

Molecular Electrostatics of Conjugated Self-Assembled Monolayers on Au(111) Using Electrostatic Force Microscopy

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The electrostatic potential produced by a variety of self-assembled monolayers on Au(111) is measured using scanning probe techniques. The molecules chosen for this study contain thiol-terminated end groups and π -conjugated orbitals, making them suitable for molecular electronics applications. We have measured the surface potential of molecules having a symmetric structure and compared these results to those obtained from similar nonsymmetric molecules. The measured potential for nonsymmetric molecules scales with the dipole moment of the molecule comprising the monolayer. For symmetric molecules, the measured surface potential is essentially the same as the substrate. This result suggests that the dipole moment formed by the Au–S bond makes a small contribution to the measured surface potential. The dipole moment of a strong electron accepting molecule was intentionally modified by reaction with a strong electron acceptor. In this case, the surface potential produced by the self-assembled monolayer was found to change polarity after the formation of the charge-transfer complex.

I. Introduction

A promising future for molecular electronics requires a subtle control of molecules at interfaces. Not only must molecules be designed to have specific electronic and structural properties, but they must then be assembled on well-characterized substrates in a controlled way. An important first step is the assembly of molecules from solution to form a homogeneous self-assembled monolayer (SAM). This self-assembly process at the molecular length scale is now well established since, for instance, a solution of thiol-terminated molecules, when exposed to a clean gold substrate, will chemisorb and form a periodic, uniform SAM.^{1,2}

An important consequence of forming a uniform SAM on a substrate is the ability to tune the electronic properties of that surface. This capability will prove to be very important in future molecular electronics applications. At the simplest level, a SAM of alkanethiols can alter the highly conducting character of a gold substrate by coating it with a thin insulating monolayer. More subtle modifications are also possible since the molecules used to form a SAM may possess interesting intrinsic electronic properties. SAMs have also been used on the metal source/drain electrodes of organic thin-film transistors in order to modify the contact resistance, with a modification of the effective work functions of the contacts being responsible for at least a portion of the effect.³

In the field of molecular electronics, it will be necessary to reproducibly form well characterized molecule/metal

and molecule/semiconductor heterostructures. While the electronic properties of an isolated molecular species can provide general guidelines for selection of a molecule with desired electronic characteristics, the formation of a chemical bond between a molecule and a substrate generally results in a transfer of charge between the molecule and substrate, as well as a broadening of the molecular levels due to electronic coupling with the substrate. The transfer of charge gives rise to a change in the electrostatic potential of the substrate when compared to that of the bare substrate. Knowledge of this electrostatic potential is essential for understanding electronic band alignments which dictate the low-field conductivity and turn-on voltages in metal–molecule–metal systems.⁴

With recent advances in scanning probe technology, systematic studies are now possible to measure the alteration of the electrostatic force experienced by a conducting tip when placed above aliphatic and aromatic thiol SAMs chemisorbed to a variety of substrates.^{5–8} By nulling out the electrostatic force with an external bias applied to the tip, it is possible to estimate the change in the electrostatic potential induced by the SAM formation. In all cases reported below, SAM formation was restricted to Au(111) single-crystal grains and all measurements of the electrostatic surface potential were referenced to a clean gold substrate in order to provide an absolute value for the resulting electrostatic potential. This referencing procedure allows for correction of uncontrolled potential offsets due to variations in the surface potential of the many different tips used in this study. In this way, we

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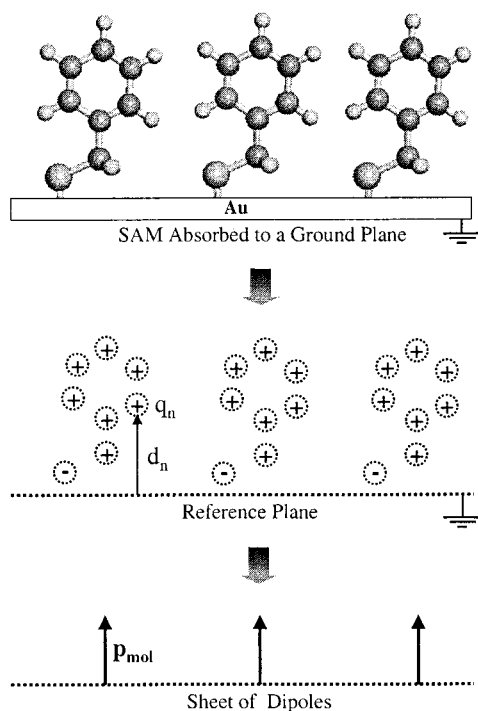


