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Structures and photoelectric properties of five benzotrithiophene isomers-based donor–acceptor copolymers

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ABSTRACT

In this paper, we have investigated the structures, electronic and optical properties of five conjugated copolymers (BTT1–BTz, BTT2–BTz, BTT3–BTz, BTT4–BTz and BTT5–BTz) featuring benzotrithiophene (BTT) isomers as donor units and benzothiadiazole (BTz) as acceptor units, linked through thiophene spacers, employing many-body perturbation theory (MBPT). We have explored the isomer effects by configuration of the sulfur atoms in BTT units, aimed to get insight into how the structural modifications to the conjugated backbone can influence the molecular structures and electronic properties of conjugated polymers. Using the trimer as the computational model, the calculated low and high energy absorption bands (660 and 413 nm) for BTT1–BTz agree well with the experimental ones (645 and 430 nm) with a small offset of ~15 nm. On the basis of our calculations, it is found that the backbones of these polymers display different coplanarities, with the dihedral angles between the two neighboring rings varying from 12.3° to 79.0°. Importantly, both BTT1–BTz and BTT2–BTz exhibit intense adsorption around 660 and 623 nm, indicating their promising application in solar cells, whereas BTT3–BTz and BTT4–BTz display the intense adsorption at 569 and 551 nm, which are also usable in the tandem solar cells. BTT5–BTz has narrow and weak adsorption in the visible and infrared region, implying it is not conducive to the sunlight absorption. The blue shift of about 150 nm from BTT1–BTz to BTT5–BTz is suggested to be originated from the shorter effective conjugation lengths.

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1. Introduction

The donor–acceptor (D–A) conjugated polymers are alternating electron-rich and electron-deficient units along their backbones, which have numerous applications in the fields of material science, such as light-emitting diodes (LEDs) [1,2], organic field-effect transistors (OFETs) [3–6], organic photovoltaics [7–9] and electrochromics [10–12]. In recent years, bulk-heterojunction (BHJ) polymer solar cells (PSCs) have attracted considerable attention owing to their special advantages, including simple, low cost fabrication, flexibility and lightweight [9]. In particular, PSCs have gained a rapid progress in the power conversion efficiency (PCE). For the conventional and inverted single-junction solar cells, PCE has been brought up to ~10% through developing novel D–A conjugated polymers with lower band gap and optimization of device fabrication [13,14]. As is well known, PCE $=$ ($J_{sc} \times V_{oc} \times$ FF) / P_{IN}, where J_{sc}, V_{oc}, FF and P_{IN} are the short-circuit current density, the photovoltage under open circuit condition, the fill factor and the incident light power, respectively. In bulk-heterojunction PSCs, the most common acceptors are fullerene derivatives, such as [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) or [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$). Hence, to obtain high power conversion efficiency, it is a good strategy to design and synthesize novel D–A conjugated polymers with low-band gap and deep HOMO energy level that can efficiently absorb the near-infrared radiation.

D–A conjugated polymers usually exhibit high effective electron delocalization along polymer backbone and strong intra- and intermolecular interactions. Due to these advantages, plenty of specific conjugated polymers have been designed and synthesized by selecting donor and acceptor moieties [15–21]. It has been found that the highest occupied molecular orbital (HOMO) energy level of D–A conjugated polymers is determined synergistically by the HOMO energy levels of the donor and acceptor, and the lowest unoccupied molecular orbital (LUMO) energy level of polymers is determined by the LUMO energy level of the acceptor. Thus, the energy levels and band gaps of D–A conjugated polymers can be tuned by choosing appropriate donor and acceptor.

The thiophene derivatives, such as thienothiophenes, benzodithiophenes and β,β'-bridged bithiophenes [22,23,24], have been emerged as a class of attractive building blocks for synthesizing D–A conjugated polymers for high performance photovoltaic devices. These thiophene derivative molecules are symmetric, perfect planar and electron-rich, which facilitate the intermolecular π–π interactions and charge transport. Besides employing these available donors, it is also important to search for more effective donor

