



Molecular engineering of donor–acceptor co-polymers for bulk heterojunction solar cells



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ARTICLE INFO

Article history:

Received 12 March 2014

Received in revised form 15 December 2014

Accepted 17 December 2014

Available online 27 December 2014

Keywords:

Density functional theory

Exchange–correlation functionals

Oligomer extrapolation technique

Reorganization energies

Excitation energies

ABSTRACT

We report a computational modeling, based on DFT and TD-DFT methodologies, on the structural, electronic, and optical properties of different donor–acceptor co-polymer system in bulk heterojunction solar cells. The donor moieties that were considered were the derivatives of thienocyclopentathiophene, fluorene, and thienobenzothiophene. We utilized for the acceptor groups the moieties of thieno[3,4-*b*]pyrrole-4,6-dione; thieno[3,4-*b*] thiophene-4,6-dione; tetrafluoro-1,3-dihydrothieno[3,4-*c*]thiophene and its non-fluorinated counterpart; various electron-donating substituents within the fused π -conjugated polymer system; and 3-fluoroselenophenothiophene. Among the donor–acceptor combination, the best in terms of molecular energy levels, energetic driving force, maximum absorption, calculated open-circuit voltage, reorganization energies, ionization potential, and electron affinity are poly[(bisthieno(bisthieno[3,2-*b*:2',3'-*d*]thiophene)-*alt*-(5-alkyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione)] and poly[(4,8-dimethyl[1,3]oxazolo[5,4-*f*] [1,3]benzoxazole)-*alt*-(thieno[3,4-*d*]pyrimidine)].

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1. Introduction

Bulk heterojunction (BHJ) solar cells have been a viable alternative to the all inorganic solar cells since it can be designed as a lightweight flexible material with minimal production costs. Initially a poly(3-hexylthiophene) (P3HT) [1] was used as the organic dye but as it exceeds its theoretical limit, scientists nowadays focus on the design of low band gap π -conjugated semiconducting polymers which usually comprises of a donor–acceptor (D–A) co-polymer system. This type of configuration shows that it can improve the photophysical properties at the same time provide a deeper highest occupied molecular orbital (HOMO) energy level as compared to P3HT [2–6]. To date, the highest performing single-junction polymer solar cell is with the use of thienobenzothiophene and 3-fluorothieno[3,4-*b*]thiophene co-polymer system, also known as PTB7, with a power conversion efficiency (PCE) of 9.2% [7]. For tandem solar cells, the best performing polymers is the combination of P3HT and poly[2,7-(5,5-bis(3,7-dimethyloctyl)-5*H*-dithieno[3,2-*b*:2',3'-*d*]pyran)-*alt*-4,7-(5,6-difluoro-2,1,3-benzothiadiazole)] (PDTP-DFBT) with PCE of 10.6% [8]. In order to further improve the efficiency of the D–A co-polymer system, we need to properly match the energy levels of these dyes to the

acceptor moiety usually with phenyl-*C*₇₁-butyric acid methyl ester (PC₇₁BM) and to the inorganic electrodes. One way of optimizing such energy levels is by assessing different molecular combinations of the donor and acceptor moieties which affects many properties such as band gap (E_g), absorption range; exciton energy; and open-circuit voltage (V_{OC}) of the dye. It is generally-known that decreasing the band gap of the co-polymer system should undergo bathochromic shift in its absorption spectra, thereby theoretically increasing its short-circuit current density (J_{SC}). In organic solar cells, when the light is absorbed by the polymers it will result in a bound electron–hole pair, called excitons, which dissociates to generate charge carriers. To be able to have an efficient charge separation, the difference between the lowest unoccupied molecular orbital (LUMO) of the polymer and PC₇₁BM should be about 0.3 eV [9]. The experimental LUMO for PC₇₁BM is –3.7 eV [10].

The open-circuit voltage of the dye is proportional to the energy difference between the HOMO of the polymer and the LUMO of PC₇₁BM, as shown in Eq. (1) [11].

$$V_{OC} \propto (\text{LUMO}_{\text{PC}_{71}\text{BM}} - \text{HOMO}_{\text{polymer}}) \quad (1)$$

Based on the Scharber's model, the V_{OC} can be estimated based on Eq. (2) [1].

$$eV_{OC} = \text{LUMO}_{\text{PC}_{71}\text{BM}} - \text{HOMO}_{\text{polymer}} - 0.3 \text{ V} \quad (2)$$

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where e is the elementary charge and the 0.3 V is the empirical value for the deviation between the built-in potential and the open-circuit voltage. This voltage loss was credited to various charge-carrier recombinations and the polymer morphology [12,13]. According to Eq. (2), a deep-lying HOMO level of the polymer could result in larger V_{OC} values.

The capability of the co-polymer system to have an efficient electron-transfer can be assessed further based on semi-classical Marcus theory self-exchange reaction, as shown in Eq. (3), which treats the reaction coordinate as a measure of both the amount of charge transferred and the polarization of the dielectric solvent [14].

$$k_{ET} = A \exp\left(-\frac{\lambda}{4k_B T}\right) \quad (3)$$

where A is a prefactor that depends on the nature of electron transfer reaction, k_B is the Boltzmann constant, T is the temperature, and λ is the reorganization energy composed of solvational and internal components. In solid thin-films, the solvent reorganization energies are considered to be negligible, thus only the internal reorganization energies are studied.

In this study, we evaluated different donor–acceptor pairs to properly tune the electronic and photophysical properties in a co-polymer system based on density functional theory (DFT) and the time-dependent DFT. We utilized the common donor moieties such as thienocyclopentathiophene; fluorene; and thienobenzothiophene macrocycles, in combination with fused π -conjugated acceptor moieties that could exist as quinoid resonance structures which increases the double bond character within the polymer backbone. We based our modifications from the highest co-polymer system, PTB7.

