Work-function modification of PEG(thiol) adsorbed on the Au(111) surface: A first-principles study

Jongmin Kim, Andris Gulans, and Claudia Draxl
Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin, Germany
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The possibility of modifying the work function of electrodes is important for optimizing the energy barriers for charge-injection (extraction) at the interface to an organic material. In this study, we perform density-functional-theory calculations to investigate the impact of dithiol-terminated polyethylene glycol (PEG(thiol)) based self-assembled monolayers (SAMs) with different numbers of PEG repeat units on the work function of the Au(111) surface. We find that a monolayer of PEG(thiol) decreases the work function of the Au(111) surface, where the magnitude of this reduction strongly depends on the length of the PEG backbone. The main contribution arises from the dipole due to the adsorption-induced charge rearrangement at the interface. Our work reveals a pronounced odd-even effect, which can be traced back to the dipole moment of the PEG(thiol) layer.

INTRODUCTION

Organic electronics devices, such as organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), and organic field-effect transistors (OFETs), are heavily affected by physical phenomena at the interface between the electrode and the organic material [1, 2]. Often, the design of such devices faces fundamental challenges due to poor charge-injection (extraction) [3, 4]. Reducing the corresponding energy barrier, can considerably improve device performance, and a number of approaches has been reported. Among them are doping of the organic semiconductor [7] or the modification of the work function of the electrode [8].

For optimal charge-injection, the work function of the anode needs to be closely aligned to the highest occupied molecular orbital (HOMO) of the organic semiconductor. Likewise, the work function of the cathode requires to be matched with the lowest unoccupied molecular orbital (LUMO) level. In other words, anode and cathode should be made of materials with high and low work functions, respectively [9]. Metals with a low work function, which are typically used for the cathode such as Ca, Mg, and Al [10, 12], are, however, immensely reactive and oxidize due to moisture or oxygen which results in an instability of devices [12, 13]. Chemically inert, such as Au and Ag, have a high work function, and thus large charge-injection (extraction) energy barriers [12], and are therefore difficult to be used as the cathode. This problem can be addressed by introducing an interlayer between the cathode and the organic semiconductor to adjust the work function of the electrode [14, 17]. Materials that have been employed as interlayers are mainly polymers, metal oxides, inorganic salts, and self-assembled monolayers (SAMs), which modulate the electrode’s work function by inducing a dipole at the interface [4, 5, 12, 15–20].

Recent experimental studies have shown that polyethylene glycol (PEG) utilized as the interlayer improves the performance of OPVs, OLEDs, and OFETs [21–25]. In addition, experimental works [21, 26] have demonstrated that PEG-based additives blended with the organic semiconductor are able to migrate to the interface, forming a self-generated interlayer by the interaction between the head groups of the additives and the electrodes. Although this technique is applicable to fabricating devices, it is difficult to accurately measure the energy-level alignment or the structural conformation because the interlayer is formed at a buried interface [26]. Alternatively, one could consider a SAM of PEG molecules as the interlayer. On the one hand, interfaces between a SAM and an electrode would be easier to analyze. On the other hand, the electronic properties of the interface could be chemically tuned, thus exploiting a common advantage of SAMs. SAMs based on alkanethiols and phenylthiols have been intensively investigated in view of modifying the properties of Au electrodes [9, 20, 27–30]. However, studies on an adsorbed SAM of PEG on the electrode material and its impact on the modulation of the work function are still lacking.

In the present work, we perform first-principles calculations to model dithiol-terminated PEG (PEG(thiol)) deposited on the Au(111) surface and show how such SAM monolayer decreases the metal’s work function. In addition, we show that the work function modification is sensitive to the length of the PEG backbone. Finally, we demonstrate that a pronounced odd-even effect originates from the relative orientation of the molecular PEG(thiol) dipole with respect to the surface normal.

COMPUTATIONAL DETAILS

We model the PEG(thiol) molecules adsorbed on Au(111), termed PEG(thiol)@Au(111), for different numbers of repeat units of the PEG backbone (1 to 4). The interface structure is shown in Fig. 1. In all considered systems, the metal substrate consists of periodi-
cally repeated 4 atomic layers. Since STM experiments of thiolate adsorbed on Au(111) show a \((\sqrt{3} \times \sqrt{3})R30^\circ\) overlayer structure [31, 32] of the thiolate, we assume a \((\sqrt{3} \times \sqrt{3})R30^\circ\) surface unit cell for all calculations. The positions of the Au atoms in the two top layers and the adsorbed PEG(thiol) are relaxed until the maximum force on each atom is smaller than 0.055 eV/Å. The bottom two layers are fixed to the positions corresponding to the bulk structure with a lattice constant of 4.192 Å. The vacuum spacing along the vertical direction is at least 14 Å to avoid spurious interactions between the periodic images.

\[
E_{\text{disp}} = -\frac{1}{2} s_6 \sum_{AB} \frac{C_{6}^{AB}}{(R_{AB})^6} f_d(R_{AB}^6), \quad (1)
\]

Here \(s_6\) is a global scaling factor for the dipole-dipole dispersion coefficients \(C_{6}^{AB}\), and \(R_{AB}^6\) is the interatomic distance between atoms A and B. The \(C_{6}^{AB}\) coefficients are calculated as a geometrical mean of fixed empirical coefficients for the atoms, and \(f_d\) is a damping function.

