

Computational Study on Optoelectronic Property Tuning of Oligothiophenes *via* Chemical Modifications for Solar Cell Applications

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Chemical modifications in conjugated polymers offers the possibility of tuning its optoelectronic properties for various applications. In this report, the optoelectronic properties of chemically modified oligomers based on poly(3-hexylthiophene-2,5-diyl) (P3HT) were investigated *via* DFT and TDDFT. The study was carried out by replacing the hydrogen in the 3'-position of the bithiophene monomer unit with several substituents. The polymer properties were predicted *via* oligomer approach where n , was varied from 1 to 10. Various electronic and optical properties were calculated: E_{HOMO} , E_{LUMO} , E_{Gap} , first singlet excitation energy (E_{Opt}) and exciton binding energy (E_{B}). Several substituents: -CN and -F were observed to have significantly lower $E_{\text{HOMO}}/E_{\text{LUMO}}$ values while having similar E_{Gap} compared to P3HT. Relevant solar cell characteristics were predicted and show that P3HT-CN and P3HT-F have significantly improved open-circuit voltage (V_{OC}). The results suggest that P3HT-CN and P3HT-F may have overall better solar cell characteristics than P3HT.

Keywords: Density functional theory, Organic solar cells, Conjugated polymers, Computational chemistry, Optoelectronic properties.

INTRODUCTION

Solar cells based on organic conjugated polymers have various potential advantages, such as, light weight, ease of fabrication and low-cost devices, thus, may be commercially attractive [1-3]. In order to be commercially competitive, various issues must be first be addressed, including improvement in stability and conversion [4,5]. Currently, the highest attained efficiency in the laboratory is 13.2 % for multijunction cell [6] and 11.7 % for single junction cell [7]. Other materials gaining attention as alternative to Si based solar cells are: perovskite [8,9], graphene [10,11] and small molecules [12].

One of the main advantages of organic materials compared to inorganic materials is the ease of chemical modifications of the materials *via* addition or substitution of various substituents to the parent molecule, which may lead to variations in its electronic [13-15], optical [16,17], or charge-transport properties [18]. By tuning the optoelectronic properties of the conjugated polymer, improvement in the material design and its intrinsic properties which may lead to improvement in its solar cell characteristics.

Fig. 1 shows the schematic diagram of the important energy levels in an organic solar cells where the active layer is a poly(3-hexylthiophene-2,5-diyl) and [6,6]-phenyl-C61-butyric acid (P3HT:PC₆₁BM) blend. The difference between the LUMO

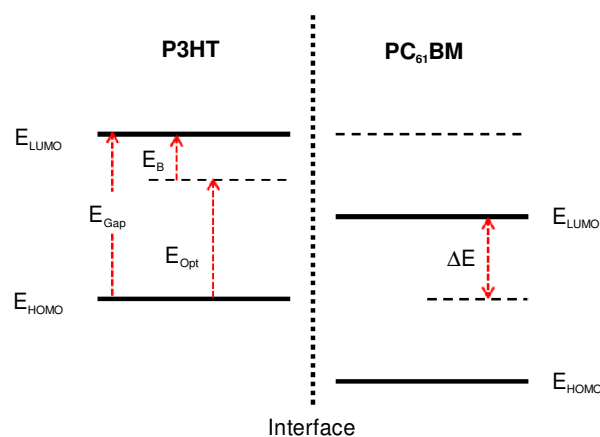


Fig. 1. Schematic diagram of the relevant energy levels in P3HT:PCBM blends

(E_{LUMO}) and HOMO (E_{HOMO}) energies is called the fundamental energy gap (E_{Gap}), while the first single excitation energy is called the optical gap (E_{Opt}) [19]. E_{Opt} is the minimum energy required for electronic transition to occur, which produces bound electron-hole pairs called exciton [20]. On the other hand, E_{Gap} is the energy required to separate electrons and holes for carrier transport [19]. Thus, E_{Gap} is usually larger than E_{Opt} for organic semiconductors and their difference is called the

exciton binding energy (E_B) [21], which may be calculated using the equation:

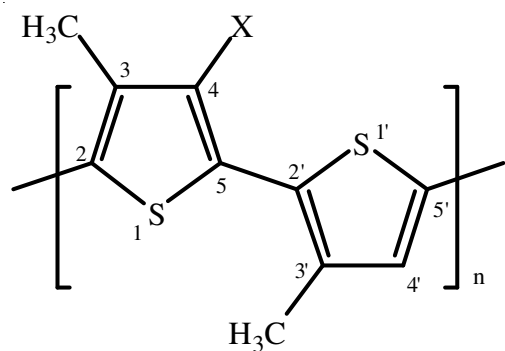
$$E_B = E_{\text{Gap}} - E_{\text{Opt}} \quad (1)$$

Density functional theory (DFT) based studies have been successful to understand and predicting the optical and electronic properties of chemically modified π -conjugated systems [22-24]. Deviations from experimental values due to the limitations of DFT have been observed for these systems [25,26]. Nevertheless, trends from DFT calculations produced values which are in good agreement with experimental findings, thus, can provide very useful insights in predicting effects of substitution in similar systems.

