Effect of Molecule-Contact Distance and Coordination Geometry of Clip Atom in I-V characteristics of Thiophenes containing Cobalt Bisdicarbollide

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Abstract: The I-V characteristics of thiophenes containing Cobalt bis(dicarbollide) are studied by forming a device where the molecule is attached to bulk Au electrodes via Au contacts. It is observed that the increase in the distance between the molecule and one of the contacts increases the conductivity for the reverse bias voltages. For the forward bias, the current increases at lower biases but decreases at higher biases. For both forward and reverse bias, conductivity increases when the coordination of the molecule with the contact is changed from hollow site to bridge site. In both cases, the increase in conductivity is attributed to the shift of the HOMO-2 towards the Fermi level.
Keywords: Carboranes, DFT, NEGF, Junction effect

1. Introduction

Carborane is a closo borane cage composed of boron and carbon atoms in which some boron atoms are replaced with carbon atoms [1]. The complexation of this anionic carborane with a variety of metal ions (e.g. Co, Fe, Ni, Mn) leads to highly stable sandwiches of metalla-bis(discarbollide) compounds [2], where the metal ion is located between the two anionic carborane cages. These organometallic complexes are popular because of their important role in the extraction of nuclides from nuclear waste [3], in molecular recognition [4], in biomedicine and in making redox switched molecular rotors [5]. The carbons facilitate further functionalization of the cages. In this work, the molecule shown in Figure 1 is used as a molecular wire, and the I-V characteristics of the system are studied computationally. This is accomplished by establishing electrical connections between the

Figure 1: Metalla- bis(discarbollide) with one thiophene side chain at each end.

thiophene substituents and gold electrodes (Figure 2). The atoms on the thiophenes that make the contact with the electrodes are called the "clip" atoms. This work focuses on two structural parameters that determine the
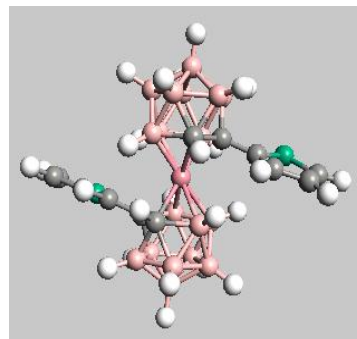
transport characteristics: (i) the distance between the molecule and the contact, and (ii) the coordination geometry of the clip atom with the contact.

2.   Methodology

In order to study the transport properties of the monomer, a system as shown in Figure 2 is modeled where the monomer is attached to bulk Au electrodes on both ends via Au contacts. The Density Functional Theory (DFT) method combined with non-equilibrium green function (NEGF) [6-8] is used for the transport calculation. The B3LYP DFT functional is used with the 6-31G* basis set. The geometry of the molecular system shown in Figure 1 is first optimized independently, and then the Au contacts are introduced. One of the hydrogen atoms in each thiophene ring is replaced with a sulfur (the "clip" atoms) to attach the monomer to the contact.
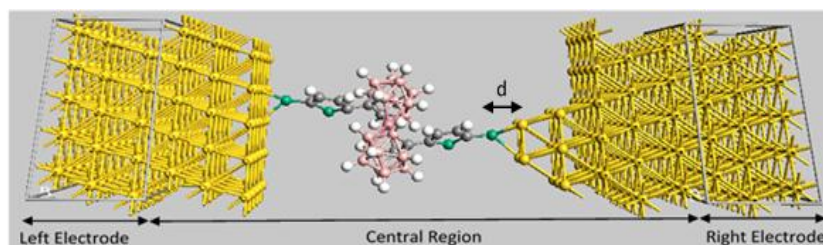

Figure 2: The device studied, showing the definitions of the terms "left electrode," "right electrode," and "central region," as used in this proceeding.

3.   Results and Discussions

The three occupied states of the molecule when attached to the contact that are closest to the Fermi level determine the low bias transport characteristics. These states are shown and labeled according to their energy ordering at a tip-S distance (labeled d in Figure 2) of 1.9 Å in Figure 3.
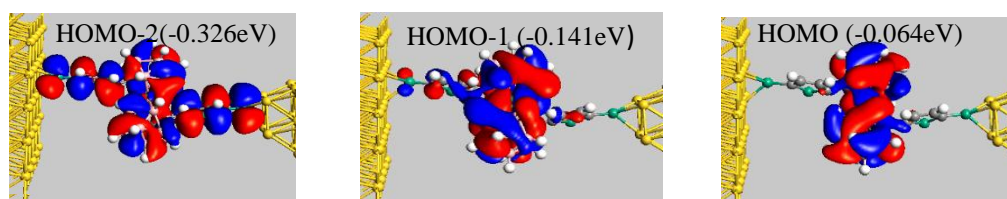

Figure 3: Orbitals of HOMO-2, HOMO-1, and HOMO for the monomer, labeled according to their energy ordering at a tip-S distance of 1.9 Å.

