PYRROLO-TTF-BASED MOLECULAR ELECTRONICS

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In the last decade we have witnessed the development of a variety of experimental techniques that enable us to sandwich single molecules between metallic electrodes and to measure their transport properties [1]. Moreover, different groups have already demonstrated that certain molecules can perform functions analogous to those of the key microelectronics components such as switches, rectifiers and electronic mixers [1]. These results have triggered the hope that maybe molecules could be used as basic building blocks for future nanoelectronics. However, although the initial results in the field of *molecular electronics* have been quite promising, there are still many basic challenges and open problems. For instance, most molecular junctions exhibit a very low conductance that decreases exponentially with the length of the molecule, i.e. it seems to be very difficult to find the simplest electronic component, namely a good molecular wire. Another important problem is that little it is still known about the relation between the structure and chemistry of the molecules and the transport properties of the junctions in which they are embedded. This is partly due to the fact that experiments probing systematically such relationship are scarce [2].

In this work we address the two fundamental problems described explicitly in the previous paragraph. In particular, we present here a comprehensive theoretical study of the transport properties of molecular junctions based on single bis(pyrrolo)tetrathiafulvalenes [bis(pyrrolo)-TTF] derivatives. These chemical compounds have several properties that make them very interesting for molecular electronics. Thus for instance, they are known to be excellent donors, they have several accessible red-ox states and a rather small HOMO-LUMO gap [3]. Using a combination of ab initio density function theory (DFT) calculations and nonequilibrium Green's functions techniques [4], we have studied the electronic structure and low-bias conductance of single-molecule junctions formed by gold electrodes and up to 20 different bis(pyrrolo)-TTF derivatives. They main conclusions of this study are:

- The electron-donating character of bis(pyrrolo)-TTF leads to a significant charge transfer between the molecules and the metallic leads, which in turn results in an unique level alignment that gives rise to very high conductance at low bias.
- The fact that the transport is dominated by resonant tunneling is manifested in a very slow decay of the low-bias conductance with molecular length. This is clearly at variance with the exponential behavior typically observed in most molecular junctions.
- We also show that the low-bias transport, which is completely dominated by the HOMO of the molecules, can be tuned to a large extent by means of the inclusion of appropriate side-groups.

In summary, our study suggests that due to the intrinsic properties of bis(pyrrolo)-TTF derivatives, they are excellent candidates for molecular wires and they are also ideal test-bed systems to study the structure-function relationship in molecular electronics. Let us finally say that experiments to test the main ideas presented in this work are currently under progress.

References:

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Figures:

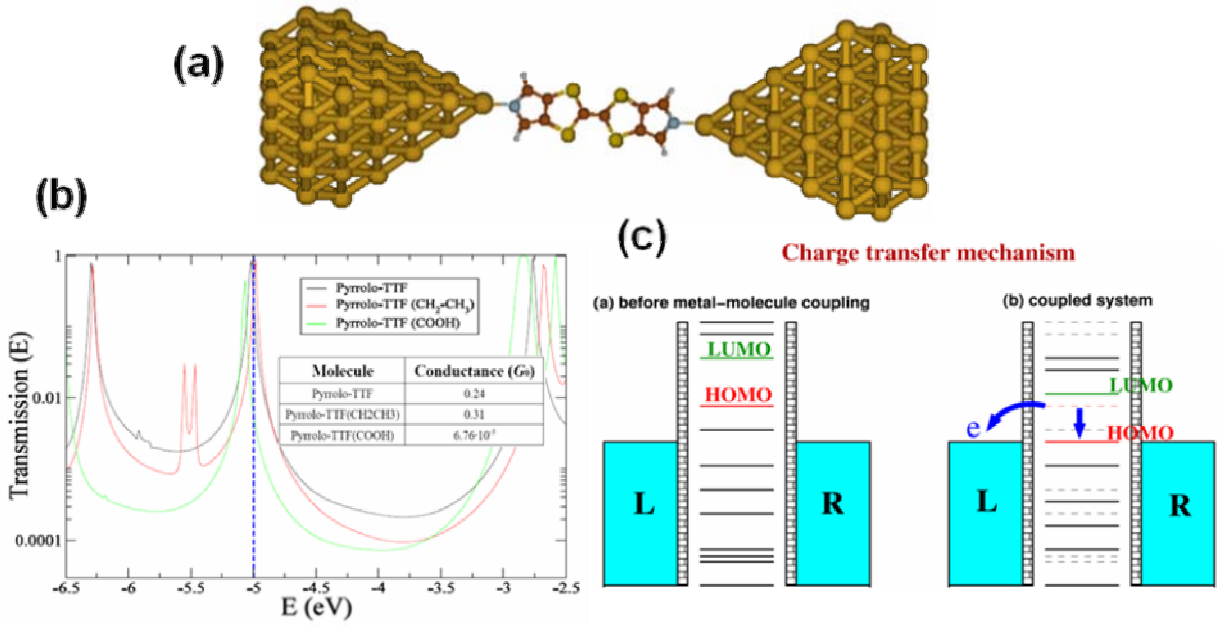

Figure 1: (a) Schematic representation of a gold-bis(pyrrolo)-TTF-gold junction studied in this work. **(b)** Transmission as a function of energy for single-molecule junctions formed with gold electrodes and several bis(pyrrolo)-TTF derivatives. Notice that the transmission is very high at the Fermi energy, the position of which is indicated by vertical dashed line. **(c)** Schematic description of the charge transfer mechanism that leads to the striking level alignment in these molecular junctions.