

# Structure and Bonding Issues at the Interface between Gold and Self-Assembled Conjugated Dithiol Monolayers

Weirong Jiang,<sup>†</sup> Nikolai Zhitenev,<sup>\*,‡</sup> Zhenan Bao,<sup>‡,§</sup> Hong Meng,<sup>||</sup>  
David Abusch-Magder,<sup>‡</sup> Don Tennant,<sup>‡</sup> and Eric Garfunkel<sup>†</sup>

Department of Chemistry and Chemical Biology, Rutgers, the State University of New Jersey, Piscataway, New Jersey 08854, Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974, Department of Chemical Engineering, Stanford University, Stanford, California 94305, and Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095

Received October 18, 2004. In Final Form: March 28, 2005

Organic thiols have received extensive attention recently because of their relative stability and ease of examination compared to other potential molecular electronic materials. In this work, scanning probe microscopy (SPM) is used to study (i) the structural properties of self-assembled monolayers (SAMs) containing conjugated dithiols and (ii) the formation of the upper molecule–metal interface on dithiol SAMs. The top gold film is deposited either by thermal evaporation or by nano-transfer printing (nTP). Generally, the utility of thermal evaporation is limited because of Au diffusion through the SAMs. However, several dithiol SAMs are identified in this work that bond well to Au overlayers and act as satisfactory diffusion barriers. Coassembly of conjugated dithiols and alkanemonthiols is suggested as a route to obtain dithiols that are denser packed and more vertical (than is obtained from pure dithiol routes). High-yield nTP is demonstrated on coassembled SAMs. Advantages and limitations of different Au deposition and transfer techniques are compared on a variety of length scales.

## Introduction

A central concept underlying current research in molecular electronics is to explore the possibility of substituting inorganic materials with organic molecules in the core regions of devices. Aliphatic and aromatic organic compounds with thiol end groups have received attention because of their relative stability in air and the ease of monolayer preparation from the solution phase. These classes of molecules are expected to span a broad range of interesting charge transport regimes ranging from insulators (alkane) to conducting molecular wires (aromatic). The most studied molecules are alkanethiols, which form well-ordered monolayers on some metal and semiconductor surfaces. These layers, usually called self-assembled monolayers (SAMs), have been studied with scanning probe microscopy, diffraction, and other methods.<sup>1–8</sup> Aromatic thiols, on the other hand, rarely display ordered overlayers.<sup>11,12</sup> Additionally, most poten-

tial devices require connecting both ends of a molecule (or molecular film) to electrodes. If sulfur is the chemical linker species, one would likely need a dithiol molecule to enable attachment of each end of the molecule to the corresponding electrodes. Dithiols are more difficult to handle experimentally than monothiols. High-resolution electron energy loss spectroscopy (HREELS), IR, X-ray absorption spectroscopy (XAS), and X-ray photoelectron spectroscopy (XPS)<sup>9–12</sup> have been used to study the structure of dithiol monolayers. HREELS studies show (by vibrational peak analysis) that alkanedithiol monolayers are not very well ordered, as is also confirmed by scanning tunneling microscopy (STM) experiments. Conjugated dithiol monolayers showed even less ordered structures. Common reported problems are formation of multilayers at surface (XPS), large tilt angles (IR and XPS), and absence of order (angle-resolved near-edge X-ray absorption fine structure, NEXAFS).

Transport properties of molecular devices are partially determined by microscopic configurations of all constituents. The formation and the properties of chemical bonds at the metal–molecule interface is one of the least understood and controlled issues in molecular electronics. Recent results<sup>13,14</sup> have given reasonable evidence that contacts and molecular–metal interfaces often do regulate overall conductance. Theoretical work has been performed on some of these systems both to understand the most likely interface bonding configurations and to simulate charge transport through the structures. Experimental

\* Corresponding author: e-mail zhitenev@lucent.com.

<sup>†</sup> Rutgers.

<sup>‡</sup> Lucent Technologies.

<sup>§</sup> Stanford.

<sup>||</sup> UCLA.