Figure 1. A dipole model used to calculate the electrostatic potential produced by a molecular SAM on a Au(111) substrate. For a uniform SAM, the potential can be modeled as an infinite sheet of dipoles located above an infinite ground plane. Therefore, no image charge correction is required.

have deduced the electrostatic potential produced by a SAM bound to a substrate. The origin of the measured potential is intimately related to the bonding and orientation as well as the chemical composition of the molecule and thus represents a quantity of considerable fundamental interest.

In this study, initial surface potential measurements on alkanethiol SAMs were conducted to build a level of confidence with our experimental techniques. This was followed by studies of aromatic thiols of interest. Studies were conducted on molecules that possessed a symmetric and nonsymmetric molecular structure in an effort to deduce the relative contributions of (i) the thiol–Au bond and (ii) the dipole moment of the molecule. Further, we have used electrostatic force microscope (EFM) techniques to monitor the formation of a charge-transfer (CT) complex by reacting a donor and an acceptor molecule in solution. We find that the sign and magnitude of the electrostatic potential of the system can be restored to its original value by removing the acceptor molecule from the SAM. These studies are interesting because they exploit the modification of a molecule's dipole moment, possibly forming a scientific basis for a sensitive chemical sensor.

II. Modeling the Surface Potential Produced by a SAM

The electrostatic surface potential produced by a SAM can be modeled by considering the dipole moments of the molecule within a uniform 2-D array of areal density N_{mol} molecules/m² (see Figure 1). The electrostatic potential that develops with respect to that of the bare metal surface is given by

$$V_{\text{SAM}} = \frac{N_{\text{mol}}(\bar{p} \cdot \hat{n})}{2K\epsilon_0} \quad (1)$$

where \bar{p} is the dipole moment per molecule, \hat{n} is a unit

vector normal to the surface, K is the relative dielectric constant of the molecular monolayer, and ϵ_0 is the permittivity of free space.

To determine \bar{p} , it is necessary to consider the magnitude and location of all charges within the molecule, given by q_n and \vec{d}_n , respectively (see Figure 1). The resulting dipole moment per molecule is

$$\bar{p} = \sum_{i=1}^n q_n \vec{d}_n \quad (2)$$

For a neutral molecule, the image charge in the metal does not contribute and the origin used to specify the \vec{d}_n 's is arbitrary. However, for cases where the molecule accepts charge from (or gives charge to) the metal surface, it is necessary to consider the effects of the net charge. In this case, the most straightforward choice is to set the origin for the \vec{d}_n 's to the point where the molecule contacts the metal surface. Using this choice, eqs 1 and 2 are suitable for describing either neutral or charged molecules.

To illustrate the magnitude of the expected potentials for typical ranges of molecular dipole moments, consider the potential that would arise from a molecular SAM comprised of molecules having a dipole moment $|\bar{p}| = 1$ D (1 debye = 3.336×10^{-30} C m) and $N_{\text{mol}} = 4 \times 10^{18}$ m⁻², which is typical for SAMs of molecules such as dodecanethiol. For a SAM in which the molecules are oriented perpendicular to the surface and in which $K = 2$, the calculated potential is $V_{\text{SAM}} \approx 380$ mV, a non-negligible potential.

Although eqs 1 and 2 appear simple to evaluate, accurate calculation of $\sum_{i=1}^n q_n \vec{d}_n$ is no easy task. To determine the location and magnitude of the charge requires the use of sophisticated quantum chemistry algorithms. The dipole moments quoted in this study were calculated using a Mulliken charge analysis performed by the quantum chemistry software package HyperChem Pro 6.0.⁹ In this initial study, our dipole calculations assumed that the molecules were neutral and ignored any molecular interaction with the Au(111) substrate.

