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Electronic and Transport Properties of Molecular Wires: Theoretical Aspects for Realization of Nanoscale Interconnection

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1. Introduction

Recently, many experimental and theoretical efforts have been carried out in order to show that instead of silicon-based microelectronics, which is likely face fundamental limitations when the lengths of circuits shrink below 100 nm, the alternative nanoscale materials can perform all the basic functions of conventional electronics components [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. For nanoelectronics, interconnections between electronic devices such as molecular wires are strongly required along with the realization of novel molecular-scale devices. They will use as power supply or ground lines for connecting metal electrodes and single molecular devices. These wires should have metallic characteristics and isolate from other wires or the substrate in order to prevent any possible current leakage.

Here, the several candidates for wire applications have been selected and their conductance properties have been investigated by the nonequilibrium Green's function formalism of quantum transport. Recently, the formation of a supramolecular complex between the conducting polymer and cyclic cyclodextrin (CD), in which CDs are placed around a conducting polymer, was realized experimentally [2]. In such inclusion complexes, the cavity size of CD can be regulated by the number of D-glucose units in each CD molecule and the conductivity of polymer wire can be controlled. Theoretical studies of structural and electronic properties of such shielded wires also indicated that CDs can be used for the stabilization of polymer with near-planar configuration [3]. Moreover, the CD molecules do not affect the conductance through the undoped polythiophene molecular wire [4]. In the present study, the conductance of the doped conducting polymers in CD molecular nanotube has been investigated in order to use this inclusion complex for active molecular wire interconnections.

The porphyrin molecule is also promising candidate for future nanoelectronics since it can be used as a building block in molecular wire. This is supported by recent discovery of different porphyrin arrays having rigid geometric structure and stability in air [5]. Using such arrays it is possible to control the π orbital delocalization which is desirable for molecular wire applications. Moreover, such porphyrin polymers can be doped by different metals that will also affect on electron transport through porphyrin chain.

Therefore, the effect of metal doping on conductance properties of porphyrin has been investigated.

2. Computational method and model

Transport calculations have been carried out using a nonequilibrium Green's function approach [5]. The calculation models include two metal contacts (Au_{22} cluster for each contact) connected at the ends of a sulfur-terminated metal-porphyrins (Fig. 1).

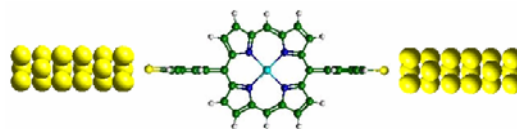


Fig. 1 Models used for transport calculations for metal-porphyrins.

The contacts and molecules are described using the sophisticated LANL2MB basis set which incorporates relativistic core pseudopotentials. The electronic structure is calculated using density functional theory with Becke-3 exchange and Lee, Yang and Parr correlation (B3LYP). 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

3a Doped conducting polymer in CD molecular nanotube

First in order to obtain the geometry and electronic structure, the calculations of sodium doped polythiophene (PT) fragment have been performed. Charge transfer from Na to the polymer chain ($0.42e$ per sodium atom) is found. The main part of the charge goes to the inner rings. The doping atoms are located above the polymer chain and they are closer to the carbons than the sulfur. There is a significant geometry modification in the inner rings which are located closer to the sodium atoms. Also, there is an interchange of the single and double C-C bonds as compared to the undoped case. Such a local transformation reveals the formation of a quinoidlike structure of PT which has metallic characteristics. The value of the HOMO-LUMO energy difference is found to be 1.346 eV which is significantly reduced as compared with the undoped case (2.382 eV). The molecular geometry and

electronic structure of the PT fragment are transformed and this is affected on its conductivity. It has been found that the conducting channel near the Fermi energy in the case of Na-doped polymer chain is larger as one in the case of non-doped polymer fragment (Fig. 2). These conductance channels correspond to the electron transport through the polymer chain.

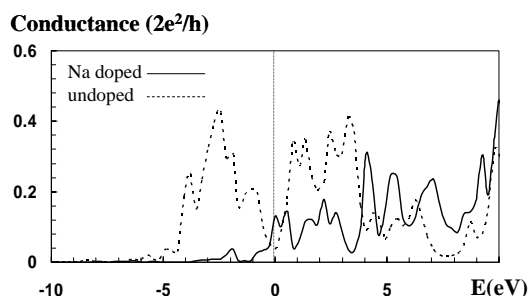


Fig. 2 Conductance for the sodium doped (dashed line) and undoped (solid line) PT fragment. The Fermi level (vertical dotted line) has been chosen as zero energy.

The structure of an *n*-type doped PT fragment in various inclusion complexes based on CD molecules was also studied. The results of calculations showed that the structures of doped PT in the case of a molecular nanotube of cross-linking α -CDs has near-planar geometry and locally transforms to quinoidlike (metallic) form, with the electronic configuration of the optimized structure of PT being practically same as the one in free space. It is found that the sodium atoms are located outside the CD molecules and for formation of an isolated metallic single polymer chain it is necessary to control the separation distance between CD molecules.

3b Metal-porphyrin

The structure, electronic and conductance properties of Metal 5, 15-di-(4-thiophenyl)-porphyrin (MDTP) have been investigated. The results have been shown that the dihedral angle between porphyrin plane and thiophenyl plane is close to the perpendicular, which means that this π conjugation in whole MDPT molecule is broken. Analysis of metal 3d orbital splitting in Zn and NiDTP have shown that in the case of NiDTP, the out-of plane interaction between metal 3d orbital and π orbital of porphyrin is larger than that in the case of ZnDTP. The results suggest that Ni metal will enhance the conductance of DTP since the transport properties in conjugated molecular systems have strong relation to molecular π orbitals.

Figure 3 show the conductance for DTP, ZnDTP and NiDTP. It has been found that the metal with the large out-of plane interaction between metal 3d orbital and π orbital of porphyrin (in our case Ni) enhance conductance of DTP more than metal with large in-plane interaction splitting which means the strong interaction between metal 3d orbital and ligand σ orbitals.

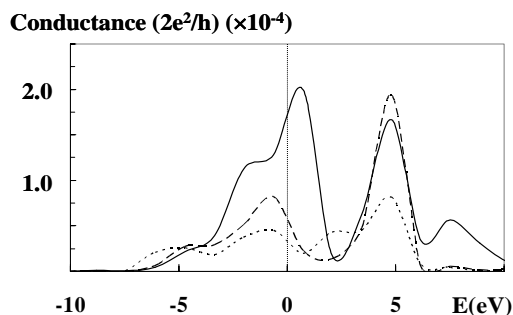


Fig. 3 Conductance for DTP(dotted line), ZnDTP (dashed line) and NiDTP (solid line).

Moreover, the conductance values are found to be a very small which can explain that the thiophenyl groups destroy the π conjugation in whole MDTP structures.

4. Conclusions

The results of the calculations reveal that the doping of conducting polymer increases the conductance through the molecular wire. In order to realize an isolated metallic single polymer chain it is necessary to control the separation distance between CD molecules. This control can be easily realized for a molecular nanotube of cross-linking α -CDs, because in this case, the CDs molecules are connected by chemical bonds. In the case of metal porphyrin, the metal atoms enhance the conductivity. In the case of MDTP, the conductance is small and depends on Au-molecule contact. Therefore, the other connections of porphyrin to electrodes should be proposed in order to realize the molecular wire for interconnections between electronic devices.

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