Simultaneously Understanding the Geometric and Electronic Structure of Anthraceneselenolate on Au(111): A Combined Theoretical and Experimental Study

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Self-assembled monolayers (SAMs) of π-conjugated organic molecules have attracted significant interest in the field of molecular and organic electronics because of their ability to change electrode work functions combined with a considerable conductivity. Studies simultaneously addressing both their geometrical and morphological structure as well as their electronic properties are, however, scarce. Here, we provide a detailed description of layers consisting of anthracene-2-selenolate on Au(111), which display extraordinarily well and long-range ordered structures. Combining experimental data with the results of slab-type band-structure calculations, we are able to unambiguously determine the alignment of the molecules on the surface. The electronic structure of the SAMs is then determined by ultraviolet photoelectron spectroscopy (UPS) and by density functional theory (DFT) based simulations. For the SAM-induced work-function modification a particular close agreement between the experimental value of −1.3 eV and the calculated −1.37 eV is found. This supports the notion that the currently available modeling approaches have the potential to quantitatively predict important aspects of the electronic structure of SAMs as long as truly well-ordered monolayers are investigated.

Introduction

Covalently bonded self-assembled monolayer (SAMs) on metals have attracted great interest due to the various applications they enable by changing the macroscopic and microscopic properties of the substrate surface. These include the modification of wetting, adhesion, and corrosion properties (macroscopic) or the change of the substrate work function, Φ (microscopic), which allows tuning the barriers for charge-carrier injection into materials in contact with SAM covered electrodes. The latter is also significantly influenced by the alignment of the electronic levels of the SAM relative to the metal substrate, which determines the tunnel barrier the carriers need to overcome when “crossing” the SAM. The energy-level alignment is also a crucial quantity in molecular electronics, where either individual molecules or monomolecular layers are the active components of the device.

When aiming at improved electronic properties of metal electrodes, semiconducting SAMs consisting of conjugated molecules are used as contact primers. They are typically linked to the metal via thiolates. The properties of such aromatic SAMs are very sensitive to their structure, which is on the one hand determined by the local chemical, electronic, and geometric structure at the metal−molecule interface. On the other hand, the properties are controlled through the intermolecular interaction of the SAM backbones. In particular the charge transport from one to the next molecule is important when looking forward to self-assembled-monomer field-effect transistors (SAMFET), where the SAM is the semiconductor (as well as the dielectric). Therefore, precisely controlled experiments are required to minimize local fluctuations and defects and to maximize homogeneity and long-range order within the SAMs. Moreover, highly ordered and well-defined layers are important model systems for deriving a conclusive relationship between the morphology and electronic structure of a SAM and the properties of the individual building blocks.

The geometrical structure of aromatic SAMs has been thoroughly studied both experimentally and theoretically in the past. Nevertheless, a combination of scattering and scanning probe techniques determining the structure of conjugated SAMs and simultaneous measurements of their electronic properties are scarce. Additionally, to interpret experiments and to elucidate the microscopic origin of the SAM properties, input from quantum-mechanical modeling is crucial. In previous modeling studies, the influence of individual molecular units of the SAM on the resulting electronic properties of the interface has been
analyzed mainly conceptually but without direct comparison to experimental data.

As an important prerequisite for such a comparative study, improved order is important. One possibility to achieve that is the introduction of a flexible spacer between the rigid π-conjugated backbone and the anchoring unit. The disadvantage of this approach is that such an aliphatic spacer decouples the electrons in the organic π-system from those in the metal. An alternative method not suffering from that disadvantage has recently been suggested. By replacing the frequently used thiolate anchoring groups of the SAM with selenolate groups, a significant increase of ordering has been observed. Of particular interest for the present study are fully conjugated SAMs utilizing rigid anthracene backbones and selenolate anchoring groups. These films not only exhibit a particularly high degree of long-range ordering but also consist of rigid molecules, which eliminate intramolecular twisting and bending as an additional degree of freedom that needs to be considered when interpreting experimental and modeling data. Moreover, the fully conjugated nature of acenes results in a reduced energy gap, compared to, for example, oligophenylene based systems, which is expected to be beneficial for charge injection.

