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Theoretical Study on Inclusion Complex of Polyaniline Covered by Cyclodextrins for Molecular Device

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1. Introduction

Recently, the molecular electronic devices have attracted considerable interest of scientists and the semiconductor industry as a "post-silicone technology" in consequence with a future applications and trends in advanced computer electronics [1]. In parallel with the progress of more effective fabrication technologies, the theoretical study of promising molecular structures based on quantum mechanical calculations is one of the key factors for designing new electronic devices with the desired physical characteristics.

One of the possible approaches for realizing the molecular devices is the formation of self-assembly supramolecular structures such as inclusion complexes [2]. It was reported that the cyclic molecules cyclodextrins (CDs) were threaded onto a polymer chain and formed a "molecular necklace" structure owing to very small cavities and close packing of the CD molecules [2-4]. In such insulated molecular nanotube, the conformation of the polymer chain remains to be close to a rodlike one. Recently, the formation of a new inclusion complex (Fig. 1), namely "insulated molecular wire", in which a conjugated conducting polymer covered by CDs, was realized [5]. Although, polyaniline itself has a good conductivity, the configuration of polyaniline in CDs is transformed and conductivity is very sensitive to molecular structure.

Fig. 1 (a) Schematic diagram of inclusion complex formation of CDs and conducting polymer. (b) Cluster model used for calculations.

In order to examine the configuration of polyaniline in CDs, we investigate the structural and electronic properties of this inclusion complex

2. Computational method and model

CDs are versatile hosts since the size of their cavities regulated by the number of D-glucose units in each molecule (6, 7, and 8 for α-, β-, and γ-CD, respectively). Their shapes resemble a short tube as shown in Figure 1a and the radius of one side is slightly larger than that of the other side. According to the experimental data, the minimal unit cell that consists from two β-CDs and polyaniline base has been selected (Fig. 1b).

Since the number of atoms in minimal unit cell is more than 300, the combined quantum mechanics and molecular mechanics (QM/MM) method has been applied. In this hybrid method part of the structure the polyaniline base (in our case, two conjugated monomer units) is treated quantum mechanically (HF/6-31G*) while the remainder of the system (CDs) is treated by molecular mechanics force field (DREIDING force field).

3. Results and Discussion

It is well-known that the source of the conductivity for a conjugated conducting polymer is a set of π-type molecular orbitals that lie above and below the plane of the molecule when it is in a planar or near planar conformation [6]. Thus it is important to know what configuration of polyaniline fragment formed into CDs.

First, we optimized the two monomer units in free space using both the full optimization in order to find the lowest energy structure and partial optimization with keeping planar configuration of polyaniline base (Fig. 2). The planar structure is higher in energy by 11.93 kcal/mol at HF/6-31G* level as compared to the most stable structure. Next, the structure of polyaniline base in two CDs has been optimized and shown in Figure 3. The result of calculations indicates that the configuration of trapped polyaniline molecule is close to planar structure.

The structure of polyaniline base in CDs lies higher in energy by 8.74 kcal/mol as compared to the most stable configuration of two monomer units in free space. Thus,
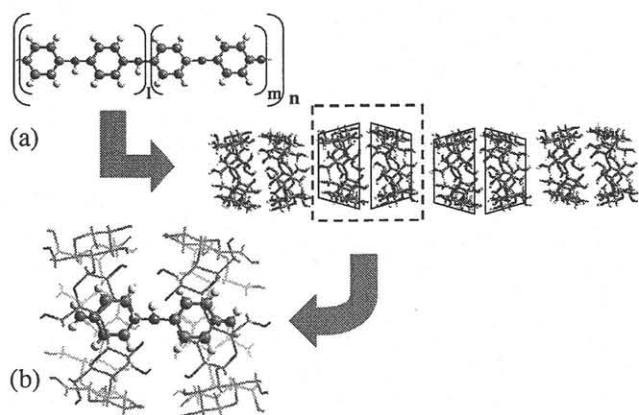
the near planar configuration of polymer chain is formed in CDs owing to the non-covalent interactions such as Coulomb and van der Waals between host framework of CDs and polyaniline guest molecule. The stoichiometry of this inclusion compound is 1:1 (CD-polyaniline monomer unit), which is in good agreement with experiment [5].
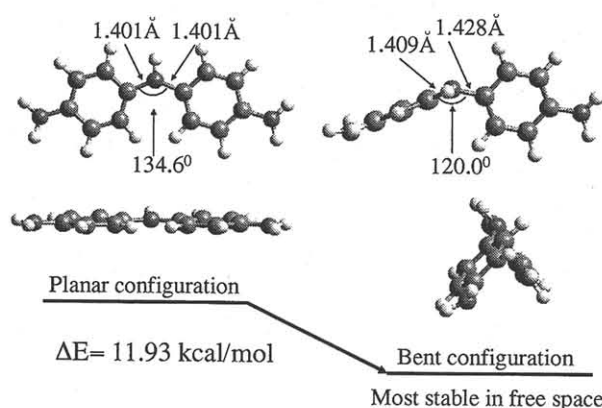

