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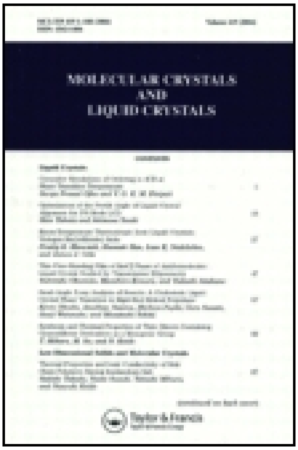

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THEORETICAL STUDY OF MOLECULAR ENAMEL WIRES BASED ON P0LYTHIOPHENE-CYCLODEXTRIN INCLUSION COMPLEXES

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THEORETICAL STUDY OF MOLECULAR ENAMEL WIRES BASED ON POLYTHIOPHENE-CYCLODEXTRIN INCLUSION COMPLEXES

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The structural configurations and electronic properties of polythiophene-cyclodextrin (PT-CD) inclusion complexes have been investigated by a combined quantum mechanics and molecular mechanics method. The results show that the structure of n-type PT in CDs has a quinoidlike form. In the cases of β-cyclodextrins and cross-linking α-cyclodextrins the electronic structure of polythiophene is almost the same as that of polythiophene in free space. The dopants are located outside the CDs, and hence for realization of a doped polymer chain it is important to control the separation distance between CDs, which can be easily achieved in the case of a molecular nanotube of cross-linking α-CDs.

Keywords: α-CD; β-CD; density functional theory; HOMO; LUMO; polythiophene

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 [1–3]. In 1974, Aviram and Ratner [4] first theoretically demonstrated the possibility of an organic molecule to function as a molecular rectifying diode, which was confirmed later by a series of experimental demonstrations [5,6]. At the present time, the main aim of investigations in molecular electronics is to demonstrate that single molecules or a finite number

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of self-assembled molecules can perform all the basic functions of conventional electronics components such as wires, diodes and transistors. Therefore, 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 [7,8].

For application to molecular electronics, the wire is a very important component because it can be used as a connection between a metal electrode and other functional molecules, such as a molecular diode or transistor, to create complex molecular circuits. It is also important that the molecular wire should have metallic characteristics. Among different candidates for molecular wires, such as conducting polymers, carbon nanotubes and DNA, the first seems to be most attractive. Their electrical conductivity can be controlled over the full range from insulator to metal by chemical or electrochemical doping and they can be synthesized with highly controlled lengths [9]. The control of the structural order of conjugated polymers is important for realization of molecular wires with good electrical conductivity because the carrier mobility and hence the electrical conductivity is limited by their structural disorder. This problem might be solved if a bulky insulating structure were to cover the single conducting polymer chain. Moreover, this "molecular enamel wire" concept should make multi-level wiring possible because it can prevent any possible shorts between the wiring [2].

Recently, formation the inclusion complex between the conducting polymer, polyaniline (PANI), and cyclic cyclodextrin (CD) molecules Figure 1 was reported [10,11]. The size of the CD cavities can be regulated by the number of D-glucose units in each molecule (6, 7, and 8 for α-, β-, and γ-CD, respectively). Moreover, a rigid molecular tube can be created by crosslinking adjacent α-CD units using a hydroxypropylene bridge [12] (see Fig. 1b). It was found that the conformation of a single polymer chain inside the CDs remains rodlike conformation (all *trans* configuration) in such a supramolecular structure. Moreover, a previous theoretical study also indicated that β-CD molecules can be used as an insulated molecular structure for stabilization of the isolated near-planar configuration of polyaniline, with the electronic configuration of the optimized structure being almost the same as that in the planar conformation [13]. Therefore, this supramolecular complex is one of the promising candidates for realizing the "molecular enamel wire" concept in molecular electronics applications.