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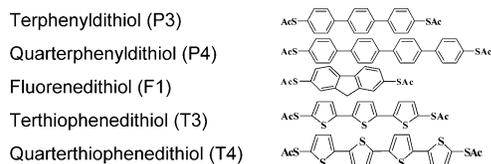
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**Figure 1.** Schematic structures of conjugated molecules studied in this paper.

studies of interface formation range from single-molecule experiments<sup>13,14</sup> to surface-averaged techniques.<sup>9,15,16</sup>

The present paper addresses two issues central for molecular electronics based on SAMs that have received only limited coverage before. First, we study the assembly of well-ordered monolayers containing aromatic dithiols. Little microscopic characterization has been performed on dithiols and even less in the case of conjugated dithiols. A small number of conjugated thiols can be introduced into alkane SAMs by substitution<sup>17</sup> reactions. The method used here is the assembly of conjugated dithiols in the presence of alkanemonthiols. Second, we study the formation of interfaces between SAMs (of either pure conjugated dithiols or mixtures of conjugated dithiols and alkanemonthiols) and Au contacts at different length scales. Au is deposited on top of the SAM by either thermal evaporation or nano-transfer printing (nTP). The two metal delivery techniques yield different microscopic topography at the metal–molecule interface. For metal evaporation, the metal topography at the top interface depends on the probability of bonding (sticking), and the relative rates of surface mobility, surface nucleation, and diffusion into the SAM. The pattern of Au clusters at the top surface/interface is a characteristic determined primarily by the nature of the SAM and can be used as a method to help identify organic film structure when molecular order cannot be resolved by scanning probe microscopy (SPM) or other methods. In the case of nTP, the topography of the Au at the top Au–SAM interface is the same for different dithiol SAMs. The quality of nTP is studied for different sizes of Au contacts, from the macroscopic scale down to a single Au grain ( $\sim 20$  nm).

### Experimental Section

Four dithiol molecules, fluorenedithiol (F1), terphenyldithiol (P3), terthiophenedithiol (T3), and quarterthiophenedithiol (T4), as shown in Figure 1, were synthesized by previously described methods.<sup>9</sup> Two types of monolayers were studied: pure dithiol monolayers and mixed monolayers consisting of a dithiol and an alkanemonthiol. The organics were deposited on atomically flat Au substrates (for STM measurements) and GaAs substrates (for nTP experiments). The main reason that motivated our use of GaAs as a substrate for the nTP studies was that Au separates from mica in the “Scotch tape test”. GaAs is flat over a large range, and past work show high-quality monolayers. Our results to date imply that the local bonding behavior of the upper (organic/Au) interface is similar on both Au and GaAs substrates. Atomically flat Au films [of predominantly (111) orientation] on mica substrates were purchased from Molecular Imaging, Inc. GaAs wafers were etched in concentrated  $\text{NH}_4\text{OH}$  solutions for 3 min to remove the oxide before deposition of the organic monolayers. GaAs and Au substrates were soaked in a tetrahydrofuran (THF) solution of the thiol (about 0.01 mM) with a few drops of 37% aqueous solution of ammonium hydroxide at room temperature for 24 h and then rinsed with THF, toluene,

and 2-propanol. Finally a thin layer of Au (nominal thickness of  $\sim 1$  nm) was thermally evaporated onto the SAMs at room temperature at a  $45^\circ$  incidence angle (deposition rate  $\sim 0.01$  nm/s). The STM and AFM studies were performed with a JEOL JSPM 4210. The STM measurements were performed with fresh mechanically cut Pt/Ir tips, with typical settings of  $\sim 1$  V bias and  $\sim 10$  pA tunneling current.

The nano-transfer printing technique used here was previously reported by Loo et al.<sup>18</sup> Both continuous Au films and Au patterned into nanoscale dots were used. For continuous Au films, flat unpatterned Si surfaces were used as a master. The master dot pattern was defined in a poly(methylmethacrylate) (PMMA) bilayer (50 nm thick film made from 50K PMMA in anisole/50 nm thick film made from 950K PMMA in xylene) on top of a Si surface by electron beam lithography (Figure 4). The purpose of such a bilayer is to define a minimal ( $\sim 10$  nm) but consistent undercut in the side walls of the stamp profile. About 10 nm of Au was deposited onto a polydimethylsiloxane (PDMS) stamp replicated from the master. The undercut ensures isolation of Au films accumulated on the protruding features of the stamp, well separated from Au deposited on the lower layers. A larger undercut hinders the replication of the PDMS stamp and is undesirable. The (patterned) Au film is imprinted onto the thiol-terminated molecular monolayer previously prepared on Au/GaAs. After printing, we confirmed Au overlayer transfer by SPM. A “Scotch tape” adhesion test was then used to estimate the relative bonding strengths between the top continuous Au layer and various dithiol monolayers. Contact-mode AFM was used to estimate the bonding strength between the top Au nano dots and various dithiol monolayers. Below we present typical SPM and nTP results and summarize other work. All experiments were performed multiple times for reproducibility.