Fig. 2 Structural analysis of different conformations of polyaniline fragment.
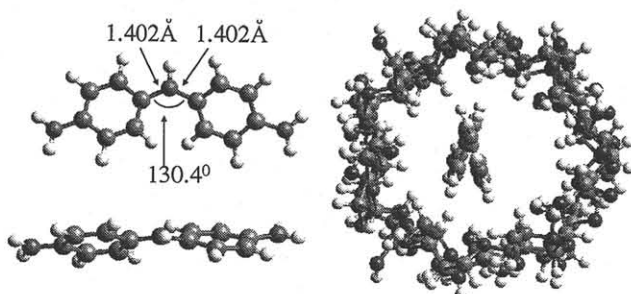

Fig. 3 Structural analysis of polyaniline in β-CDs

The analysis of molecular orbital energy diagrams for three different configurations of polyaniline base shows that the electronic structure of polyaniline in CDs is practically same as that of the planar conformation (Fig. 4). The energy levels of the HOMO (highest occupied) and the LUMO (lowest unoccupied molecular orbital) of polyaniline trapped into CDs are close to ones in the case of planar configuration of polyaniline fragment. The value of HOMO-LUMO energy difference is found to be 10.18 eV, which is close to the value of energy difference for planar structure (10.06 eV). However, in the case of inclusion complex, the energy levels of polyaniline are slightly shifted as compared with other configurations. This reveals that the molecular nanotube based on CDs can stabilize the near planar polymer and the electronic structure of this configuration is similar to the one for the same polymer in planar geometry.
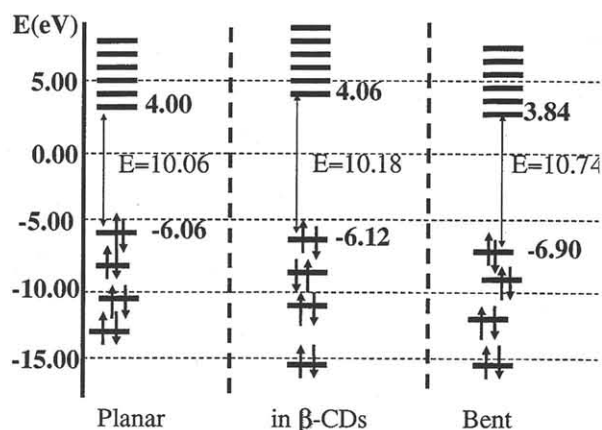

Fig. 4 Schematic MO diagram different conformations of polyaniline fragment.

4. Conclusions

In this study, the structure of polyaniline fragment in β-CDs was optimized using the combined quantum mechanics and molecular mechanics (QM/MM) method. The result of calculations showed that the structure of polyaniline in molecular nanotube had near planar geometry, with the electronic configuration of the optimized structure being practically same as the one in the planar conformation. Moreover, the host-guest stoichiometry of this inclusion compound was 1:1, which was in good agreement with experiment, and supported the realization of molecular electronic device based on this complex.

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