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units. In 2011, McCulloch and coworkers designed and synthesized a new benzotrithiophene (BTT) isomer molecule [25]. Its planarity and extended π-system makes it a potential candidate as the donor compound in D–A copolymers. Although BTT has been proved to be one of the most promising candidates for high performance photovoltaic devices with a deeper HOMO, the efficiency still needs to be further optimized. Based on the positions of sulfur atoms [26], the BTT family should have seven possible isomers, including benzo[2,1-b:-3,4-b′:5,6-c″]trithiophene (BTT1), benzo[2,1-b:-3,4-b′:5,6-b″]trithiophene (BTT2), benzo[1,2-b:-4,3-b′:5,6-c″]trithiophene (BTT3), benzo[1,2-b:4,3-b′:5,6-c″]trithiophene (BTT4), benzo[1,2-b:-3,4-c′:5,6-c″]trithiophene (BTT5), benzo[1,2-b:3,4-b′:5,6-b″]trithiophene (BTT6), benzo[1,2-c:3,4-c′:5,6-c″]trithiophene (BTT7). These BBTs have high co-planarity and extended π-conjugation, and are expected to serve as donor units for designing low-band gap D–A conjugated polymers. Four benzotrithiophene isomers (BTT1, BTT2, BTT6, BTT7) have been successfully synthesized [25, 27–30], and the corresponding D–A conjugated polymers based on substituted benzo[1,2-b:-3,4-b′:5,6-c″]trithiophene (BTT1) and benzo[2,1-b:-3,4-b′:5,6-b″]trithiophene (BTT2) have been synthesized in the past four years [31–33]. In 2012, Müllen and his coworkers [33] have found that a novel donor–acceptor copolymer P1, in which the benzo[1,2-b:-3,4-b′:5,6-c″]trithiophene (BTT1) combines directly with 2,1,3-benzothiadiazole (BTz), has no field-effected response due to the pronounced disorder in the thin film. However, another copolymer P2, in which the benzo[1,2-b:-3,4-b′:5,6-c″]trithiophene (BTT1) and BTz are linked by thiophene spacers, shows a hole mobility of 0.04 $\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ in field-effected transistors. A new BTT-based polymer, poly{benzo(1,2-b:-3-4b′:5,6-b″)trithiophene-alt-4,4′-dihexyl-2,2′-bithiazole} (BTT2–BTz), possesses a broad band gap and deeper HOMO energy level, and the assembled device based on BTT2–BTz/$\mathrm{PC_{71}BM}$ achieved the highest PCE of 5.06% among the BTT2- and BTz-based conjugated polymers [31]. These photovoltaic performances make BTT2–BTz conjugated polymer having potential application in tandem solar cells.

Computational design of new photovoltaic materials has attracted increasing interest. In some literatures, quantum-mechanical simulations have provided detailed understanding of energy level modulation for rationally designing π-conjugated polymers with desired optical properties [34–37]. Because of its moderate computational cost, the time-dependent density functional theory (TDDFT) method is one of the most commonly used approach for studying small- and medium-sized molecules, which can provide reasonable excited states for local electronic transitions. However, for the extended π-systems and charge-transfer exciton, the given TDDFT results are sometimes unreasonable and even incorrect [38,39]. Recently, the limitation of TDDFT method has been overcome by using many-body perturbation theory (MBPT) based on a set of Green's function equations [40–42]. Two key ingredients in MBPT are the electron self-energy operator Σ and the Bethe–Salpeter equation (BSE). The former can be obtained by the Hedin's equations with *GW* approximation. The accuracy of MBPT for excitation energies is within 0.1–0.2 eV, and MBPT has been widely employed for exploring the optical excitations in bulk crystals [43–45], clusters [46], polymers [47,48], biological molecules [49,50] and small inorganic and organic molecules [51–53].

To date, the three other BTT isomers, benzo[1,2-b:-4,3-b′:5,6-c″]trithiophene (BTT3), benzo[1,2-b:4,3-b′:5,6-c″]trithiophene (BTT4) and benzo[1,2-b:-3,4-c′:5,6-c″]trithiophene (BTT5) have not been synthesized yet. Thus, their D–A conjugated polymers containing BTT isomers [31,32,42] have not been experimentally investigated except for benzo[2,1-b:-3,4-b′:5,6-c″]trithiophene (BTT1) and benzo[2,1-b:-3,4-b′:5,6-b″]trithiophene (BTT2), and the structure–property relationship of the conjugated polymers is still unclear. Therefore, in this work, we calculated by using MBPT the absorption spectra and excited energies of five BTT-based conjugated polymers (Chart 1), where the BTT isomers are linked to the 2,1,3-benzothiadiazole (BTz) by thiophene spacers. This work may be beneficial for understanding how the structural modification influences the electronic structures and optical properties of benzotrithiophene isomers-based donor–acceptor copolymers.