### Results and Discussion

Monothiol-based monolayers on atomically flat Au substrates have been widely studied with STM and other techniques. Alkanes and some other monolayers exhibit close-packed, well-ordered structures.<sup>2</sup> On the other hand, scanning probe microscopic studies of dithiol monolayers have been scarce. We found that STM images of dithiol monolayers have inferior quality and lower resolution than those of monothiol monolayers and are often streaky at room temperature. The streakiness may be caused by the interaction between the sulfur (at the end of a non-rigid molecule) and the STM tip. At lower temperatures ( $< 250$  K) the quality of images improves slightly. STM images show a relatively flat surface but no ordered structures.

As an initial step in the microscopic characterization of interfaces between the SAMs and top metal contacts, we used SPM to examine thin Au films thermally evaporated onto the SAMs. While the details of the interfaces may be different for thin and thick metal films, useful information about the granularity, quality of chemical bonds, and metal atom diffusion through the SAM can be inferred from SPM images. Figure 2 shows STM images of Au deposited on various dithiol monolayers. Characteristic granular patterns are seen in all images with different cluster densities and heights. The image of the P3 monolayer uniformly covered by small clusters has the smallest roughness. Two distinct types of clusters are present in the F1 SAM image, while images of T3 and T4 monolayers with evaporated Au show bigger islands.

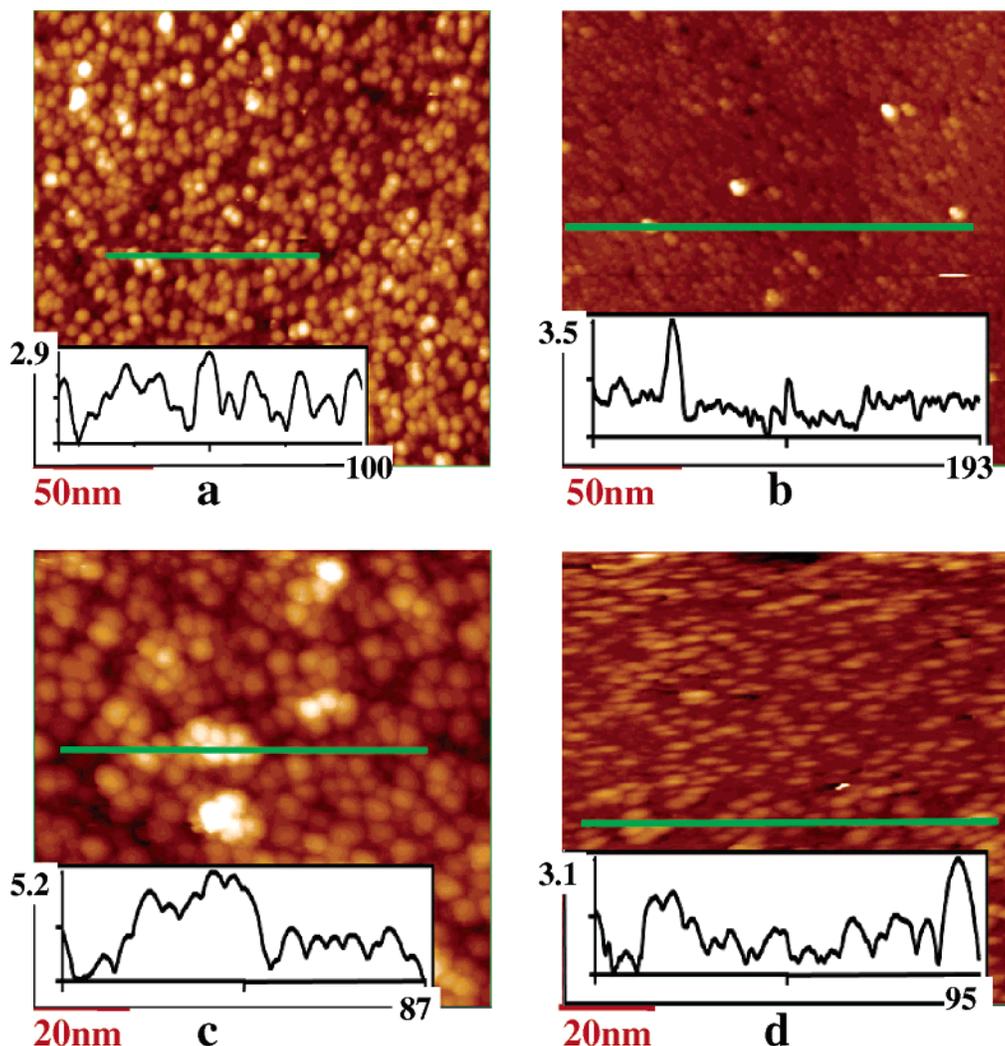
Quantitative interpretation of topographic STM images can be rather complicated.<sup>3,6</sup> The image represents a surface of constant tunneling current and is determined by both the topography and the effective local conductance. Variations of the local conductance caused by differences in bonding, or by the presence of dopants or impurities in

