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Research paper

Impact of benzothiadiazole position on the photovoltaic properties of solution-processable organic molecule materials

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ABSTRACT

Organic molecule materials (BDT-HTH-BT and BDT-BT-HTH) applied for solution-processable organic solar cells (OSCs) have been synthesized to investigate the impact of the location of acceptor unit on the photovoltaic properties. Benzothiadiazole (BT) group was introduced as an acceptor unit, which was linked to bithienyl-substituted benzodithiophene (BDT) unit directly in BDT-BT-HTH or with hexyl-thiophene unit in BDT-HTH-BT, respectively. The molecular weight of BDT-BT-HTH and BDT-HTH-BT are the same. However, due to the different position of the BT unit, BDT-HTH-BT and BDT-BT-HTH exhibit apparently different optical and electrochemistry properties, corresponding to the photovoltaic properties. The OSCs device based on a blend of BDT-BT-HTH and $PC_{71}BM$ (1:0.8, w/w, 0.5% DIO) reached a PCE (power conversion efficiency) of 3.45%, with a short-circuit current density of 6.85 mA cm^{-2}, an open-circuit voltage of 0.815 V and an fill factor of 61.8%. In comparison, the PCE of the OSCs device based on BDT-HTH-BT as donor material is recorded only 0.32% under the same experimental conditions.

1. Introduction

The development of novel materials give rise to the high photovoltaic performance of solution-processable organic solar cells (OSCs), from the polymer donor materials [1–7] to the solution-processable molecule donor materials [8–11], from the fullerene acceptor materials [12,13] to the non-fullerene acceptor materials [14–19]. In comparison with polymer materials, due to the advantages such as defined structure and less batch-to-batch variation, solution-processable molecules materials offer more research interest from the groups all over the world. Zhan et al. have published the non-fullerene solution-processable OSCs based on INIC series of molecules as the acceptor and the power conversion efficiency (PCE) have reached as high as 11.5% [20]. Efficient fullerene-free all-small-molecule OSCs have been reported to reach the PCE of 9.08% and 9.73% by Hou et al. and Li et al. respectively, which were based on the new organic molecule donor and non-fullerene acceptor materials [21,22]. A further increase in the PCE requires a deep understanding of the relationship between the structure and photovoltaic properties of the organic molecule materials, which is critical to both of the design of the novel organic molecule materials and the fabrication of the OSCs devices. So developing the new organic molecule materials is vital to the PCE improvement of OSCs.

We have synthesized two simple solution-processable photovoltaic molecule materials with benzothiadiazole (BT) as acceptor unit linking to bithienyl-substituted benzodithiophene (BDT) donor unit directly (BDT-BT-HTH) or with hexyl-thiophene (BDT-HTH-BT) [23,24], to investigate the impact of the BT position on the photovoltaic properties of the corresponding molecule materials. Although the molecular weight of BDT-BT-HTH and BDT-HTH-BT are the same, due to the different position of the BT unit, BDT-HTH-BT and BDT-BT-HTH exhibit apparently different optical and electrochemistry properties, corresponding to the photovoltaic properties. The OSCs based on the blend of BDT-BT-HTH and $PC_{71}BM$ (1:0.8, w/w, 0.5% DIO) reached a PCE of 3.45%, with a short-circuit current density of 6.85 mA cm^{-2}, an open-circuit voltage of 0.815 V and an fill factor of 61.8%. In comparison, the PCE of the OSCs based on BDT-HTH-BT and $PC_{71}BM$ was only 0.32% under the same experimental conditions.

