Preparation and Characterization of 4'-Donor Substituted Stilbene-4-thiolate Monolayers and Their Influence on the Work Function of Gold

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Self-assembled monolayers of E-stilbene-4-thiolate (SAM1), E-4’-(ethoxy)stilbene-4-thiolate (SAM2), and E-4’-(dimethylamino)stilbene-4-thiolate (SAM3) on Au(111) have been obtained from reaction of ethanol solutions of the corresponding S-acetyl derivatives with gold substrates. A combination of X-ray photoelectron spectroscopy, ellipsometry, and infrared reflection absorption spectroscopy indicates that the monolayers are dense (ca. 3.3 × 10¹⁴ molecules/cm²) and that the long molecular axes of the thiolates are approximately perpendicular to the surface. Ultraviolet photoelectron spectroscopy shows that formation of these monolayers decreases the work function of pristine Au by 0.9–1.3 eV, in part due to a bond dipole of ca. 4.4 D/molecule formed upon adsorption and partly due to the molecular dipole moment arising from the 4’-donor substituents. However, the extent of the work function variation between SAM1, 2, and 3 is smaller than anticipated from purely electrostatic considerations.

Introduction

Self-assembled monolayers (SAMs) of organic molecules on metals have received considerable attention over the last two decades.¹⁻⁴ Proposed applications of SAMs include their use as agents for improving the wettability of surfaces,⁵ anticorrosive layers,⁶ biosensors,⁷ and resists for lithography.⁴ From a purely scientific standpoint, these structurally ordered systems offer a great opportunity for studying structure–property relationships of organic–inorganic interfaces. Studies of the influence of the molecular structure on the packing of thiol on noble metal surfaces have led to important insights into the molecular scale morphology of the monolayers. It is now understood that the thiol group binds to gold, leading often to formation of long-range order in the resulting organic adlayer.⁴⁻⁸⁻¹¹ This understanding has further led to studies of the influence of synthetically accessible adsorbate structures on a variety of surface characteristics including wetting properties,⁵,⁶ electronic characteristics,¹²⁻¹⁴ and chemical reactivity.¹⁵⁻¹⁷ One of the interesting effects induced by SAMs is the modification of the work function of the metal, which is of great importance in organic electronic applications, since it is one of the parameters determining the barrier for charge-carrier injection from the metal into an organic overlayer.¹⁸⁻¹⁹ Although any adsorbate can potentially modify the work function of a metal,¹⁸,²⁰ SAMs offer the opportunity to systematically investigate the influence of molecular structure on the work function. Evans and Ulman showed that the surface potential of alkyl-thiol-coated gold surfaces is linearly dependent on the number of methylene units in the alkyl chain and is correlated to the dipole moment of the molecules residing on the metal surface.²¹ Further investigations of alkyl thiol monolayers showed that the direction and the magnitude of the dipole moment of the molecules forming the monolayer are important factors determining the work function of the underlying metal.²²⁻²⁴

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A limitation on the use of monolayers consisting of long-chain alkyl thiols for modifying injection barriers between metals and organics is the intrinsic electrically insulating characteristics of the alkyl chains. Monolayers consisting of conjugated thiols, which have been shown to exhibit considerably enhanced conductivity, may be more promising for this type of application. Sita et al. were the first to systematically study the work function modification of gold by conjugated thiols. Although since then the effects of substituted conjugated thiols on the work function of metals have been studied both theoretically and experimentally, it should be stressed that reports on the influence of the end group substituents in monolayers of conjugated thiol molecules on the work function of the underlying metal are scarce and the understanding is still rather inchoate.

Here, we describe the preparation and characterization of self-assembled monolayers of three different substituted stilbene thiolates on gold, as well as the impact of these thin films on the work function of the substrate. The schematic representation of these monolayers is presented in Figure 1. To the best of our knowledge, this is the first report on the preparation of monolayers composed of conjugated stilbene thiolates. Hence, the monolayers were characterized in detail using infrared reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS), and ellipsometry studies. Ultraviolet photoelectron spectroscopy (UPS) was employed in order to investigate the electronic structure of the SAMs. In particular, the low kinetic energy region of UPS spectra has been used to evaluate the work function of the samples. The estimated values were used, together with calculated molecular dipole moment values, to gain insight into the intrinsic dipole moment of the Au-S interface as well as the influence of the chemical substituents on the work function shift.

