Molecular Rectifiers: A new design based on asymmetric anchoring moieties

Colin Van Dyck¹, Mark A. Ratner¹

¹) Northwestern University

Corresponding author: Colin Van Dyck (cvd@northwestern.edu)

Nowadays best single molecule rectifiers exhibit limited performances, with typical rectification ratios lower than 10. In previous works, we focused on the Fermi level alignment problem in molecular junctions, more particularly the characterization of the Fermi level pinning phenomenon, at the theoretical level. This effect has a deep influence on the response of the transmission spectrum to an applied bias. Indeed, the pinning leads to a control and a splitting of the energy levels coupled to their respective electrodes. This is at the origin of a consequent orbital polarization effect.

Relying on our characterization of these effects, we introduce here three simple rules to design an efficient rectifying molecule, and demonstrate its functioning at the theoretical level, using the NEGF-DFT technique. The design rules notably require both the introduction of asymmetric anchoring moieties and a decoupling bridge. They lead to a new rectification mechanism based on the high compression and control of the HOMO/LUMO gap by the electrode Fermi levels, arising from a pinning effect. Significant rectification ratios up to 150 can easily be obtained and are theoretically predicted, as the mechanism opposes the resonant to the non-resonant tunneling transport mechanisms.

Van Dyck Nano Letters 2015 15 1577
Advanced Functional Materials 2014 24 6154