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Computational modelling of donor-acceptor-donor conjugated polymers based on benzothiadiazole

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ABSTRACT

Since the interaction between alternating donors and acceptors results in a decreased in the band gap, a narrow band gap (<1.8 eV) will be expected in polymers containing donor-acceptor-donor (D-A-D) repeating units. It is possible to decrease the band gap as much as possible or to adjust HOMO (highest occupied molecular orbital)-LUMO (lowest unoccupied molecular orbital) levels by determining the proper donor (D) and acceptor (A) groups. In this study, quantum chemical calculations are performed using density functional theory (DFT) to investigate the HOMO–LUMO energy gap of benzothiadiazole based donor-acceptor-donor type conjugated polymers. The donors include thiophene, 3,4-ethylenedioxythiophene (EDOT) and 3,4-propylene dioxythiophene (ProDOT) units. These units are functionalized with methyl groups at the 3,4-, 2,3- and 3,3-positions of thiophene, EDOT, and ProDOT, respectively, in order to observe the effect of the alkyl side chains on the band gap of the polymers. The geometries of the monomers and oligomers were optimized using the semi-empirical PM6 method in the gas phase. Density functional theory single point calculations are carried out at the B3LYP/6-31G(d, p) level using optimized geometries. The energies (HOMO, LUMO) of the oligomers are obtained at the same level. The band gaps of the studied polymers are evaluated by extrapolating oligomers gaps to infinite chain lengths. The results indicate that calculated band gap values are in good agreement with the available experimental ones in the literature. The theoretical methods used in this study are encouraging for the modeling of similar donor-acceptor-donor type novel conjugated polymers.

1. Introduction

Conducting polymers are known as synthetic metals because they exhibit electric, electronic, magnetic and optical properties that are similar to those exhibited by metals and semiconductors. That is why they are called intrinsically electroactive conjugated polymers. The discovery of high electrical conductivity in doped polyacetylene has stimulated an enormous amount of work towards the description of the electronic properties of conjugated organic polymers [1]. Conducting polymers continue to fascinate many scientists due to their potential applications in the development and the construction of new advanced materials such as sensors, photovoltaic devices, artificial muscles and displays [2–14]. Most conducting polymers have band gaps between 1.0 and 4.0 eV, which is within the range of visible light and near-infrared region [15]. The photovoltaic materials should have the lowest band gap (Eg) (<1.8 eV) [16]. Over the last two decades, the synthesis and design of new organic conducting polymers, which have low band gaps have witnessed a growing interest, related to their appealing properties. The most used method has been applied to design molecules with alternate donor-acceptor-donor (D-A-D) repeating units that are expected to have small gaps. Besides, the experimental design and synthesis studies, there has also been much theoretical design and computational studies of donor-acceptor-donor type conjugated polymers to find materials with low-band gaps [17–24]. Yamamoto et al. investigated the electronic structures of p- or n-type doped some compounds based on ab initio electronic band structure calculations and find unipolarity [25–28]. In order to solve the unipolarity problem, they proposed a co-doping method for various samples for the fabrication of the low-resistivity wide band-gap semiconductors. The co-doping method using acceptors and donors as reactive dopants simultaneously is based on ab initio electronic band structure calculations. This was verified by experiments conducted by Joseph et al. [29]. They also showed that the co-doping method is the efficient and universal doping method by which to avoid carrier compensation with an increase of the solubility of the dopant, to increase the activation rate by decreasing the ionization energy

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of acceptors and donors, and to increase the mobility of the carrier [30–33]. Therefore, quantum chemical calculations are expected to play a major role in the development of novel materials with specific and especially predicted electronic and optical properties. Recently, the benzothiadiazole (benzo[*c*][1,2,5]thiadiazole, BT) based conjugated polymers have received a great deal of attention because of the possibility to make synthetic materials with a very low band gap such as photovoltaic [34–40], solar cells [34,41–48], organic light-emitting devices [49], and organic field-effect transistors (OFETs) [50]. On the other hand, 3,4-ethylenedioxythiophene (EDOT) and 3,4-propylenedioxythiophene (ProDOT) and their improved derivatives are certainly the most attractive organic conducting polymers due to both their good conductivity and stability properties. These compounds are also known as competitors to other existing low band-gap polymers. A large amount of research has been dedicated to the preparation and investigation of properties of EDOT including donor-acceptor-donor type oligomers. The calculations of band gaps in polymers are important in the area of advanced materials research, which results in the materials with desired properties [51,52]. Before the synthesis of novel polymers with low band gaps, quantum-chemical methods have been applied to predict the band gaps of conjugated polymers. Theoretical studies provide a simple method for prediction of band gaps and optical properties and make a great contribution to support experimental results. Thus, one main aim of this study is to understand the structure-property relationship of materials systems such that specific materials properties may be achieved via molecular design and also to support experimental results. In this work, we calculated the band gaps of four alternate electron D-A-D conjugated oligomers and polymers based on benzothiadiazole as shown in Fig. 1. Thiophene (Th), EDOT or ProDOT groups are selected as donor units and 1,2,5-benzothiadiazole (BT) is chosen as the acceptor unit since these molecules are used most widely molecules in small band gap D-A-D copolymers and used to make low band gap donor-acceptor materials [53–55].