Experimental Section

A. Synthesis and Sample Preparation. General. Ethanol (200 proof, spectral grade) was acquired from Aldrich and wasdeoxygenated by bubbling with N2 gas for at least 30 min. All the other solvents and reagents were purchased and were used without further purification apart from tetrahydrofuran (THF), which was dried by passing through columns of activated alumina in a manner similar to that described in the literature. NMR spectra were recorded using a Bruker DRX 500 spectrometer. Elemental analysis was performed by Atlantic Microlabs. Ethanol (5 mL) was added to the remaining crude product, and the mixture was then dried over magnesium sulfate and filtered. The solvent was evaporated under reduced pressure. The obtained material was then recrystallized from ethanol to yield a white solid (4.23 g, 83%).

3H NMR (500 MHz, CD2Cl2) δ (ppm): 7.52 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.23–7.28 (m, 3H), 7.09 (s, 2H), 2.50 (s, 3H). 13C{1H} NMR (500 MHz, CD2Cl2) δ (ppm): 138.49, 137.70, 134.49, 134.49, 129.03, 128.25, 128.23, 127.90, 127.19, 126.79, 126.71, 15.81. Anal. Caled for C15H14S (M+), 226.08162; found, 226.08267.

E-4-(Acetylthio)stilbene (AcI). Compound M1 (4.0 g, 17.7 mmol) and sodium thio-tert-butoxide (5.0 g, 45.0 mmol) in dry DMF (50 mL) were heated to reflux for 24 h under a nitrogen atmosphere. Next, the flask was cooled down to 0 °C, and acetyl chloride (10 mL) was added at once to the mixture under a strong nitrogen gas flow. The mixture was then allowed to reach room temperature, and it was stirred under a nitrogen flow for an additional 30 min. Next, the flask was opened to air, and the mixture was poured into water (500 mL). The product was extracted with dichloromethane (200 mL) and the organic phase was washed with water (4 × 50 mL). Next, the organic phase was dried over magnesium sulfate and filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using dichloromethane/hexanes (1:1) as eluent, followed by recrystallization from ethanol. This afforded pale greenish needles (2.89 g, 64%).

<table>
<thead>
<tr>
<th>Compound</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
</tr>
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<tbody>
<tr>
<td>Chemical</td>
<td>Ethanol (5 mL)</td>
<td>Ethanol (5 mL)</td>
<td>Ethanol (5 mL)</td>
</tr>
<tr>
<td>Synthetic procedure</td>
<td>Ethanol (5 mL)</td>
<td>Ethanol (5 mL)</td>
<td>Ethanol (5 mL)</td>
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<tr>
<td>Property</td>
<td>Ethanol (5 mL)</td>
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<td>Ethanol (5 mL)</td>
</tr>
<tr>
<td>Result</td>
<td>Ethanol (5 mL)</td>
<td>Ethanol (5 mL)</td>
<td>Ethanol (5 mL)</td>
</tr>
</tbody>
</table>

Figure 1. Schematic representation of the monolayers investigated in this study under reduced pressure. Next, 150 mL of dichloromethane were added to the remaining crude product, and the mixture was washed with water (3 × 50 mL). The organic phase was then dried over magnesium sulfate and filtered. The solvent was evaporated under reduced pressure. The obtained material was then recrystallized from ethanol to yield a white solid (4.23 g, 83%).

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13C{1H} NMR (500 MHz, CD2Cl2) δ (ppm): 193.63, 138.17, 136.56, 134.44, 129.77, 128.36, 127.65, 127.08, 126.69, 126.26, 29.68. Anal. Caled for C15H14S (M+), 226.08162; found, 226.08267.

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room temperature, and it was stirred under a nitrogen atmosphere for 1.5 h. After that time, the flask was opened to air and poured into methanol (500 mL). The mixture was then cooled to −6 °C for 24 h. The solid was collected by filtration, washed with methanol, and recrystallized from ethanol to give white flakes (4.30 g, 71%).

