Fermi Level Pinning and Orbital Polarization Effects in Molecular Junctions

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Self-assembled monolayers (SAMs) provide a convenient way for tuning the work function of electrodes and controlling the hole or electron injection barriers.[1] Besides, SAMs have also promising applications in molecular electronics, where they act as a linker between two electrodes. In molecular junctions, the electronic structure of the SAM/metal interface plays a dominant role on the final electronic transport properties that do not simply reflect the properties of the molecules. The key parameters are the alignment of the SAM conducting states relative to the metal Fermi level (E_F), and the interplay between the interfacial and intramolecular electronic couplings.

Recent theoretical studies have suggested that the frontier molecular orbitals can be pinned to the Fermi level (implying that the changes in the HOMO level energy of a conjugated core upon electroactive substitution in the gas phase is not recovered in the junctions) and electronic polarized under the application of a bias.[2] To further shed light on these two phenomena, we investigate here the electronic structure of a series of organic conjugated wires varying by the nature of the central ring when deposited on Au (111) using Density Functional Theory (DFT) calculations, with a special emphasis given to the variations of the work function of the metal. We also use a Non-Equilibrium Green´s function formalism coupled to a DFT framework to simulate the I/V curves of single-molecular junctions and to rationalize them from the evolution of the transmission spectra under bias.

References

[1] (a) B. de Boer, et. al. Adv. Mater. 17 (2005) 622; (b) D. Cahen, et. al. Adv. Mater. 15 (2003) 271.
[2] (*a) Colin Van Dyck, et.al. Phys.Chem.Chem.Phys.15 (2013) 4392; (b) S. Osella, et. al. J. Phys. Chem. C, 118 (2014) 18721*.

Figures

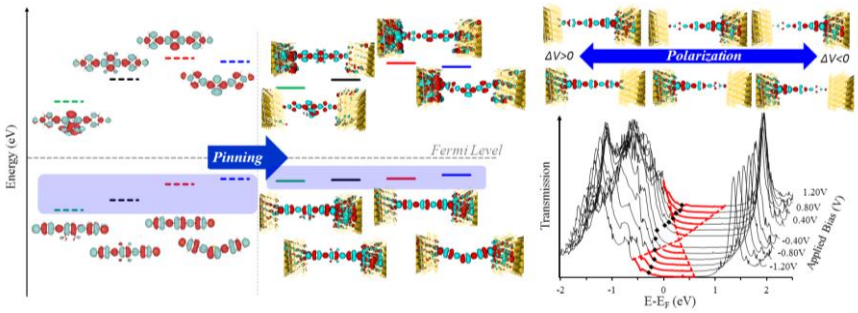

Figure 1: Schematic representation of Pinning and Polarization Effects in Molecular Junctions at equilibrium and under biases.