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Ab initio investigations of quaterthiophene molecular wire under the interaction of external electric field

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Abstract

A conducting molecular wire, quaterthiophene, has been investigated theoretically at ab initio Hartree–Fock levels by considering the interaction from an external electric field. When the external electric field increases, the single bonds become shorter, the double bonds become longer, and the molecular configuration tends to be more planar. All these features make the molecular wire more conjugated. The molecular electronic structure is sensitive to the electric field as well. With increasing the electric field, the HOMO–LUMO gap decreases. Moreover, the spatial distribution of LUMO moves to the high potential end, whereas HOMO to the low potential end.

Keywords: Quaterthiophene; External electric field; Molecular wire

1. Introduction

Since the first theoretical demonstration by Ratner and Aviram [1] that an organic molecule could be functioned as a molecular diode, the idea of employing organic molecules as functional unit in electronic devices has received great attention. Tremendous experimental efforts have been paid out on the molecular wires [2,3], diodes [4–6], switches [7,8], and storage devices [9–11] at actual molecular level. Most of these devices consist of the conjugated molecular units, which contain alternating single and double (or triple) bonds and facilitate the electron transport. α-Conjugated oligo- and polythiophenes as well as their derivatives are promising materials for a wide variety of applications in molecular electronic devices [9], such as molecular wire [12], molecular field-effect transistor [13], and molecular diode [14]. Moreover, they also offer an interesting model for understanding the electrical properties of conjugated molecular materials due to their typical conjugation structure. Therefore, they have intensely been investigated both theoretically [15] and experimentally [14].

One of the requirements to use a molecule in molecular electronics is the ability to wire it into the device architecture. In order to connect the functionalized molecules to one another or to the electrodes, wires in molecular scale are essentially necessary. Experimental investigations on molecular wires have already been carried out by using mechanically controllable break junctions [3], nano-junctions [16], and scanning probe microscopy (SPM) [17]. Together with those researches, a large number of theoretical studies have also been reported. Theoretical work can be broadly classified into two categories: one focuses on the geometry and electronic structures [18], and the other on the electron transport behavior based on non-equilibrium Green's function (NEGF) formulism [19]. However, most of the previous theoretical studies seem to less concern the surroundings, where the electronic device works. Although the non-equilibrium Green's function (NEGF) method implicitly includes the electric field effect in self-consistent calculation, the electric field dependence of the molecular structure is generally not considered [19]. It should be noted that any component in the electronic device must be subjected to a considerable external electric field. Under this particular condition, the molecular geometry as well as the electronic structure, which plays a crucial

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role in determining the conductance of molecular wire, is doubted to be the same as in the *zero*-electric field [20]. Since most previous theoretical studies on the molecular wires did not take the electric field effect into account, they rather look *ex-situ* [18,21].

Application of external electric field is feasible in theoretical simulations. For example, a number of electric field effect on the molecular properties, such as nonlinear optical (NLO) properties [22], polarizability [23], and stability [24] have been reported in the previous publications. However, the molecular wire is essentially different from those "free" molecules. In particular, the molecular wire is usually covalently bonded to the leads; it cannot be extended in the direction of the molecular axis. Therefore, a detailed study of the electric field effect on the electronic and geometric structures of molecular wire is highly desired for precisely understanding the molecular electrical properties. Unfortunately, there is no systemically investigation on these characters yet.

The purpose of this paper is to focus on a more likely *in situ* theoretical approach to the design of molecular electronic devices and further to reveal the electric field dependence of the molecular geometry, electronic structure, dipole moment, and the spatial distribution of the frontier orbitals of the molecular wire which are less concerned in previous work [25].

2. Methodology

It is well known that the performance of a molecular wire is predominated by many factors, such as the nature of the molecule itself [26], the interface between the molecule and the electrode [27], the electrode material [28], and the electrode shape [29]. Since considering all these factors looks impossible, here, we give a simplified model (Fig. 1) that a quaterthiophene bridges two chemically inert electrodes (applied here with the positive pole on the right side), meaning the effect of the electrode materials has been neglected (Fig. 2).

To select a proper calculation method, the quaterthiophene was fully optimized at HF methods with 6-31G, 6-31G*, 6-31G**, 6-31+G, 6-31++G, 6-31+G* basis sets, B3LYP method with 6-31G* basis set, and MP2 method with 6-31G* basis set under *zero*-electric field. A tight convergence criterion was applied in all the geometry calculations, and the eventual *maximum force* $< 1.5 \times 10^{-5}$, *RMS force* $< 1.0 \times 10^{-5}$, *maximum displacement* $< 6.0 \times 10^{-5}$, and *RMS displacement* $< 4.0 \times 10^{-5}$ were achieved. After a detailed comparison among the calculation methods concerned, a relative proper one (HF/6-31G*) that gives sufficient accuracy with sustainable computing period was selected and used for studying on quaterthiophene under the external electric field. Under the external electric field, the two terminal carbon atoms were fixed in space (the distance between the two terminal carbon atoms is obtained from the fully optimized molecule) to simulate the connection to the leads as shown in Fig. 1. All the other geometric parameters were, then, optimized at the same level of theory in the application of uniform external electric field. The uniform electric field ranging from *zero* to 2.57×10^9 V/m and aligned along the two terminal carbon–carbon inter-atomic vector was applied to the model molecules, which can reasonably represent the working condition of the molecular electronic device [30–32]. All the calculations were performed by Gaussian 03 [33] program.

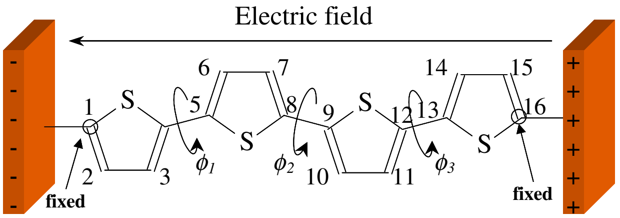

Fig. 1. A schematic description of representative molecular wire, named quaterthiophene, is connected with two chemically inert electrodes. The external electric field is aligned along the two terminal carbon–carbon inter-atomic vector C16 → C1.

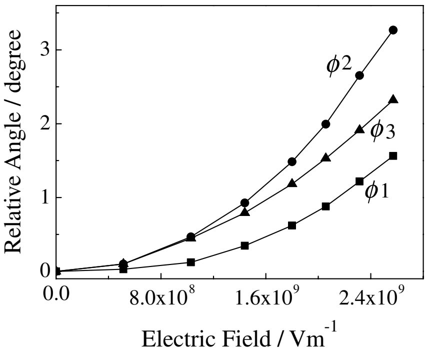

Fig. 2. Electric field dependence of torsional angle between thiophene rings calculated by HF/6-31G* method.

3. Results and discussion

3.1. Calculation methods and basis sets effect on quaterthiophene molecules

As a kind of promising material for organic electronic devices and molecular electronics devices, oligothiophenes as well as their derivatives have been investigated intensively by using various theoretical methods [20,34]. Due to the lack of experimental data, a comprehensive comparison among those different theoretical methods may offer us the relative proper one that can be used with sufficient accuracy and sustainable computing time. Since the molecular torsion is very sensitive to the calculation conditions [35], it can be used as a criterion for the determination of the proper method for the geometry optimization. In this work, the reference calculation has been performed at MP2/6-31G* level of theory. Table 1 lists the results of