

Redox State Dependence of Single Molecule Conductivity

Wolfgang Haiss,* Harm van Zalinge, Simon J. Higgins, Donald Bethell, Horst Höbenreich, David J. Schiffrin, and Richard J. Nichols

Centre for Nanoscale Science, Chemistry Department, University of Liverpool, Liverpool L69 7ZD, U.K.

Received August 29, 2003; E-mail: w.h.haiss@liv.ac.uk

There is currently intense interest in both theoretical¹ and experimental^{2–5} aspects of the electrical properties of single molecules due to their potential use in electronic devices. It has been proposed that their electrical properties can be controlled by the occupancy of energy levels within the molecules, as illustrated by the use of oligophenylene-ethynylene⁶ and viologen⁷ bridges. In both cases it was found that charge trapping in molecular states leads to changes in electrical behavior. The purpose of the current work is to demonstrate a simple technique for measuring the conductivity of single molecules as a function of their redox state.

The technique is schematically described in Figure 1. This relies on forming molecular wires between a gold surface and a gold STM tip. Very recently, Xu and Tao² have reported on similar measurements but using STM break junctions. The molecule used here, 6-[1'-(6-mercapto-hexyl)-[4,4']bipyridinium]-hexane-1-thiol iodide (6V6; see Figure 1), was chosen for several reasons. The thiol groups at both ends constitute anchoring points to the gold surface and to the STM tip. The redox group (a viologen, V) has readily accessible energy levels and is symmetrically placed between defined molecular tunneling bridges (the two alkyl chains) at either end. In addition, these molecules are highly stable in the redox states addressed here.

These molecules form a low-coverage phase on gold(111), lying parallel to the surface.⁵ STM measurements were performed on this phase, as schematically shown in Figure 1. When the STM tip was brought close enough to the Au surface, which was experimentally achieved by increasing the tunneling current setpoint (I_0), spontaneous formation of stable molecular wires between the tip and the sample was observed. The tip was then lifted while keeping a constant x - y position, and the current–distance ($I(s)$; s = relative tip–sample distance) relation was measured.

Two distinctive classes of $I(s)$ scans were observed: (i) a fast exponential decay typical of tunneling between a tip and a bare metal (curve 1 in Figure 2a) and (ii) a less abrupt decay followed by a characteristic current plateau (I_W) (curve 2). It is proposed that the plateau is related to conduction through molecular wires chemically bonded to the tip and to the substrate. Direct tunneling to the substrate does not contribute significantly to the observed current for these separations (see Figure 1). This plateau is followed by another current decay at longer distances. Figure 2b shows a plot of I_W versus $s_{1/2}$ ($s_{1/2}$ = distance for $I = I_W/2$) for 117 $I(s)$ scans taken at different locations. The average value of $s_{1/2}$ is (2.4 ± 0.6) nm. The end of the plateau is observed at approximately 2 nm from the initial setpoint distance (s_0). A realistic estimate of s_0 places the tip-to-substrate distance at approximately 2.5 nm at the end of the plateau. This is close to the length of a 6V6 molecule, given that molecular modeling of the free molecule produces a distance between the two sulfur atoms of 2.4 nm for trans oriented alkyl chains. This implies that the molecules are in a fully extended conformation before disengagement, as shown in Figure 1.

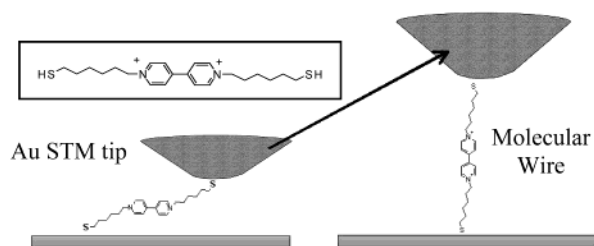


Figure 1. Schematic diagram of the experiment performed to study electrical properties of single molecules in both air and electrolyte. The inset shows the 6V6 dication.

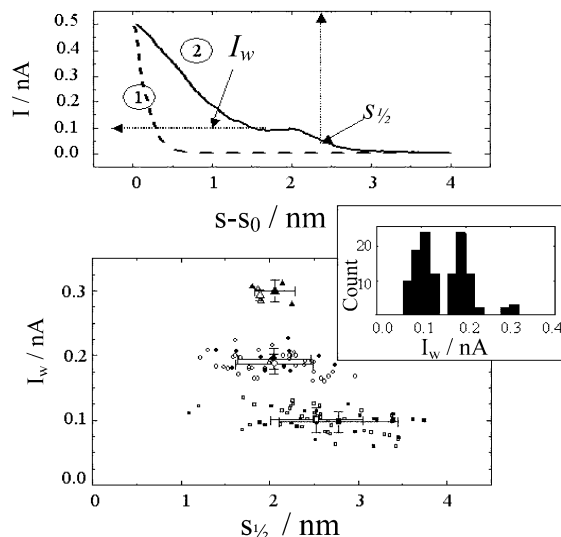


Figure 2. (a) Current decay curves ($I(s)$ scans) for 6V6 on Au(111) in air. (1) Baseline for a clean Au surface and (2) in the presence of 6V6 molecular wires between the tip and the substrate. (b) Dependence of $s_{1/2}$ on the current plateau current (I_W) for 117 $I(s)$ curves taken at different locations of the substrate (filled symbols $U_t = +0.2$ V; open symbols $U_t = -0.2$ V; where U_t is the tip-to-substrate potential difference). $I(s_0) = 0.5$ nA for all the measurements; the error bars represent the standard deviation for each class of events. Inset: Histogram of the current values from Figure 2b.