1H NMR (500 MHz, CD3Cl) δ (ppm): 7.52 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 16.3 Hz, 1H), 6.92 (d, J = 16.3 Hz, 1H), 6.72 (d, J = 8.8 Hz, 2H), 2.99 (s, 6H), 2.40 (s, 3H). 13C{1H} NMR (500 MHz, CD3Cl) δ (ppm): 194.05, 150.29, 139.31, 134.53, 130.18, 127.50, 126.20, 125.46, 124.70, 122.47, 111.97, 39.89, 29.73. Anal. Calcld for C13H19NOS (M+), 270.11044; found, 270.11040.

Monolayer Preparation. IRRAS, XPS, and ellipsometry measurements were carried out on monolayers prepared on 100 nm thick polycrystalline gold titanium-primed glass purchased from EMF Corporation. X-ray diffraction of the gold substrates in Bragg–Brentano geometry is dominated by reflections from the Au(111) surface (see the Supporting Information). All gold substrates were stored under a nitrogen atmosphere and were cleaned with freshly prepared piranha solution followed by a thorough rinse with distilled water immediately before adsorption of thiolates. Warning: Piranha acid solutions react violently with many organic materials and should be handled with great care! SAMs were prepared by immersing freshly cleaned gold substrates into ca. 0.5 mM ethanolic solutions of the appropriate 4-acetylthio-stilbene and allowing the adsorption to continue for 20 h at room temperature under a nitrogen atmosphere. Each sample was then washed copiously with ethanol, dried under a stream of nitrogen gas, and stored under nitrogen for later analysis.

UPS measurements were performed on atomically flat Au(111) on mica acquired from Agilent. The substrates were sent to us under an argon atmosphere, were unpacked in a glovebox, and were placed directly into ca. 0.5 mM ethanolic solution of the appropriate acetylthio-stilbene for 20 h. Each sample was washed copiously with ethanol, dried under a stream of nitrogen, and stored under nitrogen for later analysis.

All sample manipulations were performed under inert gas atmosphere except for the ellipsometry measurements, which were performed under ambient conditions, and for the transfer of the samples into the XPS airlock during which the samples were exposed to the atmosphere for less than 3 min.

B. Sample Characterization and Data Analysis. A nitrogen-purged Digilab FTS-600 FT-IR instrument equipped with an MCT detector was used for measuring IR absorption spectra of the solutions. A KBr window cell was used for the measurements. A total of 256 scans were collected for each spectrum with 2 cm−1 resolution. A grazing-angle accessory (80° angle of incidence, from Pike) was employed in the IRRAS studies. The light was p-polarized with a gold grid polarizer from Perkin-Elmer. The pressure was about 10−2 Torr. The photoelectron takeoff angle was 35° with respect to the surface plane, and the spot size was about 1 mm. The pressure in the photoelectron takeoff angle was 35° with respect to the surface plane, and the spot size was about 1 mm. The pressure in the vacuum chamber was 10−2 Torr. The photoelectron takeoff angle was 35° with respect to the surface plane, and the spot size was about 1 mm. The pressure in the vacuum chamber was 10−2 Torr.

(35) Dodecyl thiol-d3 was prepared in a manner similar to that reported in ref 8. Commercially available dodecyl bromide-d3 was reacted with potassium thio-}

was chosen to be 0.8 mm. The uncertainty of the monolayer thicknesses obtained from XPS data was calculated from the error propagation of the double standard deviations for the Au(4f) peak intensities, which were obtained from measurements of four different spots for each sample. For the calculations of coverage, each S(2p) peak was fitted with two mixed Gaussian–Lorenzian functions with an assumed spin–orbit splitting of 1.18 eV and with a Shirley-type background correction. The fitted function was then numerically integrated, and the square root of the sum of squares of the residuals was propagated as the error in the integrated area of the S(2p) peak. Each measured Au(4f) peak was integrated numerically after subtracting the Shirley-type background. The double standard deviation was then calculated from the data for four spots for each sample and propagated in the error analysis. Fitting and background correction were done using the free fitting software XPSPeak 4.1.