In a previous study, the structure and bonding of the anthracene-2-selenolate SAM (AntSe) have been characterized by means of low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), thermal desorption spectroscopy (TDS), reflection adsorption infrared spectroscopy (RAIRS), and near-edge X-ray absorption (NEXAFS), as described in ref 30. Sharp LEED spots reveal a (3 × 3)rect surface unit cell and imply a high degree of long-range order. Moreover, high-resolution STM images show the presence of two molecules per unit cell, which arrange in a herringbone pattern consistent with the anthracene bulk structure. From the appearance of a sharp single peak in the TDS spectra it can be concluded that the adsorption sites of the two molecules in the unit cell are isoenergetic. In spite of this multitude of experimental data, a certain degree of ambiguity exists regarding the details of the molecular arrangement within the SAM because the molecules exhibit no axial symmetry, thus leading to different possible molecular packing arrangements within the film (vide infra).

Here, we show that quantum-mechanical modeling can help to distinguish between different molecular packing arrangements. Knowing the actual film structure, we can then use the calculations to predict the electronic properties of the SAM. The validity of those data and, thus, the applicability of the chosen methodology can eventually be benchmarked by comparing the calculated work-function modification, ∆Φ, and the density of states in the molecular region (MDOS) to the corresponding data obtained by UV-photoemission spectroscopy (UPS). This is of particular interest in the present case, as, to the best of our knowledge, this study is the first one in which it is ensured that the structure assumed in the calculations is equivalent to that of the sample for which the electronic properties are determined experimentally. Finally, we show how information on the electronic coupling between the molecules can be gained from the lateral (i.e., in-plane) band structure of the SAM.

Methodology

Computational Approach. We performed density functional theory (DFT) based slab-type band structure calculations using the VASP code. Exchange and correlation were treated with the generalized gradient approximation (GGA), choosing the PW91 functional. The valence Kohn–Sham pseudo wave functions were expanded in a plane-wave basis set with a cutoff energy of 20.13 Ry, and the projector augmented-wave (PAW) method was employed to describe valence–core interactions.

To model the anthracene-2-selenolate (AntSe) monolayer on the Au(111) surface, we studied two molecules per unit cell arranged in a herringbone pattern in the experimentally determined (3 × 3)rect surface unit cell. From the appearance of a sharp single peak in the TDS spectra it can be concluded that the adsorption sites of the two molecules in the unit cell are isoenergetic. In spite of this multitude of experimental data, a significant increase of ordering has been observed. Of particular interest for the present study are fully conjugated SAMs utilizing rigid anthracene backbones and selenolate anchoring groups. These films not only exhibit a particularly high degree of long-range ordering but also consist of rigid molecules, which eliminate intramolecular twisting and bending as an additional degree of freedom that needs to be considered when interpreting experimental and modeling data. Moreover, the fully conjugated nature of acenes results in a reduced energy gap, compared to, for example, oligophenylene based systems, which is expected to be beneficial for charge injection.

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the local density of states (LDOS) was integrated between the Fermi energy ($E_F$) of the system and the energy $E_F - 0.2$ eV, which corresponds to the experimental sample bias of $-200$ mV.\textsuperscript{30,58} Furthermore, STM images were produced including the complete highest occupied molecular orbital (HOMO), setting the second integration boundary to 1.64, 1.75, and 1.71 eV below $E_F$ for the three investigated molecular packing arrangements (A–C), respectively. To obtain more realistic images and to account for the finite experimental resolution, the calculated LDOS was averaged over 59 points on the model of a spherical tip with a diameter of $\sim 2$ Å.\textsuperscript{31} All molecular structures and calculated STM images were visualized with the XcrysDen program.\textsuperscript{59}

The quantity compared to the experimental UPS spectra is the molecular density of states (MDOS) which represents the DOS projected onto the atoms of the SAM.

To obtain the band structure along high-symmetry directions, calculations were performed with a $k$-point mesh from $\Gamma$ [1/2, 0, 0] along the $k_x$-axis to $\Gamma$ [0, 0, 0] and $\Gamma$ along the $k_y$-axis to $\Gamma$ [0, 1/2, 0] with 50 points in each direction. The calculations were performed in a non-self-consistent manner, relying on the charge density from the above-described ($8 \times 4 \times 1$) Monkhorst–Pack grid. Band structures were computed for the isolated H-saturated SAM as well as for the full slab with the SAM bonded to the metal substrate (see the Supporting Information).

