Charge Transport with Single Molecules – An Electrochemical Approach

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Introduction

The integration of molecular structures in electronic circuits is currently an active field of fundamental research inspired by the visionary concepts of molecular electronics. A particular challenging topic represents the charge transport in nanoscale molecular systems with device-like functions. Addressing a metal│molecule│metal junction requires a source and a drain electrode as well as localized electronic levels. The role of source and drain may be represented by the tip of an STM combined with an appropriate substrate [1,2] or a pair of planar nanoelectrodes. [3]. Working in an electrochemical environment has the advantage that two potential differences can be tuned individually, the bias voltage between the two working electrodes WE 1 and WE 2, and the potential drop between one working electrode and the reference electrode RE (**Fig. 1**). The latter acts as a gate electrode.
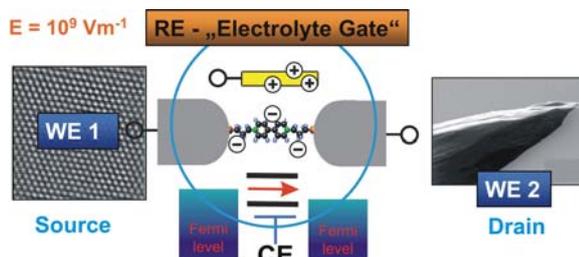

Fig, 1 Principle of the chosen „electrolyte gate" configuration. The role of source and drain electrodes are represented by a Au(111) substrate (WE 1) and a gold STM tip (WE 2). Tuning of the Fermi levels of WE 1 and WE 2 relative to the molecular energy levels enables measuring of current (i) – voltage (E)

Results and Discussion

We developed a new STM-type approach [1,2,4] to measure single junction conductance data of two molecular systems: alkanedithiols and redox-active N,N'-bis(6-thio-alkyl)-4,4'-bipyridinium bromide (HS-nVn-SH), n = 5 to 10, immobilized at a solid│liquid interface. The approach is based on the repeated formation and breaking of symmetric molecular junctions between a coated gold STM tip, except the very end of the apex, and a Au(111)-(1x1) electrode modified with reactant molecules (**Fig. 2**), and the subsequent recording of current-distance traces with high dynamics and speed in 1 pA $< i_T <$ 230 μA [6,7]. These traces are often non-exponential and exhibit a series of characteristic plateaus separated by abrupt steps. The steps were identified as breaking of single respective multiple molecular junctions. The statistical analysis of up to 3000 individual pulling curves yielded values of the single junction conductance [4].
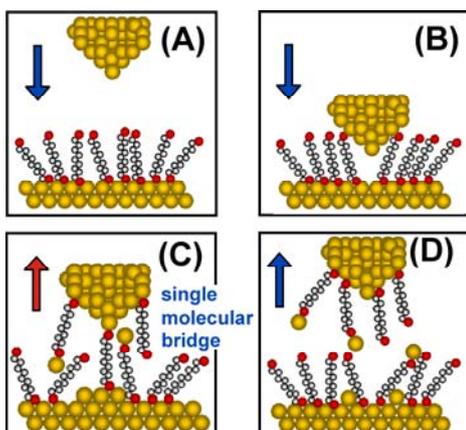
Fig. 2. Principle of the electrochemical single molecule stretching experiment: (A) Approach; (B) formation of molecular junctions; (C) stretching with a constant pulling rate of 6 nm s⁻¹; (D) breaking of the contact and switching on the feedback control.
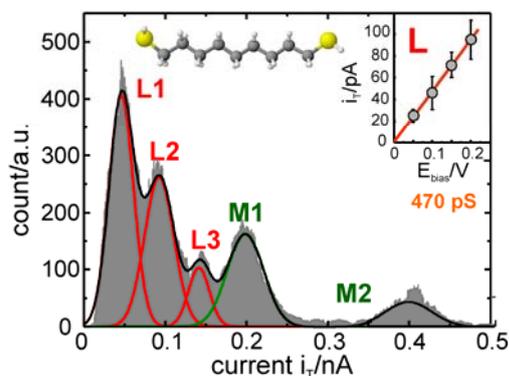
Fig. 3. Conductance histogram constructed from current – distance "stretching curves" for 0.1 mM 1,9-nonanedithiol in 1,3,5-trimethylbenzene in $0 < i_T < 0.5$ nA. 1100 individual traces were recorded.

