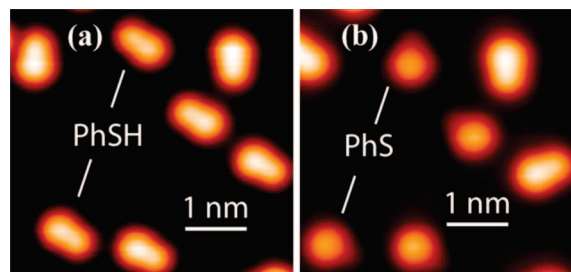


Figure 1. Benzenethiol (PhSH) and phenylthiolate (PhS) on Au(111) at 5 K. PhS species in (b) were produced at 5 K by applying a 2.7 V pulse on top of PhSH molecules in (a). Au adatoms are not involved in these species.

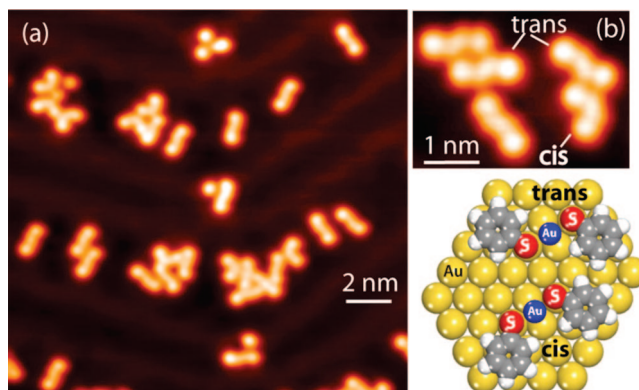


Figure 2. Surface complexes of phenylthiolate (PhS–Au–PhS) observed after heating Au(111) with PhSH to 300 K. (a) Large scale image showing the dominance of the trans-complex. (b) Close-up STM image showing trans- and cis-PhS–Au–SPh complexes. Schematic ball models are shown on the left (the Au adatom is blue).

in the form of an elongated structure (complex) with two large lobes. Each lobe corresponds to the phenyl group because its apparent height is nearly the same as that of the large lobe in the undissociated PhSH molecule (Figure 1). The STM profile along the length of the complex has $\text{fwhm} = 1.63 \pm 0.07$ nm, slightly less than double the apparent length of the STM image of a PhSH molecule. Each complex is therefore composed of two PhS fragments (Figure 2). The phenyl groups in the complex can be either in cis- or trans-configuration relative to each other (Figure 2b). The trans-conformer is dominant. Many complexes are observed to coalesce into spacious structures, most likely due to weak hydrogen bonding (e.g., C–H \cdots S).¹² The phenylthiolate complexes do not form long compact chains as observed in the alkanethiolate stripe phase on Au(111) because of the steric hindrance associated with the large phenyl group.¹³

Favorable formation of the PhS complex at high temperature as well as its STM image implies that the complex is not a diphenyldithiol molecule (PhSSPh) where two PhS fragments are bonded by a S–S bond. The adsorption energy of PhSSPh was predicted to be very small¹⁰ and

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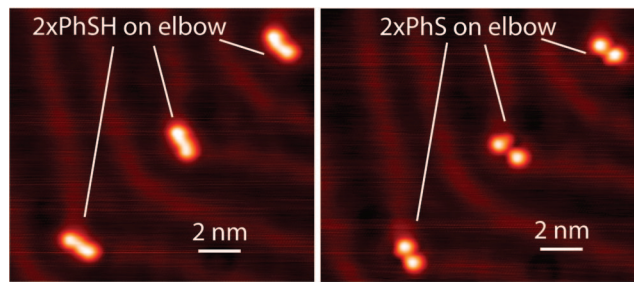


Figure 3. Pairing of PhSH molecules on the elbow site at $T \sim 70$ K. The S–H groups are facing each other. Au adatoms are not involved at this temperature. The overall geometry of the pair is closely reminiscent of the PhS–Au–SPh complex formed at higher temperature (Figure 2). Each pair in the left panel was pulsed with a 2.7–3.0 V pulse. Pulsing converts PhSH to PhS (right panel) via S–H bond scission.