III. Previous Surface Potential Studies of SAMs

Evans and Ulman first studied the surface potentials of self-assembled alkanethiols of different chain lengths adsorbed on polycrystalline gold substrates.¹⁰ These measurements were conducted using a macroscopic Kelvin probe. Since the probe diameter was on the order of a few millimeters, the surface potential produced by a large number of molecules ($\approx 10^{13}$) was measured. The results of these measurements indicated a dependence of the electrostatic surface potential on the number of CH₂ groups that formed the backbone of the alkanethiols. A change of ~ 10 mV per CH₂ group was observed. Their study suggested two contributions to the surface potential: one arising from the Au–S bond and another from charge separation along the length of the molecule itself.

More recently, Lu et al. have used a Kelvin force microscope (KFM) to measure the surface potential of alkanethiol SAMs transferred to a gold substrate using microcontact printing techniques.^{11,12} Since the measure-

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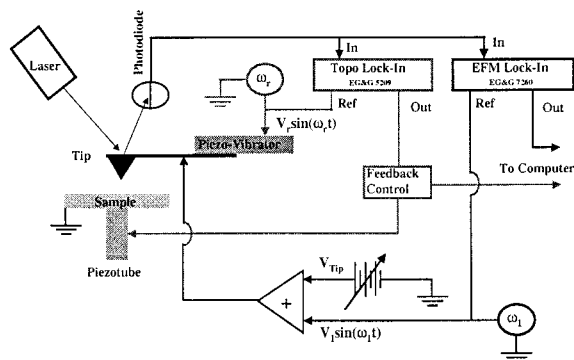


Figure 2. A schematic diagram of the electrostatic force microscope apparatus.

ments were made using KFM, lateral resolution of the surface potential measurement was reduced to ≈ 50 nm. These measurements also indicated a similar dependence of the surface potential on the chain length of alkanethiols. A dependence of ~ 14 mV per CH_2 group was observed.

Taken together, these two previous studies show a dependence in the polarity and magnitude of the electrostatic surface potential on the number of CH_2 groups present in an alkanethiol molecule. In these previous studies,^{10–12} the SAMs were modeled as a two-dimensional ensemble of dipoles with length l , where l is approximately the length of the molecule. A layer of negative charge resides close to the gold substrate, while the positive charge was thought to lie at the tail of the molecule, approximately a distance l above the gold substrate. The orientation of the dipole moment is inferred from the positive slope in the surface potential as the chain length is increased. This implies that the increase in potential measured with increasing alkane chain length is directly related to the distance between the two charge sheets. Since the molecules investigated in these prior studies were non-conjugated, the molecular SAMs are relatively nonconducting and the dipoles were modeled by charge sheets located at the two ends of the molecule.

IV. Experimental Details

A. The Electrostatic Force Apparatus. A commercial scanning probe microscope (SPM), capable of operating in a dry nitrogen environment, was used throughout this study.¹³ A standard optical beam bounce detection scheme was employed to detect both the surface and the electrostatic forces. The reported measurements were made using heavily doped silicon tips with a nominal spring constant of 2 N/m.¹⁴ These tips were found to have excellent characteristics both for detecting the electrostatic force and for imaging the sample substrate. The electrostatic surface potential was measured using a standard noncontact force detection technique.^{15–19} The tip was held at a fixed distance of approximately 100 nm above the sample using a noncontact topographic feedback system.