In this context, it is important to study the configuration of doping polymers in CDs. The molecular geometry of the polymer can be

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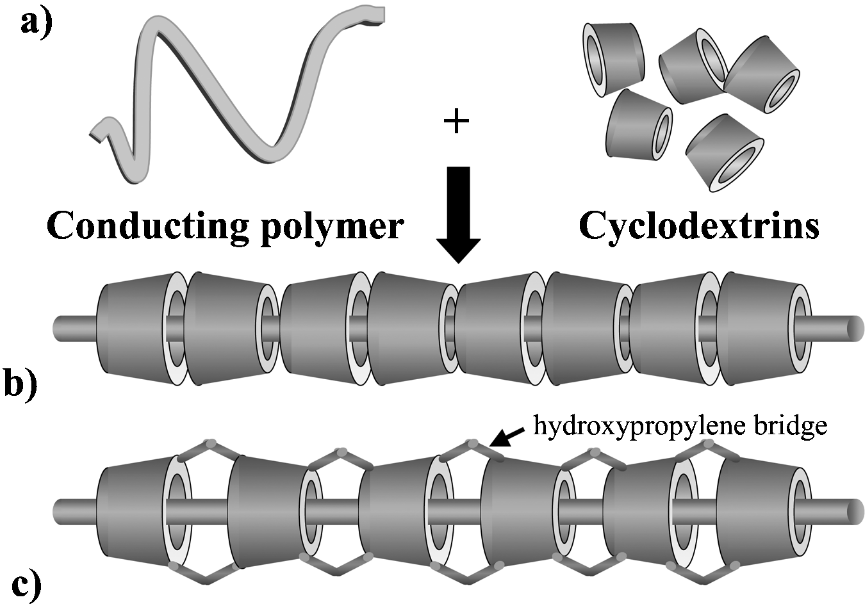

FIGURE 1 Schematic diagram of (a) the polymer and cyclodextrins; (b) inclusion complex formation of CDs and conducting polymer called a "molecular necklace"; (c) polymer chain into a molecular nanotube of crosslinking α-CDs.

transformed and hence affect its conductivity. For this reason, we investigate the structural and electronic properties of different polythiophene-CD inclusion complexes. The aim of this study is to demonstrate the possibility of the formation of isolated molecular wires having metallic characteristics using quantum mechanical simulations.

2. COMPUTATIONAL METHODS

The calculations on the geometries of both the undoped and highly doped polymer chains have been performed under density functional theory (DFT) at the B3PW91/LanL2DZ level of theory. The notation B3 indicates a three-parameter Becke exchange functional [14] and PW91 indicates the Perdew-Wang 91 correlation functional [15]. The use of a hybrid functional in the DFT formalism is fully justified due to the fact that it is a first-principles tool able to accurately predict the energy difference between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. As dopant agents, sodium atoms have been chosen and hence the effect of n-type doping has been studied.

The two-layered "Own N-layered Integrated molecular Orbital and molecular Mechanics" (ONIOM) method [16], which combines quantum mechanics and molecular mechanics calculations, has been applied for optimization of the polymer structure in the CDs molecular nanotube as in our previous work [13] because of the huge number of atoms in the studied inclusion complexes. In this hybrid method, the structure of the polymer fragment is treated quantum mechanically (at B3PW91/LanL2DZ level) while the remainder of the system (the CD molecules) is treated by a molecular mechanics force field (DREIDING force field). Using this method the structure of the selected cluster model has been optimized. In order to examine the possible charge transfer as well as the interaction between polymer fragments and CDs, a single-point energy calculation has been performed for the optimal configuration of this inclusion complex at the B3PW91/LanL2DZ level of theory. These calculations have been performed using the Gaussian 98 set of programs [17].

3. RESULTS AND DISCUSSION

In order to realize the concept of a molecular enamel wire it is important to understand the stability and electronic properties of the conducting polymers in the metallic state when they are encapsulated into a molecular nanotube. Moreover, it is important to know the configuration of the polymer chain formed in the CDs because the source of conductivity for a conjugated conducting polymer is a set of π-type molecular orbitals that lie above and below the plane of the molecule. Among the various conducting polymers, heterocyclic polymers such as polythiophene and polypyrrole have been most extensively studied because high-quality stable films of these polymers can be prepared. Polythiophene [poly(2,5-thienylene)] can be synthesized from dihalogenated thiophene, leading to a fairly well-ordered material, stable in air at room temperature [18]. Investigation of n-type doping is important for practical applications but rarely realized because of greater difficulties as compared to p-type doping. Thus, there are only a few papers on n-type doping of polythiophene [19].