In contrast, MBD@rsSCS goes beyond just adding pairwise interatomic contributions. Compared to DFT-D2, it also includes screening effects. The dispersion energy is written as [37]

\[
E_{\text{disp}} = -\sum_k w_k \int_0^\infty \frac{dk}{2\pi} \text{Tr}\{ \ln(1 - \mathbf{A}_{LR}(\omega) \mathbf{T}_{LR}(k)) \}, \quad (2)
\]

where \(w_k\) represents the weighting factor of the \(k\)-points, and \(\mathbf{A}_{LR}\) and \(\mathbf{T}_{LR}\) are the frequency-dependent polarizability and the long-range interaction tensor in reciprocal space, respectively. For structure optimizations involving the long-range correlation, in the MBD@rsSCS method, interatomic forces are computed from the dispersion-energy gradient. Both methods are implemented in the exciting code.

RESULTS AND DISCUSSION

Adsortion geometry

The main structural features of the relaxed PEG(thiol)@Au(111) system are reported in Table I. The molecules are chemically bound to the surface through their S atom of the head group, situated at the bridge site with a slight shift toward the hollow site as can be seen in the side view depicted in Fig. 1. This adsorption configuration is similar to what was found by various theoretical studies of thiolate adsorbed on Au(111) [35, 36]. In our MBD@rsSCS calculations, the PEG(thiol) molecules are tilted from the surface normal by 29.5° - 31.9° depending on the number of repeat units. Similar tilting angles for n-alkanethiols on the Au surface are reported in Refs. 41 and 42. The calculated adsorption distances, \(d\), between the S atom and the average position of Au surface atoms are 1.93 – 1.95 Å, depending on the molecular length. In contrast, the tilting angles and adsorption distances, are not sensitive to the latter.
TABLE I. Adsorption geometry of PEG(thiol) molecules adsorbed on the Au(111) surface using MBD@rsSCS and DFT-D2 for van der Waals corrections on top of PBE (see also Fig. 1).

| Repeat units | MBD@rsSCS | DFT-D2 |
|--------------|-----------|--------|
| n            | θ [°]     | d [Å]  | θ [°] | d [Å] |
| 1            | 31.9      | 1.94   | 35.3  | 1.92  |
| 2            | 29.5      | 1.95   | 32.0  | 1.93  |
| 3            | 31.3      | 1.94   | 32.3  | 1.92  |
| 4            | 30.7      | 1.93   | 30.7  | 1.92  |

Work-function change

In a next step, we study the influence of the adsorbed PEG(thiol) molecules on the work function of Au(111). Figure 2 displays the calculated plane-averaged electrostatic potential of the investigated system obtained by MBD@rsSCS for the case of \( n = 1 \) (1-PEG(thiol)@Au(111)). The work function is defined as the difference of the electrostatic potential energy at the vacuum level, \( E_{\text{vac}} \), and the Fermi energy, \( E_f \), i.e.,

\[
\Phi = E_{\text{vac}} - E_f.
\]

Note that the two sides of the slab have different values of \( E_{\text{vac}} \). The side with the clean Au(111) surface reflects the work function of gold, \( \Phi_{\text{Au}} \), for which our calculation yields a value of \( \Phi_{\text{Au}} = 5.15 \) eV. It agrees well with 5.15 eV obtained from an UPS experiment [43] as well as previous DFT-PBE studies where values of 5.15 eV [44] and 5.12 eV [44] were reported. The other side of the slab has the work function, modified by the molecular adsorption, \( \Phi_{\text{mod}} = 4.39 \) eV. Thus, the effect of the adsorbed SAM is given by the difference \( \Delta \Phi = \Phi_{\text{mod}} - \Phi_{\text{Au}} = -0.76 \) eV. This quantity is presented in Table I as a function of \( n \). We observe that (i) the PEG(thiol) monolayer significantly decreases the work function of Au(111) in all cases and (ii) there are strong oscillations of \( \Delta \Phi \) with respect to \( n \). An odd (even) number of repeat units results in the smallest (largest) work-function modification. This phenomenon is known as an odd-even effect [28, 29].

