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Distance Dependence of Electron Tunneling through Self-Assembled Monolayers Measured by Conducting Probe Atomic Force Microscopy: Unsaturated versus Saturated Molecular Junctions

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Electron tunneling through self-assembled monolayers (SAMs) composed of either unsaturated or saturated molecules was investigated using conducting probe atomic force microscopy (CP-AFM). SAMs of unsaturated oligophenylene thiolates or saturated alkanethiolates were assembled on Au substrates and contacted with a Au-coated AFM tip at constant applied load. The current–voltage (I–V) characteristics of both types of SAMs were linear over ± 0.3 V. Resistance (R) increased exponentially with molecular length (s) in both cases according to the expected relationship, $R = R_0 \exp(\beta s)$, but the rate of increase, as quantified by the structure-dependent factor β, was much less for the unsaturated SAMs than for the saturated alkanethiolate SAMs. Average β values were 0.42 ± 0.07 Å^{-1} for the oligophenylene thiolate SAMs and 0.94 ± 0.06 Å^{-1} for the alkanethiolate SAMs. Extrapolation of semilog plots of resistance versus molecular length to zero length yielded an estimate of the metal–molecule contact resistance, which was 10^4 Ω for a 50 nm radius Au-coated tip in contact with either the oligophenylene thiolates or alkanethiolates. This study establishes that CP-AFM can be used to probe transport in molecular junctions as a function of molecular dimensions and structure.

Understanding electron tunneling through thin molecular films is an important component of the fundamental science supporting molecular electronics. As early as the 1960s, Lambe and Jaklevic examined the current–voltage (I–V) characteristics of junctions formed by sandwiching a thin evaporated molecular layer between an oxide-covered Al electrode and another metal, for example, Au, Al, or Pb.[1] In another pioneering study, Mann and Kuhn fabricated tunnel junctions from multilayered Lang-muir–Blodgett films of fatty acids and showed that the junction conductance decreased exponentially with the number of layers.[2] Sagiv and Polymeropoulos followed up this work with a study of tunneling through single monolayers of fatty acids and perfluorinated fatty acids adsorbed on oxidized aluminum.[3] Renewed interest in the properties of tunnel junctions based on molecular films and individual molecules is motivated by possible applications of these junctions in molecule-based electronics.[4] Recently, researchers have demonstrated that metal–molecule–metal junctions formed by either Langmuir–Blodgett[5] or self-assembly techniques[6] can display useful electrical behavior such as rectification,[5d] negative differential resistance,[6a] and electrochemical switching.[5a,c]

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CHART 1: Scheme of the Conducting Probe Atomic Force Microscopy Experiment[a]
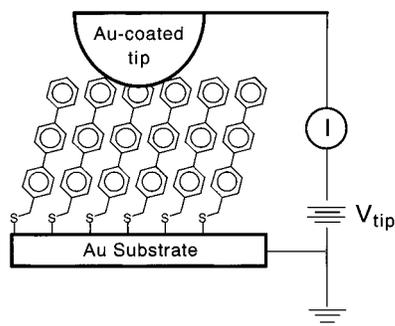
[a] A metal−molecule−metal junction is formed by contacting a Au-supported self-assembled monolayer (SAM) with a Au-coated AFM tip. Voltages are applied to the tip; the substrate is kept at ground. Measurements are performed in air. Tip is not to scale.

Although interesting *I−V* characteristics for specific junctions have been identified, understanding of the full spectrum of factors influencing the electrical properties of metal−molecule−metal junctions remains an important goal.[7] Specific transport mechanisms are unclear, particularly when redox groups are present in the junction, and the electrical contact between molecules and metal electrodes is poorly understood. Currently, it is not possible to calculate the *I−V* characteristic for a given metal−molecule−metal junction a priori.[8]

Examining the dependence of the junction resistance (or conductance) on molecular length is one approach to examining mechanisms of transport. For example, in the case of coherent, nonresonant tunneling, the prediction is that the junction resistance, *R*, will scale exponentially with separation between the contacts:[7e]

$$R = R_0 \exp(\beta s) \qquad (1)$$

where *s* is the interelectrode separation defined by the molecular length, β is a structure-dependent factor that depends on bonding and functional group patterns in the molecules, and R_0 is an effective contact resistance. Other length dependencies of resistance are possible, corresponding to alternative transport mechanisms; for example, resistance is expected to scale linearly with electrode separation in the case of diffusive transport. There are few reports on the distance dependence of electron transport within metal−molecule−metal junctions,[9] though the distance dependence of electron transfer in soluble molecular systems, such as proteins[10] and donor−bridge−acceptor compounds,[11] has been studied extensively.

