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Theoretical Study of conductance through Polycyclic Aromatic Hydrocarbons

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• Introduction

The use of organic molecules as electronic devices has attracted considerable attention in recent years. Electron transport through molecules has been investigated experimentally by scanning tunneling microscopy and mechanically controllable break junction approaches. Theoretical studies gave a better inside view on the electron conductance based on the nonequilibrium Green's function (NEGF) method and Landauer's formula and described the important factors, which control the conductance, i.e. spatial distribution of the frontier orbitals, the effect of the external electric field, and the delocalization of the π–electron system. On the basis of NEGF method and Landauer's formula, an orbital symmetry rule has been proposed for polycyclic aromatic hydrocarbons (PAHs) in molecular junctions[1]. Possible connections of molecules for effective electron transport can be predicted by analyzing the orbital phases and amplitudes of the HOMO and LUMO. For PAHs, their spatial distribution of frontier orbitals and HOMO-LOMO gaps can be influenced significantly by the molecular size and edge type structure[2] and the presence of impurity defects. In this study, the orbital concept is applied on PAHs with different molecule sizes and edge type structures and with heteroatomic defects, which are connected to the electrodes at different sites. We investigate the electron transport phenomena of these systems and attempt to see whether the orbital symmetry rule is applicable with these perturbations.

• Methods

For the molecules having weak contact with electrodes (Figure 1a), various connections for good and poor conductance are predicted by looking at their frontier orbitals with orbital symmetry rule, and the transmission probabilities of different connections are calculated at Hückel level of theory combined with nonequilibrium Green's function (NEGF) method.

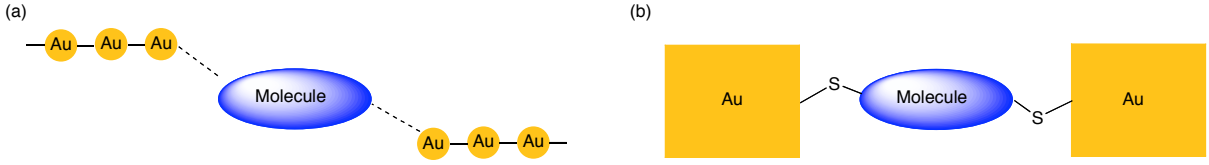

Figure 1. Models of molecular junctions for (a) weak coupling and (b) strong coupling systems.

For the molecular junctions, which have strong coupling between a molecule and two gold electrodes through Au-S bonds (Figure 1b), calculations are performed by NEGF-DFT method in ATK 2008.10 program. The current *I* can be calculated from the eq.1 for applied biases in the range from 0.0 to 1.0 V.

$$I(V) = G_0 \int_{-\infty}^{+\infty} n(E)T(E,V)d\mathrm{E} \tag{1}$$

- **Results and Conclusions**

Good transmission probability of these molecules can be found in connecting sites between atoms in which the phases of HOMO and LUMO are different and the amplitudes of the frontier orbitals are large. The predictions made for weak coupling systems are almost consistent with the DFT results. For the effect of impurity defect by heteroatoms, orbital symmetry rule becomes more effective with the decreasing in proportion of N atom in the molecules. Overall, the orbital symmetry rule works well both in big acene edge type and phenanthrene edge type structures[3] and in the system with heteroatoms impurity defect.

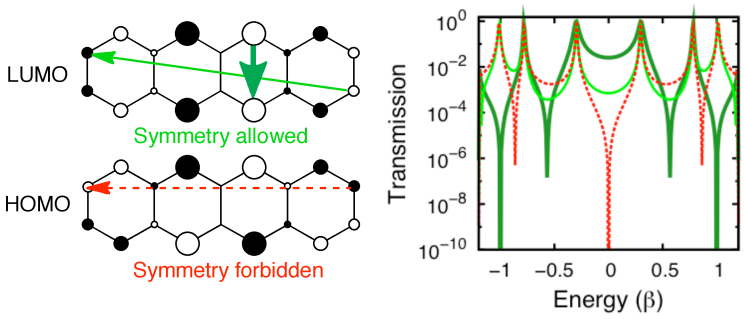

Figure 2. Frontier orbitals of tetracene and symmetry-allowed and –forbidden routes and the transmission spectra calculated with NEGF-HMO method.

(1) Yoshizawa, K.; Tada, T.; Staykov, A. *J. Am. Chem. Soc.* **2008**, *130*, 9406.
(2) Tada, T.; Nozaki, D.; Kondo, M.; Hamayama, S.; Yoshizawa, K. *J. Am. Chem. Soc*. **2004**, *126*, 14182
(3) Li, XQ.; Staykov, A.; Yoshizawa, K. *J. Phys. Chem. C,* **2010**, *114*, 9997-10003.