A diagram of the measurement scheme is given in Figure 2. The electrostatic force acting on the tip was measured by placing a controlled combination of a dc bias voltage (V_{Tip}) and a time varying dither voltage ($V_1 \sin \omega_1 t$) on a conducting atomic force

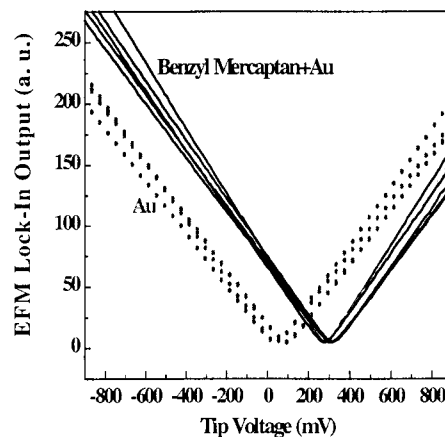


Figure 3. A measurement of the absolute value of the electrostatic force in eq 7 for a bare Au substrate and the benzyl mercaptan SAM. When the electrostatic force goes to zero, the applied tip potential (V_{Tip}) equals the local surface potential ($V_{\text{surf}}(x, y)$). Each curve plotted is a measure of the force as a function of the applied tip voltage V_{Tip} . The individual curves were taken at random locations across the sample. The uncertainty in determining the zero force condition is used as an estimate for the experimental error in determining the surface potential.

microscope (AFM) tip. The modified potential difference between the tip and sample produces an electrostatic force given by

$$F(\omega_1) \propto \frac{dC}{dz} [V_{\text{surf}}(x, y) - V_{\text{Tip}}] V_1 \sin(\omega_1 t) \quad (3)$$

where dC/dz is the capacitance gradient between the tip and substrate. If the substrate is covered with a SAM, then $V_{\text{surf}} = V_{\text{SAM}}$.

The ω_1 component of the force can be detected using standard phase sensitive detection. By varying the dc bias voltage applied to the tip (V_{Tip}), the sample's electrostatic surface potential was measured by determining the dc tip voltage required to minimize the magnitude of the ω_1 component of the electrostatic force. In these measurements, ω_1 was ~ 80 kHz and V_1 was 2 V root mean square (rms).

Many tests were conducted to verify that the dc bias needed to minimize the electrostatic force was independent of parameters such as the magnitude of the dither voltage, the driving frequency ω_1 , and the tip-sample separation. In addition, a minimum detectable potential change determined to be ~ 10 mV was established by biasing a bare gold substrate with a stable, external voltage source.

The surface potentials of different SAM samples were measured with the same AFM tip and referenced with respect to a Au reference sample. Because the measurements were made over a uniform sample, electrostatic convolution effects produced by the cantilever beam are minimized.²⁰ Small variations in the electrostatic potential from point to point across the surface are expected and observed and are thought to be related to defects in SAM formation as well as grain boundaries and foreign adsorbates on the substrate. Typical data obtained following this procedure are given in Figure 3.

B. Molecular Synthesis. Benzyl mercaptan (BM), α, α' -xylyldithiol (XYL), 2,3,5,6-tetramethyl-*p*-xylene- α, α' -diol, tetracyanoethylene (TCNE), and pentamethylbenzyl alcohol were obtained from Aldrich. 2,3,5,6-Tetramethyl-*p*-xylene- α, α' dithiol (TMXYL) and pentamethylbenzyl mercaptan (PMBM) were prepared from the respective alcohols as described previously.²¹ The procedures developed to prepare the tetramethyl xylyl dithiol-tetracyanoethylene (TMXYL-TCNE) charge-transfer complex are described elsewhere.²¹

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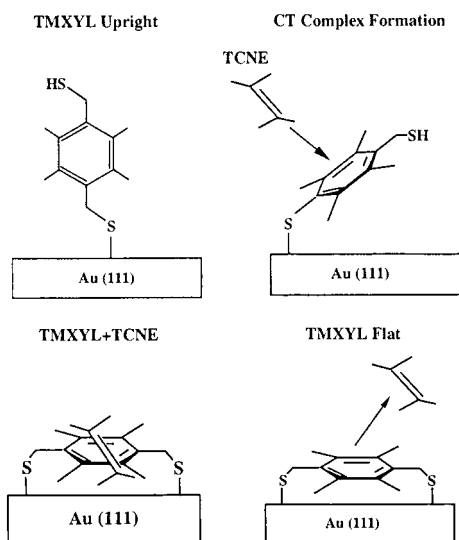


Figure 4. Orientation of TMXYL before and after its reaction with TCNE and after removal of TCNE from the charge-transfer complex.