A Woollam M-2000 spectroscopic ellipsometer was used for the determination of the ellipsometric thickness. All the measurements were performed at a 70° angle of incidence in the spectral range of 370–1000 nm. Three spots were measured for each sample, and a mean value of thickness and a standard deviation were calculated. The uncertainty in the measurement is assumed to be the sum of the standard deviation in the measurement and a typical error of the fitting procedure given by the fitting software (0.1 Å). It has been demonstrated that upon thiol adsorption on gold a new optical transition is present in the reflection spectrum of gold, which has to be included in the model for fitting ellipsometric data. In order to include the effects of the gold–thiol layer, a new optical transition is present in the reflection spectrum of gold with optical constants measured for the cleaned gold slide, optical constants of the Au21.4 Å of an octadecane monolayer with an index of refraction (ODT). An initial model was built, which consisted of 1000 Å of solution as well as for a gold slide coated with octadecanethiol (DDT). The double standard deviation was then calculated from the data for four spots for each sample and propagated in the error analysis. Fitting and background correction were done using the free fitting software XPSPeak 4.1.

The major IR modes of the molecules are present in the vibrational frequencies, and IR transition dipoles of isolated molecules on gold. However, the carbonyl stretching vibration, and IR transition dipoles of isolated 4′-substituted 4-stilbene thiol in vacuum were performed within the modified Perdew–Wang (mpW) exchange(40) and the Lee–Yang–Parr (LYP) correlation functional(41) in conjunction with a 4-31G** basis set as implemented in Gaussian98.(42)

### Results

#### Synthesis and Monolayer Preparation

For this study, three stilbene thiol derivatives were synthesized, with two of them containing an electron-donating group in the 4′-position. In order to avoid the known issue of air oxidation of aromatic thiols to form disulfides, which are often insoluble, we prepared acetyl-protected thiols.43,44 Figure 2 shows the general synthetic scheme describing the preparation of the protected thiols, 4C1–3. The Horner–Wadsworth–Emmons reaction between diethyl 4-(methylthio)benzylphosphonate (1) and commercial 4-substituted benzaldehydes was utilized to prepare the S-methylated stilbene thiols, M1–3, in good yields.(43) The acetyl group was introduced by treating each thiomethylated stilbene with sodium thio-tert-butoxide in refluxing DMF and quenching the resulting thiolate anion with acetyl chloride.45 This approach gave moderate yields of 40–64%.

The acetyl-protected stilbene thiols were used in the preparation of monolayers directly without deprotection.(44,49,50) Figure 3 shows a comparison of FT-IR spectra of CDC13 solutions of 4C1, 4C2, and 4C3 with IRRAS spectra of the corresponding monolayers (SAM1, SAM2, and SAM3, respectively) on gold. The major IR modes of the molecules are present in the IRRAS spectra of the monolayers confirming the adsorption of the molecules on gold. However, the carbonyl stretching mode (∼1700 cm⁻¹) present in the spectra of CDC13 solutions

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(45) 1 was prepared from 4-(methylthio)benzyl alcohol according to a slightly modified published procedure. Xue, C.; Luo, F.-T. J. Org. Chem. 2003, 68, 447–442.
of the acetyl-protected molecules is absent in the IRRAS spectra of the SAMs, indicating that the adsorbed species do not contain the carbonyl group, consistent with the formation of thiolate monolayers. The IRRAS spectra are discussed in more detail in a subsequent section.

XPS provides additional evidence for the adsorption of the thiolates on gold. Figure 4 shows XPS spectra of SAM1–SAM3. The data in the S(2p) region confirm the presence of sulfur with the peak maximum around 162.7 eV, consistent with the literature for other conjugated thiolate monolayers. All SAMs show the main C(1s) peak around 284.2 eV, which is in agreement with literature values obtained for biphenyl thiolate SAMs. There is a pronounced shoulder on the high binding energy side in the case of SAM2 and SAM3. This is consistent with the existence of carbon attached to an electronegative atom (O and N for SAM2 and SAM3, respectively). The spectra in the binding energy region of O(1s) core electrons are also presented in Figure 4. SAM2 shows a strong signal around 533.1 eV, which can be attributed to the oxygen attached to a phenyl ring. Additionally, SAM3 shows a signal around 532.3 eV, which is also barely visible in the spectrum of SAM1. This signal may be attributable to water molecules adsorbed on the monolayers. As expected, only SAM3 shows a signal from nitrogen core electrons (Supporting Information).