**Experimental Methodology.** AntSe SAMs were prepared by immersing Au(111) substrates into an ethanolic solution (0.1 $\mu$M) of selenoaetic-acid-Se-anthracene-2-yl-ester for at least 24 h, followed by thorough rinsing with ethanol and drying in a nitrogen stream. The acetate protection group was used to avoid the formation of insoluble aromatic diselenides as well as a possible oxidation of selenium, hence enabling the preparation of monolayer films by immersion (for synthesis and details see ref 30). The gold substrates were prepared by evaporating 140 nm of gold at 450 K under high-vacuum conditions onto freshly cleaved mica sheets, which had previously been heated to 590 K for 48 h to remove residual crystal water. After deposition, the gold/mica substrates were flame-annealed in a butane/oxygen flame, yielding high-quality Au films with flat terraces of several 100 nm exhibiting a (111) surface orientation. In a previous study, the adsorption and formation of AntSe-SAMs was characterized by means of RAIRS, TDS, XPS, NEXAFS, low-current microchannel plate LEED, and STM as described in ref 30.

Moreover, the electronic valence structure was characterized by employing photoelectron spectroscopy using a gas discharge He-I vacuum UV light source (21.22 eV) and a hemispherical electron energy analyzer (Leybold EA200). All UPS spectra were recorded at normal emission with an acceptance angle of $\sim 10^\circ$. The energy scale is referenced to the Fermi edge of the Au substrate.

The STM data were recorded under ambient conditions with a Jeol JSPM 4210 microscope using tips prepared mechanically by cutting a 0.25 mm Pt$_{0.8}$Ir$_{0.2}$ wire (Goodfellow). Typically low tunneling currents of 150 pA were used in current-contant mode at $-200$ mV sample bias, thus avoiding tip-induced changes to the SAM. No differences were found in the STM images acquired before and after the UPS measurements, indicating that possible radiation damage of the SAM can be safely excluded.

**Results and Discussion**

**Structural Aspects.** In a previous study it has been shown that AntSe-SAMs on Au(111) form a ($\sqrt{3} \times 4$)rect structure with two molecules per unit cell. In addition to the herringbone arrangement of adjacent molecules, characteristic stripes along the (112) direction can be observed in the STM data (see Figure 1), suggesting an inhomogeneous molecular packing within the SAM. Since the AntSe molecules exhibit no axial symmetry – the Se anchoring unit is necessarily attached to the lowest ring of the anthracene backbone in a nonsymmetric fashion – one can distinguish between different inclinations and positions (i.e., left or right) of the anthracene backbone relative to the Se–C bond (cf. Figure 1, molecular packing arrangements A–C). As a consequence, different relative molecular packing arrangements can be realized that comply with the same lateral periodicity. Thus, in spite of the multitude of experimental data (cf. Introduction), still a certain degree of ambiguity exists regarding the details of the molecular arrangement within the monolayer. Further clarification might be provided by X-ray scattering experiments, which are, however, difficult to perform for SAMs on Au(111).\textsuperscript{50} Therefore, in this study a different approach is adopted. The geometry of several possible molecular packing arrangements is optimized computationally and a number of observables are calculated. By comparing them with the experiment, the best agreement is proposed as the most likely structure.

Three molecular packing arrangements (labeled as A, B, and C) can be envisioned that are a priori consistent with the above-mentioned lateral periodicity: i.e., they all have the same unit cell dimensions with molecules packed in a herringbone pattern, including characteristic stripes in the STM images. The resulting three molecular packing arrangements are sketched in the bottom part of Figure 1. At this point it is worth mentioning that the apparent (dark) stripes seen in the tunneling micrographs reflect...
Table 1: Differences in the Total Energies per Unit Cell (ΔE), the Tilt Angle φ, and the Herringbone Angle Θ as Calculated for the Three Molecular Packing Arrangements and Measured by NEXAFS and STM (Experimental Data from Reference 30).

<table>
<thead>
<tr>
<th>molecular packing arrangement</th>
<th>ΔE/eV</th>
<th>φ/°</th>
<th>Θ/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.013</td>
<td>19/10</td>
<td>48</td>
</tr>
<tr>
<td>B</td>
<td>0.138</td>
<td>8/55</td>
<td>86</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>11/12</td>
<td>79</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td>33 (NEXAFS)</td>
<td>48 ± 3 (STM)</td>
</tr>
</tbody>
</table>

* For a definition of those angles see Figure 2.