In this letter, we report a comparison of the distance dependence of electron tunneling in metal−molecule−metal junctions based on self-assembled monolayers (SAMs) of saturated and unsaturated molecules. To form the junctions, we have developed a conducting probe atomic force microscopy (CP-AFM) approach, Chart 1.[12,13] Au-coated AFM tips were used to contact SAMs formed by adsorption of oligophenylene derivatives **I−III** or alkanethiols ($CH_3(CH_2)_nSH$, $1 \le n \le 7$) to
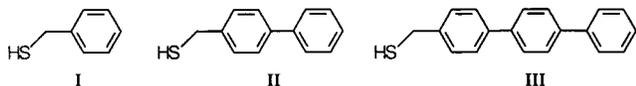
Au.[14] Current through the SAMs was recorded as a function of applied tip voltage. The salient features of this method are as follows: (1) the junctions are easy to assemble; (2) the contact areas are small (on the order of 10 nm^2) so that as few as 100
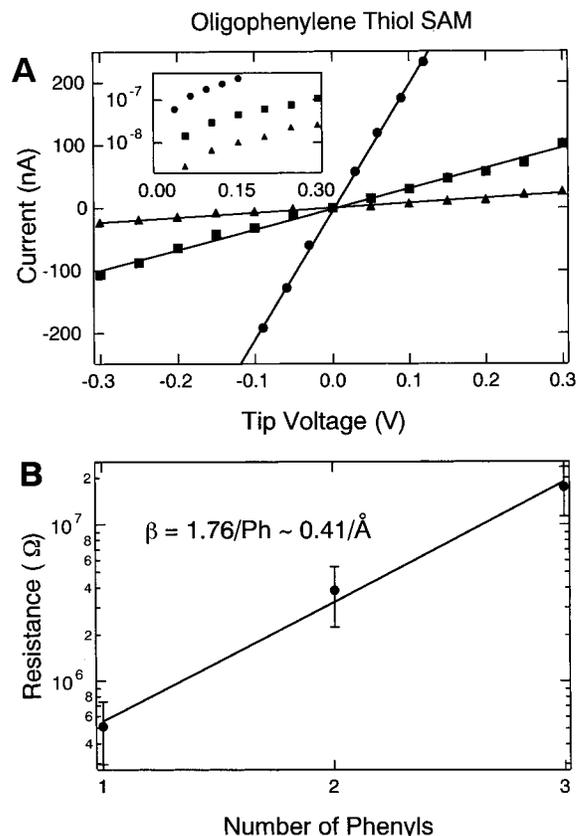

Figure 1. (A) Current versus tip voltage between ±0.3 V for SAMs of **I** (●), **II** (■), and **III** (▲). Straight lines are fits to the data. Inset shows a semilog plot. Panel B shows a semilog plot of average resistance versus number of phenyl groups in SAMs of **I−III**. Resistances were determined from the slopes of linear fits to the *I−V* characteristics as shown in panel A. Average resistance was determined for five separate *I−V* measurements for each SAM. The error bars represent the standard deviations. The solid line is a linear fit, yielding a β value of 1.76 per phenyl, or 0.41 Å^{-1}.

molecules compose the junction.[12a] Previously, we have shown that conducting probes make reproducible electrical contacts to alkanethiolate SAMs, and we have used CP-AFM to measure the distance dependence of electron tunneling through alkane-thiolate SAMs.[12] Here, we have extended the method to SAMs of conjugated molecules **I−III**, demonstrating the generality of the CP-AFM approach for the formation and characterization of metal−molecule−metal junctions involving different classes of molecules.

Figure 1A shows typical *I−V* characteristics between ±0.3 V for a Au-coated tip in contact with SAMs of **I−III**. The *I−V* traces were acquired with the *same tip* at an applied load of 2 nN. The traces are linear over the sweep range. Importantly, a semilog plot of the junction resistance (taken as the reciprocal of the slope of each *I−V* trace in 1A) versus molecular length (number of phenyl groups) is linear, Figure 1B. Each point in the Figure 1B plot represents the average of five measurements taken on the same sample; the error bars are the standard deviation. The linear dependence in Figure 1B is consistent with coherent, nonresonant electron tunneling across the junction. The fit yields a β value of 1.76 per phenyl group or 0.41 Å^{-1}, assuming a through-bond mechanism.[15,16]

