Revealing the role of anchoring groups in the electrical conduction through single-molecule junctions

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Great effort has been devoted recently to understand the role of the anchoring groups in the transport properties of single-molecule junctions [1,2]. 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. 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 how these groups affect the internal electronic structure of the molecules.

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 [3]. 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 ending groups, while it is much lower for cyano and nitro groups. 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 [4]. 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.

References:

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Figures:

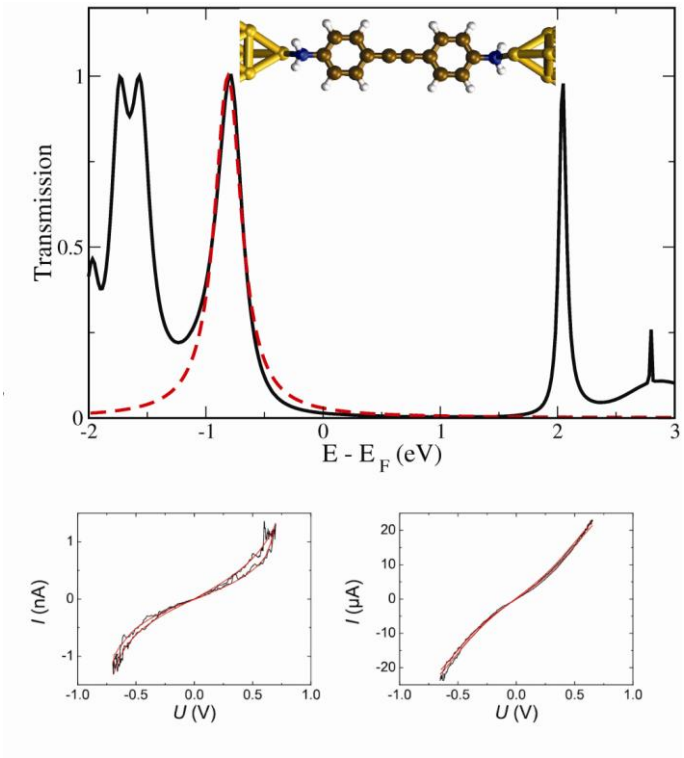

Figure 1 Upper: First principle calculations of the transmission through the Au|1,2-bis(4-aminophenyl)ethyne|Au junction. Lower: Experimental I-V curves of junctions formed with thiol and nitro terminated molecules