We first optimized undoped and Na-doped fragments of polythiophene (PT), which consists of seven monomer units in free space. The undoped PT fragment remains in the planar aromatic form Figure 2a, with one single and two double C–C bonds inside the heterocyclic ring and single C–C bonds between rings. The calculated bond lengths are as follows: $d_{C-S} = 1.811\,\text{Å}$, $d_{C=C} = 1.386\,\text{Å}$, $d_{C-C} = 1.424\,\text{Å}$ for the ring; and $d_{C-C} = 1.436\,\text{Å}$ for the ring-connection. All these values are in good agreement with the experimental x-ray geometries of bithiophene [20] (where $d_{C-S} = 1.712\,\text{Å}$, $d_{C=C} = 1.357\,\text{Å}$, $d_{C-C} = 1.433\,\text{Å}$ and

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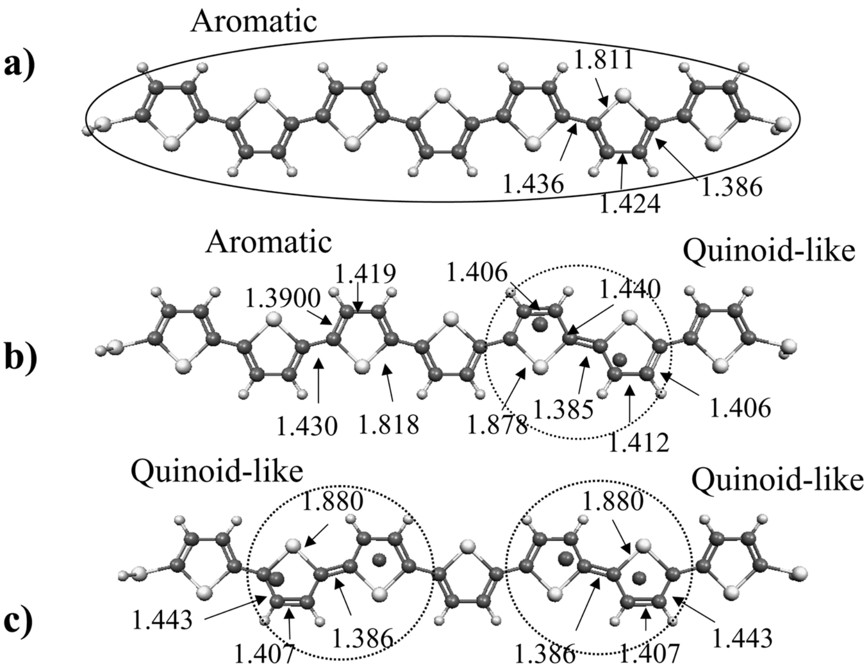

FIGURE 2 Structural analysis of the most stable configurations of PT fragments in free space: (a) undoped PT fragment; (b) Na-doped (28.6%) PT fragment; and (c) Na-doped (57.1%) PT fragment.

$d_{C=C} = 1.480\,\text{Å}$). The value of the HOMO-LUMO energy difference is found to be 2.382 eV, close to experimental value 2.1 eV [19] which indicates a semiconducting state for undoped polythiophene.

The geometries of the sodium-doped PTs are shown in Figure 2(b,c). Charge transfer from Na to the polymer chain (0.42*e* 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 (see Fig. 2). 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 in good agreement with the experimental observed adsorption peak of about 1.6 eV [19]. This energy value is significantly reduced as compared with the undoped case (2.382 eV). Electronic structure analysis also shows charge transfer from the Na atoms to PT Figure 3. The lowest unoccupied orbital

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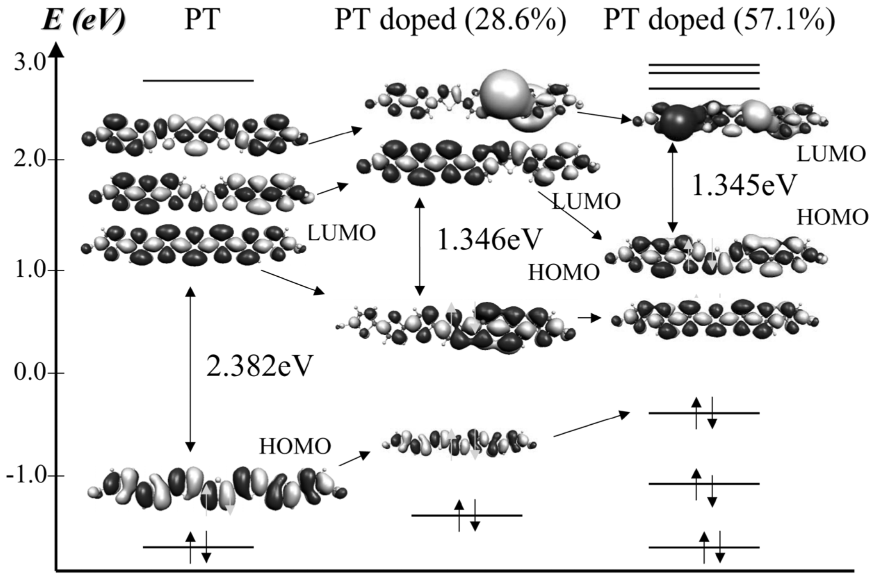

FIGURE 3 Schematic MO diagrams of the most stable configurations of PT fragments in free space: (a) undoped PT fragment; (b) Na-doped (28.6%) PT fragment; and (c) Na-doped (57.1%) PT fragment.

