

Charge Transport in Metal-Molecule-Metal Junctions Probed by Conducting Atomic Force Microscopy

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Charge transport through molecular monolayers has been extensively studied for scientific and technological interest.¹ It is now possible to measure charge transport through single molecules or small molecular groups bridging macroscopic external contacts with the rapid development of various measuring techniques.² For example, conducting atomic force microscopy (CAFM) is a widely used technique to achieve reliable electrical contacts to self-assembled monolayers (SAMs).³ In this study, we report a study of charge transport in alkanedithiol SAMs formed in metal-molecule-metal junctions using CAFM in combination with a variety of molecular transport techniques including temperature- and length-variable transport measurements and transition voltage spectroscopy. The main goal of this study is to probe the intrinsic transport properties of component molecules using CAFM, but not parasitic or defect-related effects.

For our experiments, alkanedithiol (from Assemblon) SAMs of various molecular lengths were prepared on Au substrates. Molecular junctions were formed by placing a Au/Cr-coated AFM tip in the stationary point contact on alkanedithiol SAMs under a controlled tip-loading force (1 nN), as shown in the inset of Figure 1. All electrical measurements were carried out inside a nitrogen-filled AFM chamber.

Temperature-variable current (I)-voltage (V) measurement is necessary to investigate the conduction mechanism. Figure 1 shows representative temperature-variable $I(V)$ curves of a 1,8-octanedithiol SAM measured by CAFM with a heating and cooling stage. The $I(V)$ curves were measured between 280 and 320 K, and no temperature dependence was observed. The temperature-independent $I(V)$ characteristic is a clear manifestation of tunneling and eliminates many of the potential alternative mechanisms such as thermionic or hopping conduction. Thus far, a consistent picture has emerged for the off-resonant tunneling mechanism with saturated alkyl chains,⁴ which can be reasonably expected when the Fermi energy of the electrode lies within a large energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of short molecules as in the case of alkanedithiols. To confirm tunneling mechanism, we performed further transport measurements for the molecular junctions (see below) in addition to the $I(V)$ results within a small temperature variation.

Another well-established validation method to interrogate

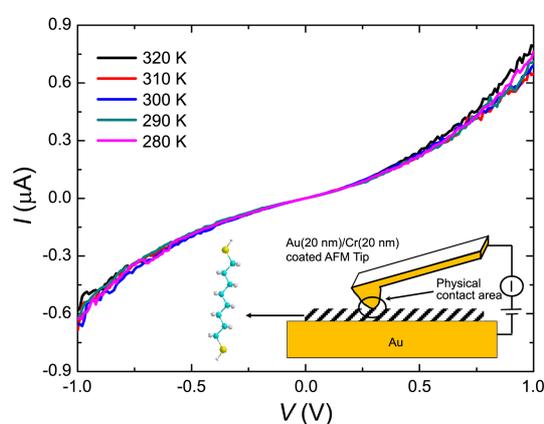


Figure 1. Temperature-variable $I(V)$ characteristics of 1,8-octanedithiol SAM. Inset shows a schematic of the CAFM measurement.

the transport mechanism of molecular junctions is to examine the dependence of conductance on molecular length.

The charge transport mechanism of a molecular junction can be revealed by the characteristic length dependences. In particular, off-resonant tunneling has been extensively discussed in the literature,¹ which dominates through relatively short, nonconjugated molecular systems (such as alkyl chains). For example, in the case of coherent, off-resonant tunneling, alkanedithiol molecules display an exponential decrease in conductance with molecular length. In particular, the conductance (G) is expected to be proportional to $\exp(-\beta N)$, where N is the number of carbon atoms in the alkanedithiol molecule and β is the tunneling decay coefficient. In order to investigate length-dependent conductance, we examined the conductance of five different alkanedithiols with various chain lengths: 1,8-octanedithiol (HS-C₈H₁₆-SH, denoted as DC8 for the number of carbon atoms), 1,9-nonanedithiol (HS-C₉H₁₈-SH, DC9), 1,10-decanedithiol (HS-C₁₀H₂₀-SH, DC10), 1,11-undecanedithiol (HS-C₁₁H₂₂-SH, DC11), and 1,12-dodecanedithiol (HS-C₁₂H₂₄-SH, DC12). As illustrated in the inset of Figure 2, the conductance values were obtained by the least-squares linear fit from the low-bias regimes ($-0.1 \text{ V} \leq V \leq 0.1 \text{ V}$) of $I(V)$ characteristics. As anticipated above, a semilog plot of the conductance values versus the molecular length was linear as shown in Figure 2. Each conductance value in Figure 2 represents the average of repeated measurements (at least 100), and the error bars are the