The observation that the decrease of the current for larger tip–sample separations following the plateau (Figure 2a) occurs over a distance range and not abruptly is possibly caused by the extension of the molecular assembly, which includes the molecular wire as well as a group of surface and tip atoms, prior to a break of the chemical contact of the molecular wire, either at the tip or at the substrate junction. At sufficiently large tip–sample separations, chemical contact of the molecular wire to the tip or to the surface is broken and, hence, the current drops to zero.

Three different groups of events can be distinguished in Figure 2b: group 1 (squares), group 2 (circles), and group 3 (triangles). The measured values of I_W cluster around integer multiples of a basic current value of (98 ± 16) pA. These steps in conductivity

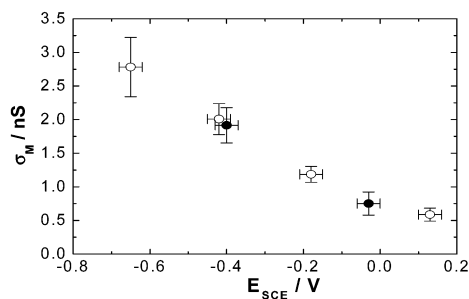


Figure 3. Measurements performed under electrochemical control in 0.1 M phosphate buffer solution. Potential dependence of the conductivity at constant U_T (0.2 V) of a single 6V6 molecule as determined from group 1 events. σ_m error bars represent the standard deviation for each group of measurements. Filled and open symbols correspond to two different samples.

are attributed to the presence of a discrete number of molecules between the tip and the sample. The simplest explanation of the results is that the lowest conductivity unit (group 1 events) and the respective subsequent steps (groups 2 and 3 events) correspond to conduction through a single molecule and the others to two and three molecules, respectively.

From the above results, the conductivity of a single molecule (σ_M) at $U_t = 0.2$ V is (0.49 ± 0.08) nS (where U_t is the tip-to-substrate potential difference). The inset in Figure 2 shows a histogram of the current values in Figure 2b. The conductivity can be compared with results in which the wiring is realized by chemical attachment of nanoparticles to 6V6 molecules incorporated in an hexanethiol monolayer on gold which gave a value of (0.56 ± 0.03) nS.^{5,7c} The similarity of the conductivity measured from both techniques indicates that this new method for the measurement of single molecule electrical properties is reliable.

Having established the reliability of single molecule conductivity measurements using the present STM method, we now show that this can be used in an electrolyte, where the redox state of the molecular bridge can be altered. The fundamental question we wish to address is how the conductivity changes as a result of the redox state of the molecule. Discrete steps in I_w due to the presence of an integral number of molecules tethered between tip and sample were clearly observed, similar to the results in air described above. By analyzing the group of conductance events corresponding to a single molecule measured at different potentials, it was possible to determine the conductance of single molecules as a function of the applied electrode potential (Figure 3). Reversible conductivity changes from 0.5 to 2.8 nS were observed when the molecule was electrochemically switched from the oxidized to the reduced state.

These observations have implications for electron transport through molecular wires containing chemically or electrochemically oxidizable or reducible groups. The measured conductivity of a single 6V6 molecule at 0 V vs SCE (0.44 ± 0.04) nS can be compared with that of a single dodecanedithiol molecule (0.122 ± 0.014) nS, determined by Cui et al. using a conducting AFM.⁴ From this comparison, it can be concluded that the presence of the bipyridinium center has a pronounced effect on the conductivity of the whole molecule. This could result from inelastic tunneling leading to a transient occupation of the reduced state of the bipyridinium moiety.⁸ The coupling with the nuclear degrees of freedom will determine whether the electron transfer is best described as a sequential or superexchange process or an intermediate situation.⁹

The pronounced conductivity increase in the region between -0.2 and -0.6 V is attributed to the well-known reversible one-electron reduction of the bipyridinium moiety (V) from V^{2+} to the radical V^{+} .¹⁰ Upon reduction, the electron density in the bipyridinium moiety increases, concomitant with the alignment of the Fermi level of the gold electrode relative to the LUMO of the bipyridinium group, consistent with potential dependent STM contrast measurements.¹¹ The associated potential-induced change in conductivity quantified here for a single molecule tethered between two gold electrodes is qualitatively consistent with the results of standard electrochemical experiments, where electron transport through the bipyridinium moiety to an external redox couple is enhanced upon reduction from V^{2+} to V^{+} .^{7b} However, for the case of the experiments discussed here, the conductivity changes are moderated by both the presence of sulfur contacts and the presence of connecting alkyl chains.

In summary, a simple and reproducible method to measure the conductivity of single molecules has been demonstrated utilizing the spontaneous formation of molecular wires between an STM tip and substrate. This method can be applied in an electrochemical environment, enabling the redox state of molecules to be controlled during such measurements.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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