In order to analyze the nature of the work-function change, we perform an analysis following Refs. 46 – 48 and decompose \( \Delta \Phi \), as follows:

\[
\Delta \Phi = \Delta V_{\text{BD}} + \Delta V_{\text{SAM}} + \Delta V_{\text{relax} - \text{Au}}.
\]

\( \Delta V_{\text{BD}} \) is the contribution due to the charge rearrangement caused by the formation of new chemical bonds which leads to a dipole between PEG(thiol) and Au(111). \( \Delta V_{\text{SAM}} \) is the shift of the electrostatic potential created by the intrinsic dipole moment of the PEG(thiol) layer relative to the surface normal. \( \Delta V_{\text{relax} - \text{Au}} \) indicates the work function change of the isolated Au surface due to the surface relaxation caused by the adsorption of PEG(thiol). We define \( \Delta V_{\text{SAM}} \) as the difference of the electrostatic potential energy between the two sides of the PEG(thiol) molecules. Likewise, the difference of the potential energy between the two sides of the isolated Au(111) slab is termed \( \Delta V_{\text{relax} - \text{Au}} \).

To obtain \( \Delta V_{\text{BD}} \), we consider the change of the charge density caused by the chemical bonding. The latter induces a change in the electrostatic potential, \( \Delta V \), which satisfies the Poisson equation. In practice, it is sufficient to consider a plane-averaged density change, \( \Delta \rho \), to solve

\[
\frac{d^2 \Delta V}{dz^2} = -4\pi \Delta \rho.
\]

by numerical integration. The difference of \( \Delta V \) between two sides of the slab corresponds to \( \Delta V_{\text{BD}} \) (see Fig. 2).

In PEG(thiol)@Au(111), when PEG(thiol) molecules are attached to the Au surface, the S–H bond of thiol is replaced by an S–Au bond, followed by release of H\(_2\) [28 49]. Therefore, \( \Delta \rho \) is defined as

\[
\Delta \rho = \rho_{\text{tot}} - (\rho_{\text{SAM}} + \rho_{\text{surf}} - \rho_H),
\]

where \( \rho_{\text{tot}} \), \( \rho_{\text{SAM}} \), \( \rho_{\text{surf}} \), and \( \rho_H \) correspond to the plane-averaged charge densities of the total PEG(thiol)@Au(111) system, the free-standing PEG(thiol) monolayer, the isolated Au(111) surface from the total system, and the isolated layer of H atoms, respectively.

Figure 2 provides the results of \( \Delta V_{\text{BD}} \) and \( \Delta V_{\text{SAM}} \) obtained with MBD@rsSCS for the case of 1-PEG(thiol)@Au(111) (shown in Fig. 2). The left panel shows the plane-averaged \( \Delta \rho \) and \( \Delta V_{\text{BD}} \) along the vertical direction. Significant oscillations of the former are found at the interface. In other words, the charge rearrangement is mainly confined to the interface region, in particular, near the S atom and the topmost layer.
Au layer. The charge density is increased in the topmost Au layer and depleted right above it. For 1-PEG(thiol)@Au(111), the individual contributions to ∆Φ amount to ∆V_{relax-Au} = -0.04 eV, ∆V_{SAM} = 0.36 eV, and ∆V_{relax-Au} = -0.04 eV. The dominant contribution in determining ∆Φ is ∆V_{BD}, whereas ∆V_{relax-Au} is tiny compared to ∆V_{BD} and ∆V_{SAM}.

Let us now examine the dependence of the three contributions on the molecular length, n, and the origin of the observed odd-even effect in ∆Φ. The corresponding values of ∆Φ, ∆V_{BD}, ∆V_{SAM}, and ∆V_{relax-Au} are listed in Table II. ∆V_{BD} decreases the work function of the surface in all four cases. However, in contrast to ∆Φ, ∆V_{BD} has similar values irrespective of n, which therefore has basically no influence on the odd-even effect. ∆V_{relax-Au} is also insensitive to n, and its magnitude is negligible compared to ∆V_{BD} and ∆V_{SAM}. This indicates that the surface relaxation upon adsorption does not play a role in the odd-even effect. Unlike ∆V_{BD} and ∆V_{relax-Au}, a pronounced odd-even effect is revealed for ∆V_{SAM}. It should be noted that values of ∆V_{SAM} positive potential shifts are obtained in case of odd n while for even n they are basically zero. The latter is caused by PEG(thiol) with even n having an inversion center that cancels out the effect of the molecular dipole moment. Therefore, we attribute the odd-even effect to the PEG(thiol) dipole moment parallel to the surface, while the bond dipole contribution due to the adsorption-induced charge redistribution as well as the surface-relaxation contribution due to adsorption are relatively small.