In this study, DFT and time-dependent density functional theory (TD-DFT) calculations were performed to determine the effects on optoelectronic properties of substituted oligothiophenes based on P3HT. The hydrogen of a bithiophene monomer unit was replaced with various substituents and the electronic and optoelectronic properties were determined. Also, important solar cell characteristics were estimated and P3HT derivatives with improved solar cell characteristics were suggested.

COMPUTATIONAL METHODS

The chemical structures of the chemically modified oligothiophenes based on poly(3-hexylthiophene-2,5-diyl) (P3HT) is shown in Fig. 2. Several electron-donating and electron-withdrawing groups replaced the hydrogen in the 4-position of a bithiophene monomer unit. It was observed previously, that the alkyl side chain does not significantly affect the optoelectronic properties of conjugated polymers, thus, the hexyl chain attached to the 3- and 3'-positions were replaced with a methyl group in order to reduce computational costs [27]. Structural optimizations were carried out using MOPAC2016 [28] using PM6 semiempirical methods. The terminals of the oligothiophenes were terminated with hydrogen. All optimizations were carried out without any restrictions and in gas-phase. Total energy calculations were carried out with PC-GAMESS/Firefly QC package [29] which is partially based from GAMESS (US) source code [30] using the B3LYP hybrid functional with 20 % HF exchange and 6-31(d) as the basis set. The first singlet excited states were determined using TD-DFT, also at the B3LYP/6-31G(d) level. The open-circuit voltage was calculated using the equation [21]:



X = F, Cl, CN, NH₂, NO₂, OH and SH

Fig. 2. Chemical structures of P3HT derivatives

$$V_{\text{OC}} = 1/e \left[\left| E_{\text{HOMO}}^{\text{P3HT-X}} \right| - \left| E_{\text{LUMO}}^{\text{PCBM}} \right| - 0.3 \text{ eV} \right] \quad (2)$$

where e is the elementary charge and 0.3 eV is an empirical factor, a quantity related to the quasi Fermi energies of electrons and holes of the acceptor and donor materials [19]. The ionization potential (IP), was estimated using the negative of the E_{HOMO} based from Koopman's theorem [31].

RESULTS AND DISCUSSION

Optoelectronic properties: Fig. 3 shows the variation of the calculated frontier orbital energy values for the oligothiophenes from $n = 1$ to 10 bithiophene units. It can be observed that the E_{HOMO} , E_{LUMO} and E_{Gap} values converge around $n = 8$ to 10 bithiophene units, therefore, shorter oligomer chain length is sufficient to approximate the polymer values. E_{HOMO} , E_{LUMO} and E_{Gap} values at $n = 10$ were observed to be -4.42 eV, -2.22 eV and 1.91 eV, respectively. Compared with the experimental energy values: $E_{\text{HOMO}} = -4.76$ eV, $E_{\text{LUMO}} = -2.46$ eV and $E_{\text{Gap}} = -2.30$, deviations of 7, 9.7 and 17.0 % were observed, respectively. The deviations of the calculated values from the experimental values are consistent with previous calculations carried out using DFT/B3LYP method [32-34]. Also, since we are mainly interested in the trends of P3HT substitution, the DFT/B3LYP method is sufficient for this study.

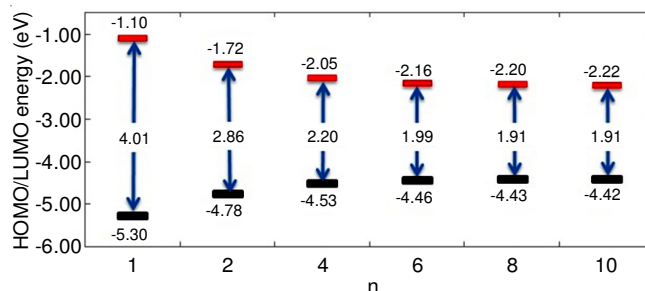


Fig. 3. Calculated energy values for P3HT at the DFT/B3LYP/6-31G(d) level: E_{HOMO} , E_{LUMO} , E_{Gap} , with respect to the number of monomer units n

Fig. 4 shows the calculated energy values for $n = 10$ bithiophene units for the P3HT derivatives. It can be observed that several P3HT derivatives have greatly increased in their E_{Gap} : P3HT-NH₂, P3HT-NO₂, P3HT-OH and P3HT-SH. These derivatives were observed to have large deviations from planarity and as a result, the energies of the aromatic and quinoid structures are very different (more stabilized E_{HOMO} and less stabilized E_{LUMO}) resulting to large increase in the E_{Gap} [35]. On the other hand, several derivatives were observed to have smaller or almost unchanged E_{Gap} : P3HT-CN and P3HT-F. For these derivatives, it was observed that the structures are planar which results to good overlap between molecular orbitals and having closer energy between the quinoid and aromatic structures [35]. F and CN are electron-withdrawing substituents [36,37] and lower the energies of the frontier orbitals. On the other hand, P3HT-Cl, although produced a planar structure, increased in E_{Gap} since the decrease in E_{HOMO} was more than the decrease in E_{LUMO} resulting to enlargement of E_{Gap} .

