Conductance properties of single-molecule junctions

H. B. Weber [a,1], J. Reichert [a], R. Ochs [a] D. Beckmann [a] M. Mayor [a] H. v. Löhneysen [b]

[a] *Forschungszentrum Karlsruhe, Institut für Nanotechnologie, D-76021 Karlsruhe*

[b] *Physikalisches Institut, Universität Karlsruhe, D-76128 Karlsruhe and Forschungszentrum Karlsruhe, Institut für Festkörperphysik, D-76021 Karlsruhe*

Abstract

We have performed conductance measurements with a gold-molecule-gold junction employing the mechanically controlled break-junction technique. The organic sample molecules form a stable covalent bridge between the electrodes. Two molecules, which differ essentially by their spatial symmetry, showed discrete stable conductance patterns (IVs), which reflect the symmetry/asymmetry of the sample molecules. A third molecule with an additional tunnel barrier in the central axis shows a strongly suppressed conductance. The correlation between these obvious properties of the molecules and the observed IVs unambigously shows that the junction is indeed formed of the sample molecules. Vice versa, these observations demonstrate that IV characteristics can be appropriately designed by a proper choice of molecules.

Key words: molecular electronics; single-molecule junctions

The use of metal-molecule-metal junctions as a building block for electronic devices provides interesting advantages compared to traditional materials. The possibility of self assembly may facilitate the production process. A major advantage is, however, the tunability of the electronic properties by an appropriate choice of molecules. This is demonstrated in this paper. Conceptually, a junction containing only one molecule is the simplest system which we try to understand first. To provide sufficient stability of the molecular junction, we chose an organic molecule with functional end groups that form covalent bonds to the gold electrode pair, realized by a mechanically controlled break junction. Similar experiments were reported in [1,2], but without convincing arguments that indeed single molecules were observed.

The molecules are shown in Fig. 1. They are stiff, rod like (length $l = 2$ nm) and have thiol endgroups. The experimental procedure is described in [3,4]. Briefly, we use the self assembly of molecules in solution to attach a sub-monolayer of molecules to the surface of the electrode pair. After blowing away the solvent, the measurement is done under vacuum conditions at room temperature. As no direct imaging of the molecule in between the electrode pair is possible, the only information can be obtained by the conductance data. While approaching the two electrodes, we apply a finite bias voltage, which allows the molecule to be directed towards the opposite electrode and allows further for current measurements. In the tunneling regime ($2 - 10$ nm), the current is rising exponentially with the distance and is very unstable, indicating rearrangements in the electrode gap. Suddenly, the current locks into a rather stable state. In this state, the molecule bridges the gap and it is possible to record IV characteristics which are often well reproducible. This behavior is very similar for the three different molecules investigated here. This suggests a direct comparison of the IVs thus observed.

Fig.2a) shows the IV observed in the locked-in regime for molecule **1**. The current has clearly a non-linear form. Whereas at low voltage the current is

---

[1] Corresponding author. Present address: Forschungszentrum Karlsruhe, Institut für Nanotechnologie, Postfach 3640, D-76021 Karlsruhe E-mail: heiko.weber@int.fzk.de

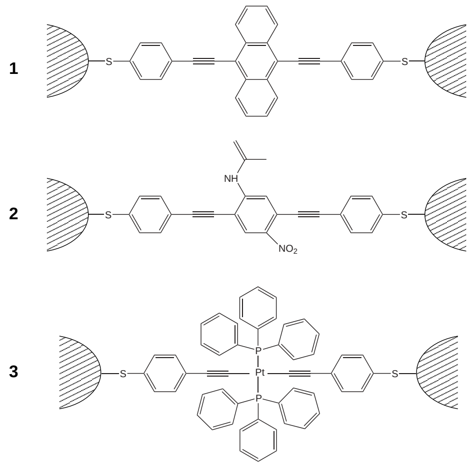

Fig. 1. Scheme of a single molecule junction with gold electrodes and the three molecules **1**,**2**,**3** investigated.

strongly suppressed, a step-like, strongly broadened increase of the current is observed at ±0.3 V. This is presumably due to an electron-transmitting molecular orbital which contributes to the conductivity as soon as the bias voltage is sufficiently high. Similar data shown in [3] strongly suggest that we are sensitive to single molecules. It should be mentioned, that even identical molecules create varying IVs due to the high sensitivity to microscopic details in the vicinity of the molecule. Such sample to sample fluctuations can barely be avoided when a single molecule is chemically connected to an irregularly shaped surface.