Monolayer Thickness and Molecular Coverage. XPS data can also be used to establish the thickness of the monolayers. The relative attenuation of photoelectrons originating from the photoionization of the substrate is a measure of the thickness of an adlayer residing above the substrate as described by

\[
\ln \frac{I_1}{I_2} = \frac{d_2 - d_1}{\gamma \sin \phi}
\]

where \(I_1\) and \(I_2\) are measured Au(4f7/2) photoelectron intensities of sample 1 and sample 2, respectively, \(d_1\) and \(d_2\) are the thickness of the adlayer in sample 1 and sample 2, respectively, \(\gamma\) is the attenuation length of Au(4f7/2) photoelectrons caused by the organic adlayer, and \(\phi\) is the photoelectron takeoff angle with respect to the sample surface. Table 1 shows the thickness values obtained from XPS results on SAM1, SAM2, and SAM3 using a dodecanethiol-coated gold slide as a reference with the assumed thickness of the DDT monolayer of 15.2 Å. The extracted XPS thickness values are slightly smaller than the DFT calculated long molecular axis lengths for all three monolayers (Figure 5). This is consistent with the existence of dense monolayers with the molecules slightly tilted from the surface normal.

Figure 3. Comparison of IR spectra of CDCl3 solutions of compounds Ac1, Ac2, and Ac3 and IRRAS spectra of the corresponding monolayers.

Figure 4. XPS spectra of stilbene thiolate SAMs in different spectral regions. Spectra are displaced vertically for clarity.

(56) The equation assumes the same attenuation length of photoelectrons for sample 1 and sample 2. We used \(\gamma = 42\) Å according to ref 12.

(59) An octadecane-thiol-coated gold slide was also measured. The calculated thickness of the octadecanethiol monolayer was 21.1 ± 0.4 Å.
(60) An alternative interpretation is a slightly less dense non tilted layer.
ness of monolayers on noble metals\textsuperscript{1,10,39,53} and thus to measure the monolayers. We used this technique to obtain an thickness values of the monolayers on gold.\textsuperscript{30,61,62,64} Additionally the polar substituents values are similar to those obtained for other conjugated thiol the monolayers studied here is shown in Table 1. The obtained thickness extracted from the measurement of the octadecanethiol-coated gold slide.\textsuperscript{63} The coverage of the dodecanethiol-coated gold slide was assumed to be 10\textsuperscript{12} molecules/cm\textsuperscript{2}, which is a value based on ref 3. Following the procedure data in the spectral range of 600–1000 nm were used for fitting.\textsuperscript{39} Each stilbene adlayer was assumed to be a Cauchy layer with each monolayer is shown in the Supporting Information. The ellipsometric thicknesses for SAM1 and SAM2 are slightly smaller than the calculated molecular lengths and consistent with the XPS estimates of the thickness (Figure 5). However, SAM3 appears somewhat thicker. This may be due to adsorption of water onto the monolayer under the ambient conditions used for the ellipsometry measurements. Moreover, this is consistent with the presence of oxygen in the XPS spectrum of SAM3 (see above).

### Infrared Reflection Absorption Spectra
Infrared reflection absorption spectroscopy (IRRAS) has proven to be very useful in the characterization of monolayers on metals.\textsuperscript{1,10,36,67} It is, in principle, possible to establish the molecular orientation of the constituents of a self-assembled monolayer by comparing the IR spectrum of adsorbate-like free molecules with the IRRAS spectrum of the monolayer.\textsuperscript{10,36,67} The selection rule for light absorption by molecules on metallic surfaces states that only transitions with transition dipole moments (TDMs) that have nonzero projection onto the surface normal are allowed.\textsuperscript{67} There

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Table 1. Thickness and Coverage Data of Stilbene Thiolate Monolayers on Gold