Fig. 3 illustrates a typical histogram for Au│nonanedithiol│Au junctions (for display purposes) in the limited current range $0 < i_T < 0.5$ nA. Two distinctly different sequences of equally separated maxima were identified. A third sequence exists at $i_T > 1.0$ nA. The first peaks of each sequence were attributed to a low (L), a medium (M) and a high (H) single junction conductance. Identical results were obtained in argon, 1,3,5-trimethylbenzene and aqueous electrolyte. The M and H values of the single junction conductance in logarithmic scale are linearly dependent on the alkyl spacer length. The decay constants amount to $\kappa = 0.96$ and 0.94 respectively. The L values do not exhibit a linear dependence. Comparison with first principle quantum chemical calculations, which lead to energy dependent transmission functions, provide the following conclusions: The M conductance junctions represent an all-trans conformation of the alkyl chain with both sulfur atoms bound in atop position to single gold atoms. An all-trans chain with sulfur atoms bound to two gold atoms in bridge position represents the high conductance junction, a factor 4 larger than the former. The low conductance values L could be identified to a sequence of gauche isomers with atop binding sites.

The above strategy was also applied to molecular junctions, composed of redox-active N,N'-bis(n-thioalkyl)-4,4'-bipyridinium bromide (HS-nVn-SH) as functional unit. HS-nVn-SH may exist in three different states, as dication in the stable oxidation state V^{2+}, and the two reduced forms radical cation $V^{+\cdot}$ and neutral species V^o, depending on the applied electrode potential [1]. The corresponding one-electron transfer steps are reversible. The single conductance current shows a
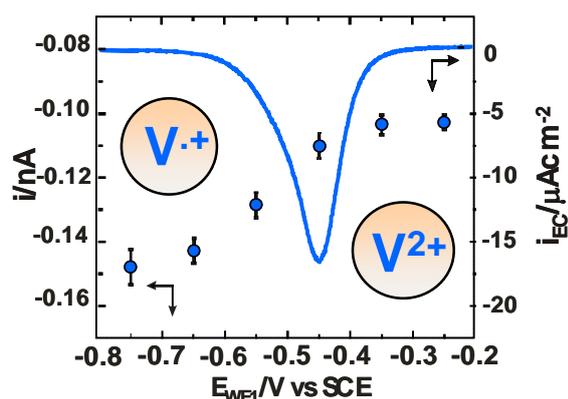

Fig. 4. Single molecule conductance current of Au-S-6V6-S-Au junctions vs. the substrate potential E_{WE1} at fixed bias $(E_{WE1}-E_{WE2}) = -0.10$ V, individual points. Each data point was obtained from histograms of more than 500 individual traces. The solid blue line corresponds to the macroscopic current-voltage curve for the reduction of $V^{2+} \rightarrow V^{+\cdot}$ on Au(111)-(1x1).

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clear dependence on the redox state of HS-nVn-SH (**Fig. 4**). It is rather constant in the stability range of the oxidized dication V^{2+}, decreases at E_{WE1} < -0.40 V and reaches a plateau at E_{WE1} < -0.70 V, e.g. past the formal potential of the one electron redox process $V^{2+} \leftrightarrow V^{+\cdot}$. The sigmoid increase of the molecular conductance current up to 50 % is ascribed to the higher electron density and higher conjugation of the immobilized radical monocation $V^{+\cdot}$ as compared to the dication V^{2+}. The switching rate between the two redox-states could be as high as 0.10 ms [1]. Comparison to our experiments with symmetric Au│HS-nVn-SH│Au junctions points to an all-trans conformation of the two alkyl chains with both sulfur atoms bound in atop position. The construction of asymmetric tunneling junctions Au│H-nVn-SH │Au leads to a transistor- and/or diode-like current voltage response employing the concept of "electrolyte gating" [1].

Current efforts are focused on implementing the conceptual and technological knowledge developed in the vertical STM configuration into a horizontal assembly of nanoelectrodes prepared by combining lithographic and electrochemical techniques. A dedicated four-electrode bipotentiostat was developed for controlling the electrochemical fabrication process and for monitoring the electrical characteristics [3,5,6]. We could achieve Cu and Au nanocontacts and stable molecular-sized gaps, which exhibit characteristic quantized tunneling currents. The major next challenge comprises the development of strategies for the controlled fabrication of single and/or small numbers of (redox-) active and addressable molecular junctions. First results will be discussed.

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