

REVEALING THE ROLE OF ANCHORING GROUPS IN THE ELECTRICAL CONDUCTION THROUGH SINGLE-MOLECULE JUNCTIONS

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Recent advances in nanofabrication techniques have made possible to contact individual molecules between metallic electrodes and to measure their electronic transport properties. This fact has triggered the hope that single molecules could be used as electronically active elements in a variety of applications. This has given rise to the birth of a new interdisciplinary field already known as *Molecular Electronics*. Although the initial results are promising, the future of this field still depends crucially on our ability to understand the basic transport mechanisms that determine the electrical current at the single-molecule scale.

With this idea in mind, a great effort has been devoted recently to understand how the transport properties of molecular junctions can be tuned by modifying chemically the molecules under study [1]. In this sense, one of the main problems that have been addressed is the role of anchoring groups in the transport through single-molecule junctions [2,3]. However, these studies have been largely based on the analysis of the low-bias conductance, which does not allow to elucidate the exact influence of the terminal groups in both the electronic structure and transport characteristics of the junctions.

In this work we present a combined theoretical and experimental study of the transport properties of ethyne single molecules chemically modified by the introducing thiol, nitro and cyano terminal groups. The measurements were performed using the mechanically controllable break-junction (MCBJ) technique. The advantage of this experimental approach is that it allows us to record the current-voltage (I-V) characteristics, which provide valuable information not contained in the linear conductance. We show that the observed I-V curves can be accurately fitted with a single-level resonant tunneling model. From the fits, we are able to extract both the width of the resonant level that dominates the transport, which is a measure of the strength of the metal-molecule coupling, and the position of this level. Thus, we are able for the first time to establish quantitatively how different end groups determine the metal-molecule coupling and to show these groups affect the internal electronic structure of the molecules.

In order to support the previous conclusions, we have performed first principles calculations of the transport properties of these molecules using a combination of density functional theory and non-equilibrium Green's function techniques [4]. Our computational results show that for all molecules the conductance is dominated by a single level, the closest one to the gold Fermi level. The strength of the coupling and the molecular level energy position were extracted from the first principles calculations and they were found to be in good agreement with our experimental results. We find that the coupling strength is similar for thiol, amino [5] and nitro ending groups, while it is much lower for the cyano group. Moreover, for thiol- and amino-terminated molecules the current proceeds through the highest occupied molecular orbital (HOMO), while in the case of nitro- and cyano-terminated molecules, the conductance was found to be dominated by the lowest unoccupied molecular orbital (LUMO), in agreement with the findings of recent thermopower experiments [6]. These results demonstrate that end groups

not only determine the metal-molecule coupling, but they also strongly modified the internal electronic structure of the molecules, changing in turn the nature of the electrical conduction.

The ensemble of our results constitutes an important step forward in the understanding of the relation between the electronic structure of single molecules and the transport properties of the junctions in which they are embedded.

References:

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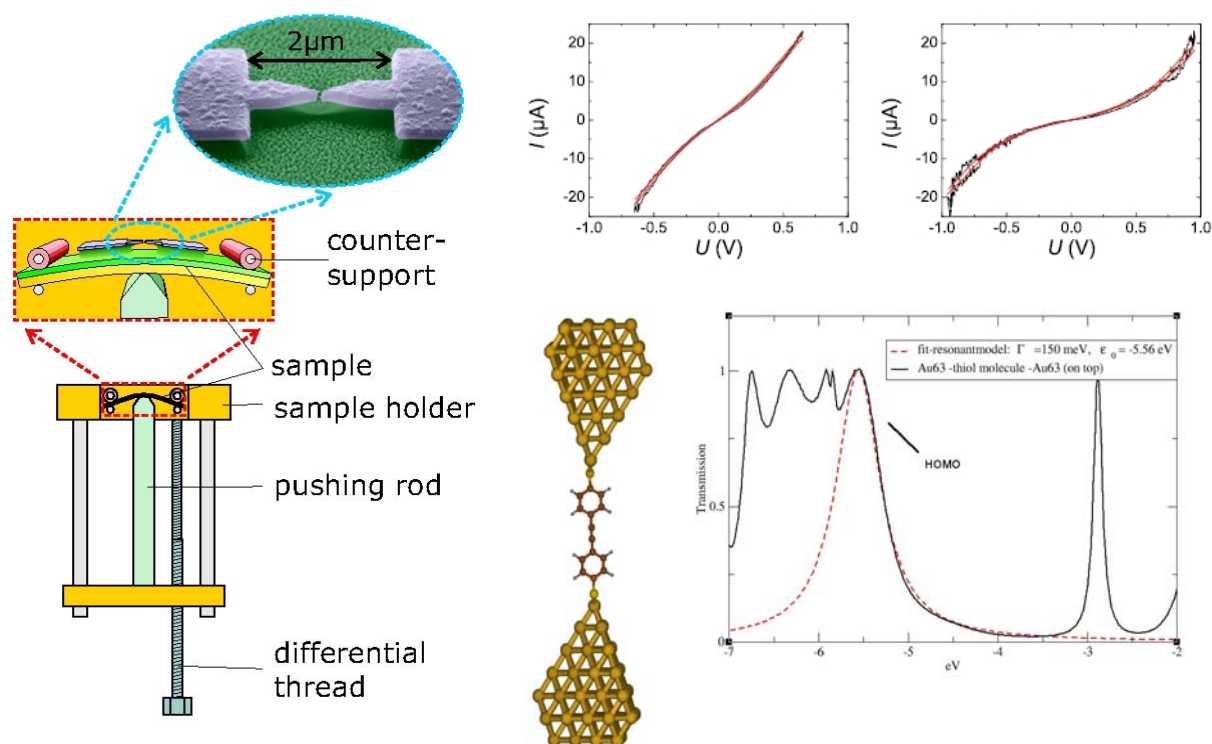


Figure 1: Left: Microfabricated mechanically controllable break-junction set-up. Upper right: Experimental I-V curves of Au |1,2-bis(4-thiolphenyl)ethyne|Au junctions. Lower right: First principle calculations of the transmission through this junction.