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I. Introduction

Molecular devices are potential candidates for this next step, and they would make it possible to realize the most advantageous devices. However, source of expenditure is necessary that such a large number of organic molecules can be obtained by synthetic chemistry, so any means of exploring their properties and behavior in order to predict the relevant properties of a molecule in advance of its synthesis would be extremely useful.

The 3d metallocenes, such as ferrocene, are also promising candidates for future nanoelectronics because they can be used as building blocks in molecular circuits. A high degree of chemical and thermal stability in different environments and a wealth of synthetic methods for the construction of a variety of relatively complex ferrocene-based systems are the advantages of ferrocenes in molecular circuits.[1] Moreover, such molecules can be doped by different metals that will also affect electron transport through the cyclopentadienyl ring, and molecular wires based on ferrocene molecules are compact and linear, which allows one to incorporate such wires into bulky molecules, such as cyclodextrins, to create a shielded molecular wire. Therefore, it can be expected that the ferrocene molecule is a promising material for constructing molecular devices. However, to our knowledge, there are no theoretical reports describing the transport properties of a single ferrocene. Recently, it has been shown that the incorporation of a ferrocene unit into a conjugated phenylethynyl molecular system significantly increases the conductance compared with a similar-in-length, all-organic conjugated phenylethynyl oligomer.[2] In this study the electronic and transport properties of ferrocenedithiolate have been studied using the nonequilibrium Green's function formalism (NEGF) of quantum transport and density functional theory.

II. Computational Methods

Transport calculations have been carried out using the nonequilibrium Green's function approach.[3] The calculation models include two metal contacts connected at the ends of a sulfur-terminated ferrocene (see Fig. 1). Two systems with different five-member ring connections have been taken into account. The 1,3'-ferrocenedithiolate and 1,3-ferrocenedithiolate molecules were selected for this study and are shown in Figs. 1(a) and 1(b), respectively. Their transport properties have been calculated using the TranSIESTA-C program.[4] It is assumed that the gold electrodes are infinitely long. The contacts and molecules are described using the double-zeta plus polarization basis set for molecules and the double zeta basis set for Au electrodes. The electronic structure is calculated using the density functional

theory with local spin density approximation within the parameterization of Perdew and Zunger (LSDA- PZ).

III. Results and Discussion

First, the geometry and electronic structure of an isolated ferrocene molecule have been calculated. The optimized geometry of ferrocene agrees with experimental data. Figure 2 shows the transmission coefficients for 1,3'-ferrocenedithiolate and 1,3-ferrocenedithiolate molecules at zero bias. In both cases, several conductance channels are observed above and below the Fermi energy. These peaks have practically the same features and are located in the same energy region. However, there is a small peak approximately 0.1 units tall just below -2 eV which appears only in the case of 1,3-ferrocenedithiolate molecule. This molecule also exhibits non-zero broadening near the Fermi level in contrast to the zero transmission estimated for 1,3' - ferrocenedithiolate, indicating that the difference in conductance is mainly due to different molecule-electrode couplings. Moreover, 1,3-ferrocenedithiolate system has a wider peak in the energy interval from -4 to -3 eV.

The transmission coefficient changes under the applied bias as shown in Fig. 3. In both systems, all the peaks shift and some of them change shape. In the case of 1,3' - ferrocenedithiolate molecule, there are no significant changes in the first conductance peaks above and below the Fermi level, which means that nearly the same conductance behavior occurs at these voltages. Different features are found for 1,3-ferrocenedithiolate molecule. In this case [see Fig. 3(b)], a new small peak appears near the Fermi level at 2 V. This is most likely due to the splitting of molecular levels of 1,3-ferrocenedithiolate molecule under the applied bias. The difference in the transmission coefficient affects the current-voltage (I-V) characteristics of 1,3-ferrocenedithiolate molecule.