<table>
<thead>
<tr>
<th>Sample</th>
<th>XPS thickness [Å]</th>
<th>Ellipsometric thickness [Å]</th>
<th>Coverage ([10^{14} \text{ molecules/cm}^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM1</td>
<td>12.1 ± 0.6</td>
<td>11.1 ± 0.5</td>
<td>3.2 ± 0.23</td>
</tr>
<tr>
<td>SAM2</td>
<td>13.7 ± 0.5</td>
<td>12.7 ± 0.1</td>
<td>3.2 ± 0.23</td>
</tr>
<tr>
<td>SAM3</td>
<td>12.8 ± 0.7</td>
<td>15.7 ± 0.7</td>
<td>3.1 ± 0.23</td>
</tr>
</tbody>
</table>

\(^a\) Coverage was obtained from XPS measurements.
are two main assumptions one must make in order to extract the molecular orientation from comparison of relative intensities in the FT-IR spectrum of the bulk adsorbate-like species and the IRRAS spectrum of the monolayer: first, that the TDMs of the vibrational modes of interest are the same for the adsorbate and the adsorbate-like species and, second, that the free adsorbate-like sample is isotropic. The second assumption is of course valid if one uses liquid solutions of the adsorbate-like species.

The FT-IR spectra of solutions of M3 and the IRRAS spectrum of SAM3 are compared in Figure 6. The mode at 1610 cm⁻¹ (assigned to the phenyl quadrant stretching, with TDM along the long molecular axis) and the mode at 1523 cm⁻¹ (assigned to the phenyl semicircle stretch mode, also with TDM along the long molecular axis) show practically the same relative intensity in the FT-IR spectrum of a CDCl₃ solution of M3 and in the IRRAS spectrum of SAM3. The second phenyl semicircle stretch mode with TDM along the long molecular axis was assigned to the band at 1483 cm⁻¹, with TDM perpendicular to the long molecular axis, is greatly reduced in the monolayer spectrum. These observations suggest that the orientation of the long molecular axis of the adsorbate and the adsorbate-like species and, second, that the free adsorbate-like sample is isotropic. The second assumption is of course valid if one uses liquid solutions of the adsorbate-like species.

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Figure 7. Secondary photoelectron cutoff regions of the UPS spectra of stilbene thiolate monolayers on gold.

behavior for the three stilbene thiolate derivatives studied here is similar to that previously observed in biphenyl thiolate SAMs, for which a tilt angle from the surface normal of ca. 20° has been reported.

Work Function of Monolayers. Figure 7 shows the low kinetic energy portion of UPS spectra of the stilbene thiolate monolayers on gold. This spectral region is often referred to as the secondary photoelectron cutoff, and the position of the sharp rise of the signal (characterized by an electron kinetic energy of E_{min}) is used to establish the position of the vacuum level of the sample and its work function, Φ, according to the relation: Φ = E_{F} - (E_{F} - E_{min}), where E_{F} is the photon energy (21.2 eV in this study) and E_{F} is the kinetic energy of photoelectrons from the Fermi level.

The extracted work functions (Figure 8) for all three monolayers are significantly smaller than values reported for Au(111), which are typically in the range 5.2–5.3 eV. The work function of 4.30 eV measured for the unsubstituted stilbene thiolate monolayer, SAM1, is very close to the values measured for monolayers of other conjugated thiophenes without polar substituents; for example, values of 4.20 and 4.30 eV have been reported for the work function of Au(111) coated with 4,4'-(ethynylphenyl)-1-benzothienylene and 4-terphenylthiophene, respectively. Substitution of the terminal phenyl ring of the stilbene backbone with a π donor group in the para position leads to a further drop in the work function, as shown in Figure 8.

It is interesting to compare the experimental modifications of the work function with those anticipated on a purely electrostatic basis. The work function change, ΔΦ, caused by a sheet of dipoles residing on the surface can be estimated using the

Table 2. Vibrational Frequencies (in cm⁻¹) of Prominent IR Modes Measured for Solutions of 4'-Substituted 4-(Methylthio)stilbenes and the Corresponding SAMs

<table>
<thead>
<tr>
<th>solution</th>
<th>M1</th>
<th>SAM1</th>
<th>I_{SAM1}/I_{M1}</th>
<th>solution</th>
<th>M2</th>
<th>SAM2</th>
<th>I_{SAM2}/I_{M2}</th>
<th>solution</th>
<th>M3</th>
<th>SAM3</th>
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a Assignment is based on literature and DFT-calculated vibrational modes of the isolated molecules; str. = stretching mode, bend. = bending mode, wag = wagging mode, ip = in plane, op = out of plane, par = TDM parallel to the long molecular axis, perp = TDM perpendicular to the long molecular axis. b Ratios of experimental intensities for a given mode in a SAM and in the solution of the corresponding free molecule.

