

Electronic and Transport Properties of Ferrocene Molecule: Theoretical Study

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1. Introduction

Recently, molecular electronics which probes a single molecule as electric device, such as wire, diode or transistor, has advanced significantly because of future limits of silicon-based technology, which is likely, face fundamental limitations when the lengths of circuits shrink below 100 nm [1]. Theoretical studies based on first-principles calculations have been mainly related to the understanding of conduction mechanisms through molecular structures. Despite the fact that the first-principles methods are either computationally expensive, they are important because can propose novel nanodevices as well as enrich experimental intuition.

The 3d metallocenes, such as ferrocene are also promising candidates for future nanoelectronics since it can be used as a building block in molecular circuit. High degree of chemical and thermal stability in different environments and a wealth of synthetic methods for construction of a variety of relatively complex ferrocene-based systems are the advantages of a ferrocene application to molecular circuits [2]. Moreover, such molecules can be doped by different metals that will also affect on electron transport through cyclopentadienyl ring.

Here, the electronic and transport properties of ferrocene has been studied using the non-equilibrium Green's function formalism of quantum transport and the density functional theory.

2. Computational method and model

Transport calculations have been carried out using a nonequilibrium Green's function approach [3]. The calculation models include two metal contacts connected at the ends of a sulfur-terminated ferrocene (Fig. 1). TranSIESTA-C program is used for this calculation. The contacts and molecules are described using the double-zeta plus polarization basis set for molecules and the double zeta basis set for Au electrode. The electronic structure is calculated using density functional theory with LSDA-PZ.

Using the Hamiltonian and the overlap matrices corresponding to the gold contacts, the surface Green's functions describing the semi-infinite electrodes attached to the molecules from the left and right sides are derived. Green's function in this study is given by

$$G(\epsilon) = [\epsilon - H - \Sigma_L - \Sigma_R]^{-1} \quad (1)$$

The terms Σ_L and Σ_R are called the self-energies of the electrodes. The current of the system is calculated from Green's function using a nonequilibrium Green's function (NEGF) theory.

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} T(\epsilon) [n_F(\epsilon - \mu_L) - n_F(\epsilon - \mu_R)] \quad (2)$$

where n_F is the Fermi distribution function and T is transmission coefficient derived from Hamiltonian and self energies of electrodes

$$T(\epsilon) = \text{Tr}[\text{Im}\Sigma_L(\epsilon)G^\dagger(\epsilon)\text{Im}\Sigma_R(\epsilon)G(\epsilon)] \quad (3)$$

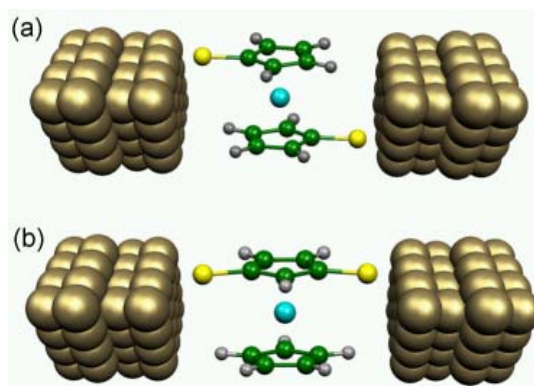


Fig. 1 Models used for transport calculations: (a) 1,1'-dithiol-ferrocene; (b) 1,3-dithiol-ferrocene.

3. Results and Discussion

First, the geometry and electronic structure of isolated ferrocene molecule have been calculated. The optimized geometry of ferrocene is in agreement

with experimental data [4]. Figure 2 shows the transmission coefficient for ferrocene molecules at zero bias. It has been found that the conducting channel near the Fermi energy in the case of 1,3-dithiol-ferrocene is larger as one in the case of 1,1'-dithiol-ferrocene. There several conductance channels below and above Fermi energy are also observed. Thus, 1,3-dithiol-ferrocene has wider peak in the energy interval from -5 to -3 eV.

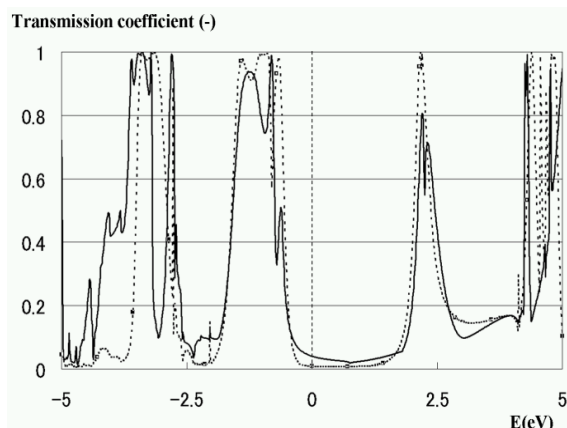


Fig. 2 Transmission coefficient for 1,1'-dithiol-ferrocene (dashed line) and 1,3-dithiol-ferrocene (solid line). The Fermi level (vertical dotted line) has been chosen as zero energy.

Molecular orbital analysis shows that in this energy region, 1,3-dithiol-ferrocene has molecular orbitals that span the length of the molecule (see Fig. 3b). These orbitals, which can be termed as the conduction MOs, should be responsible for the electron transport at non-zero bias and these orbitals can be termed as the conduction MOs.

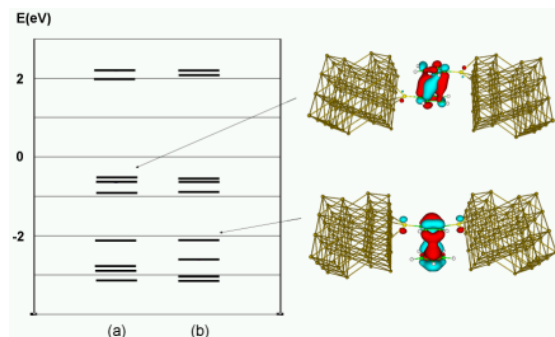


Fig. 3 Molecular orbitals (MO) of (a) 1,1'-dithiol-ferrocene and (b) 1,3-dithiol-ferrocene.

The I-V curves for both structures are shown in Fig. 4. It is found that the conductivity through 1,3-dithiol-ferrocene is higher electrical conductivity

when the same cyclopentadienyl ring is connected to Au electrode by sulfur atoms.

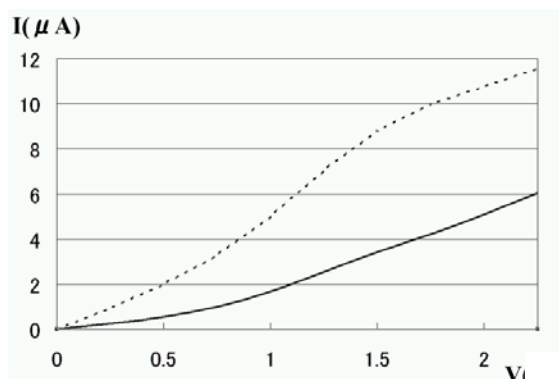


Fig. 4 I-V curve for 1,1'-dithiol-ferrocene (solid line) and 1,3-dithiol-ferrocene (dashed line).

4. Conclusions

The results of the calculations reveal that the conductance through the ferrocene molecule depends on position of S atoms. It is shown that the molecule has higher electrical conductivity when the same cyclopentadienyl ring is connected to Au electrode by sulfur atoms. The I-V characteristic shows that in the case of 1,3-dithiol-ferrocene the transport properties of molecule has a metallic feature.

Acknowledgments

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