



Full paper/Mémoire

Theoretical investigation of structures and electronic states of a series of phenyl-capped oligothiophenes

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ARTICLE INFO

Article history:

Received 8 September 2013

Accepted after revision 4 November 2013

Available online 10 July 2014

Keywords:

Phenyl-capped thiophene (PnT)

Oligomer

Density functional theory (DFT)

Semi-conductor

ABSTRACT

The structures and electronic states of a series of phenyl-capped oligothiophenes (PnTs) and their ionic species were investigated by means of the density functional theory (DFT). The calculations were performed on the oligomers formed by n repeating units, where n ranges from 2 to 6, using the B3LYP/6-31G** level of theory. The results obtained show that the end-substitution plays a fine-tuning effect on the geometries, electronics, and excitation states. It was found that the oligomers in the doped state have more satisfactory structural and electronic characteristics for the conducting polymers. The conjugated system in the doped oligomers has more aromaticity, with expanded and planar chains. The calculated energy gap values between the frontal molecular orbitals for the PnTs indicate that with increasing the oligomer chain length, the conductive band gap decreases. The calculated first excitation energies of the PnTs at the TD-B3LYP/6-31G** level reveal that the doped PnTs have lower excitation energies than the neutral states. The oligomer chains with a phenyl ring as the end-capped group display red shifts in their absorption spectra. The end-capped substituted oligothiophenes display better characteristics than the unsubstituted ones. It could be anticipated that the phenyl-capped substitution would be helpful to charge-carrier hopings between chains, and thereby, enhance the conductivity.

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1. Introduction

Five-membered oligoheterocyclic compounds, such as oligothiophene, oligopyrrole, and oligofuran have raised an extensive interest in the last decade because they display fascinating semi-conductivity, photo-conductivity, and electroluminescence properties [1,2]. Intrinsic conducting polymers with conjugated double bonds are newly considered as a very important class of electroactive and photoactive materials. Some of these polymers exhibit physical properties that lend them to the development of display devices, transistors, sensors, etc. [3–5]. These applications have received a great deal of attention from

both the academic and industrial research centres [6–9]. During the past decade, thiophene-based electronic materials have been extensively investigated. The ease in the chemical modification of the structures of these materials can potentially allow us to fine-tune their optical and electronic properties [10–14]. These properties strongly depend upon the degree of electronic delocalization present in such materials, effective conjugated length (ECL), and introduction of substituents at specific positions. However, a significant drawback of oligothiophenes is their low fluorescence and poor stability with respect to the oligomers consisting of substituted derivatives [15].

In order to develop a higher performance of oligothiophene, several modified oligothiophenes have been synthesized, and their electronic properties symmetrically investigated. One approach is to substitute the side-chain of the thiophene ring. Substituents at the β -position of the monomer rings prevent the undesirable α - β couplings

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that decrease the conjugated length and solubility of the polymers, and also the substitution plays an important role in the electrical and electro-optical properties of the polymers [16]. Conducting polymers with modified solubility in some industrially important solvents have recently been synthesized by introducing a proper substitution on the monomer ring [17,18]. It is clear that the electronic and structural properties of a substituent contribute to the delocalization of the polymer π -conjugate system, and the introduction of an electron-donating substituent at the β -position of the thiophene ring might be an interesting strategy to prevent defects, and withhold or even surpass the desirable properties of polymers [19–23].

The other approach is to synthesize the capped oligothiophene, where both ends of the thiophene chain are capped by the substituted groups [24–29]. The capped oligothiophenes have a well-defined molecular size and a high chemical stability. Recently, it has been found that phenyl groups as the end-substituents have novel light-emitting properties [24–29]. Although these features, obtained experimentally, are one of the interesting points in capped-oligoheterocyclics, the electronic structures of both neutral and doped states of the capped-oligoheterocyclics are not clearly understood due to the lack of theoretical works. However, in the last few decades, theoretical calculations have been employed to investigate different aspects related to the molecular and electronic structures of thiophene and its β -position substituted derivatives using *ab initio* and DFT calculations [30–37]. In our previous works [38,39], we studied a series of substituted pyrroles as potential monomers for the synthesis of conductive polymers and the corresponding oligomers with modified physical and electrical characteristics.