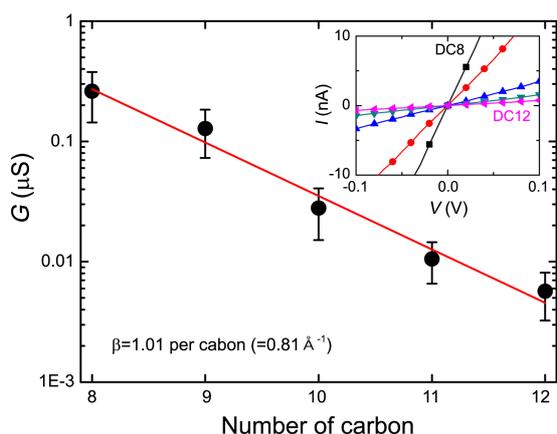


Figure 2. Semilog plot of the conductance versus the number of carbon atoms for five different length alkanedithiols. The decay coefficient (β) can be determined from the linear fit (the solid line), yielding a β value of 1.01 ($= 0.81 \text{ \AA}^{-1}$) per carbon atom. The inset shows length-dependent $I(V)$ curves in the low-bias linear regime, where a conductance value is obtained from linear fitting of the data.

standard deviation. From the linear fit (the solid line across data points) in Figure 2, a β value of 1.01 ($= 0.81 \text{ \AA}^{-1}$) per carbon atom was determined assuming through-bond tunneling. This β value is in good agreement with previously reported literature values.^{1,4}

Consequently, a correct exponential decrease of conductance upon molecular length increase, temperature dependence of $I(V)$ characteristics, and agreement with decay coefficients all point to a valid molecular junction.

Transition voltage spectroscopy (TVS) is a very promising spectroscopic method for molecular junctions.³ Specifically, TVS is used to estimate the energy barrier height (Φ_B) between an electrode's Fermi level and the nearest molecular level, and length-dependent TVS measurements for saturated alkyl chains can provide a critical test for distinguishing true molecular junctions from a vacuum tunnel junction with no molecules.¹ Thus, we performed TVS measurements on a series of alkanedithiol molecules of different lengths ranging from DC8 to DC12, employing CAFM. Measurements of V_{trans} in alkanedithiol junctions are shown in Figure 3(a). To prepare Figure 3(a), a representative $I(V)$ curve displayed in the inset of Figure 3(a) was transformed to axes of $\ln(I/V^2)$ against $1/V$, known as a Fowler-Nordheim plot where the inflection point denotes V_{trans} (indicated by the vertical dashed line in Figure 3(a)). V_{trans} for the series of alkanedithiol molecules is illustrated graphically in Figure 3(b). The average value of V_{trans} , represented by the solid line in Figure 3(a), falls within the standard deviation (within two dashed lines) of the measured values for each of the molecules, indicating that V_{trans} is invariant with alkanedithiol molecular length. This result is consistent with the HOMO-LUMO gap of these molecules being virtually length independent, which also agrees with the data of Beebe *et al.*³ Similarly, ultraviolet photoelectron spectroscopy measurements have shown that the energy offset between the HOMO and the electrode's Fermi level is constant for different length alkyl chains.⁵

We note that such length constancy in V_{trans} for alkane-

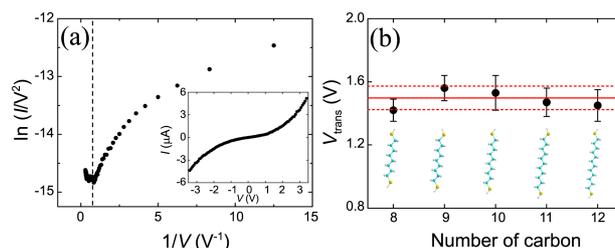


Figure 3. (a) Fowler-Nordheim plot for DC8, where the vertical dashed line denotes transition voltage (V_{trans}). Inset shows the corresponding $I(V)$ curves. (b) V_{trans} as a function of molecular length for alkanedithiols DC8 to DC12. The solid line represents the mean value of V_{trans} for the five different alkanedithiols, and the two dashed lines show the standard deviation for averaging. Error bars on each data point denote the standard deviation across individual measurements for different alkanedithiols. Chemical structures for each molecule are displayed in the inset.

dithiol junctions is fully in agreement with the results expected from a molecular transport model based on the Landauer formula, *i.e.*, V_{trans} is independent of molecular length (longer than $\sim 8 \text{ \AA}$) for constant Φ_B .⁶ On the other hand, V_{trans} is expected to be inversely proportional to tunneling length for the case of a tunnel junction without molecules obeying the Simmons model.⁶ Only within the molecular transport picture, V_{trans} can be directly scaled with Φ_B , thus giving valid information on molecular energy levels. Therefore, our findings from length-dependent TVS measurements provide additional verification of the molecular junction formation by CAFM.

In conclusion, we have demonstrated a proof of intrinsic charge transport properties in alkanedithiol molecular junctions using a multiprobe approach combining a variety of transport techniques. The temperature-independent $I(V)$ behavior and the correct exponential decay of conductance with respect to molecular length shows that the dominant charge transport mechanism is off-resonant tunneling. Length-dependent TVS measurements for the saturated alkanedithiol series indicate that we did indeed probe a molecular system with CAFM. These results can provide stringent criteria to establish a valid molecular transport junction via a probabilistic measurement technique.

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