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2. Experimental

2.1. Materials

2.1.1. BDT-HTH-BT

A mixture of monomer **(1)** (774.77 mg, 1 mmol), monomer **(2)** (836 mg, 2.2 mmol), $Pd_2(dba)_3$ (14 mg), $[(CH_3)_3C]_3PBF_4$ (18 mg) and K_3PO_4 (24 ml, 2 M in aqueous solution) were added and stirred in degassed toluene (30 ml) under the protection of N_2 flow. The solution was heated at 80 °C for 24 h. Then the cooled mixture was poured into water, extracted with dichloromethane. The combined organic part was washed by saturated salt solution, dried over anhydrous $MgSO_4$. After evaporating the solvent, the crude product was purified by column chromatography (silica gel, petroleum/CH_2Cl_2, 1:1) to produce 608.2 mg of compound **BDT-HTH-BT** as red solid with a yield of 54.2%. MALDI-TOF MS: 1122.3, calculated for $C_{62}H_{66}N_4S_8$ 1122.31. ^1H NMR (500 MHz, $CDCl_3$): δ ppm 7.90 (s, 2H), 7.84 (d, 2H), 7.82 (d, 2H), 7.76 (s, 2H), 7.62 (t, 2H), 7.38 (d, 2H), 6.95 (d, 2H), 2.97 (m, 8H), 1.85 (m, 8H), 1.48 (m, 8H), 1.38 (m, 16H), 0.94 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 155.6, 152.1, 147.3, 141.9, 139.1, 138.1, 137.1, 137.0, 136.8, 136.5, 132.5, 131.3, 129.6, 127.9, 127.2, 125.1, 124.4, 123.4, 121.7, 120.1, 31.7, 31.6, 31.6, 30.7, 30.3, 29.9, 29.4, 29.0, 22.7, 22.6, 14.1. Anal. Calcd for $C_{62}H_{66}N_4S_8$: C, 66.29; H, 5.88; N, 4.98. Found: C, 65.49; H, 5.89; N, 4.95.

2.1.2. BDT-BT-HTH

The synthesis and purification procedure of **BDT-BT-HTH** was similar with that of **BDT-HTH-BT** but using precursor **(3)** instead of **(2)**. The mixture was purified by column chromatography (silica gel, petroleum/CH_2Cl_2, 4:1) to produce 520.6 mg of compound **BDT-BT-HTH** with a yield of 46.4%. MALDI-TOF MS: 1122.4, calcd for $C_{62}H_{66}N_4S_8$ 1122.31. ^1H NMR ($CDCl_3$, 500 MHz): δ [ppm] 8.58 (s, 2H), 7.69 (s, 2H), 7.57 (m, 4H), 7.34 (d, 2H), 7.00 (d, 2H), 6.84 (s, 2H), 3.07 (t, 4H), 2.54 (t, 4H), 1.96 (m, 4H), 1.59 (d, 6H), 1.32 (d, 16H), 1.02 (t, 6H), 0.91(t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 152.4, 152.3, 147.0, 144.1, 139.4, 138.7, 138.3, 137.5, 137.1, 128.7, 128.2, 126.8, 126.4, 125.0, 124.9, 124.3, 124.3, 123.7, 121.5, 31.8, 31.7, 31.7, 30.5, 30.5, 30.3, 29.7, 29.1, 29.1, 22.7, 22.7, 14.2, 14.1. Anal. Calcd for $C_{62}H_{66}N_4S_8$: C, 66.29; H, 5.88; N, 4.98. Found: C, 66.15; H, 6.01; N, 4.92.

2.2. Methods

Nuclear magnetic resonance (NMR) spectra, MALDI-TOF spectra, elemental analysis, absorption spectra and the electrochemical cyclic voltammogram were recorded referring to the works published before [25]. The structure, the fabrication procedure and the measurement of OSCs were as the same as the reference [23].

3. Results and discussion

3.1. Synthesis of the compounds

Scheme 1 shows the synthetic routes of BDT-HTH-BT and BDT-BT-HTH. Monomer 1, 2 and 3 were synthesized according to the references [23,26–28]. BDT-HTH-BT and BDT-BT-HTH were obtained by Suzuki reaction with a yield of 54.2% and 46.4%, respectively. BDT-BT-HTH has better solubility than BDT-HTH-BT in organic solvents even they are similar in the structure.