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**Figure 2.** STM images of pure dithiol monolayers with  $\sim 1$  nm Au thermally evaporated on SAMs. Two characteristic types of clusters can be seen: type A are flat clusters one or two Au layers thick; type B clusters are bigger and have rounded shape. (a) T4, B-type Au clusters dominated; (b) P3, A-type Au clusters dominated; (c) T3, B-type Au clusters dominated; (d) F1, mix of A- and B-type clusters. Length and height units are nanometers.

monolayers, can affect the apparent height of clusters and molecules.<sup>19–21</sup> For example, Au clusters residing on top of the monolayer with good chemical bonds might appear taller than poorly bonded neighboring islands of similar physical “height”. Additionally, vapor-deposited Au can diffuse through monolayers of alkanes and some conjugated thiols,<sup>22</sup> forming islands (usually flat two-dimensional) below the layers. By comparatively studying Au deposition on conjugated dithiols and on mixed alkanethiol/dithiol monolayers, we observed systematic changes of the cluster patterns and identify some key characteristics of these interfaces.

The motivation to study the mixed layers is 2-fold: (i) to observe isolated individual dithiol molecules in an “inert” monothiol matrix<sup>19,20</sup> and (ii) to help generate ordered and oriented dithiol films (with the monothiol as a seed and orienting layer to be partially displaced by

dithiols). Previous studies have addressed mostly substitutions of conjugated dithiols and alkanedithiols into alkane SAMs.<sup>19,20</sup> This useful technique has been used to introduce a small number of molecules into the alkane matrix for the first reason noted above, incorporated mostly around defects of the molecular lattice. It is not clear whether the substitution of a small percentage of molecules will display different electrical behavior than pure films in SAM-based devices. Here, we assemble alkanemonothiols simultaneously with conjugated dithiols.

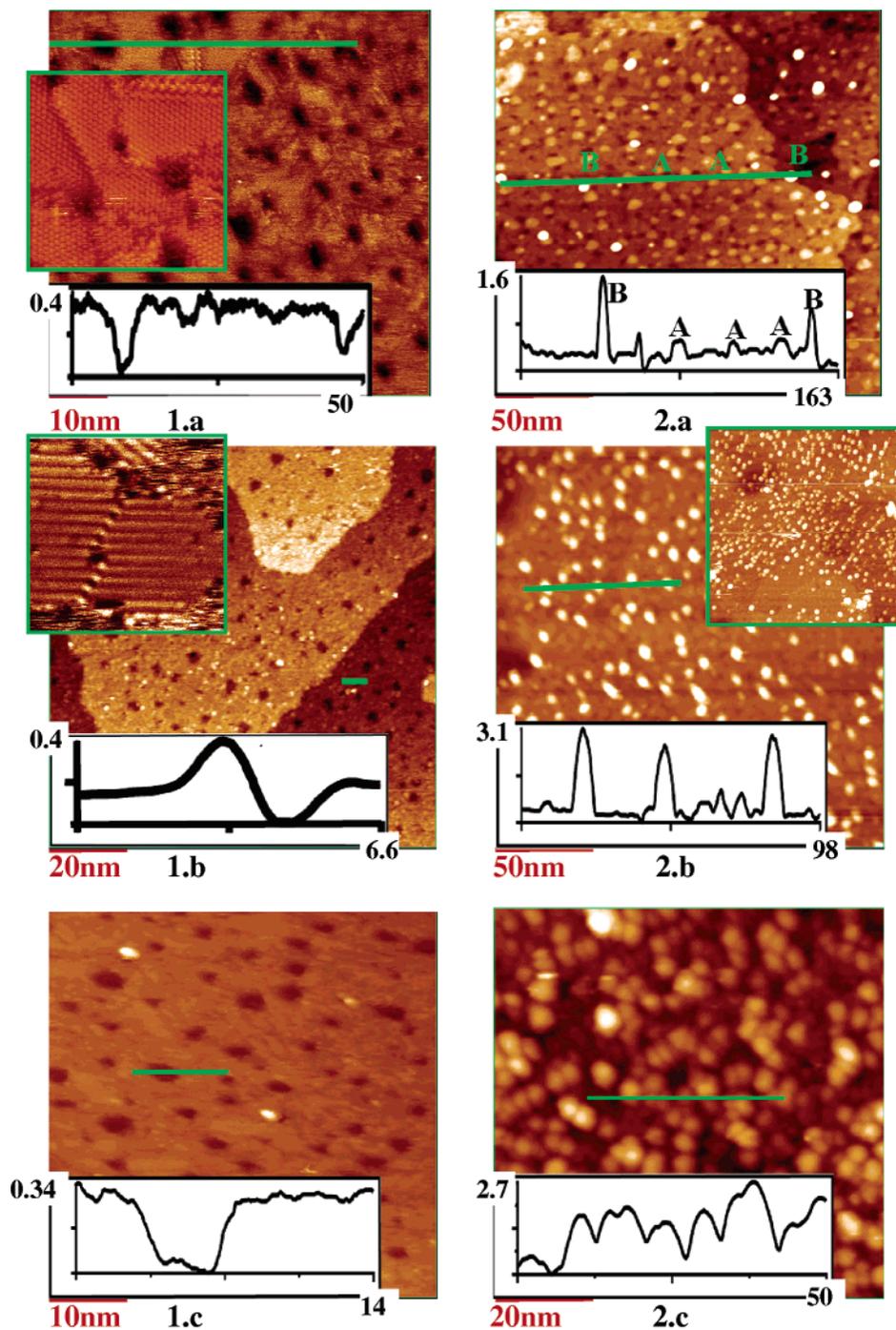
Au substrates were soaked in THF solutions containing a certain ratio of monothiol and conjugated dithiol molecules for 24 h. The starting concentration ratio of monothiols to various conjugated dithiols was 10:1. However, STM images appeared to be of low quality for some dithiol molecules, resembling those of pure dithiol SAMs. The concentration of these dithiol solutions was reduced until stable STM images were obtained. Figure 3 shows STM images of (column 1) mixed octanethiol (C8) and various conjugated dithiols and (column 2) the same mixed SAM films with thermally evaporated Au on top of mixed SAMs. The ratio of C8 to F1 (top panels) in the THF solution is 10:1, the ratio of C8 to T3 (middle panels) is