Molecule **1** has a spatial mirror symmetry (see Fig.1) and the conductance of the junction is expected to be independent of the current direction. Hence one would expect symmetric IVs (with respect to the bias sign). This symmetry is broken for molecule **2** by two attached side groups. For this molecule, asymmetric IVs might be expected. Indeed, the IVs observed for the molecules **1** and **2** are symmetric and asymmetric, respectively (an additional case where asymmetric IVs are observed is reported in [3]). In molecule **3**, the Pt atom in the central part intersects the conjugated molecule into two weakly coupled parts [5]. It is expected to act as an additional tunnel barrier which suppresses the current with respect to molecule **1**. Indeed, the observed currents are reduced by four orders of magnitude, compared with molecule **1**. Furthermore, the peak-like structure observed for **1** is not observed in **3**[6]. Instead, the current behavior can be well described by a tunnel characteristic [7] with a barrier height of ≈ 2.5 eV.

In conclusion, we have demonstrated that the conductance properties of three different molecules can be related to obvious properties of the molecular structure. This proves that electronic properties of molecular junctions can be tuned by an appropriate design of the molecule.

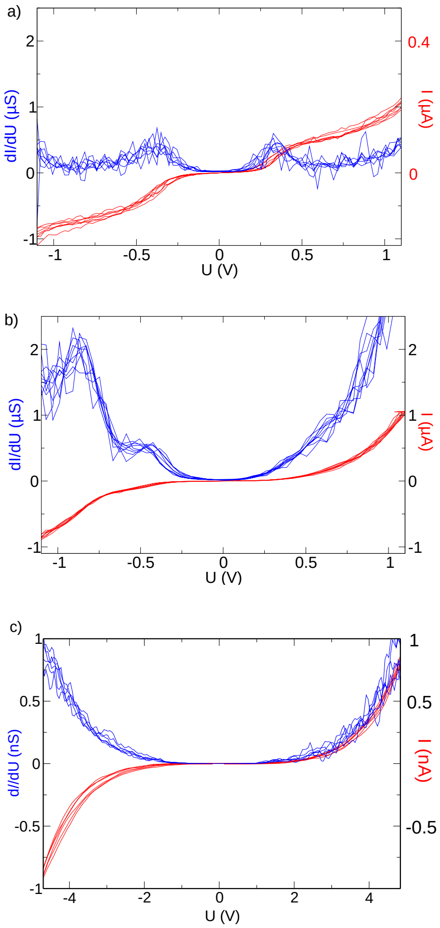

Fig. 2. a)-c): Current-voltage data and differential conductance dI/dU observed in the stability regime for molecules 1-3 (cf Fig. 1), respectively.

References

[1] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, Science **278** (1997) 252.

[2] C. Kergueris *et al.*, Phys. Rev. B **59** (1999) 12505.

[3] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. v. Löhneysen, Phys. Rev. Lett. **88** (2002) 176804.

[4] H. B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Ahlrichs, H. v. Löhneysen, to be published in Chem. Phys .

[5] P. Siemsen, U. Gubler, C. Bosshard, P. Günther, F. Diederich, Chem. Eur. J. **7** (2001) 1333.

[6] M. Mayor, C. v. Hänisch, H. B. Weber, J. Reichert, D. Beckmann, Angew. Chem. Int. Ed. **41** (2002) 1183.

[7] J. G. Simmons, J. Appl. Phys. **34** (1963) 1753.