The I-V characteristics of both molecules are shown in Fig. 4. For 1,3-ferrocenedithiolate system, the slope of the I-V curve is large at low bias due to its higher transmission coefficient near E_F as discussed previously. It is suggested that the gold electrode orbitals near E_F contribute to transport. In both systems, the current increases sharply around 3 V because conductance involves the first transmission peaks (see Fig. 3) in the electric transport at relatively high bias. At low bias, only the low energy transmission coefficient is in the integral interval. However, the high energy transmission coefficient enters into the integral interval at higher bias. The 1,3-ferrocenedithiolate molecule shows the metallic features of conductance, and this supports the application of this molecule as a building block for molecular wires. To examine the difference in I-V characteristics at low bias, the molecular orbitals of electrode-molecule-electrode systems were analyzed. In the case of the electrode-1,3'-ferrocenedithiolate-electrode system, the molecular orbitals are primarily localized on the molecule and on one electrode. On the other hand, the molecular orbitals of the

electrode-1,3-ferrocenedithiolate-electrode system distribute from the left to the right electrodes, and hence make a conducting pathway across the 1,3-ferrocenedithiolate molecule. This results in a higher transmission coefficient and transport properties of the 1,3-ferrocenedithiolate system at low bias. These results reveal, in agreement with previously reported data,[2] that the ferrocene molecule is a promising candidate as a component for molecular wires compared with all-organic oligomers. Moreover, it can be expected that the system of ferrocene oligomers will provide even a better conductance due to the reduction in the energy gap between occupied and unoccupied levels as in the case of porphyrin arrays.[5, 6]

IV. Conclusions

The transport properties of two ferrocenedithiolate systems with different five-member ring connections have been estimated using the nonequilibrium Green's function formalism of quantum transport and the density functional theory.[7] The results of the calculations reveal that the conductance through the ferrocene molecule depends on the position of sulfur atoms. The molecule has a higher electrical conductivity at low bias when the same cyclopentadienyl ring is connected to an Au electrode by sulfur atoms. The transmission coefficients of ferrocenedithiolate molecules changed with applied bias. This is attributable to the shift of energy levels and the change of molecular orbital shape by the electric field. The I-V characteristics show that, in the case of 1,3-ferrocenedithiolate system the transport properties of the molecule have metallic features.

References:

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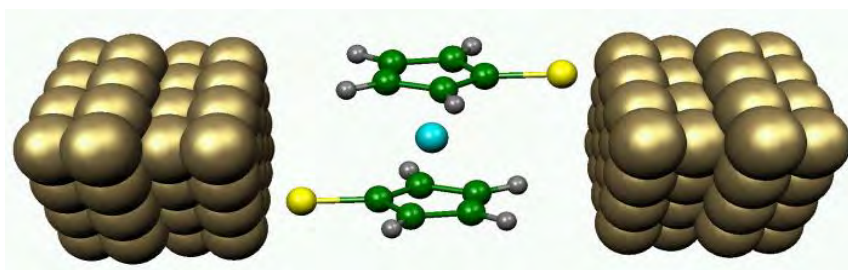
Fig. 1. Models used for transport calculations: (a) 1,3'-ferrocenedithiolate; and (b) 1,3-ferrocenedithiolate molecules connected to gold electrodes.

Fig. 2. Transmission coefficients of 1,3'-ferrocenedithiolate (blue line) and 1,3-ferrocenedithiolate molecules (red line). The Fermi level (vertical dotted line) has been chosen as zero energy.

Fig. 3. Transmission coefficient for zero bias (blue line) and for applied 2 V bias (green line). Figure 3(a) shows the transmission coefficient for 1,3'-ferrocenedithiolate, and Fig. 3(b) shows the transmission coefficient for 1,3-ferrocenedithiolate.

Fig. 4. I-V characteristics of 1,3'-ferrocenedithiolate (blue line) and 1,3-ferrocenedithiolate systems (red line).