C. Gold Substrates. The Au(111) substrates used in this study were prepared from commercially available substrates made by evaporating 10 nm of Cr and then 200 nm of Au on a glass substrate having dimensions of 1 cm \times 1 cm.²³

All Au substrates are front-side flamed until dull red for 30–40 s producing flat grains of a few microns in diameter having a Au(111) orientation. The flame-annealed substrates were cleaned in high-purity ethanol prior to SAM deposition. After SAM preparation, the samples were either quickly inserted into the SPM apparatus or stored in nitrogen-filled boxes or vacuum desiccators until the measurements were made.

As a precaution, the electrostatic surface potential of each flamed gold substrate, as well as a preselected gold reference substrate prepared at the same time, was measured prior to any SAM deposition. These measurements were used as a screen for good substrates; only those substrates having a surface potential within a 50 mV range of that measured for a designated Au(111) reference substrate were used for SAM deposition. Typically, for data taken at multiple positions over any one substrate, the surface potential varied by not more than ± 30 mV.

D. SAM Deposition. SAMs of XYL, BM, and PMBM were prepared by immersing an annealed Au(111) substrate into 1–5 mM solutions overnight. For the case of XYL and BM, EtOH was used as a solvent. For PMBM, CH_2Cl_2 was used as a solvent. After SAM formation, the substrates were carefully rinsed in the appropriate solvent, dried under a stream of clean nitrogen, and stored in a vacuum desiccator until just prior to insertion into the SPM apparatus.

A SAM of the CT complex was synthesized in a number of steps as summarized schematically in Figure 4. The first step was the formation of an upright SAM of TMXYL on Au(111). The second step involved the immersion of the TMXYL-coated Au(111) substrate in a concentrated solution of TCNE (0.1 M) in CH_2Cl_2 . The third step required a SAM of TMXYL, but with the TCNE removed by immersion in a solution of the strong electron donor trimethyl tetrahydrofulvalene (Me_3TTF).

A SAM of TMXYL upright was prepared by immersing an annealed Au(111) substrate into ca. 1 mM CH_2Cl_2 solutions of the respective compound for 12–16 h. The substrates were then thoroughly rinsed with CH_2Cl_2 and dried overnight under a stream of nitrogen.

A SAM of TMXYL–TCNE was prepared by immersing an annealed Au(111) substrate previously coated with TMXYL upright in a concentrated solution (ca. 7 mL) of TCNE in CH_2Cl_2 , for 48 h. The substrate was rinsed with CH_2Cl_2 and dried under nitrogen.

A SAM of TMXYL flat with two thiol bonds to the Au(111) substrate was prepared by immersing the TMXYL–TCNE SAM in a concentrated solution of Me_3TTF in CH_2Cl_2 for 30 h.

E. SAM Characterization. The ellipsometric data and reflection–absorption infrared (RAIR) spectra of XYL have been reported previously.²⁴ The experimental thickness for XYL is 0.83 nm, consistent with a tilted molecular orientation ($\sim 24^\circ$) and only one thiol attached to the substrate. This tilt is apparently due to the presence of methylene carbon atoms in XYL. The thickness of the benzyl mercaptan SAM is 0.45 nm, indicating that the molecule is also tilted to the substrate since the expected length of the molecule is 0.55 nm. The measured thicknesses of the PMBM and TMXYL SAMs are 0.67 and 0.8 nm,²¹ respectively, and are consistent with the molecule standing up on gold.

