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# **Molecular Enamel Wires for Electronic Device: Theoretical Study**

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# **1. Introduction**

The main challenge in molecular electronics is to establish that single molecules, or a finite number of self-assembled molecules, can perform all the basic functions of conventional electronics components such as wires, diodes and transistors. Over the past several years there have been significant advances in the realization of electronic devices integrated on molecular scale<sup>1,2)</sup>.

Among different candidates for molecular wire, the conducting polymers are very attractive materials for several reasons; they can be synthesized with highly controlled length, their electrical conductivity can be controlled over the full range from insulator to metal by chemical or electrochemical doping<sup>3)</sup> and they can be chemically bonded without changes of their electronic properties with other functional molecules to create circuits with more complex functionality. However, the carrier mobility is limited by structural disorder of conducting polymer and hence in metallic state, it limits the electrical conductivity. Thus, the control of structural order of conjugated polymers is important for realization of molecular wire with good electrical conductivity. This problem might be solved using the "molecular enamel wire" concept<sup>2)</sup>. According to this concept, the single conducting polymer chain is encapsulated within bulky insulated supramolecular structure. Moreover, such complex can prevent the interfacial interaction between polymer chain and substrate.



Fig. 1 Schematic diagram of molecular circuit. (a) Inclusion complex of CDs and conducting polymer. (b) Polymer chain within molecular nanotube of cross-linking  $\alpha$ -CDs.

One of the possible approaches for realizing this concept is the formation of inclusion complex, which can be incorporated into molecular circuit (Fig. 1), between the conducting polymer and cyclic cyclodextrin (CD) molecules. CDs are versatile hosts since the size of their cavities regulated by the number of D-glucose units in each molecule. The molecular tube can be created by cross-linking the adjacent  $\alpha$ -CD units using the hydroxypropylene bridge (Fig. 1b). Recently, the formation of such inclusion complexes in which a conducting polymer, polyaniline (PANI) covered by CDs was realized<sup>4,5)</sup>. It was found that the conformation of the polymer chain remains rodlike (all *trans* conformation) in CD molecular nanotube. The theoretical study also indicates that  $\beta$ -CD molecules can be used as insulated molecular nanotube for stabilization of the isolated near-planar configuration of polyaniline<sup>6)</sup>.

Here we investigate the structural, electronic properties and current transport characteristics of different CDs-conducting polymer inclusion complexes. The aim of this study is to demonstrate the possibility of the formation of isolated molecular enamel wires using quantum mechanical simulations.

### 2. Computational method

Since the treated inclusion complexes consists of a huge number of atoms, the combined quantum mechanics and molecular mechanics calculations (QM/MM) has been applied for optimization of polymer structure into CDs molecular nanotube. In order to examine the possible charge transfer as well as the interaction between polymer chain and CDs, the single point energy performed calculation has been for optimal configurations of these inclusion complexes using the B3PW91/Lanl2dz level. From these calculations, the Hamiltonian of the system is derived, which is then used in calculating the transport characteristics. Transport calculation is based upon determining the electronic transfer probability across the conducting polymer via the Green's function approach<sup>7)</sup>.

#### 3. Results and Discussion

It has been found that the polythiophene (PT) fragment retains the planar configuration (Fig. 2a) in free space. The structures of the PT fragment in  $\alpha$ -CDs, molecular nanotube of cross-linking  $\alpha$ -CDs and  $\beta$ -CDs have been optimized and are shown in Fig. 2b, 2c, and 2d, respectively. The result of calculations indicates that the configurations of trapped PT are close to the planar structure in the cases of molecular nanotube of cross-linking  $\alpha$ -CDs and  $\beta$ -CDs. The structures of the PT fragment in molecular nanotube of cross-linking  $\alpha$ -CDs and  $\beta$ -CDs lie higher in energy by 0.723 and 0.296 kcal/mol, respectively, as compared to the configuration of five monomer units in free space. It has also been found that in these cases, there are no charge transfer between polymer fragment and host frameworks of CDs, and hence the interaction between polymer and CD molecules has a non-covalent character.



Fig. 2 Structural analysis of PT fragment: (a) in free space; (b) in  $\alpha$ -CDs; (c) in molecular nanotube of cross-linking  $\alpha$ -CDs; and (d) in  $\beta$ -CDs.

The different results have been obtained in the case of  $\alpha$ -CDs-polythiophene inclusion complex (Fig. 2b). Thus the configuration of PT fragment lies in higher in energy by 2.525 kcal/mol as compared to the most stable configuration of five monomer units. Moreover, the CD molecules are distorted and lose the structural order along the polymer chain. Analysis of molecular orbital energy diagrams for PT fragment in three different CD host frameworks shows that the electronic structure of PT is almost the same as that of the most stable conformation. The HOMO and LUMO, LUMO+1 energy levels of PT fragment trapped in CDs are similar to those in the case of planar configuration of the PT fragment in free space.



Fig. 3 Contour of LUMO+2 for four different complexes: (a) PT in (b) PT in  $\alpha$ -CDs; (c) PT in molecular nanotube of cross-linking  $\alpha$ -CDs; and (d) PT in  $\beta$ -CDs.

However, in the case of the LUMO+2 energy level the overlapping between  $\alpha$ -CDs and PT fragment is observed (Fig. 3b). This reveals that the inclusion complex based on  $\alpha$ -CDs host framework cannot be used for realization of molecular enamel wire.

In order to realize the concept of "molecular enamel wire" it is important to understand the stability of the conducting polymers in metallic state when they are encapsulated within molecular nanotube. For this purpose, the PANI fragment in metallic (emeraldine salt) state has been optimized inside the CD molecular nanotube. The results show that the emeraldine salt of PANI in the cases of molecular nanotube of cross-linking  $\alpha$ -CDs and  $\beta$ -CDs has near-planar structure and its electronic configuration is similar to that of the planar conformation of emeraldine salt of PANI in free space.

### 4. Conclusions

In this study, the structures of PT and PANI fragments in various inclusion complexes based on CD molecules were optimized using the QM/MM method. The result of calculations showed that the structures of conducting polymer in the cases of molecular nanotube of cross-linking  $\alpha$ -CDs and  $\beta$ -CDs had near-planar geometry, with the electronic configuration of the optimized structure being practically same as the one in the planar conformation. Moreover, the metallic form of PANI chain can be also covered by insulating molecular nanotube, and supports the realization of molecular electronic device based on this complex.

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