(LUMO) of PT accepts electrons and becomes the highest occupied orbital (HOMO) in the case of 28.6% doping. It is also found that increasing the doping concentration to 57.1% does not lead to a reduction in the band gap (1.345 eV) as compared to the case of 28.6% doping. Structure modifications in this case also have local character (Fig. 2c). This can be explained by the experimental data that the carriers in *n*-type doped PT are not as mobile as the *p*-type doped PT [19].

Recently, the structure of an undoped PT fragment in various inclusion complexes based on CD molecules was theoretically investigated using the same calculation procedure as reported here [21]. The results of calculations showed that the planar structure of single undoped polythiophene can be stabilized in the cases of β-CDs and molecular nanotube of cross-linking α-CDs. It has also been found that in these cases, there is no charge transfer between the polymer fragment and host framework of CDs [21]. Therefore, in the present study, the structures of the Na-doped PT fragment in β-CDs and in a molecular nanotube of cross-linking α-CDs with different configuration of Na atoms have been optimized and are shown in Figure 4. For the β-CDs, two initial structures have been selected in which the Na atoms are located inside and outside the CD molecules (Fig. 4a and 4b, respectively). In the first case, after optimization strong deformation of

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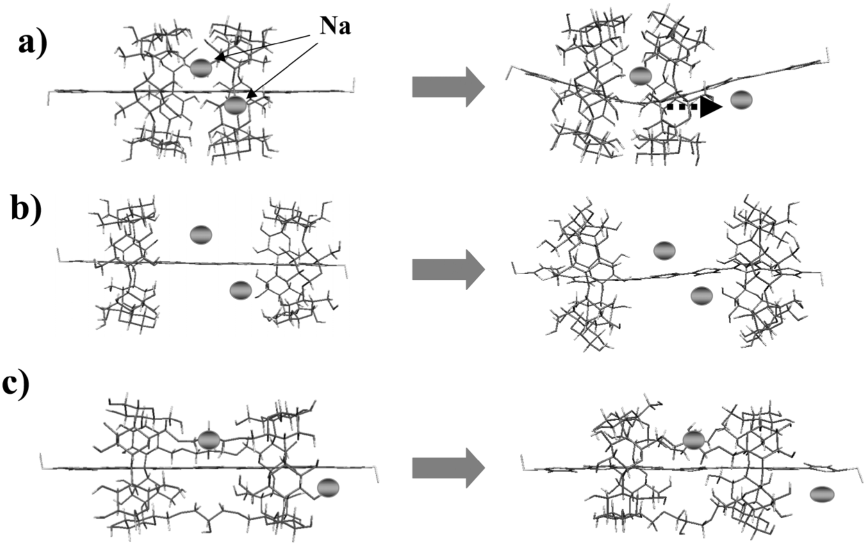

FIGURE 4 Initial and optimized geometries of Na-doped (28.6%) PT fragment: (a,b) in β-CDs; (c) in a molecular nanotube of crosslinking α-CDs.

the PT fragment is observed. Moreover, one of the Na atoms is moved outside the CD molecules. In the second case, the doping atoms remain closer to their initial positions but the distance between the CD molecules increases. This indicates that doping of PT in the case of the β-CDs is difficult because one must control the separation distance between the β-CD molecules in order to prevent a large deformation of the PT chain. However, in the case of a molecular nanotube of cross-linking α-CDs (Fig. 4c), such control can be easily realized because the CD molecules are connected by chemical bonds. As in the case of doped PT in free space, the geometry modifications in the inner rings of PT provoke, along the carbon path, the interchange of the single- and double-like bonds (see Figure 5). The bonds between rings decrease from 1.436 Å to 1.380 Å, which means a local transformation of PT from aromatic to quinoid form as in the case of doping PT without covering by CD molecules.