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**Figure 3.** STM images of monolayers of mixed dithiol and octanethiol molecules before (column 1) and after (column 2) thermal evaporation of  $\sim 1$  nm Au. (a, top panels) C8:F1 = 10:1; inset in panel 1a is the zoom-in of monolayer lattice, which is identical to pure octanemonothiol lattice. (b, middle panels) C8:T3 = 20:1; inset in panel 1b (30 by 30 nm) is the zoom-in of monolayer lattice, which shows ordered structures different than alkane matrix; inset in panel 2b (300 by 300 nm) shows Au dots pattern at different surface area of same sample, which shows linear ordering related to the orientation of mixed lattice. (c, bottom panels) C8:T4 = 100:1; STM image shows no ordered molecular lattice.

20:1, and the ratio of C8 to T4 (bottom panels) is 100:1. In all solutions, the concentration of C8 was 1 mM.

The coassembled mixed SAMs show much flatter surfaces and better morphology than pure dithiol SAMs. Three different types of assembly can be identified: random incorporation of dithiol molecules into a matrix of monothiols (Figure 3.1a), mixed assembly with ordered structures that are different from the monothiol matrix (Figure 3.1b), and assembly of predominantly conjugated dithiols (Figure 3.1c).

The prominent features seen in Figure 3.1a,b are dark areas typically observed during the assembly of al-

kanemonothiols on Au. These are monatomic depressions in the substrate Au surface induced by the process of self-assembly. The areal density of surface/interface Au changes with thiol adsorption and the diffusion is such that voids or protrusions result. In addition, rare bright dots are seen over the images that can be interpreted as dithiol molecules.<sup>19,20</sup> Conjugated dithiol molecules are expected to be more conductive than alkanemonothiols, and thus an equivalently sized dithiol molecule should appear taller in the STM images. The concentration of bright dots is higher in Figure 3.1b than in 3.1a, suggestive of a higher percentage of dithiol incorporation. Different

molecular order is observed for these two SAMs. The ordered structure seen in the inset to Figure 3.1a is typical for an alkane matrix, while the ordering seen in Figure 3.1b is substantially different. We believe that this is a mixed lattice consisting of both conjugated and alkane molecules.