Theoretical investigations on a series of end-substituted oligoheterocycles are thereby desirable for designing novel functional materials, which is the main purpose of this work. In the present study, we investigated the phenyl group effect as the end-substitution on the structural and electronic properties of a series of oligothiophenes in the ground and excited forms and their doped states, as obtained with the aid of DFT calculations. To this end, we investigated characteristics of the π -conjugate system and bond length alternation pattern, HOMO–LUMO gaps, electron affinity (EA), ionization potential energy (IP), and the first excited energies of a series of PnTs including di-, tri-, tetra-, penta-, and hexamers.

2. Computational details

The ground-state geometry of each oligomer studied in this work was fully optimized using gradient procedures at the hybrid density functional B3LYP level of theory. A preliminary basis set test carried out for calculations on the electronic ground state showed that 6-31G** was the best basis set that can be used within our available hardware/software facilities within a reasonable time. Our previous studies [38,39] and reports by others [40–46] have shown that the DFT appeared notably adapted to describe oligoheterocyclics. Thus, the DFT-B3LYP level of theory was selected for the present study of PnTs using the

6-31G** basis set as implemented in the Gaussian 03 program package [47].

The optimized geometries were calculated for both the neutral and doped states of the oligomers. There was no symmetric constraint on geometry optimization. The nature of the optimized stationary point was characterized by frequency calculations at the same level of theory with the same basis set. The analysis of the obtained results showed that all the optimized structures were obtained as minima on the potential energy surface without any imaginary mode. The energies of the different states in the relevant geometries were obtained for calculating the IP values using the Koopman theorem [48]. The time-dependent density functional theory (TD-DFT) [49,50] was employed to calculate the optical properties on the basis of B3LYP/6-31G** optimized geometries. Ten lowest excitation states of each compound were computed, from which the excitation spectra were theoretically simulated with a Gaussian broadening of 0.6 eV of full-width half maximum.

3. Results and discussion

3.1. Molecular geometry

The sketch map of the structure for the hexamer type ($n = 6$), P6Ts, is depicted in Scheme 1, as an example of the PnTs. It is noticeable that the carbon atoms adjacent to the heteroatom in the thiophene ring α positions are branching centers in the electropolymerization/electro-polymerization process, and thus controls the stereochemistry of the polymer chains. Also, the β carbon atoms are in appropriate positions for substitution. However, in this study, the phenyl substitution was fixed at the head and tail of an oligomer chain. It is known that the well-defined polymer structure contains almost exclusively the head-to-tail (HT) conformation, due to the α – α couplings between adjacent heterocyclic monomers in the backbone of polymer chains [38,39]. Thus, geometry optimization of PnTs was performed on the HT conformation at the B3LYP/6-31G** level of theory.

One of the important factors related to the extent of the π -conjugation is the chain planarity, which can be reflected by the torsional angle D , as defined in Scheme 1. Dihedral angles defining the torsion between two adjacent building units along the oligomer chain for nTs, PnTs, and their ionic species were collected in Table 1. The calculations indicate that nTs and PnTs, in neutral states, are non-planar structures, in which the phenyl ring substituents are largely twisted from the plane of backbone structure of PnTs due to their steric hindrances. These angles are largely changed in the ionic states. With increase in the repeating units, there is a significant reduction in the inter-ring torsion angle at the centre of the oligomer, compared to the outside. It is interesting that the doped oligomers have less torsion angles than the corresponding neutral ones. It is known that the planarity of the polymer chains plays an important role in their electric conductivity. In general, crystalline oligothiophenes have been found to be nearly planar, as a result

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