To understand the electron transport through PT, we have analyzed the spatial extent of the frontier orbital, which provides a strategy by which the transport properties of these systems can be understood. Analysis of the molecular orbital energy diagrams Figure 6 for the configurations of doped PT in the CDs host framework shows that the HOMO and LUMO+2 orbitals (as well as LUMO and LUMO+1) are located on the polymer fragment and their contours are similar to those in the case of the planar configuration of doped PT in free space. This result may be important from

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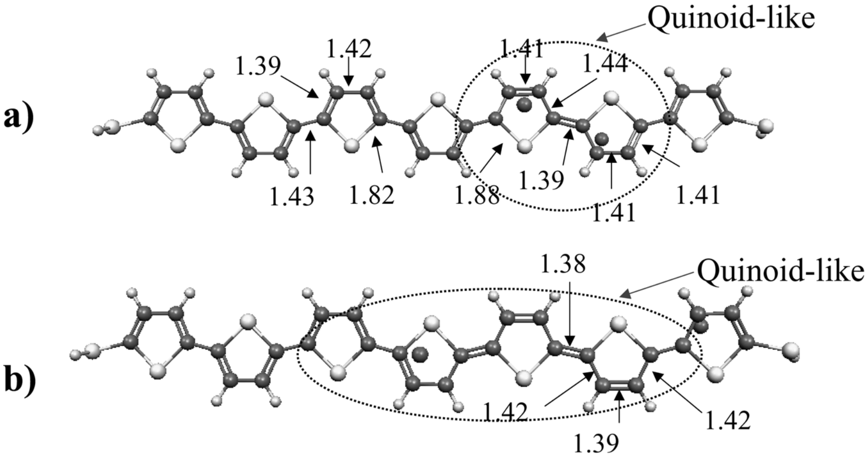

FIGURE 5 Structural analysis of Na-doped (28.6%) PT fragment: (a) in β-CDs; (c) in a molecular nanotube of crosslinking α-CDs.

a practical point of view since the experimental realization of polyaniline, which has a larger diameter compared with polythiophene, in a crosslinking α-CD nanotube has been already reported, and AFM and STM observation indicated the formation of an inclusion complex in which the

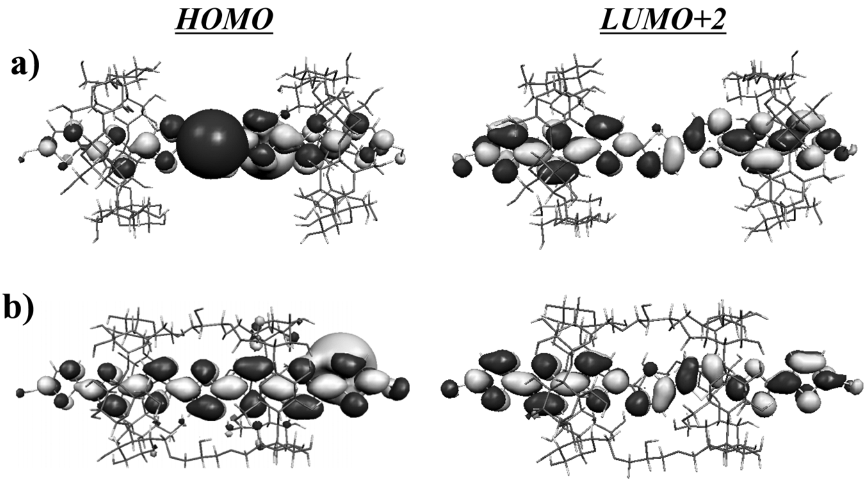

FIGURE 6 Contour of the HOMO and LUMO+2 orbitals for Na-doped (28.6%) PT-CDs inclusion complexes: (a) in β-CDs; (b) in a molecular nanotube of crosslinking α-CDs.

polymer is fully covered by a molecular nanotube [9]. These experimental data in combination with the present theoretical results provide support for the "molecular enamel wire" concept [2] and hence can suggest this supramolecular system as a good candidate for realizing this concept in molecular electronics.

4. CONCLUSIONS

In this study, the structure of an *n*-type doped PT fragment in various inclusion complexes based on CD molecules was optimized using the combined quantum mechanics and molecular mechanics (QM/MM) method. 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 in order to prevent large deformation of the PT chain. 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. The theoretical results, in agreement with experimental data [10,11], may also suggest the application of such inclusion complexes in complex molecular circuits.

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