In Figure 3.2a, there are two classes of features on the surface: A-type monatomic height clusters and B-type bigger ones. Most of the surface area is covered by the monatomic height clusters. These clusters are created by Au atoms penetrating through C8 SAMs as established in previous works.<sup>23</sup> B-type clusters have not been detected for Au films evaporated on alkanemonothiols. They are unique for the mixed monolayers and are related to the presence of conjugated dithiols. If exposed at the surface, the second S atom of dithiols can react with Au deposited on the surface and work as a nucleation center for the formation of bigger clusters. Two similar types of clusters are also seen in Figure 3.2b. Consistent with the assumption of higher dithiol percentage and Au nucleation around exposed sulfur atoms, there are more B-type clusters in Figure 3.2b (T3/C8) than in Figure 3.2a (F1/C8). The A-type clusters in Figure 3.2b are also formed underneath the SAM by the penetrating Au atoms. They display slightly different, more rounded surface features than in Figure 3.1b. The shape is possibly affected since the clusters are formed under the mixed molecular lattice.

Two types of clusters are also observed on pure dithiol SAMs (see Figure 2). Both type A and type B clusters are present in Figure 2d. Other SAMs display patterns with either cluster A (Figure 2b) or B (Figure 2a,c) dominating. Type A clusters are distinctly flat with a thickness of 1–2 Au layers. We suggest that this feature is formed if Au diffuses through SAMs. The nucleation and growth of lower interface features are mostly determined by the interaction of incoming Au with the Au substrate and are only slightly affected by the interaction of Au with the SAM. Type B clusters likely rest on top of the SAM. The rounded shape of the taller B-type clusters is typical for Au island nucleation on many other surfaces. Other experimental results are consistent with these assignments. In the case of alkanethiols, the molecular lattice is often seen on top of A-type clusters.<sup>23</sup> While no molecular lattice can be observed on top of type A clusters for dithiol molecules, the increased noise characteristic of STM imaging of exposed S bonds is detected in the corresponding areas, suggesting that the molecules reside on top of the A clusters. On the other hand, there are groups of a few neighboring type B clusters often appearing taller in the images (Figure 2a). This can be accounted for if these clusters are electrically connected within the group but isolated from other neighboring clusters. This is possible only if B-type clusters are residing on top of the SAM.

For the mixed T4 + C8 monolayer (Figure 3.1c), we observe no bright inclusions in the STM image. The T4 molecule is about 5 Å longer than T3 and C8, and it is likely to be internally more conductive than C8. No molecular order is seen for T4 films. It is likely that the sample surface is covered by an almost pure monolayer of either C8 or T4. Figure 3.2c is an image of the surface after Au is deposited onto a monolayer prepared in a solution with a 100:1 ratio of C8 and T4. This image is very similar to the image of Au deposited onto a pure T4 monolayer (Figure 2a). This observation, combined with the nTP result discussed later, implies that Figure 3.1c is an image of almost pure T4.

**Table 1. Efficiency of Au Transfer to Organic Monolayers for Different Molecules<sup>a</sup> and Qualitative Adhesion Strength<sup>b</sup>**

	C8	C8th	P3	P4	T3	T4
SAM						
% transfer	0	>90	10	<10	~50	>90
adhesion test		+	–	–	–	+
Mixed SAM						
	C8th/C8		P4/C8	T3/C8	T4/C8	
% transfer		>90	>90	>90	>90	>90
adhesion test		–	–	–	–	+

<sup>a</sup> By printing. <sup>b</sup> By scotch tape test.

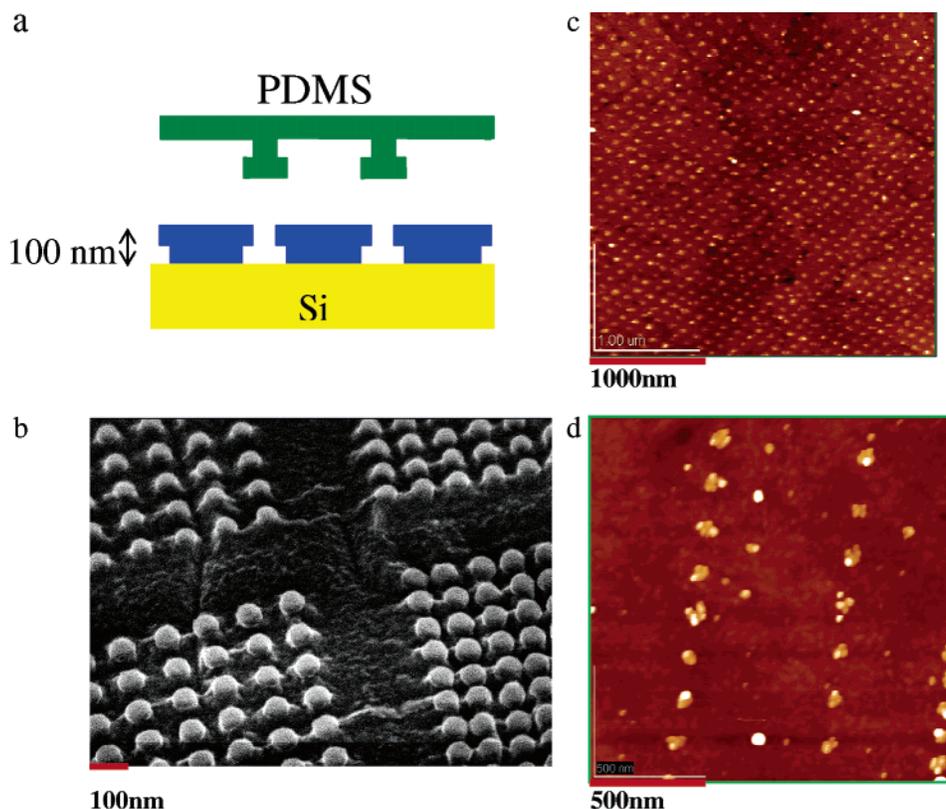
The interface pattern created during evaporation of Au is specific for every monolayer. In contrast, nano-transfer printing allows a comparison of interfaces with similar metal topography. Au was evaporated onto a PDMS film and the Au was then brought into contact with different SAMs. The interface properties (interaction strength, flatness, etc.) between the printed Au overlayer and the various dithiol monolayers were examined by the efficiency of Au transfer to the SAM (measuring the fractional amount transferred) and the bonding strength (from the Scotch tape adhesion test). Both continuous Au films and nanosized patterned dot transfer were examined. The results of continuous Au film printing are shown in Table 1.

