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In Situ Wiring of Single Molecules Into Electrical Circuit via Electrochemical Distance Tunneling Spectroscopy

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Abstract

The electrical conductance of single n-alkanethiol and α,ω -alkanedithiol molecules was measured via in situ distance tunneling spectroscopy in aqueous 0.1M KOH solution. The statistical analysis of the conductance values show that the α,ω -alkanedithiol molecule trapped in the STM break junction can adopt two distinct geometries that result in “lower” and “higher” conductivity values. In contrast, n-alkanethiol molecules trapped in the junction show only a single conductivity value characteristic for a particular molecule. Furthermore, the “lower” conductivity value determined for α,ω -alkanedithiol is virtually identical to the electrical conductivity of the n-alkanethiol containing the same number of atoms in the backbone. Moreover when the STM tip is polarized to electrochemical potential preventing a chemical reaction between terminal -SH group and Au, only “lower” conductivity values are observed for α,ω -alkanedithiols.

Keywords

scanning tunneling distance spectroscopy; electrochemical STM; single molecule conductivity; alkanethiols

Development of reliable methods to measure electrical conductivity of single molecules is of key importance in building the foundations of molecular electronics.¹⁻⁴ Recently, several groups have used the STM break junction method to measure the conductance of variety of molecules containing -SH, or -NH₂ groups at both ends of a molecule.⁵⁻⁸ In this approach the STM tip is moved in and out of the surface of a flat metal electrode and current-distance curves are recorded. The molecules present in the vicinity of the junction (in a solution or on the surface of either contact) may bridge the STM gap resulting in a stable metal - molecule - metal structure of well defined conductance. Under these conditions distinct steps are observed on the current-distance curves. The statistical analysis of the current values represented by these steps reveals clear peaks at the integer multiples of the fundamental conductance value characteristic for a particular molecule.⁵⁻⁸

While many of the experiments conducted thus far rely on measurements performed in an inert solvent or in air, the aqueous electrolyte solution provides several advantages for studies of biologically relevant molecules like DNA, proteins, or peptides.⁹⁻¹¹ Additionally, the tunneling

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spectroscopy performed in the electrochemical cell allows us to apply well controlled electrochemical potentials to both metal contacts thus the redox properties of the bridging molecule can be tuned.¹² Lastly, under appropriate experimental conditions the electrochemical reaction between the end group of a molecule and the metal contact can be induced or prevented in situ thus allowing us to “wire” the molecule into the electrical circuit. We have recently demonstrated such wiring for monolayers of α,ω -alkanedithiols using macroscopic Hg drop junction approach.¹³

We report here measurements of electrical conductivity of several aliphatic thiol molecules using in situ electrochemically controlled tunneling spectroscopy in aqueous 0.1M KOH solution.¹⁴ We show that both α,ω -alkanedithiols as well as n-alkanethiols can be trapped in a tunnel junction formed between the Au STM tip and the Au(111) electrode in the presence of the molecules of interest on Au(111). Furthermore we demonstrate that the ability to control the electrochemical potential of the STM tip allows us to induce or prevent the reaction between the terminal –SH group and the STM tip thus allowing us to investigate, in situ, the effect of the formation of covalent bond between the molecule and the metal contact on the electrical properties of the system.

In our experimental approach shown schematically in figure 1 the STM tip¹⁵ is first brought to the Au(111) electrode at the desired set-point current (typically 1 - 4 nA). Subsequently the tip is lifted using z piezo drive while keeping the x-y position constant at the rate of 17nm/s and the current-distance curve is recorded. The advantage of this approach is that the bias voltage can be kept constant while both E_{TIP} and $E_{SUBSTRATE}$ potentials can be simultaneously changed to induce desired interactions between the molecule and a metal contact.

The experiment is performed in a deoxygenated water solution containing 0.1M KOH as the supporting electrolyte. The composition of the solution allows us to study, in situ, the influence of the reaction between the terminal -SH group of a molecule and the STM tip on the overall conductance of the system. In particular, the reaction between the terminal –SH group and the STM tip would not occur if the tip is polarized to the potential more negative than the reductive cleavage of the Au-S- bond.¹⁶⁻¹⁷

Since statistical analysis of the data is necessary in such experiments, we recorded up to five thousand current-distance curves for each set of experimental conditions reported later in the paper. The representative example of the current – distance curve recorded in the absence of thiolated molecules is shown in figure 1A. A typical exponential decay expected for tunneling process through layers of water was observed in virtually all of the experiments as long as rigorously clean cells were used.¹⁴ A different behavior is observed in the presence of a low surface coverage sub-monolayer of thiolated molecules on the Au(111) electrode surface.¹⁸ Under these conditions, thus without molecules present in a solution, about 5% of current-distance curves for di-thiols and ca. 2% of current-distance curves for mono-thiols show characteristic plateaus as clearly visible in figure 1B. Similar plateaus were observed by Schirfrin and Nichols⁸ for α,ω -dithiols in air for the two-terminal STM gap, however in our current experiment in water we have observed virtually identical plateaus for both α,ω -dithiols and for n-alkanethiols.