An unequal lateral separation of the topmost rings of the aromatic backbones which are essentially imaged by STM (as shown below). This does, however, not necessarily reflect the actual positions and the relative arrangement of the anchoring units, since the molecules are not perfectly upright-oriented but tilted. In all molecular packing arrangements the selenium atoms (green circles in Figure 1) adopt an inhomogeneous lateral packing with alternating separations of 1.5 and 2.5 Å gold rows along the ⟨110⟩ direction. Interestingly, only in molecular packing arrangement A, all Se atoms are equivalently oriented with respect to the backbone and their larger separation coincides with the dark stripes. In contrast, in molecular packing arrangements B and C neighboring backbones are tilted in opposite directions and the separation of the anchoring units is out-of-plane with the dark stripes.

A first estimate of which of the molecular packing arrangements is most likely adopted can be made from the total energy per unit cell calculated for all three structures. Molecular packing arrangement A is found to have the lowest energy, whereas in the molecular packing arrangements B and C the energies are higher by 0.013 and 0.138 eV, respectively (see Table 1). Since the total energies of A and B are rather similar, no unambiguous conclusions regarding the lowest energy structures can be made. Regarding the accuracy of such calculations, it must be kept in mind that in DFT studies based on local or gradient-corrected functionals, van der Waals interactions are not properly accounted for. Previously, it has been shown by a combined theoretical and experimental study that this plays no role for the orientation of the molecules in the bulk anthracene crystals as a function of pressure.2 Still, it cannot be excluded that variations in the van der Waals energy of the different molecular packing arrangements are larger than the obtained energy differences for the various geometries. Therefore, to determine the actual microstructure, one has to go beyond purely energetic reasoning.

Additional insight can be gained from comparing a number of experimental observables such as the tilt angle, φ, the herringbone angle, Θ, and STM images to the corresponding calculated quantities. The tilt angle of the molecules, φ, is defined as the angle between the molecular plane of the anthracene backbone and the surface normal (see Figure 2). Relatively small tilt angles of 11° and 12° (for the two nonequivalent molecules in the unit cell) are found for molecular packing arrangement C, which decrease slightly for B to values of 8° and 5°. The average tilt is maximized in molecular packing arrangement A, where tilt angles of 19° and 10° are found (see Table 1). The latter orientation correlates best with an average tilt angle of 33° determined from NEXAFS measurements. A possible origin of the discrepancy between calculation and experiment could be residual disorder of the molecules on the surface (e.g., existence of less ordered domains and adsorption at defects); also a dynamic contribution cannot be excluded originating from the fact that the experiments have been performed at room temperature, while the calculations correspond to the situation at 0 K. Moreover, even though DFT performs very well when calculating the tilt angles in anthracene crystals,63 the neglect of van der Waals interactions can have some impact.

To test the impact of inter-molecular interactions, we also performed geometry optimizations using LDA instead of GGA, as the former is known to overestimate (rather than underestimate) the binding between aromatic systems,50 which to some extent compensates the neglect of van der Waals interactions in DFT. This results in significantly increased tilt angles of 44° and 42° in molecular packing arrangement A, now clearly larger than the experimental value, which implies that here stronger intermolecular interactions indeed favor larger tilt angles.

We also tested the impact of introducing an additional gold atom exactly underneath the Se atom for molecular packing arrangement A to generate a layer of adatoms as suggested in refs 54 and 55 for thiolate SAMs. Here, a smaller impact on the tilt angles (24 and 13°) is observed, and the results would, in principle, fit the experimental data better. However, the resulting work-function modification for this geometry is found to significantly deviate from the experimental value (vide infra).