We have carried out this measurement two additional times using two different tips and have obtained β values of 0.50 and 0.35 Å^{-1} in those separate experiments. Figure 2A shows resistance versus molecular length for all three sets of data. The cause of the variation between experiments is not clear at this
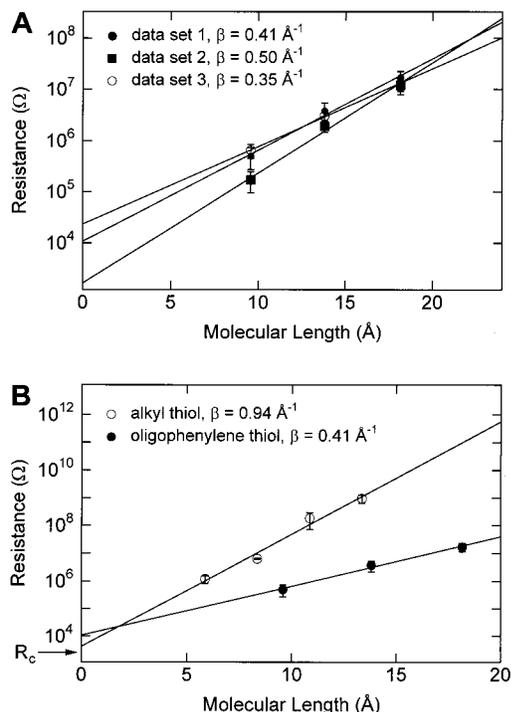
Figure 2. (A) Semilog plot of resistance versus molecular length for junctions based on molecules **I**−**III**. Data are shown for 3 different trials. A different Au-coated tip was used for each trial. The lines are best fits. Panel B shows a semilog plot of average resistance versus molecular length for junctions based on oligophenylene thiolates (●) and alkanethiolates (○). Determination of molecular lengths is described in refs 16 and 18. The lines are best fits yielding β values of 0.41 Å^{-1} and 0.94 Å^{-1} as shown. For both lines, the zero-length intercept is the effective contact resistance, R_0. The data for the oligophenylene thiolates in panel B are also shown in panel A.

time; we speculate that it is due to differences in tip radii leading to different areas of contact and different extents of SAM compression for the same nominal load. It may also reflect local variations in the structures of the SAMs.

The average β value from the three data sets is 0.42 ± 0.07 Å^{-1}. This is somewhat lower than the value (0.67 ± 0.1 Å^{-1}) obtained by Rampi and Whitesides using Hg drop contacts to oligophenylene thiolate SAMs assembled on Ag substrates.[9a] We note, however, that 0.42 Å^{-1} falls in the range of β values (0.35−0.57 Å^{-1}) obtained for similar aromatic SAMs by electrochemical methods.[17] The discrepancy between our current CP-AFM results and the Hg drop experiments may be due to inherent differences in the measurement methods. For example, there is a factor of 10^{10} difference in contact area for AFM tip contacts versus Hg drop contacts, which may lead to different amounts of SAM deformation,[9c] as well as differences in sensitivity to defects. There may also be structural differences between oligophenylene thiolate SAMs on Au and Ag that affect the measured β values in the two experiments.

Figure 2B shows a comparison of resistance versus length data for SAMs of **I**−**III** and SAMs of alkanethiols.[15,16,18] The data for the two types of SAMs were obtained using two separate Au-coated tips each having a radius of ∼50 nm. The plot shows that the slopes and the corresponding β values are different. The β value for the alkanethiol junctions is 0.94 ± 0.06 Å^{-1}, consistent with previous studies of tunneling through alkanethiols;[19] the β value for the oligophenylene derivatives is 0.41 Å^{-1} (data set 1 in Figure 2A). Thus, for the same molecular length, the resistance for junctions based on unsaturated molecules is significantly lower than that for

junctions based on saturated molecules. For example, at a molecular length of 12 Å, the resistance equals ∼10^8 Ω for the alkanethiolate SAM and 10^6 Ω for the unsaturated SAM. The resistance is expected to be lower for coherent, nonresonant tunneling through conjugated systems than for saturated ones.[7,11a]

The effective contact resistance, R_0 (given by the zero-length intercept on the vertical axis in Figure 2B), is approximately 10^4 Ω for both saturated and unsaturated systems. In principle, the contact resistance between the probe tip and the SAMs could be expected to be different. Although the probe tips have similar radii and therefore the contact areas should be comparable, the Au-coated tip contacts terminal methyl groups with alkanethiolate SAMs and it contacts phenyl rings in the case of the oligophenylene thiolate SAMs. The fact that the contact resistances are indistinguishable (within our experimental uncertainty) suggests either that the electrical properties of the tip−CH_3 and tip−phenyl contacts are comparable or that the contact resistance is dominated by the properties of the *other* contact, that is, the Au−thiol interface. More studies of the properties of Au−SAM contacts are necessary to clarify this point. It is, however, an important aspect of our measurements that the contact resistance can be estimated from the length dependence of the tunneling resistance.

In summary, we have measured the resistance of SAMs to nonresonant tunneling as a function of molecular length and composition using CP-AFM. The dependence of resistance on molecular length is much weaker for the conjugated SAMs than for the aliphatic SAMs. This study establishes that CP-AFM is a productive approach to examining the electron-transport characteristics of molecular junctions composed of different classes of molecules. We emphasize that examination of the distance dependence of electron transfer through metal−molecule−metal junctions is a useful approach for determining transport mechanisms and for quantifying the electrical resistance of metal−molecule contacts.

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