2E05 Theoretical Study of Donor-π-bridge-Acceptor Unimolecular Electric Rectifier

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Abstract

Electrical rectifying properties of a single molecule nanowire from the type donor-π-bridge-acceptor are investigated by means of non-equilibrium Green's function method combined with density functional theory (NEGF-DFT). The investigated nanowire is an oligo 1,4-phenylene ethylene with π-donor and π-acceptor groups attached on opposite sides of the molecule. The donor and the acceptor wires are separated by a π-bridge in contrast to the Aviram-Ratner rectifier - a donor-σ-bridge-acceptor diode. A model closer to the real molecular electronic device is considered with relaxation of the molecular geometry under the interaction with external electric field taking into account its influence on the electronic properties of the nanowire. Asymmetric I-V diagram is observed with a conductance ratio of 7. The analysis of the spatial distribution of frontier orbitals, the HOMO-LUMO gaps, and the transmission spectra give an inside view of the observed results.

1 Introduction

Aviram and Ratner [1] are the first who proposed a molecular diode in order to illustrate the possibility of making molecular components with the same functionality as semiconductor devices. The donor-σ-bridge-acceptor (DσA) diode consists of two π-conjugated segments separated by one or several σ-bonds. The σ-bonds introduce an insulating barrier to the electron transfer between the wires like in the PIN-type diode. A π-donor group is attached to the D wire, while a π-acceptor group is attached to the A wire. Stokbro et al. [2] have investigated the rectifying properties of single molecule Aviram-Ratner diode with recently developed first-principle Green's function method combined with density functional theory [3]. They have observed symmetrical I-V characteristic for DσA unimolecule diode. The purpose of our study is to give a theoretical answer to the question, whether the unimolecule nanowire has itself rectifying properties or the experimentally observed asymmetric I-V characteristic is a result of the aliphatic chain attached to one end of the molecule. We investigate an alternative donor-π-bridge-acceptor (DπA) diode, shown in Figure 1, between two gold electrodes with first-principle Green's function method combined with density functional theory [3].

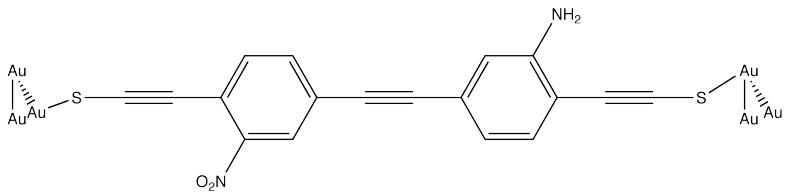

Figure 1: DπA nanowire - unimolecular electric rectifier bridged between two Au(111) electrodes.

2 Discussion

The calculated current as a function of the applied bias, for the DπA-nanowire and its geometries optimized in an external electric field, is plotted in Figure 2. The calculated rectifier ratio is highest for an applied bias of 1.5 V - 7 times. Although the observed ratio is not very high, it is sufficient to show that the investigated nanowire possesses itself diode-like properties and can be used as an unimolecular electric rectifier.

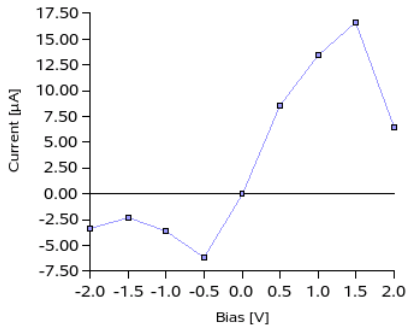

Figure 2: Asymmetrical I-V characteristic of DπA nanowire.

This result can be explained with the difference in the HOMO-LUMO gaps and spatial distribution of the frontier orbitals of the DπA-nanowire as a result of its perturbation by external electric fields in opposite directions induced between the electrodes. The π-electron conjugation and the HOMO-LUMO gap are two important factors that determine the conductance of the molecular wire [4].

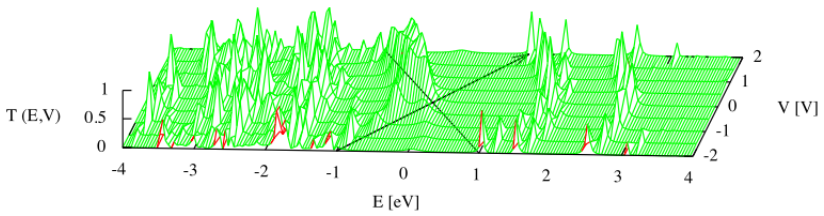

Figure 3: Transmission spectrum of DπA diode.

The zero bias transmission spectrum is not sufficient to determine the rectifying properties of the nanowire. It is necessary to investigate the change of the transmission spectrum under the applied bias in both opposite directions, Figure 3.

References

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