When the distance between the tip and the S clip is increased, reverse bias conductivity is found to increase (Figure 4a). For forward bias, the current initially increases but decreases at higher voltage. The increase in conductivity is the result of the shift of the HOMO-2 towards the Fermi level as tip-S distance is increased (Figure 4b). As HOMO-2 shifts, the corresponding peak in the transmission function shifts towards the Fermi
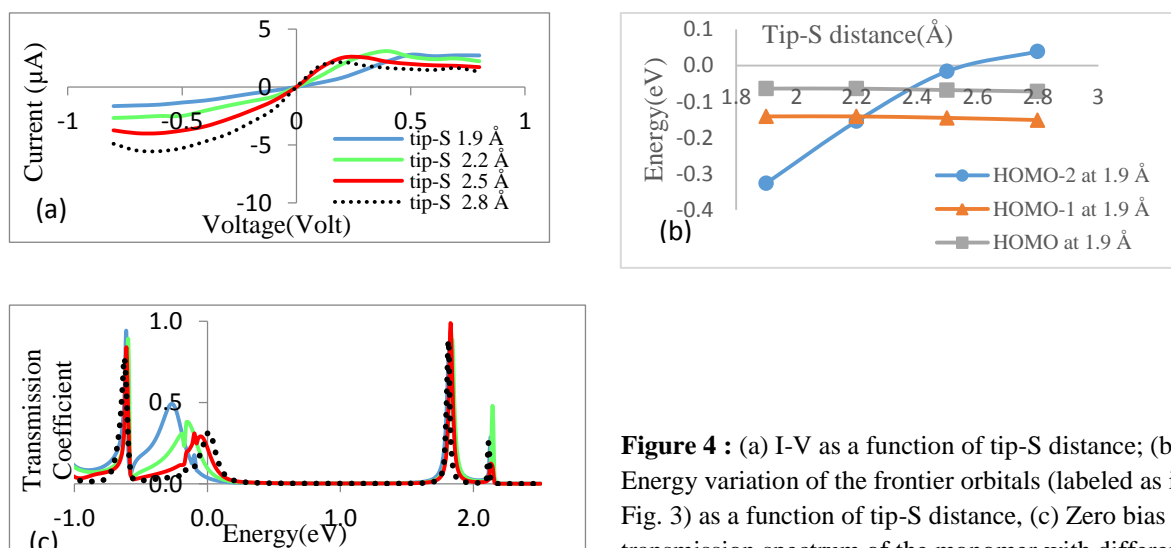
Figure 4 : (a) I-V as a function of tip-S distance; (b) Energy variation of the frontier orbitals (labeled as in Fig. 3) as a function of tip-S distance, (c) Zero bias transmission spectrum of the monomer with different tip-S distances.

level (Figure 4c), and hence there is an increase in the current. An asymmetry in the I-V curve with high current when the right electrode is positive is observed because the distance between the terminal S atom is different in the left contact compared to the right contact.
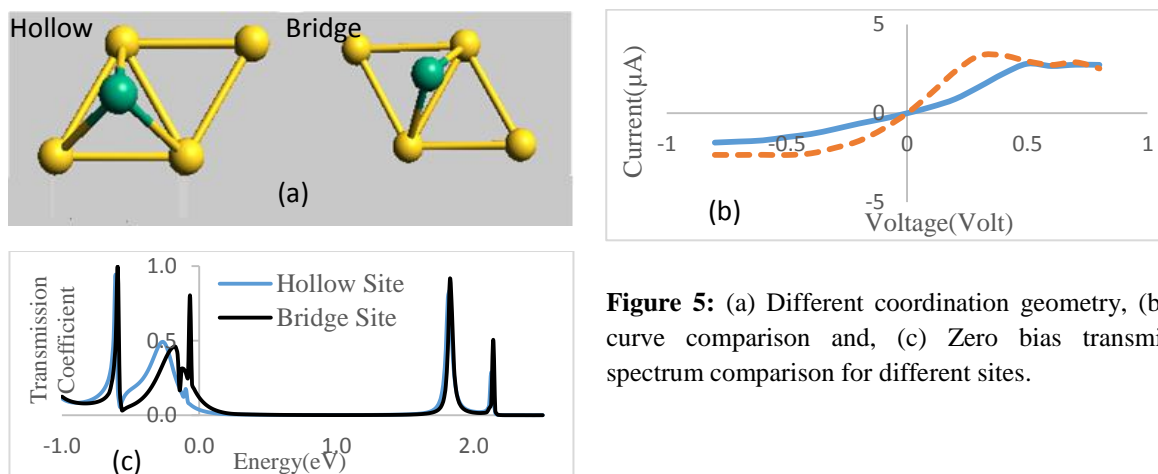

Figure 5: (a) Different coordination geometry, (b) I-V curve comparison and, (c) Zero bias transmission spectrum comparison for different sites.

When the coordination geometry of S clips with the contact is changed from hollow site to bridge site (Figure 5a) keeping the distance between tip and S at 1.9 Å, an increase in conductivity is observed for both, forward bias and reverse bias voltages (Figure 5b). As in the case when the tip-S distance in changed, this is found to be caused by the shift of the HOMO-2 toward the Fermi level what results in the transmission function to also move closer to the Fermi level leading an increase in conductivity.

4. Conclusion

The occupied states close to the Fermi level determine the low-bias transport characteristics. The orbital HOMO-2 that has interaction with the contact gets affected by the change in the molecule-contact interface and shift its energy which produce different transport characteristics. The HOMO and HOMO-1 that has almost no interaction with the contact are hardly affected by changes in the interface.

5. Acknowledgments

6. References

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