The research is divided into three parts: First, is the modification of the donor moiety retaining the 3-fluorothieno[3,4-*b*]thiophene at the acceptor part. Second, is the use of different acceptor moieties retaining the thienobenzothiophene as the donor. And lastly, based on the optimized structures obtained from the modifications of the donor and acceptor moieties, we designed new co-polymer dyes in an effort to attain a highly efficient organic polymer dye. The results show that the newly designed dyes attain a narrower band gap, deeper HOMO levels, acceptable exciton energies, better absorption coverage, and high charge-transfer capabilities, which reveals that by properly matching the donor and acceptor pairs is an efficient way to improve the performance of the D–A conjugated co-polymer systems.

2. Computational method

All calculations were done in Gaussian 09 [15] software package. The ground-state geometries (2–4 repeating units) were optimized using DFT without symmetry constraints using full alkyl-branched chains. Most of the theoretical calculations uses a shortened alkyl chain for computational speed purposes and normally do not have much contribution on the excited-state energies, however, the length and bulkiness of the alkyl chains for the studied compounds are very vital especially for the proper conformation of the co-polymer system.

We employed the oligomer extrapolation method [16–18] in our calculation of the effective conjugation length (ECL) and in turn the maximum absorption wavelength by extrapolating the equation of the line based on the excitation energies against the reciprocal chain length within the threshold of 0.01 eV. The band gap was taken from the y-intercept of the equation of the line. The calculated ECL was used to determine the HOMO energy level according to the linearity between the HOMO energies and reciprocal

chain length. The LUMO energy is determined from the difference between the extrapolated HOMO energy and the band gap.

The neutral, cationic, and anionic forms of a dimer structure of the co-polymer system calculated at B3LYP/6–31G(d) were used to compute the ionization potential (IP); electron affinity (EA); internal hole and electron reorganization energies (λ_{hole} and $\lambda_{electron}$, respectively); hole and electron extraction potential (HEP and EEP, respectively), and “small-polaron” stabilization energies for hole (SPE(h)) and electron (SPE(e)). Their corresponding equations are shown in Eqs. (4)–(8).

$$\text{Ionization potential : } IP_V = E_0^+ - E_0 \text{ and } IP_A = E_+ - E_0 \quad (4)$$

$$\text{Electron affinity : } EA_V = E_0 - E_0^- \text{ and } EA_A = E_0 - E_- \quad (5)$$

$$\text{HEP} = E_+ - E_+^0; \text{ EEP} = E_-^0 - E_- \quad (6)$$

$$\lambda_{hole} = IP_V - \text{HEP}; \lambda_{electron} = \text{EEP} - EA_V \quad (7)$$

$$\text{SPE(h)} = IP_V - IP_A; \text{ SPE(e)} = EA_A - EA_V \quad (8)$$

The subscripts V and A, in the ionization potential and electron affinity of Eqs. (3) and (4), represent vertical and adiabatic approach in the calculations. $E_0^{+(-)}$ is the energy of the cation (anion) calculated with the optimized structure of the neutral molecule. $E_{+(-)}^0$ is the energy of the neutral molecule calculated at the cationic (anionic) state. E_0 , E_+ , and E_- are the energies of the neutral, cationic, and anionic ground-state structures.

In order to assess which polymer is a suitable alternative to PTB7, we develop a criteria based on the properties that were calculated as follows: (1) the band gap should be <1.8 eV; (2) difference between the LUMO of the polymer and the LUMO of PC₇₁BM (ΔE_{L-L}) which relates to the energetics of the driving force of the system should fall within the range of $0.3 < \Delta E_{L-L} < 0.6$ eV; (3) the maximum absorption, λ_{max} , of the polymer should be greater than 670 nm; (4) the open-circuit voltage calculated based on Eq. (2) should be >0.8 V; (5) the reorganization energy, $\lambda_{total} < 0.7$ eV with equal λ_{hole} and $\lambda_{electron}$ values to have more balanced charge-transfer (CT) process; (6) the ionization potential which is indirectly proportional to the creation of holes in the polymeric materials should be less than 5.62 eV, while the electron affinity should have a value greater than 1.85 eV to efficiently inject electrons; and (7) the “small-polaron” stabilization energies for both holes and electrons based on Eq. (8) should have a value less than 0.2 eV in order to have more pronounced ion displacements which could improve the charge carrier-injection and -transporting characteristics of the polymer.

An initial assessment of the appropriate exchange–correlation (xc) functional was performed to identify the proper geometric structure and the molecular orbital energies using 6–31G(d) basis set. For the ground-state optimization we compared the commonly used xc functional, B3LYP with the mPWHandHPW91, which was found to have close correlation with the dihedral angles between adjacent thiophene species [19]. The mPWHandPW91 xc functional is a modified version of the mPWPW91 developed by Perdew and Wang’s 1991 exchange–correlation functional [20,21] having a Hartree–Fock exchange of 50%. For the energies, we compared B3LYP with M06–2X xc functional, which has close agreement with experimental results [22]. The identification of an appropriate xc functional for excited-state calculation was based on B3LYP and its long-range xc functional counterpart, the coulomb-attenuated method B3LYP (CAM-B3LYP). As shown in Table S1 in Supporting information, among the xc functionals, the most appropriate method for the depiction of the energy levels and band gap is using TD-B3LYP/6–31G(d)//mPWHandHPW91/6–31G(d) theoretical methodology with a mean absolute difference

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