even slightly negative¹⁴ on Au(111), while its dissociation to be facile with a barrier of less than 0.3 eV, thus rapid at 300 K.¹⁰ Furthermore, calculations show that the phenyl rings in the PhSSPh molecule adsorbed on the Au(111) surface are oriented nearly normal to the surface.¹⁰ In contrast, the apparent height of the large lobes in the complex is nearly the same as that in the undissociated PhSH molecule, which implies orientation of phenyl rings parallel to the surface. Furthermore, an isolated PhS complex is very stable against high voltage/current pulses from the STM tip: no topographic changes (diffusion, dissociation) are observed even at a pulse voltage as high as 3.5 V and a tunneling current of 100 pA. In contrast, the PhSH molecule with a relatively strong S–H bond dissociates at 2.7 V and above, while the S–S bond in the CH_3SSCH_3 molecule on the Au(111) surface dissociates at 1.4 V and above.^{2,10} We therefore propose that the PhS complexes incorporate Au adatoms by analogy with the self-assembled surface complexes of CH_3S at low coverage.² Schematic structural models for the PhS–Au–PhS complexes in the cis- and trans-conformations are shown in Figure 2, where the structure of the anchor bond was assumed to be similar to that of $\text{CH}_3\text{S–Au–SCH}_3$, with each S atom making one bond to a surface Au atom and the other to the Au adatom.²

The formation of PhS complexes is accompanied by partial lifting of the herringbone reconstruction (Figure S1). The periodicity of the soliton lines along the $[1\bar{1}0]$ close-packed directions on Au(111) is ~ 7.5 nm in Figure S1, significantly larger than 6.3 nm on the clean surface. In a previous publication, we carried out statistical analysis of this phenomenon in the case of methylthiolate self-assembly which also involves Au adatoms.² Following the same procedure for Figure S1, the extra coverage of Au atoms embedded in the residual regions of the herringbone reconstruction is 0.48 Au atoms/nm² compared to 0.67 Au atoms/nm² on the clean surface. At the same time, the surface coverage of the PhS complexes is 0.14 units/nm². The reduction in the coverage of embedded Au atoms in the herringbone reconstruction is thus nearly the same as the coverage of the PhS complexes, which implies that each complex does indeed incorporate one Au adatom extracted from the reconstructed surface layer of Au(111).²

Notably, our findings and the corresponding structure of the adatom complexes are in excellent overall agreement with a recent analysis of self-assembled arenethiolate species on gold nanoparticles as small as 1.4 nm diameter.¹⁵

An intriguing observation of the elbow sites of the herringbone reconstruction was made at a very low coverage of PhSH, slightly below its dissociation temperature. As seen in Figure 3, PhSH molecules are preferentially adsorbed on the elbow sites, which is a general behavior seen for many molecules on Au(111) owing to the presence of the lattice defect (a threading dislocation) at the elbow

site. The undissociated state of PhSH molecules in each pair on the elbow site can be readily verified by dissociating the molecules with 2.7–3.0 V pulses from the STM tip, producing PhS species (Figure 3). Upon closer inspection, we find that the PhSH are also aligned in a geometry that appears to be very similar to that in the trans-complex PhS–Au–SPh (Figure 2b). The main difference is a slightly larger separation of the peripheral lobes between two PhSH molecules at the elbow, $\text{fwhm} = 1.74 \pm 0.04$ Å. Similar aligned pairs were also observed in the case of CH_3SH adsorption on Au(111).¹⁶ These observations suggest that, in addition to being the likely source of reactive Au adatoms at low adsorbate coverage,² the elbow site can also act as a template for the RSH dissociation and subsequent or simultaneous formation of the Au adatom complex. Prealignment of the reagent molecules on particular surface sites was recently suggested to facilitate subsequent reactions¹⁷ and, in the case of PhSH molecules, may also shed light on the much debated fate of hydrogen atoms in the dissociation of the S–H bond.^{1,18} DFT calculations showed that on a defect-free surface the energy gain due to the dissociation of the S–H bond (forming an adsorbed H atom) is very small because of the relative strength of the S–H bond and weakness of H bonding to the Au(111) surface.¹⁹ The additional gain of the binding energy due to the Au adatoms and the possibility of forming a H_2 molecule in the dissociation of the prealigned RSH molecules may shift the energetic balance to strongly favor S–H bond dissociation.

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Supporting Information Available: Statistical analysis of the lifting of the herringbone reconstruction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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