A discussion of the RAIR and ellipsometric characterization of the TMXYL upright, TMXYL–TCNE, and TMXYL flat was more involved. The RAIR spectrum of this complex shows an intense band at 1378 cm^{-1} , corresponding to the CH_2 out-of-plane bending mode of TMXYL. In contrast, the in-plane mode at 1437 cm^{-1} decreases significantly in intensity. This suggests that TMXYL is now lying flat with respect to the Au(111) substrate, bound through both thiol groups. In addition, the out-of-plane “puckering” mode of TCNE at 554 cm^{-1} shows a significant increase in intensity. These data suggest that TCNE is also lying flat with respect to the metal substrate, presumably on top of TMXYL. Finally, a SAM of TMXYL was studied in the flat configuration, but with the TCNE removed. The RAIR spectrum from this sample showed the same intense band at 1378 cm^{-1} , as shown in the RAIR spectrum of the CT SAM, suggesting that TMXYL remains flat on Au(111). The absence of the out-of-plane bending mode at 554 cm^{-1} confirms the removal of TCNE from the substrate.

All optical ellipsometry measurements were carried out on a rotating analyzer ellipsometer equipped with a HeNe laser source, operated at 633 nm. The angle of incidence was 70° . Several areas on the sample were measured. The refractive indices of the organic films were taken as 1.5. The thickness of TMXYL upright was measured to be 0.8 nm by ellipsometry, a value consistent with the theoretical lengths obtained with the molecular axis normal with respect to the surface. In contrast, ellipsometry data on samples of TMXYL–TCNE give a thickness of 0.6 nm, indicating that the film thickness is less than the sum of the two components, thereby suggesting that the charge-transfer complex is no longer normal to the surface. Instead, we conclude that TMXYL–TCNE is now lying flat, with its molecular axis parallel to the surface. This is consistent with the conclusions drawn from the RAIR data above. Similarly, ellipsometry data on TMXYL flat indicate that the TMXYL remains flat after the removal of the TCNE. In summary, the two-component SAM of TMXYL–TCNE is found by ellipsometry to have a thickness that is 0.2 nm less than that of a SAM of TMXYL alone.

Advancing water contact angles were obtained with a home-built goniometer. All measurements were performed at room temperature. The sample chamber atmosphere was saturated with water vapor by filling the well of the chamber with water. The advancing contact angle was measured by lowering the needle to the surface and injecting 1 mL of water on the surface of the wafer. Both sides of the drop were measured. This procedure was repeated over several areas of the sample, and the results were averaged.

Contact angle measurements on TMXYL upright give a value of 80° , indicating that it is a densely packed structure and hence has a hydrophobic character. The data are in reasonable agreement with those obtained on a SAM of the analogous molecule, XYL, which give a contact angle of 70° . However, it is not as hydrophobic as octadecanethiol or dodecanethiol SAMs (111° – 114°).²² In contrast, a SAM of TMXYL–TCNE gives a contact angle of 71° and suggests that upon doping of TMXYL, to generate a CT complex, the structure becomes more hydrophilic.

We conclude that RAIR spectroscopy, ellipsometry, and contact angle measurements are all consistent with the proposed horizontal orientation of TMXYL+TCNE shown in Figure 4.

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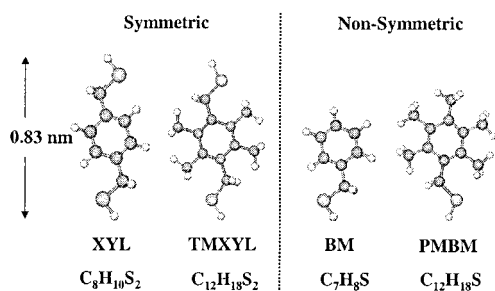


Figure 5. A schematic diagram of the various molecules used in this study.

Table 1. Values for V_{SAM} for Molecules on Au(111)^a

designation	V_{SAM} (in mV)	$p_{\text{calculated}}$ (in debye)
XYL	50 ± 30	0
BM	240 ± 50	1.0
TMXYL	20 ± 70	0
PMBM	150 ± 50	0.9

^a The calculated dipole moment for each molecule is also listed.