The trend in the work-function modification for n-alkanethiols and CF₃-terminated n-alkanethiols on Au was also observed in previous studies, and it has been shown to originate from differences in the terminal dipole orientations of the molecular monolayer [29, 50]. Interestingly, the differences of ∆Φ between odd and even chains of n-alkanethiols and CF₃-terminated n-alkanethiols are noticeably lower than those of the PEG(thiol)s [30]. For example, the maximum amount of such energy differences is approximately 0.30 eV for the former and 0.77 eV for the latter.

Since van der Waals (vdW) forces play a crucial role at organic/metal interfaces [50, 52], as well as in the intermolecular interactions [53], we finally investigate how sensitive the work-function modification is to the choice of the vdW correction. To this extent, we perform additional calculations by means of the semiempirical DFT-D2 functional [35], which employs a pairwise-additive model account for the long-range dispersion. The results on the adsorption geometry and the work function

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**TABLE II. PEG(thiol)-induced change in work function, ∆Φ, and its main components for different numbers of repeat units of the PEG backbone, n. All results obtained using MBD@rsSCS and DFT-D2, respectively, are given in eV.**

| Repeat units | MBD@rsSCS | DFT-D2 |
|--------------|-----------|--------|
| n            | ∆Φ        | ∆V_{BD} | ∆V_{SAM} | ∆V_{relax-Au} | ∆Φ    | ∆V_{BD} | ∆V_{SAM} | ∆V_{relax-Au} |
| 1            | -0.76     | -1.08   | 0.36     | -0.04         | -0.24 | -1.01   | 0.79     | -0.02         |
| 2            | -1.11     | -1.06   | 0.00     | -0.05         | -0.82 | -1.00   | 0.22     | -0.04         |
| 3            | -0.39     | -1.12   | 0.78     | -0.05         | -0.26 | -1.06   | 0.84     | -0.04         |
| 4            | -1.16     | -1.10   | 0.00     | -0.06         | -0.95 | -1.02   | 0.08     | -0.01         |
modifications are given in Fig. 4 and Table II.

The tilting angles, $\theta$, calculated with the DFT-D2 are higher than those obtained with the MBD@rsSCS. The difference is getting smaller with longer molecular length, and the two approaches give the same answer for $n = 4$. The inclusion of screening effects has a minor effect on $\theta$ for small $n$ because the screening is less effective.

The adsorption distances, $d$, obtained from DFT-D2 and MBD@rsSCS are 1.92 – 1.93 Å and 1.93 – 1.95 Å, respectively. These values clearly reflect that there are no noticeable differences between the two approaches.

$\Delta \Phi$ as computed with both approaches is shown at Fig. 4(b), exhibiting a qualitatively similar trend. Both types of calculations show a decrease in the work function for all four $n$, and a pronounced odd-even effect is observed. However, in the MBD@rsSCS case, a greater reduction of the work function is obtained when the PEG(thiol) molecules approaches the Au(111) surface compared to the DFT-D2 method. In the MBD@rsSCS calculations, the difference of $\Delta \Phi$ between $n = 2$ and $n = 4$ is only 0.05 eV, whereas a much greater difference of 0.37 eV is observed between odd values of $n$. The PEG backbone with $n = 1$ is more twisted and bent than the others due to screening effects, leading to a large difference of $\Delta \Phi$ between odd $n$. On the other hand, this difference is only 0.02 eV in case of DFT-D2. Figs. 4(c) and 4(d) show $\Delta V_{BD}$ and $\Delta V_{SAM}$. Here, $\Delta V_{BD}$ obtained from both methods is found to be negative but the values are slightly different. In contrast, $\Delta V_{SAM}$ associated with the dipole moment of the PEG(thiol) monolayer is sensitive to the type of long-range corrections. The difference between the MBD@rsSCS and the DFT-D2 reflects variations in the structure of the adsorbed PEG(thiol) molecules including the tilting angle as mentioned before. Overall, despite many differences between the results of the two methods, we note that the main message of our paper does not change if the DFT-D2 is used instead of the MBD@rsSCS.

CONCLUSIONS

In summary, we have carried out first-principles calculations of the work-function modification induced by the adsorption of a PEG(thiol) SAM on the Au(111) surface, considering different numbers of PEG backbone repeat units. We have found that the PEG(thiol) molecules are adsorbed with an average tilting angle of the PEG backbone of $\sim 30^\circ$ with respect to the surface normal. Importantly, the work function of Au(111) is always reduced, regardless of the molecular length. We observe a pronounced odd-even effect in the work-function shift as a function of the number of repeat units. An even number of repeat units reduces the work function of Au(111) more than an odd one. This effect stems mainly from a dipole moment of the PEG(thiol) molecules. The tunable work function of the cathode signifies that PEG(thiol)@Au(111) is a promising candidate for applications in organic and molecular electronics.

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* claudia.draxl@physik.hu-berlin.de

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