(a)



(b)

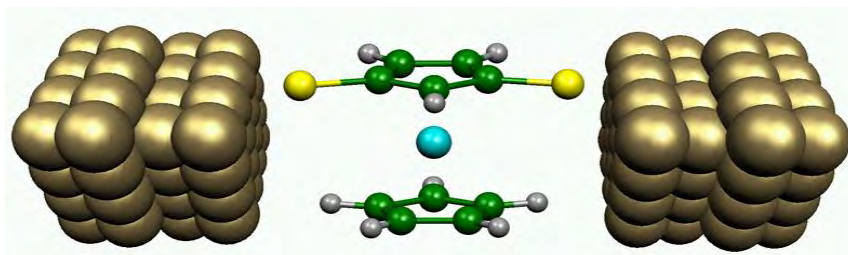


Fig. 1

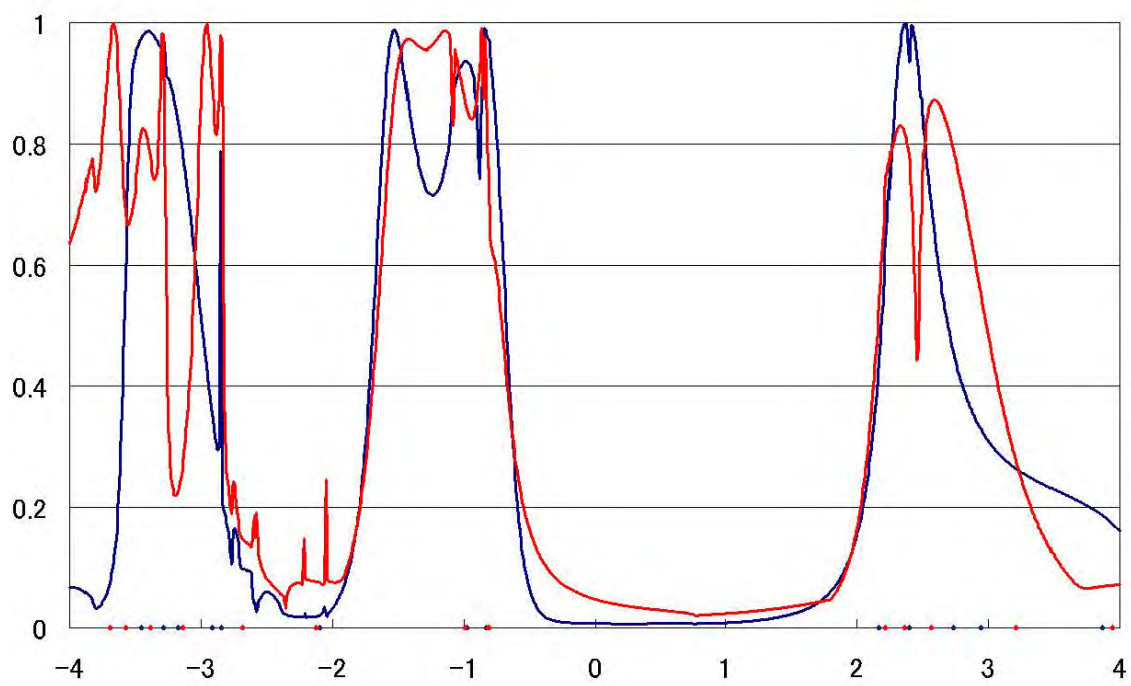
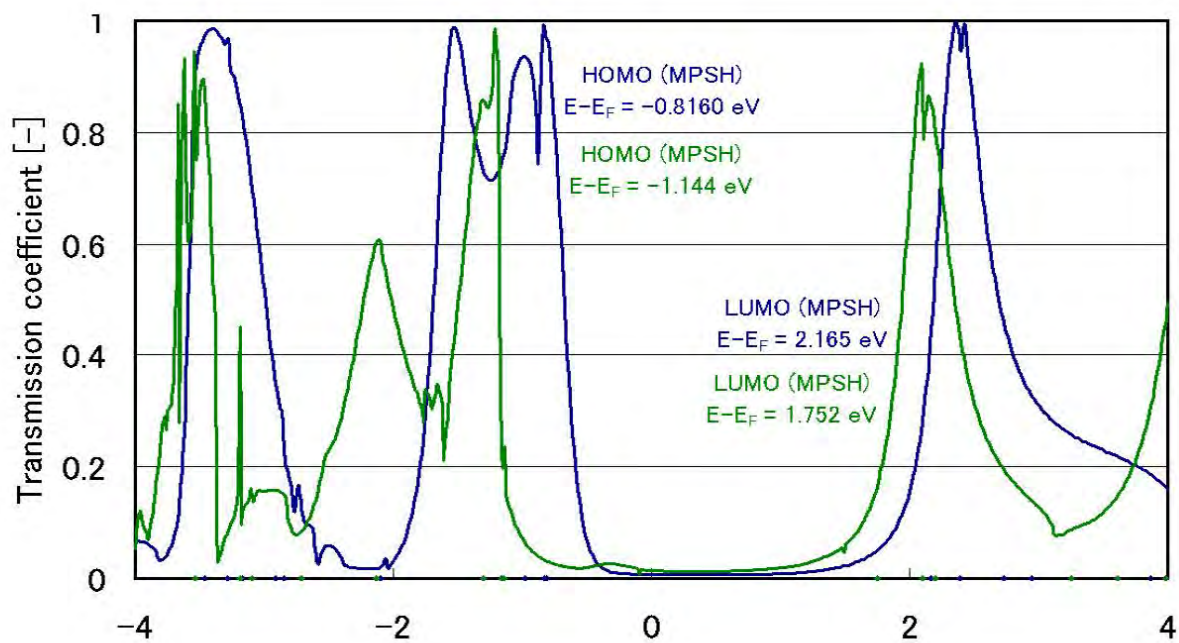