While the exact origin of the plateaus on the current-distance curves is a matter of discussion, it seems clear that the abrupt drop in the current value indicated by an arrow in figure 1B corresponds to the breakage of the electrical contact between the molecule and the metal tip or the electrode. Thus the current measured at the breakage point is assumed to represent the conductivity of a molecule or molecules trapped in a junction.⁵⁻⁸ Furthermore, the exponential current-voltage curves are observed for the junction indicating that the superexchange tunneling is predominant mechanism of conduction. Similar dependence for two-terminal

junction was recently reported by Tao et al.¹⁹ Analysis of the current values obtained in the course of our measurements indicates that, for each molecule, currents are grouped around particular values. We have calculated the mean value and the standard deviation for each group of currents. These values are shown in Table 1.

It is clear that for n-alkanethiols the mean values of current are integer multiples of the fundamental current value. For example, the distributions of current values for n-heptanethiol shows 5 average values at $n \times 99$ pA, ($n=1, 2, 3, 4, 5$). Analogously, mean current values for n-nonenethiol can be described as $n \times 41$ pA, ($n = 1, 2, 3, 4$), and mean current values for n-decanethiol can be described as $n \times 26$ pA. ($n = 1, 2, 3, 4, 5, 6$). This result indicates that several molecules can be trapped within a junction.⁵⁻⁸

The analysis of average current values observed for α,ω -alkanedithiols is more complicated. For 1,6-hexanedithiol molecule current values 1 through 7 appear to be multiple integers of the fundamental current value, 98 pA. These mean current values follow the general relationship described by $n \times 98$ pA, ($n = 1, 2, 3, 4, 5, 6, 7$). Second distribution of values is seen, however, for currents 8 through 10 with general description of $n \times 1038$ pA ($n = 1, 2, 3$). This behavior is similar to that reported very recently by Tao et al for the α,ω -alkanedithiols in a two-terminal STM break junction in an inert solvent.¹⁹ Thus it appears that α,ω -alkanedithiols bridge the gap between the STM tip and the Au(111) electrode by adopting at least two sets of distinctly different geometries resulting in different conductivities. We will describe these conductivities as “small conductivity” and “large conductivity” for each dithiol molecule. Further inspection of the current values reported in table 1 indicates that the fundamental “small conductivity” values observed for α,ω -alkanedithiols are virtually identical to the fundamental conductivity values observed for n-alkanethiols having the same number of atoms along the backbone. For example, the fundamental current value for 1-heptanethiol is 99 ± 9 pA while the fundamental “small current” value for 1,6-hexanedithiol is 98 ± 11 pA. Analogous dependencies, albeit with some irregularities, are observed for all investigated molecules as seen in table 1. It appears therefore that the interactions between the terminal –SH group and the STM tip are responsible for the observed dual distribution of conductivities for α,ω -alkanedithiols.

Clearly, for both n-alkanethiols and α,ω -alkanedithiols the molecule must be attached to the surface of both Au contacts, either covalently or by physical adsorption, in order to produce a plateau on the current-distance curve. It is worth noticing that the physical adsorption of the terminal –SH group on the STM tip might, in some cases, result in a geometry that prevents formation of the Au-S bond within the millisecond time scale of the tunneling spectroscopy experiment. Yet, the reaction between the terminal –SH group and the STM tip could be altogether prevented if the STM tip is electrochemically polarized to the potential negative of the standard electrochemical potential of the –S-Au bond cleavage. It was reported previously that the reduction of the Au-S- bond occurs around -1 V vs. an Ag/AgCl (SSCE) electrode.¹⁶⁻¹⁷

Therefore we have investigated the influence of the electrochemical potential of the STM tip on the distribution of currents for α,ω -alkanedithiols and n-alkanethiols in a STM break junction. The example of the dependence of the fundamental mean current value for 1,6-hexanedithiol on the electrochemical potential of the STM tip is shown in figure 2. In this experiment the tip potential was changed from -0.6 V vs. SSCE to -1.1 V vs. SSCE while the bias voltage between the Au(111) substrate and the Au tip was kept constant. It is clear that both “large” and “small” current values are observed for all potentials except for the most negative potential of -1050 mV vs. SSCE.²⁰ This potential corresponds to the reductive cleavage of the –S-Au bond indicating that the lack of the Au-S- bond is responsible for “lower conductivity” values for α,ω -alkanedithiols.