Next, the herringbone angle, Θ, which is defined as the angle between the vectors normal to the planes of the two neighboring AntSe molecules (see Figure 2) has been considered. For molecular packing arrangements B and C the anthracene backbones are arranged nearly perpendicular (Θ equals 86° for molecular packing arrangement B and 79° for molecular packing arrangement C), while for structure A an angle of 48° is obtained in excellent agreement with the experimental herringbone angle of 48 ± 3°, determined from STM data.30,67

The data presented above point toward molecular packing arrangement A to be prevalent in the AntSe-SAMs. As a next step, STM images obtained by tunneling through states between EF and 0.2 eV below EF (corresponding to the experimental sample bias) as well as between EF and a voltage chosen to include the HOMO of the SAM (cf. Methodology) have been calculated. The small bias voltage in the experiments had to be used, as at larger voltages indications for a degradation of the SAM were observed. Since no SAM-related features are discernible within the narrow energy range between EF and −0.2 eV, the STM images are consistent with the molecular packing arrangement A.
A first estimate of what is to be expected in the STM images can be made on the basis of the shape of the HOMO of an isolated AntSe molecule, which is shown in the top left panel of Figure 3. When tunneling from the STM tip into the HOMO of the molecule, ideally four lobes of the HOMO orbital (two on each side of the molecular plane) should be visible in the STM experiments for perfectly upright-aligned molecules and appropriate resolution. For a nonperpendicular (i.e., a not perfectly upright) alignment of the molecules, the shape of the STM spots depends in a subtle way on the molecular orientation: A tilt of the molecular plane ($\phi$ in Figure 2) will result in STM images where only the “upper” $\pi$-lobes of the molecular plane are clearly visible. The experimental line scan shown in the top part of Figure 3 indeed exhibits a pronounced double-peak structure for one of the features, and the observed separation between the two $\pi$-lobes on one side of the molecular plane closely matches the separation between the molecular orbital lobes (as indicated in the figure). A tilt of the long molecular axis within the molecular plane will result in the dominance of one of the two $\pi$-lobes of the HOMO from one side of the molecular plane. This reasoning can be used to directly link the shapes of the simulated STM images to the molecular orientation.

For molecular packing arrangement B, indeed, all four HOMO $\pi$-lobes are resolved at least for one of the molecules in the unit cell in the STM images calculated at an assumed sample bias of $-1.75$ V. The HOMO-related $\pi$-lobes partly overlap with those from the neighboring molecules, although the ones “below” the molecular plane are clearly weaker. The latter trend is even more pronounced in the molecular packing arrangement C, which is consistent with the larger tilt angles (see Table 1). At $-0.2$ V sample bias the separation between the two lobes on each side of the molecular plane diminishes in the calculated STM images. This is the result of the changed tunneling situation with the tip Fermi level being so close to $E_F$ that tunneling occurs only through intragap hybrid states. These hybrid states can be associated with the tails of the features originating from various molecular orbitals. However, independent of the tip bias, the occurrence of STM spots above and below the molecular plane and the large apparent herringbone angle for molecular packing arrangements B and C are inconsistent with the experimental data. Due to the large tilt $\phi$ of the molecules in molecular packing arrangement A, only one of the “upper” two $\pi$-lobes are visible; i.e., also as far as the STM pictures are concerned, the calculated results for molecular packing arrangement A are in best agreement with experiments.

Nevertheless, also here certain deviations to the experimental STM images are observed. In particular, the calculated STM features are less elongated than the experimental ones; i.e., they are close to spherical. This hints toward a deviation in the “in-plane tilt” angles $\phi_i$ between experiments and calculations. In this context it should, however, also be kept in mind that the actual shape of the tip in the experiments is not known and thus cannot be taken into account in the simulations.

**Electronic Structure of Anthraceneselenolate SAM.** In the following, the focus will lie on the electronic structure of AntSe-SAMs on Au(111) using molecular packing arrangement A.

Conceptually, the work-function modification due to SAM formation can be separated into two contributions.\(^{31,33,68}\) First, the chemical bond between SAM and surface affects the electron potential energy. This effect is denoted as the bond dipole ($\Delta E_{\text{Bond}}$). $\Delta E_{\text{Bond}}$ results from charge rearrangements in the region of the metal–SAM interface due to the bond formation (which is here defined as replacing the Se–H by a Se–Au bond).\(^{69}\) It can be calculated by solving the one-dimensional Poisson equation with the $xy$-plane-averaged charge rearrangements, $\Delta \rho(z)$ from the DFT calculations as the source term. The latter is given by\(^{68}\)

$$\Delta \rho(z) = [\rho_{\text{System}}(z) - (\rho_{\text{Ad}}(z) + \rho_{\text{SAM}}(z) - \rho_{\text{H}}(z))]$$