Figure 8. Work function changes caused by substituted stilbene thiolate monolayers on gold as a function of DFT-calculated dipole moments along the long molecular axis of the corresponding thiols projected on the surface normal: the circles are experimentally determined from UPS measurements, and the squares are calculated from the Helmholtz equation assuming $\mu_{BD} = 0$; the solid and dashed lines are the corresponding linear fits for each data set.

projection of the molecular dipole moment onto the surface normal, $\mu_{\text{mono}}$ and the coverage of the surface, $\theta$, employing the Helmholtz equation:

$$\Delta \Phi = \frac{\theta}{\varepsilon_0} \left( \frac{\mu_{\text{mono}}}{\kappa_{\text{mono}}} + \frac{\mu_{BD}}{\kappa_{BD}} \right)$$

where $\mu_{BD}$ is the dipole moment induced by binding to the surface (bond dipole, BD) which, generally, may include contributions from Pauli push-back, charge-transfer, and/or the formation of polar chemical bonds between metal and molecule. $\kappa_{\text{mono}}$ and $\kappa_{BD}$ are the depolarization factors of the molecular dipole layer and BD layer, respectively, and $\varepsilon_0$ is the vacuum permittivity. If $\mu_{BD}$ is assumed to be independent of the substitution pattern of the stilbene thiolate and the coverage is assumed to be constant from sample to sample, the equation also implies that the $y$-intercept of a linear fit of the experimental values of $\Delta \Phi$ against the projection of the calculated molecular dipole moments onto the surface normal (Figure 8, solid line) is the measure of the work function change originating solely from the BD layer. The extracted value is $\Delta \Phi = -0.85$ eV, which, assuming $\theta = 3.3 \times 10^{14}$ molecules/cm$^2$, is the average value of the XPS estimated coverages for the SAMs studied here, and a depolarization factor of BD layer, $\kappa_{BD}$, of 6.4 corresponds to the projection of the dipole moment induced by adsorption on the surface normal of around 4.4 D/molecule. To put this value into perspective, using the data of Alloway et al. for the surface normal of around 4.4 D/molecule. To put this

Our results indicate the presence of oxygen, likely arising from water, especially in the case of SAM3, alignment or partial alignment of water molecules within this adlayer would give rise to an additional dipole layer which, according to the Helmholtz equation, could be anticipated to influence the work function. In any case, the studied self-assembled monolayers of stilbene thiolates show the expected trend in the modification of the work function of the underlying metal with substituents of different electron-donating ability.

Conclusions

Conjugated 4'-substituted 4-stilbene acetyltio derivatives react to form dense self-assembled monolayers of stilbene thiolates on gold when deposited from ethanolic solutions. The long axes of the molecules are oriented almost perpendicularly to the surface, consistent with the report of a tilt from the surface normal of ca. 20° for biphenyl thiolate SAMs. These conclusions have been supported by evidence obtained by a variety of techniques that have been used here to characterize the thin films. UPS studies indicate that substituted stilbene thiolate monolayers can be used to modify the work function of the underlying metal. While the qualitative dependence of the work function change on the substituents in the 4' position of the stilbene molecules can be rationalized in terms of a simple electrostatic model, the magnitude of the variation is smaller than expected by these electrostatic considerations, perhaps due to the effect of water adsorbed onto the monolayers. Nevertheless, we have shown that the work function of gold can be lowered by as much as 1.3 eV using a conjugated thiolate monolayer and that the degree to which it is lowered can be controlled by the substituents; this is significant from the perspective of facilitating hole injection and/or suppressing electron injection from gold electrodes into organic charge-transport materials in organic electronics applications.

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Supporting Information Available: X-ray diffraction of gold substrates, N(1s) region XPS spectrum of SAM3, influence of the assumed refractive index on the extracted thickness values of SAM1–3, IRRAS spectra of SAM1 and SAM2. This material is available free of charge via the Internet at http://pubs.acs.org.