V. Results

A. EFM Measurements for Alkanethiols. Our initial surface potential measurements were made on dodecanethiol (DDT) and octadecylthiol (ODT) SAMs prepared in the manner described in section IV.D. The V_{SAM} with respect to bare Au(111) for DDT and ODT was found to be 100 ± 20 mV and 230 ± 30 mV, respectively. These measurements give us a slope of 20 mV/CH₂ compared to Evans' value of 10 mV/CH₂ group¹⁰ and Lu's value of 14 mV/CH₂ group.^{11,12}

Equation 1 can be used to estimate the surface potential of DDT and ODT based on their dipole moments. A commercial quantum chemistry program HyperChem Pro 6 was used to calculate the dipole moment for the pair of alkanethiols used in this initial study. The calculated dipole moment for DDT and ODT is 0.67 and 0.74 D, respectively. Assuming a packing density of 4.5×10^{18} molecules/m², a tilt of 30°, and a monolayer dielectric of 2.0 (typical parameters for alkanethiols), the surface potential for DDT and ODT is estimated to be 280 and 310 mV, respectively, giving a slope of 5 mV/CH₂ group. This simple model displays a similar trend that has been observed experimentally. However, the low value of the calculated slope indicates that this simple model may still require further refinement to include charge transfer between molecule and substrate.

B. EFM Measurements of Symmetric and Non-symmetric Molecules. Having completed initial studies on alkanethiols, surface potential measurements of aromatic thiols were conducted using the same technique to provide an insight into the charge distribution for a conjugated molecular system. These experiments were devised to test the hypothesis that the symmetry of the molecular structure influences the surface potential.

The molecules used for this study were classified into two groups. Each set contained a symmetric molecule in addition to a nonsymmetric variant. The first group consisted of XYL (C₈H₁₀S₂) and BM (C₇H₈S). The second group consisted of TMXYL (C₁₂H₁₈S₂) and PMBM (C₁₂H₁₈S). A schematic diagram of the molecules is given in Figure 5.

The results of the EFM measurements are summarized in Table 1. In addition, the calculated dipole moment ($|\bar{p}|$) obtained from HyperChem Pro 6 is listed for each molecule. At this time, due to uncertainties in the factors N_{mol} , θ , and ϵ appearing in eq 6, it is not realistic to calculate an

accurate estimate of V_{SAM} from theory. However, the measured V_{SAM} values do scale with the calculated $|\bar{p}|$ values and are in the range expected from the discussion found in section II.

The molecules that have a symmetric structure, XYL and TMXYL, give a small surface potential with respect to Au, while the nonsymmetric molecules showed significantly higher values. More significantly, benzyl mercaptan, which is equivalent to replacing one of the -CH₂SH groups of XYL with a hydrogen atom, yielded an average surface potential that is 240 mV with respect to gold. Similarly, replacement of one -CH₂SH of TMXYL with a -CH₃ group (PMBM) results in a large surface potential with respect to bare Au(111).

To understand these results, we must consider the structures of these molecules. Examination of their chemical structures suggests that the dipole moment of XYL and TMXYL should be small due to the symmetry in the molecule. Attachment of one sulfur atom to a Au(111) substrate evidently does not create a significant nonsymmetric charge distribution. The symmetry is significantly perturbed in the benzyl mercaptan SAM, and thus, a significant surface potential is observed when compared to XYL. Similar effects in the surface potential are observed when we compare the structure of TMXYL to that of PMBM (Figure 5).

These initial measurements suggest that the surface potential developed by the formation of a monolayer of molecules is dominated by the molecular structure and imply a weak influence from the charge transfer associated with the bonding to the Au surface. These initial measurements support the simple physical picture that the molecular structure affects the relative magnitude of the molecule's surface potential. Our results seem to fit two rather broad principles:

(1) The symmetric molecules produce a small potential shift with respect to bare Au as the net dipole arising from the S-Au bond cancels the dipole associated with the top H-S end group.

(2) There is relatively little charge that is transferred between the molecule and the Au substrate, at least for this class of molecules. An estimate of the net charge transferred can be obtained using eq 1. If we consider the net charge transferred to reside at the centroid of a 1 nm long molecule, there must be less than 0.01 electron transferred. This estimate assumes a typical dipole moment 0.1 D per molecule.