Here, $\rho_{\text{System}}(z)$, $\rho_{\text{Ad}}(z)$, $\rho_{\text{SAM}}(z)$, and $\rho_{\text{H}}(z)$ represent the plane-averaged charge densities of the combined system, the gold slab only, the free-standing SAM with the selene atoms saturated by hydrogens, and these saturating H-atoms only (all in their final geometries), respectively.\(^{33}\)

As a second contribution, the change of the electron potential energy across the SAM in the hypothetical situation of an ordered layer not bonded to the surface is given by $\Delta E_{\text{vac}}$. $\Delta E_{\text{vac}}$ arises from the permanent dipoles of the SAM forming molecules and, thus, is a measure for the molecular contribution...
direct comparison of peak intensities is not possible, in cross-sections are not considered in the calculations. Thus, a background has been subtracted. Note that the photoionization secondary electrons (from the gold substrate), a smooth, cubic molecular species and to compensate for the emission of comparison with the measured UPS data where, to accentuate the SAM (MDOS) is calculated. It is depicted in Figure 5 for ordered monolayers of known structure.

This indicates that the applied methodology has the potential Au(111) surface to 3.9 eV for Au covered with the AntSe SAM.

The resulting electron potential energy across the metal slab (light gray line) and for the SAM-covered slab (black line) are shown in the top part of Figure 4. A reduction of the vacuum level above the SAM with respect to the clean metal slab is clearly visible for the combined system, corresponding to a net work-function decrease due to SAM adsorption. The contributions of $\Delta E_{\text{BD}}$ and $\Delta E_{\text{vac}}$, shown in the bottom part of Figure 4, clearly reveal the dominant role of the bond dipole. It decreases the work function by $-1.20$ eV, while $\Delta E_{\text{vac}}$ results in a work-function shift of only $-0.17$ eV, consistent with the fact that the SAM-forming molecules do not contain polar substituents. In this context it should be mentioned that a very similar value for $\Delta E_{\text{BD}}$ has been calculated for thiolate anchoring groups as long as a similar SAM packing density is assumed. As a net effect, the calculated work function of the Au(111) surface is decreased by $-1.37$ eV from 5.22 to 3.85 eV due to AntSe SAM. These values are in excellent agreement with those determined by the measured valence band UP spectra (see Figure 5). The secondary cutoffs (not shown) point to an experimental work-function shift $\Delta \Phi = -1.3$ eV from 5.2 eV for the pristine Au(111) surface to 3.9 eV for Au covered with the AntSe SAM. This indicates that the applied methodology has the potential to quantitatively predict SAM-induced work-function modifications, at least as long as experiments are performed on well-ordered monolayers of known structure.

Finally, the density of states projected onto all the atoms of the SAM (MDOS) is calculated. It is depicted in Figure 5 for comparison with the measured UPS data where, to accentuate the position of the photoemission peaks arising from the molecular species and to compensate for the emission of secondary electrons (from the gold substrate), a smooth, cubic background has been subtracted. Note that the photoionization cross-sections are not considered in the calculations. Thus, a direct comparison of peak intensities is not possible, in particular, when considering the very pronounced dependence of the relative peak intensities on the experimental takeoff angle, as measured, for example, for pentacene. It should also be mentioned that DFT is a ground-state method while UPS is a final-state spectroscopic technique. The calculated MDOS in Figure 5 is shifted by $-1.17$ eV. This is inevitable, because band gaps are severely underestimated as a result of the lack of derivative discontinuities of (semi)local exchange-correlation functionals. With this shift applied (compare ref 47), the obtained correspondence between the experimental spectrum and the MDOS is quite satisfactory. Similar observations have been made for alkyl chains on semiconductors, where DFT calculations reproduced the experimental work-function changes, but, for the reasons mentioned above, a satisfactory agreement between UPS and inverse photoelectron spectra and the calculated DOS was obtained only after properly increasing the HOMO–LUMO gap. We note that, without in situ cleaning of the substrate, the fine structure of the gold d-band cannot be resolved, reflecting the influence of adsorbates on the surface density of states.

