Electron Transport in Molecular Enamel Wires

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1. Introduction

Despite a remarkable miniaturization trend in the semiconductor industry, in the next 10-15 years, conventional Si-based microelectronics is likely face fundamental limitations when feature lengths shrink below 100 nm. Thus, there have been many experimental efforts, resulting in significant advances in fabrication of molecular wires, molecular diodes and two-terminal electrical switches made from single molecules [1-3]. Theoretical studies have been mainly devoted to the understanding of conduction mechanisms through promising molecular structures and how the electronic structure of the molecule and the geometry of the molecule/metal interface affect the conduction characteristics.

For molecular electronics applications, it is important that the conducting part of a molecular wire should have metallic characteristics and this part should be isolated from other wires or the substrate in order to prevent any possible current leakage. Therefore, it would be better if a single molecular wire was to be encapsulated into a bulky insulated structure and hence forming a molecular enamel wire. The "molecular enamel wire" concept, in which insulators are placed around a conducting center, was first proposed by Wada *et al.* [1].

One of the possible approaches for utilizing isolated molecular wires for the realization of this concept is the formation of a self-assembled supramolecular complex between the conducting polymer and cyclic cyclodextrin (CD) molecules as shown in Fig. 1.



Fig. 1 Inclusion complexes between CDs and conducting polymer.

The cavity size of CD can be regulated by the number of D-glucose units in each CD molecule and a molecular tube can be created by cross-linking adjacent α -CD units using a hydroxypropylene bridge. Recently, the formation of such inclusion complexes between a conducting polymer, polyaniline with emeraldine base, and CDs was realized [4,5]. Theoretical studies also indicated that β -CD molecules

and cross-linking α -CD molecular nanotubes can be used for stabilization of the isolated near-planar configuration of polyaniline in semiconductor state [6] as well as in a metallic [7] state.

For applications these inclusion complexes in molecular electronics as enamel wires, it is important to understand the conductance properties of these supramolecular structures. For this purpose, the first-principles calculations and nonequlibrium Green function technique have been performed in order to understand the effect of encapsulation on the electronic transport through a polythiophene (PT) chain in different CD complexes.

2. Computational method and model

Transport calculations have been carried out using a nonequilibrium Green's function approach [8]. The calculation models include two metal contacts (Au₂₂ cluster for each contact) connected at the ends of a sulfur-terminated fragment of polythiophene chain (in our case, 7 thiophene monomers) without CDs (Fig. 2a) and inside the CDs molecular nanotube (Fig. 2b).



Fig. 2 Models used for transport calculations.

The contacts and molecules are described using the sophisticated LANL2DZ basis set which incorporates relativistic core pseudopotentials. The electronic structure is calculated using density functional theory with Becke-3 exchange and Perdew-Wang 91 correlation. 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. These surface Green's functions together with the Hamiltonians and overlap matrices of the molecule, and the molecule-electrode part, are then used in order to determine the conductance of the system.

3. Results and Discussion

First, we optimized both the PT fragment with and

without CD molecular nanotubes connected to Au contacts. It can be assumed that for a conjugated molecular wire, the lowest unoccupied orbitals that span the length of the molecule are responsible for the electron transport and these orbital can be termed as the conduction MOs. Figure 3 shows the HOMO and LUMO+K (K values are taken up to the first conduction MO) energy values with and without metal atoms attached. In the case of the free molecular wire the HOMO and LUMO orbitals are delocalized over the thiophene oligomer. In the case of attachment of gold atoms, the LUMO orbital of the free molecule resembles the LUMO+4 of the metal-oligomer complex due to the localization of LUMO, LUMO+1, LUMO+2, and LUMO+3 on the metal clusters. The energy difference between the HOMO and conduction MO in the case of the metal-wire complex (2.66 eV) is practically the same as that in the case of the free molecular wire (2.38 eV), as shown in Fig. 3. This result indicates that the metal-molecule interaction is localized to the interfacial region and hence the metal contacts do not modify the conduction properties of the long molecular wires.



Fig. 3 Schematic MO diagrams of the most stable configurations of the PT fragments: (a) without gold and (b) connected with gold contacts.

The results of the conductance calculations are shown in Fig. 4. It has been found that in the case of polymer chain trapped in CDs the first conducting channels are practically same to those in the case of single polymer fragment.



Fig. 4 Conductance (units of 2e²/h) vs. energy (Hartree) for the isolated PT fragment and encapsulated in β -CDs.

Analysis of the molecular orbital for the PT-CD complex connected to the gold contacts in that energy region (about 0.1 Ha) shows that these unoccupied orbitals span the length of the whole polymer chain is the same as the LUMO of the isolated PT fragment (Fig 3a). Therefore, these conductance channels correspond to electron transport through the polymer chain even in the case of CDs-polymer inclusion complex. The conductance channel in the high energy region (0.4 Ha) is related to the conductance of CDs and it can be activated only under very high applied bias. The small value of conductance indicates that the polythiophene fragment is in semiconductor state in agreement with electronic calculations of that oligomer which shows a large HOMO-LUMO energy gap (2.38 eV). Therefore, in order to use these inclusion complexes as molecular wires, the metallic state of polymer inside CDs should be realized.

4. Conclusions

The results of the calculations reveal that the attachment of Au clusters do not modify the electronic properties of the polymer chain encapsulated in a CD molecular nanotube and there is no significant effect on the conduction MOs of the studied molecular wires. Major conducting channels in all structures correspond to the states extended along the whole length of the system. Encapsulating PT in β -CDs might be a good method for obtaining isolated single molecular wire, especially if accompanied by doping in order to enhance the conductance.

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