

Theory of Rectification Applied on Nitrogen and Boron Doped Nanographenes and Cyclophanes

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The electron-transport properties of boron and nitrogen doped polycyclic aromatic hydrocarbons and cyclophanes are investigated with the non-equilibrium Green's function method and are compared to the transport properties of the unsubstituted species. Aim of the study is to derive the effect of the heteroatomic defects on the conductance of nanographenes and to suggest new effective ways for current control and design of carbon devices. Of special interest are the electrical current rectifying properties of asymmetrically doped nanographenes and cyclophanes, as well as the rectification mechanism. The mechanisms of donor- π bridge-acceptor and donor- σ bridge-acceptor rectification are used to explain the diode-like properties of asymmetrically doped nanographenes and cyclophanes.¹ The electron-rich nitrogen and electron-poor boron heteroatoms introduce conductance channels within the HOMO-LUMO gaps of the hydrocarbons and cyclophanes and significantly enhance the conductance. The combination of nitrogen and boron impurities in one polycyclic aromatic hydrocarbon leads to asymmetrical I/V curve with rectification ratio of 2.

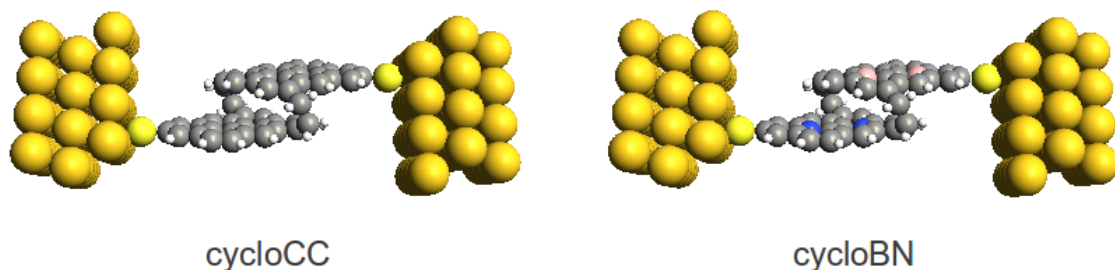


Figure 1: Cyclophane and boron, nitrogen-doped cyclophane junctions. cycloCC denotes the unperturbed cyclophane and cycloBN denotes the boron, nitrogen-doped cyclophane. Nitrogen is shown with blue color and boron is shown with pink color.

The rectification is further enhanced in the cyclophanes where the boron impurities are located in one of the layers and the nitrogen impurities in the other. Due to the efficient separation of the donor and acceptor parts, rectification ratio of 7 was estimated. The rectifying properties of the asymmetrically doped carbon materials are analytically derived from the non-equilibrium Green's function theory. Qualitative calculations are performed with the non-equilibrium Green's function method combined with the Hückel theory. Quantitative calculations are performed with the non-equilibrium Green's function method

combined with the density functional theory. The geometry of the cyclophanes is optimized with MP2.

It was shown that diode-like properties in short molecules can arise as a result of interaction of the external electric field induced between the electrodes with the molecular orbitals. The effect of the field is added as linear potential within the junction and as polarization perturbation to the molecular orbitals. The external field has strong effect on the orbital amplitudes of asymmetrical molecules and can lead to localization of conductance channels when applied in one direction and delocalization of the channels when applied in the opposite direction. Localized channels result in low transmission probability, i.e. low values of the computed current, while the delocalized channels result in high transmission probability and high values of the computed current. Within the ballistic electron transport regime the Aviram-Ratner² hopping rectification mechanism would not be applicable due to the limited effect of the external electric field on each of the π -electron systems. However, in the incoherent electron transport regime where electron hopping is essential the Aviram-Ratner model should be dominant.

Reference:

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2. Aviram, A., Ratner, M. Molecular rectifiers. *Chem. Phys. Lett.* **29**, 277-283 (1974).