The values of current recorded for molecules of different lengths are expected to follow the model of super-exchange through-bond tunneling with current decaying exponentially with distance according to $i = \exp(-\beta d)$, where d is distance and β is tunneling coefficient.¹ The plot of the natural logarithm of the fundamental current values for both “small” and “large” current steps as a function of the length of a molecule is shown in figure 2. Line C represents “large” current steps for α,ω -alkanedithiol molecules with a slope yielding the tunneling coefficient $\beta=0.83/\text{CH}_2$. This is consistent with previous measurements of the tunneling coefficient for saturated hydrocarbons reported by other authors.^{1, 4-8, 12} Markedly a different result is obtained for “small” current steps or for n-alkanethiols. In these cases the plot of the logarithm of current vs. the nominal length of a molecule (# of atoms along the backbone) shows significantly smaller tunneling coefficient ($\beta=0.41/\text{CH}_2$) which is inconsistent with values reported earlier for hydrocarbon chains.

We postulate that the low value of the measured tunneling coefficient is an artifact associated with the geometry of the molecule within the junction in the absence of a strong interactions between the end group of the molecule and the STM tip. As described earlier, the covalent bond between the terminal sulfur atom of an α,ω -alkanedithiol molecule and the STM tip provides an efficient pathway for electron tunneling along the molecule. Therefore in the course of the distance spectroscopy measurement (when the molecule is stretched) the distance between the STM tip and the Au(111) surface changes while the length of the main tunneling pathway remains constant.²¹ Under these conditions a plateau is observed on the current-distance curve. On the other hand various fragments of the n-alkanethiol molecule backbone can be conceivably adsorbed on the Au tip surface in the course of measurement. Thus, considering the statistical nature of this experiment, the n-alkanethiol molecules can not be stretched to the same extent as α,ω -alkanedithiols. Therefore, for n-alkanethiols, the change in the nominal length of a molecule results in the smaller change of the true length of tunneling pathway than anticipated. Consequently, if both ends of the molecule are not firmly attached to the metal contacts, the distance axis in figure 2 does not properly reflect the true geometric distance between the STM tip and a substrate. This conclusion is somewhat supported by the measurements of the length of the current-distance transient. Even though the absolute distance at which the molecule dislodges from the junction (see arrow in figure 1) is burdened by a large experimental error, it is apparent that the length of the transient for the α,ω -alkanedithiols is, in general, larger than the length of the transient for monothiols containing the same number of atoms in the molecule backbone.²²

In summary, we show that both n-alkanethiols and α,ω -alkanedithiols can be trapped in an in situ electrochemically controlled STM break junction in water and the current-distance curves show clear plateaus for both types of molecules. Furthermore the chemical interactions between the end group of the molecule and the metal contact can be tuned by applying appropriate electrochemical potentials resulting in varying electrical conductivities. The electrochemical wiring of single molecules into electrical circuits could be useful in a multitude of molecular electronics applications.

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Figure 1.

Scheme of the experiment showing flat Au(111) electrode modified by a low coverage sub-monolayer of the α,ω -alkanedithiol, immersed in a deoxygenated electrolyte solution of 0.1 M potassium hydroxide. The Au electrode is polarized to the potential $E_{\text{SUBSTRATE}}$ vs. a reference electrode (RE, saturated silver / silver chloride electrode) and an Au STM tip is polarized to the E_{TIP} potential. The circuit is completed with a Pt counter electrode. The bias voltage between the STM tip and an Au electrode is $\Delta E = |E_{\text{SUBSTRATE}} - E_{\text{TIP}}|$. The distance tunneling spectroscopy is performed by lifting an STM tip from the initial position while keeping the x-y position constant. A typical i-s curve recorded for the set-point current $i_0 = 4$ nA and the bias voltage is +0.4 V on: (A) bare Au(111) surface, (B) in the presence of a low coverage pre-adsorbed 1,6-hexanedithiol molecules on Au(111) electrode.

Figure 2.

Dependence of the natural logarithm of the “large” and the “small” fundamental current values on the length of the molecule (expressed as the total number of atoms in the molecule backbone). (A) n-alkanethiols; (B) α,ω -alkanedithiols, “small current” values; (C) α,ω -alkanedithiols, “large current” values. “Small” and “large” current values for 1,6-hexanedithiol as a function of the STM tip potential. The Au electrode potential was changed simultaneously to keep bias voltage of 400 mV. Experiments were performed in deoxygenated 0.1M KOH solution.

Table 1

The average values (pA) for current steps. The fundamental current values are in bold (see text for details)

Current (pA)	1	2	3	4	5	6	7	8	9	10
C7-SH	99±9	199±16	805±12	405±19	517±15					
C9-SH	41±3	79±3	117±6	177±20						
C10-SH	26±3	50±2	74±3	101±3	124±5	149±2				
HS-C6-SH	98±11	188±11	293±10	386±14	489±15	602±8	695±12	1038±80	1989±118	3050±131
HS-C8-SH	45±7	97±18	129±11	194±18	415±32	685±27	1010±30	1246±40		
HS-C9-SH	26±1	54±8	88±7	154±20	221±13	339±47	492±19			