There is essentially no transfer between stamp and organic films for (saturated hydrocarbon) monothiols. For dithiol molecules, the films prepared from pure alkanedithiol or pure T4 show a high efficiency of transfer (>90% area was transferred). Both overlayers also survived the adhesion test, implying good coverage, and large areas of contact. On the other hand, P3, P4, and T3 showed lower transfer efficiency and bond strength. There are at least two possible reasons that might be responsible for the low transfer efficiency of P3, P4, and T3: (i) poor SAM structure with only a small percentage of exposed S atoms that can interact with Au or (ii) poor S–Au bonding strength.

The same experiments performed on mixed SAMs demonstrate high transfer efficiency, although only the T4/C8 mixed film survived the adhesion test. This implies that higher orientational ordering (as occurs in very few pure dithiol systems but more often in the monothiol/dithiol mixtures) indeed improves the efficiency of nTP. Mixed monolayers improve the flatness of the monolayer and, therefore, the probability that the top thiol groups can interact with the Au atoms in the film. On the other hand, this may be showing us that most pure dithiol monolayers have very poor structural quality. These experiments also provide further evidence that for the sample prepared in a 1:100 T4/C8 mixture solution we obtain almost pure T4 monolayers because Au nTP transfer cannot succeed on a pure octanemonothiol film.

The nTP of nanosize patterned dots shows high transfer efficiency for all SAMs with dithiols. As an example, the transfer of dots to P3 SAMs displaying the lowest yield for the continuous film is shown in Figure 4c. However, there is a noticeable difference in the adhesion, consistent with the results of a continuous film. The imprinted dots on different SAMs show different resistance to AFM contact scanning. The dots imprinted on T4 are the most stable, while the dots on other SAMs can be removed by the AFM tip at the same load (~10 nN). Figure 4d shows that the smallest imprinted dots consist (based on size) of a few Au grains. Typically the Au overlayer surface topography is rather coarse in comparison with the flatness

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**Figure 4.** (a) Diagram of double-layer PMMA master; (b) SEM image of PDMS stamp made from double-layer PMMA master; (c) patterned dots transferred onto P3 SAM with double-layer PMMA master; (d) printed Au dots show only one or a few Au grains.

of the substrate Au, even with SAMs present. It is likely that there is a low density of chemical bonds formed at the top interface between the SAM and the imprinted dots.

The present results demonstrate a possible route to achieve higher structural order of monolayers with a high concentration of conjugated dithiols. Pure dithiol monolayers do not display a regular molecular arrangement in STM experiments. The absence of distinct order hinders unambiguous identification of the preferable molecular packing. Competing herringbone and p-p stacking<sup>24–26</sup> and different configurations of the Au–S bond<sup>27</sup> have been proposed to account for the high disorder. Contact angle, ellipsometry, and grazing angle Fourier transform infrared spectroscopy (FTIR)<sup>9</sup> performed for conjugated dithiols used in the present study proved high packing and nearly vertical averaged orientation of the molecules in SAMs. A high density of exposed sulfur at the SAM top surface might thus be expected. However, the quality of nTP is generally low for pure dithiol SAMs. This can be explained by high disorder in the orientation of the terminal S group. This disorder could result in less S–Au bonding per unit area and thus reduced averaged bonding strength to the Au film.

nTP works significantly better for mixed films with large dithiol concentrations. The average density of exposed S is smaller in this case compared to the pure dithiol SAMs, but a higher degree of orientational order of S apparently

is highly beneficial for bond formation. The high structural order is clearly visible in insets to Figure 3.1a,b.