Linear alkyl chains could lead to a decrease in the energy gap of the polymer [56–58]. This is a result of the inductive electron donating effect created by the addition of the alkyl side chains. The addition of alkyl side chains decrease the band gap, because of the electronic substituent effect formed by the addition of the alkyl side chains is larger than the steric hindrance generated by the alkyl side chains. On the other hand, although alkyl side chains are more advantageous to reduce the energy gap, also causes the steric hindrance by breaking the coplanarity of molecular chain. Another important issue about this subject is that the presence of alkyl substituents on the copolymers exhibit good solubility for various organic solvents [55,59,60]. Therefore, thiophene, EDOT, and ProDOT are functionalized with methyl groups at the 3,4; 2,3 and 3,3 positions in order to observe the effect of the alkyl side chains on the band gap of the studied polymers. Methyl substituents were chosen to simplify the calculations with the computational cost. The semi-empirical PM6 method was applied to calculate the geometric structures of selected polymers, and the density function theory (DFT) based on B3LYP/6-31G(d,p) level was used to calculation of the HOMO–LUMO energy gaps of polymers based benzothiadiazole, namely are poly{4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole} **(P1a),** poly{4,7-di(3,4-dimethylthiophen-2-yl)benzo[c][1,2,5]thiadiazole} **(P1b),** poly{4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole} **(P2a**), poly{4,7-bis(2,2,3,3-tetramethyl-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzo[c][1,2,5]thiadiazole} (**P2b),** poly{4,7-bis(3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole} **(P3a)** poly{4,7-bis(3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)benzo[c][1,2,5]thiadiazole} **(P3b**), poly{4,7-bis(3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-5,6-diphenylbenzo[c][1,2,5]thiadiazole} **(P4a)** and poly{4,7-bis(3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-5,6-diphenylbenzo[c][1,2,5]thiadiazole} **(P4b).** We chose density functional theory (DFT) methods because they have a good balance between accuracy and the computational time required. We compared the calculated band gaps with available experimental values and then assessed the reliability of the given methodology in predicting band gaps of the studied compounds.

According to our literature search, polymers **P1a** [49,61–70] and **P2a** [66,68,70–75] were previously synthesized with excellent performance on photovoltaics devices or solar cells. However, alkyl derivatives of **P1b** [66,68], which substituted with hexyl- and dodecyl groups in 3- position of thiophene and dialkyl derivatives of **P3b** [76,77], which substituted with butyl, hexyl and decyl groups in 3,3-positions of ProDOT were reported. The band gaps of **P1a** [78], and **P2a** [79] were also calculated theoretically using a different level of theory. Polymers **P1b, P2b, P3a, P3b, P4a,** and **P4b** are not investigated experimentally and theoretically, hence these are investigated in this study for the first time.

2. Computational methods

All calculations were performed with Gaussian 09W (Revision D.01 (n = number of the monomer units, n = 1–3)) and UNIX (n = 4–7) versions program packages [80] and GaussView 5.0.8 molecular visualization program [81]. In the first step of the computational studies, the conformers, which had the lowest energy values for each oligomer (with n ranging from 1 to 3), were determined by conformational analysis. In scan calculations, the semi-empirical quantum mechanical PM6 method [82] was employed.

In the second step of the study, once the stable conformers of monomer and oligomers were verified, full geometry optimizations for only the most stable (global minimum on the potential energy surface) conformers were carried using the PM6 method in gas phase without any symmetry constraints, and with all atoms allowed to relax. Electron correlation effects were considered by reoptimizing the geometry of the conformers using the Density Functional Theory (DFT) [83,84] single point calculations with the B3LYP (Becke three-parameter hybrid correlation functional combined with Lee–Yang–Parr correlation functional) [85,86] with 6-31G(d,p) basis set [87]. It is shown that B3LYP calculations give a quite correct band gap for a wide variety of polymer systems such as polythiophene, polypyrrole, polyfuran, polyselenophene, and benzothiazole [49,88–91] without the significant computational cost and can also serve as a reference to facilitate comparison with the literature. The vibrational analysis shows that all optimized conformers have no imaginary frequencies and are minima on potential energy surfaces.

In the third step of the study, the band gap values ($Eg = E_{HOMO} - E_{LUMO}$) of the monomer and oligomers were calculated using B3LYP/6-31G(d,p) level to obtain the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital energies. Calculations continued on the oligomers with increasing the chain length adding monomer units one by one until the Eg difference between the consecutive oligomers (ΔEg) change less than 0.05 eV to be able to estimate the typical Eg value of the polymer. This target value shows an insignificant change in the energy gap differences and, therefore, the Eg of the largest oligomer is considered to be stable in spite of the addition of more monomer units [92].

In the fourth step of the study, after a certain oligomer length was reached with the specified ΔEg criteria, the band gap values of the polymers were estimated. Structures of oligomers with 1–5 and, in some cases, 6 or 7 repeat units were optimized without enforcing planarity. The Eg values of the monomer and oligomers were plotted against the reciprocal of the polymer length ($1/n$), where n is the number of monomer units within the oligomer