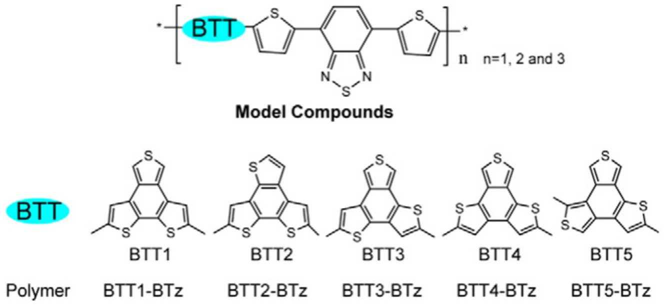

Chart 1. Structures of five benzotrithiophene (BTT) isomers used as donor units: benzo[2,1-b:-3,4-b′:5,6-c″]trithiophene (BTT1), benzo[2,1-b:-3,4-b′:5,6-b″]trithiophene (BTT2), benzo[1,2-b:-4,3-b′:5,6-c″]trithiophene (BTT3); benzo[1,2-b:4,3-b′:5,6-c″]trithiophene (BTT4); benzo[1,2-b:-3,4-c′:5,6-c″]trithiophene (BTT5).

2. Computational methods

The geometries of all BTT-based conjugated polymers were fully optimized employing the Gaussian 09 package with B3LYP hybrid functional in conjunction with the 6-311G(d,p) basis set. Previous study has proved that the alkyl side chains only play role in improving the solubility and have minor influence on the total density of states of conjugated polymer chains [54]. Thus, to reduce the computational cost, the alkyl side chains on BTT isomer units were replaced by hydrogen atoms.

The electronic and optical excitations of designed copolymers can be calculated by MBPT. In the MBPT calculations, the basis sets are constructed by atom-centered Gaussian orbitals of the form:

$$\phi_{ijk}(r) = A_{ijk} x^i y^j z^k e^{-\alpha r^2}. \tag{1}$$

Four decay constants (α) are used for C, N and S atoms (0.2, 0.5, 1.25 and 3.2 in a.u.), while three decay constants are used for H atom (0.1, 0.4 and 1.5 in a.u.). Gaussian orbitals with s, p, d and s* symmetry are included for each atom. The decay constants have been tested to give converged orbitals and excitation energies.

First, the molecular orbitals and energies are calculated according to the Kohn–Sham equation:

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{\mathrm{PS}}(\mathrm{r}) + V_H(r) + V_{XC}(r)\right\}\Psi_n^{DFT}(r) = E_n^{DFT}\Psi_n^{DFT}(r) \tag{2}$$

where $V_{PS}(r)$ and $V_H(r)$ are the pseudopotential and the Hartree potential, respectively, and $V_{XC}(r)$ is the exchange-correlation potential. It must be accepted that the Kohn–Sham energies, which are obtained with standard local exchange-correlation functions, fail to accurately reflect the single-particle excitation energies. In MBPT [42], the exchange-correlation potential in DFT is replaced by a nonlocal and energy-dependent self-energy operator $\Sigma(r,r',E)$, and the Kohn–Sham equation is replaced by the quasi-particle (QP) equation [55]:

$$\begin{aligned}&\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{ps}(r) + V_H(r)\right\}\Psi_n^{QP}(r) + \int \Sigma\left(r, r', E_n^{QP}\right)\Psi_n^{QP}(r')dr' \\ &= E_n^{QP}\Psi_n^{QP}(r).\end{aligned} \tag{3}$$

Here, the self-energy operator $\Sigma(r,r',E)$ can be evaluated by

$$\Sigma(r,r',E) = \frac{i}{2\pi}\int e^{-i\omega 0^+} G(r,r',E-\omega)W(r,r',\omega)d\omega \tag{4}$$

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