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Theoretical study in orbital views of electron transport properties in polycyclic aromatic hydrocarbons and transport effects by heteroatoms

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- Introduction

Theoretical studies revealed that the molecular size and edge structure[1], as well as the structure defects[2] in π-conjugated systems of polycyclic aromatic hydrocarbons play important roles in their chemical and electronic properties. Orbital analysis based on first principle calculations shows a close relationship between the frontier orbitals and the electron transport properties in π-conjugated systems. In previous work[3], we proposed an orbital symmetry rule for electron transport properties using metal-molecule-metal junctions, which consist of some small size molecules: naphthalene, phenanthrene and anthracene. On the basis of orbital analysis of the phase and amplitude of the HOMO and LUMO, we were able to predict possible connections for effective electron transport in π-conjugated systems. In this study, the electrical conductance of polycyclic aromatic hydrocarbons with acene edge type and phenanthrene edge type structures, which are connected to the electrodes with different sites, are investigated in terms of the orbital concept by the nonequilibrium Green's function (NEGF) method. To derive heteroatomic effects in electron transport systems, molecules involving N atoms are treated.

- Methods

We analyze the conductance of the molecules, which have weak contact with electrodes, by looking at their frontier orbitals with orbital symmetry rule and calculating at Hückel level of theory. The qualitative predictions are compared with calculations performed by NEGF-DFT method for more realistic molecular junctions, which have strong connections between a molecule and two gold electrodes through Au-S bonds. The *I-V* curves are obtained for applied biases in the range from 0.0 to 1.5 V. The DFT calculations are carried out in ATK 2008.07 program.

- Results and Conclusions

In different edge type of polycyclic aromatic hydrocarbons, the calculated results are in agreement with our expectations. 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. In phenanthrene edge structure molecules, the orbital amplitude on sulfur atoms seems to have an effect on the transport properties on some possible

connecting sites. Overall, the orbital symmetry rule also works well in big acene edge type and phenanthrene edge type structures. 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.

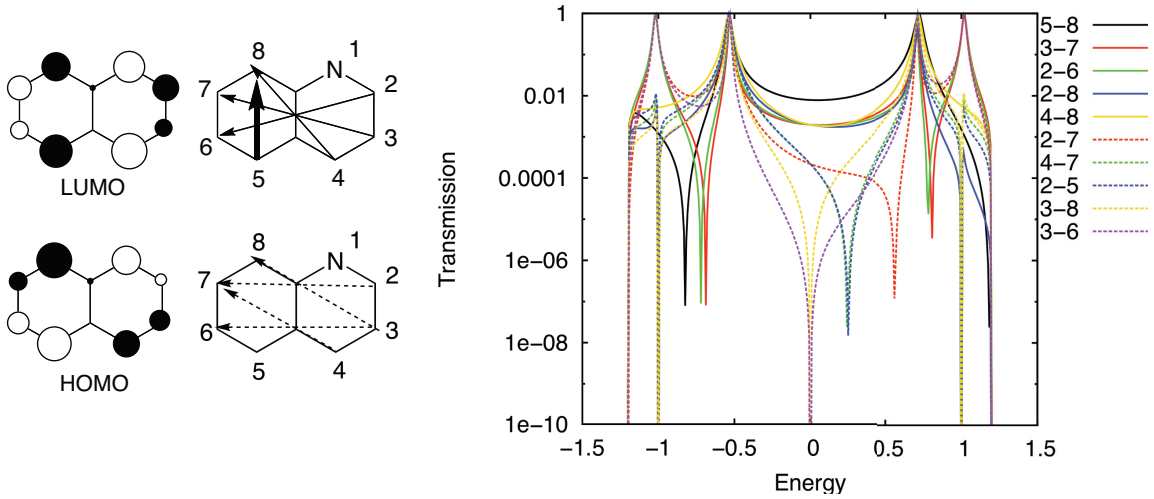

Figure 1. Frontier orbitals of quinoline and symmetry-allowed and –forbidden routes for electron transmission. Computed transmission spectra for the routes at the Hückel level of theory.

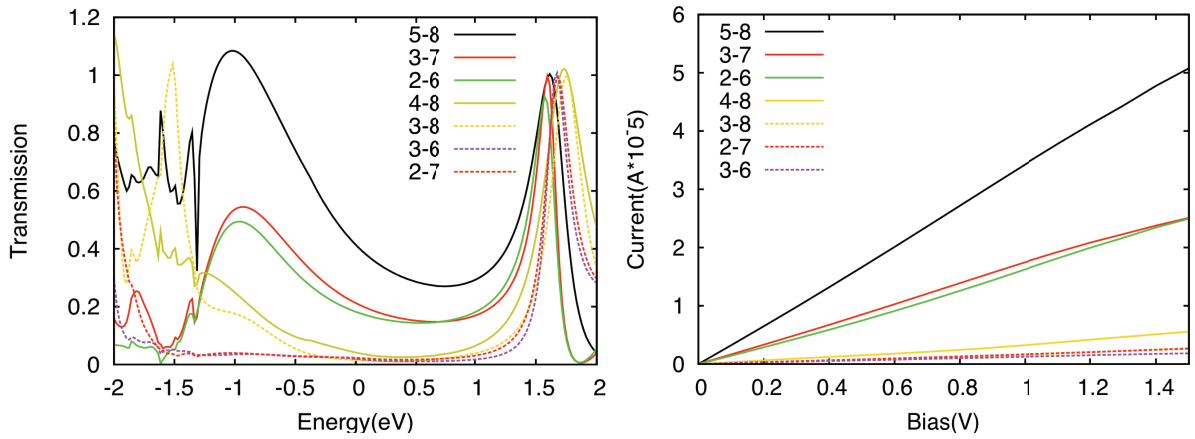

Figure 2. Calculated transmission spectra and *I-V* curves for quinoline dithiolate junctions at the Perdew-Zunger LDA level of theory.

(1) Tada, T.; Nozaki, D.; Kondo, M.; Hamayama, S.; Yoshizawa, K. *J. Am. Chem. Soc.* **2004**, *126*, 14182.
(2) Tada, T.; Yoshizawa, K. *J. Phys. Chem. B* **2003**, *107*, 8789.
(3) Yoshizawa, K.; Tada, T.; Staykov, A. *J. Am. Chem. Soc.* **2008**, *130*, 9406.