To rationalize the distinct behavior of different dithiol molecules in our experiments, we suggest that the interactions between neighboring molecules in the layers are critically important and differ strongly depending on the molecular type. A qualitative sequence of the interaction strength consistent with our data is T4 > T3 > (C8 ~ P3 ~ F1). The interaction strength is directly related to the degree of overlap of molecular orbitals. This interaction can partly control both the rate of molecular assembly from solution and the diffusion of metal atoms through the layers. It should be noted that the oxidation potentials determined for T4, T3, F1, and P3 (0.81, 0.98, 1.33, and 1.35 V, respectively) follow the same sequence.<sup>9</sup>

The degree of diffusion of evaporated Au through the underlying molecular layer is quite different for the SAMs studied here. In the case of T3 and T4 SAMs, most of the Au is trapped at the top interface. This suggests a denser packing compared to well-ordered alkanes and other dithiol SAMs and a high density of exposed S bonds at the top interface acting as nucleation centers. The density of exposed S is also related to the yield of the nTP. Indeed, the results of nTP are the most successful on T4 SAMs, confirming the high percentage of available bonding sites.

The suggested higher interaction of T4 relative to other conjugated dithiols is displayed also in the results of the coassembly experiments. During the assembly from the mixed solution, conjugated dithiols compete with the larger number of alkanemonthiols for positions on the surface. The ratio between alkanes and conjugated molecules in the SAM is quite different from the initial ratio in the solution. The extreme example is the coassembly of T4/C8 (1:100) resulting in assembly of almost pure T4

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SAMs. The rate of molecular inclusion of T4 in the layers is much faster than the C8 rate, apparently being dominated by the strong interaction between neighboring T4 molecules. Similarly, the fact that there are more T3 species on the surface than F1, despite the fact that the ratio of T3 to C8 in solution (1:20) is 2 times smaller than the ratio of F1 to C8 (1:10) in solution, implies that T3 has a higher probability to be incorporated in the SAM than F1.

A possible alternative model phenomenologically accounting for the differences in molecule–Au interface formation, Au diffusion through the SAMs, nTP yield, and assembly rate can be related to different thiol reactivity. Although a previous theoretical study has implicitly assumed that dithiols have similar S–Au bonding strengths, the sensitivity to exact local bonding configurations (as discussed in the literature)<sup>27,28</sup> implies that different packing (angle, density, etc.) may result in quite different bond strengths.

To summarize, we have studied the formation of Au interfaces on top of different SAMs with a high percentage of conjugated dithiol molecules. The study clearly demonstrates the opportunities and limitations of known techniques used for contacting molecular layers. Two techniques of Au deposition are presented. The first one is thermal evaporation of Au. The SAMs assembled from T3 and T4 are satisfactory diffusion barriers for the top Au

contact made by evaporation. Almost all Au is stopped at the top interface. Favorable factors blocking Au indiffusion are the large numbers of exposed S sites acting as nucleation centers and strong interactions between neighboring molecules within the SAM. Evaporated Au easily penetrates through SAMs assembled from other dithiols and through mixed SAMs with a large percentage of alkanethiols. The technique of nano-transfer printing can be applied to a broader range of SAMs. A small percentage of exposed S sites suffices to satisfactorily accept patterned metal on top of the SAM. The yield of the technique is higher with flatter and better-ordered SAMs. Better structural quality of the SAMs is achieved by the coassembly of conjugated dithiols and alkanethiols. However, both techniques are limited in the atomic quality of the interfaces. Evaporated Au forms granular interfaces with the characteristic grain size  $\sim 5$ –10 nm. It is likely that just a few chemical bonds per grain are formed. In thicker films, the bonds also could be highly stressed once the clusters merge, affecting the electronic properties of molecular devices. Metal contacts patterned by nTP demonstrate granular structure determined by Au growth on the stamps. The metal surface is not expected to conform to the SAM on the microscopic scale. Additionally, the granularity limits the precision of the patterns that can be defined on top of the SAM.

**Acknowledgment.** We thank the NJCST, the SRC, and the NSF for support; Yueh-Lin Loo and J. Zaumseil for helping on nTP; and Y. Chabal, B. De Boer, and M. Frank for useful discussions.

LA0474316

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