Fig. 2

(a)



(b)

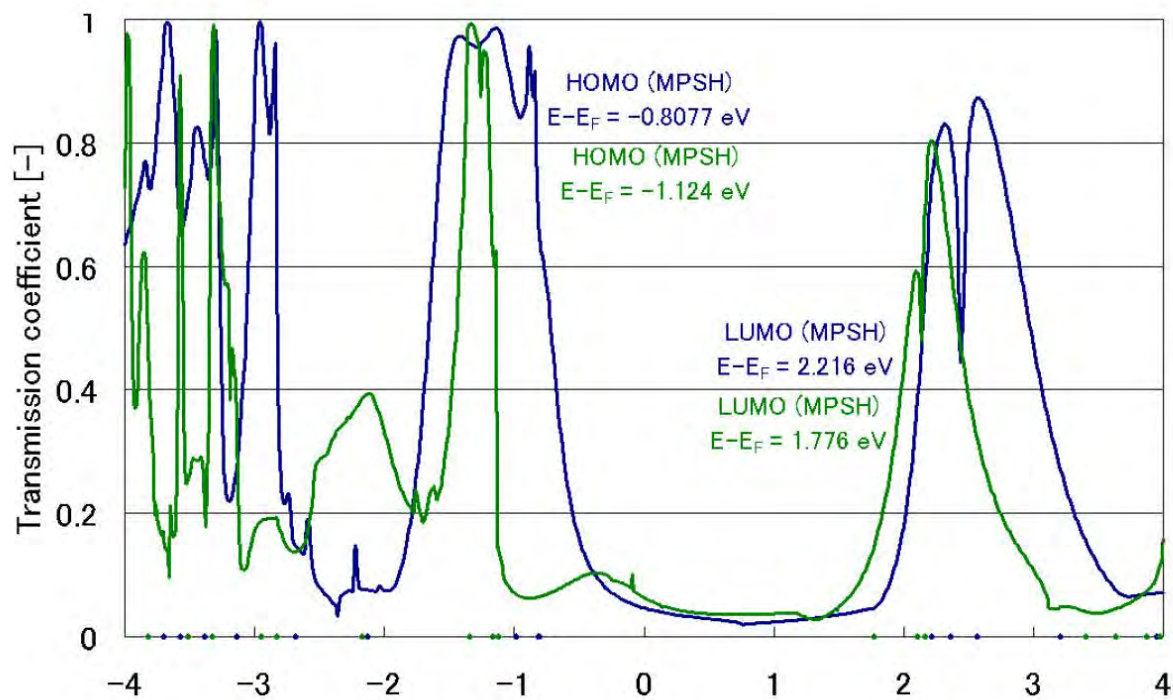


Fig. 3

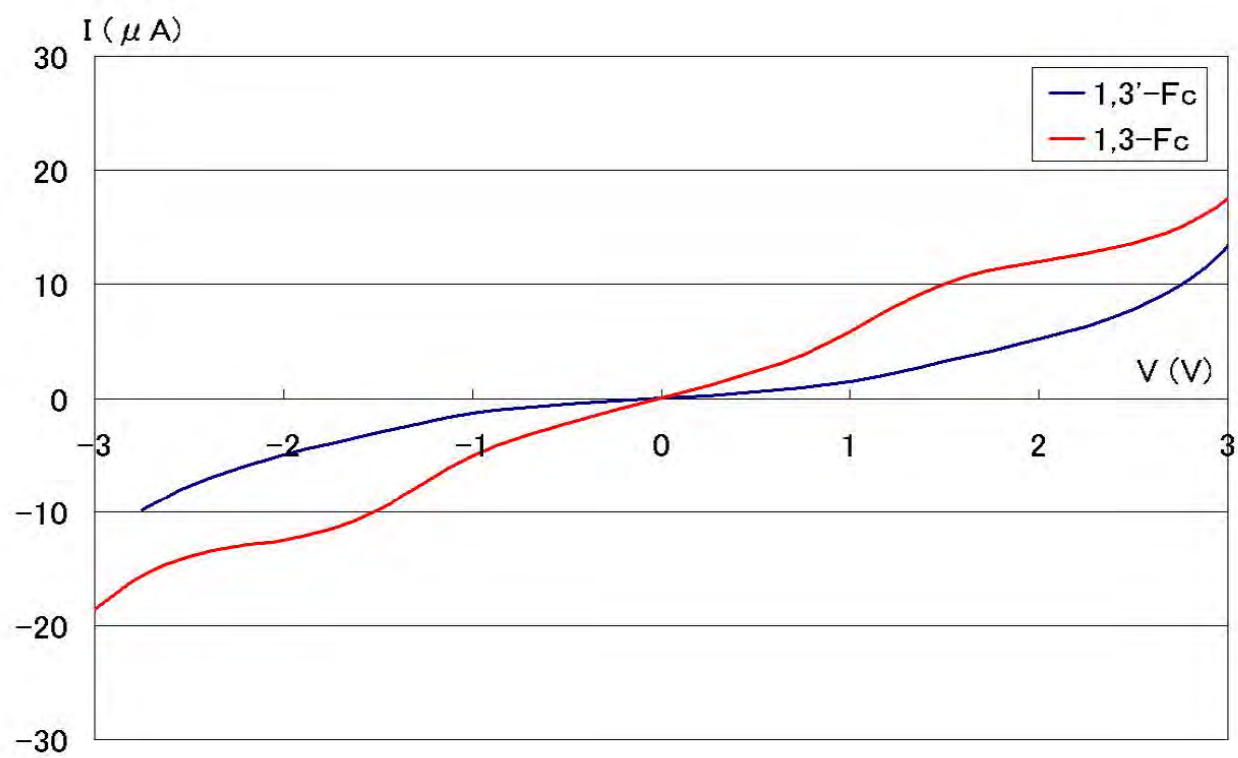


Fig. 4