On the basis of the work-function modification as the most relevant and most directly comparable experimental observable, a comparison of the results for molecular packing arrangement A with those obtained for the other investigated structures yields the following three results: (i) similar work-function changes are obtained for the used LDA and GGA functionals (cf. Methodology; with LDA an only slightly increased $\Delta \Phi$ of $-1.43$ eV is obtained in spite of the considerably larger tilt angle); (ii) a work-function change of only $-0.92$ eV is calculated for the geometry including an adatom at the fcc-hollow site, which is inconsistent with experiment; (iii) very similar values of $\Delta \Phi = -1.43$ eV are obtained for the molecular packing arrangement B and $\Delta \Phi = -1.36$ eV for molecular packing arrangement C. Here, also very similar molecular densities of states were obtained (see Supporting Information).

The only minor dependence of the work-function modification on the tilt angle is at least in part a consequence of the vanishing intrinsic molecular dipole moment of the anthracene backbones, which do not contain electron donating or withdrawing substituents.

However, this apparent similarity in the electronic structure of the three molecular packing arrangements vanishes when, instead of the MDOS, the full lateral 2D band structure of the
Summary and Conclusions

We present a joint theoretical and experimental characterization of a self-assembled monolayer of anthracene-2-selenolates on Au(111). This system can be considered as a prototypical π-conjugated SAMs, as it exhibits a particularly high degree of order, which has been well characterized by LEED, STM, NEXAFS, RAIRS, and TDS experiments (cf. ref 30). Interestingly, even this large number of characterization techniques turns out to be not sufficient to unambiguously determine the details of the molecular packing arrangement. Therefore, in this study, the measured physical observables are compared to the results of calculations carried out for various possible molecular packing arrangements of the SAM. This allows identification of the most probable SAM structure.

Knowing the atomistic structure of the SAM, its electronic properties are calculated in a second step. The calculated work-function reduction is in excellent agreement with the experimental value derived from UV photoelectron spectroscopy, lending credibility to the applied theoretical methodology. This is further supported by the fact that also the calculated molecular density of states and the UPS spectrum agree reasonably well. A much less favorable agreement between theory and experiment is observed when studying, e.g., a structure with a Au adatom between the selenolate group and the fcc-hollow site of the Au(111) surface.

While differences in the studied molecular packing arrangement have little impact on the work-function modifications, the resulting changes in the intermolecular interactions significantly affect the dispersion of the 2D band structures in the SAMs.

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Supporting Information Available: MDOS of the molecular packing arrangement B and the molecular packing arrangement C and details of the band structure of the bonded anthracene-2-selenolate–SAM on Au(111) for the molecular packing arrangements A–C. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

In this context, one, however, has to keep in mind that this does not exactly reflect the experimental observation, due to the deviations in level alignment between theory and experiment resulting from the underestimation of the energy gap by GGA-based DFT discussed in more detail when comparing the experimental UPS spectrum and the calculated density of states.


(61) The mirror domain of motif A, where the backbones are tilted in the opposite way relative to the Se–C bond, is not exactly symmetry equivalent to motif A due to the ABC stacking along the Au[111] direction. Since the differences are found only in the second Au row, which is found to have an only minor impact on the SAM-adsorption energetics (compare, for example, the very small differences in fcc and hcp docking sites), this motif will not be separately considered here.


(65) In the determination of the tilt angle by NEXAFS also the herringbone angle is considered, as mentioned in the supporting information of ref 30 and described in detail for anthracenethiolates in ref 19. In this analysis it is assumed that the twist angle of the molecular plane around the long molecular axis for the two molecules in the unit cell is given by \( \pm (\text{herringbone angle})^2 \), which is a reasonable assumption considering the possible packing arrangements shown in Figure 1. An analytical relationship between the resulting tilt angle and the molecular twist angle has been derived for the symmetric case (i.e., a herringbone arrangement) in ref 19.


(67) In this context, we note that because of the molecular tilt relative to the surface sample normal, the STM data provide only a 2D projection of the aromatic backbone planes which can differ slightly from the true herringbone angle.


(69) An alternative partitioning scheme would be to consider -Se• radicals as intermediate states; then \( \Delta E_{BD} \) would represent the formation of a Se–Au bond, the actual partitioning, while determining \( \Delta E_{BD} \) has no impact on the net work-function change as explicitly shown in: Heimel, G.; Romarer, L.; Zojer, E.; Bredas, J.-L. Proc. SPIE 2008, 6999, 699919.