At this point, a better calculation including the Au-S bond and the packing density is needed before a more quantitative comparison can be made to our data. Preliminary results from more detailed calculations including bonding to Au do in fact show that the dipole moment of symmetric thiol molecules is not affected significantly by the attachment to a gold substrate.²⁵

C. Surface Potential Measurements of a Charge-Transfer Complex. The measurements discussed above relied on symmetry of molecular structure to control surface potential. Within this context, it is interesting to determine whether chemistry alone can be used to modify the surface potential of a SAM. For this reason, a CT complex was formed by reacting a strong electron acceptor such as TCNE with a SAM of TMXYL (an electron donor).²¹ In the complex, an acceptor molecule pulls a portion of an electron out of a donor molecule. This movement of charge hybridizes the energy levels of the molecular system and should produce a measurable change in the surface potential of the SAM. To study this system, the electro-

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Table 2. Values of V_{SAM} for the Charge-Transfer Complex TMXYL–TCNE on Au(111)^a

molecular designation	V_{SAM} (in mV)
TMXYL upright	20 ± 70
TMXYL–TCNE	-140 ± 25
TMXYL flat	30 ± 60

^a The solvent used in preparation of these SAMs was CH_2Cl_2 .

static surface potential was measured for samples of TMXYL, TMXYL–TCNE (charge-transfer complex), and TMXYL after removal of TCNE.

The electrostatic surface potentials for SAMs of TMXYL, TMXYL–TCNE, and TMXYL after TCNE removal are shown in Table 2. All measurements are referenced with respect to a Au(111) substrate.

The surface potential of TMXYL is close to that of Au(111). As mentioned earlier, this is probably due to the molecule's symmetric structure. However, in measurements of the TMXYL with the addition of TCNE, the resulting charge-transfer complex displays a different behavior. These measurements indicate that when TCNE reacts with TMXYL, the surface potential of the CT complex is negative with respect to bare Au by -140 ± 25 mV. This negative surface potential is the result of the accumulation of negative charge near the top of the charge-transfer complex. Since the TCNE is a strong π electron acceptor, a significant amount of electron density is withdrawn from the TMXYL molecule and redistributed in the TCNE portion of the complex. This picture is consistent with our experimental data. The data in Table 2 show that after the removal of TCNE, the surface potential of TMXYL returns to nearly the same value as before its reaction with TCNE. This fact further supports the complete removal of the TCNE after a prolonged exposure to a strong electron donor solution and is consistent with our RAIR data.

VI. Conclusions

A systematic study of the electrostatic surface potentials for a variety of SAMs has been performed using scanning probe techniques. The molecules chosen for study are aliphatic and aromatic thiol molecules forming a S–Au bond on Au(111). Since SPM techniques are employed, measurements of the surface potential with submicron resolution are possible.

Our data support the hypothesis that the electrostatic surface potential developed upon SAM formation scales with the intrinsic dipole moment of the molecule. By studying both molecules that are symmetric and those that are nonsymmetric, the surface potential can be adjusted from near zero (for the symmetric case) to a few hundred millivolts (the nonsymmetric case). By studying the surface potential of the charge-transfer complex TMXYL–TCNE, we have demonstrated that the sign of the surface potential can be altered in a manner consistent with the polarity of the transferred charge in the complex. This result further suggests that the control and adjustment of surface potentials above substrates is possible by SAM formation.

A quantitative comparison of our data to theoretical expectations must include a realistic model that accounts for the detailed bonding of the molecule to the Au(111) substrate as well as the packing density for the resulting SAM. Our data indicate that the details of this bonding for the case of a Au–S bond should not produce effects that overwhelm the contribution from the intrinsic dipole moment of the molecule.

In summary, a spatially resolved measurement of the surface potential produced by a SAM provides a simple and effective way to characterize the uniformity of SAM formation. A quantitative interpretation of these data should allow the development of realistic models of charge transfer at an interface. Furthermore, the ability to controllably adjust the electrostatic potential at a surface will have important implications for engineering in future electronic technologies relying on self-assembled molecules.

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