Table-1 shows the calculated first singlet excitation energy, E_{Opt} and the exciton binding energy, E_B . It can be observed that the trends are similar to the trends for E_{Gap} , where P3HT-Cl,

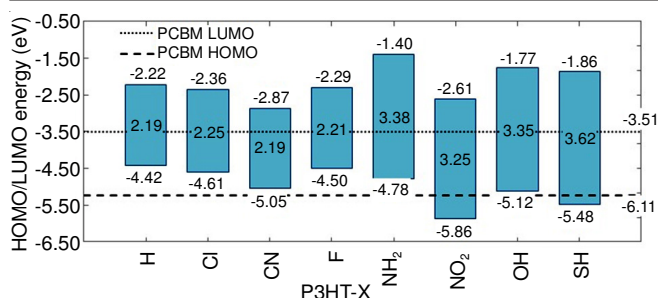


Fig. 4. Calculated energy values ($n = 10$) of the P3HT derivatives using DFT at the B3LYP/6-31G(d) level: E_{HOMO} , E_{LUMO} and E_{Gap} . The calculated E_{HOMO} (dotted line) and E_{LUMO} (dashed line) for PC₆₁BM are also included for reference

TABLE-1

CALCULATED FIRST SINGLET EXCITATION ENERGY (E_{Opt}) AND EXCITON BINDING ENERGY (E_{B}) VALUES ($n = 10$) OF POLY(3-HEXYLTHIOPHENE-2,5-DIYL (P3HT) DERIVATIVES USING TDDFT AT B3LYP/6-31G(d) LEVEL

P3HT-X	E_{Opt} (eV)	E_{B} (eV)
P3HT	1.86	0.33
P3HT-Cl	1.91	0.34
P3HT-CN	1.84	0.35
P3HT-F	1.88	0.33
P3HT-NH ₂	2.91	0.47
P3HT-NO ₂	2.79	0.47
P3HT-OH	2.90	0.46
P3HT-SH	3.13	0.49

P3HT-CN and P3HT-F produced similar or smaller E_{Opt} than P3HT, while P3HT-NH₂, P3HT-NO₂, P3HT-OH and P3HT-SH have much larger E_{Opt} than P3HT. The calculated E_{B} of the derivatives show that planar structures have lower E_{B} which may result to better exciton dissociation at the donor-acceptor materials junction and improved solar cell characteristics. Non-planar structures have higher E_{B} , which may be due to their localized structure, thus hindering the transfer of excitons.

Solar cell characteristics: Table-2 summarizes the calculated solar cell properties of the P3HT derivatives used in this study: IP, V_{OC} and E_{Gap} values. The calculated V_{OC} for P3HT was 0.61 V, which is in good agreement with the experimental V_{OC} for P3HT of 0.60 V [38]. It can be observed that all P3HT derivatives in this study have improved V_{OC} and IP, which is due to the decrease in the E_{HOMO} values. The increase in V_{OC} may possibly translate to increase in photovoltage of the solar cell, while the increase in IP will lead to increase in oxidation stability. However, the non-planar derivatives have greatly increased in E_{Gap} which would result to great decrease in light absorption and lower photocurrent density. Therefore, on the

TABLE-2

PREDICTED SOLAR CELL CHARACTERISTICS OF POLY(3-HEXYLTHIOPHENE-2,5-DIYL (P3HT) DERIVATIVES

P3HT-X	V_{OC} (V)	IP (eV)	E_{Gap} (eV)
P3HT	0.61	4.42	2.19
P3HT-Cl	0.80	4.61	2.25
P3HT-CN	1.25	5.05	2.19
P3HT-F	0.69	4.50	2.21
P3HT-NH ₂	0.97	4.78	3.38
P3HT-NO ₂	2.05	5.86	3.25
P3HT-OH	1.31	5.12	3.35
P3HT-SH	1.67	5.48	3.62

basis of the improvement in the intrinsic material properties of P3HT-CN (increase in V_{OC} , decrease in E_{Gap}) and P3HT-F (increase in V_{OC} , similar E_{Gap}) compared to P3HT, these two P3HT derivatives may be good candidates as polymer materials for organic solar cells.

Conclusion

The optoelectronic properties of chemically modified P3HT were calculated using DFT and TD-DFT. Variation in the optoelectronic properties and predicted solar cell properties of chemically modified P3HT were analyzed and compared to P3HT. P3HT-F and P3HT-CN may have better overall solar cell properties: photocurrent density, open-circuit voltage and oxidation stability than P3HT.

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