3.2. TGA analysis

The thermal stability of BDT-HTH-BT and BDT-BT-HTH were investigated by thermogravimetric analysis (TGA) and the temperatures with 5% weight loss for BDT-HTH-BT and BDT-BT-HTH were at 373 °C and 395 °C, respectively (Fig. 1). Comparing with BDT-BT-HTH, the temperature with 5% weight loss for BDT-HTH-BT is about 20 °C lower due to the different position of BT unit in the molecule structure.

3.3. Absorption spectra

Fig. 2 shows the UV–vis absorption spectra of BDT-HTH-BT and BDT-BT-HTH in $CHCl_3$ solution and film. The optical properties are summarized in Table 1. The absorption spectrum of BDT-HTH-BT in $CHCl_3$ solution exhibited an absorbance in the wavelength range from 350 to 550 nm with four absorption peaks. The two peaks of 318 and 343 nm were assigned to the π–π* transition absorption and the other two absorption peaks of 400 and 464 nm could be corresponded to the intramolecular charge transfer transition between the BDT and the BT units. Because the different BT position in molecular structure, there were approximate four absorption peaks (325, 379, 466 and 526 nm) in the absorption spectrum of BDT-BT-HTH, but 60 nm red-shifted in the 400–600 nm wavelength comparing with BDT-HTH-BT. The molar absorptivity of BDT-HTH-BT and BDT-BT-HTH were investigated to be 6.63×10^4 and 8.61×10^4, respectively, which indicates that BDT-BT-HTH showed a stronger absorption ability. For both of the two molecules, the absorption of the films red shifted about 100 nm in comparison with that of their solutions, which indicates aggregation existed in the film state. The absorbance range of BDT-BT-HTH in film (300–640 nm) was about 30 nm broader than that of BDT-HTH-BT (300–610 nm) and the absorption peak of BDT-BT-HTH red-shifted about 20 nm comparing with BDT-HTH-BT, which can be assigned to the contribution of the end hexyl-thiophene group in the molecular structure. The absorption edge of BDT-HTH-BT and BDT-BT-HTH films were at ca. 647 nm and ca. 692 nm, respectively, corresponding to the calculated optical bandgap of 1.91 eV and 1.81 eV.

3.4. Electrochemical properties

Electrochemical property of photovoltaic molecule materials is very important for the OSCs device performance. Electrochemical cyclic voltammetry was carried out to measure the energy levels of BDT-HTH-BT and BDT-BT-HTH. Fig. 3 shows the cyclic voltammograms of BDT-HTH-BT and BDT-BT-HTH in the negative and positive potential range, respectively. The onset oxidation potentials ($E_{\mathrm{onset}}^{\mathrm{ox}}$) of BDT-HTH-BT and BDT-BT-HTH are 1.11 V and 1.01 V vs. Ag/AgCl, respectively. Then the highest occupied molecular orbital (HOMO) energy levels were estimated to be −5.51 eV for BDT-HTH-BT and −5.41 eV for BDT-BT-HTH, according to the equation: $E_{\mathrm{HOMO}} = -e\,(E_{\mathrm{onset}}^{\mathrm{ox}} + 4.40)$ (eV) [29]. The lowest unoccupied molecular orbital (LUMO) energy levels of the compounds were calculated from $E_{\mathrm{LUMO}} = -e\,(E_{\mathrm{onset}}^{\mathrm{red}} + 4.40)$ (eV) [29]. The values of the energy levels were also listed in Table 1. BDT-BT-HTH exhibits a little deeper HOMO energy level than that of BDT-HTH-BT, although the bandgap of BDT-BT-HTH is narrowed.

We have investigated the theoretical calculations by density functional theory (DFT) using LDA\PWC to understand the molecular geometry. The theoretical results indicate the following: (a) the calculated HOMO and LUMO energies of the ground state optimized geometry of BDT-HTH-BT were −4.48 and −3.58 eV, whereas for BDT-BT-HTH they were −4.28 and −3.67 eV, respectively. (b) The optimized geometry of BDT-HTH-BT (Fig. 3c) shows that there is steric hindrance between the hexyl groups linked to BDT unit and thiophene ring. In the contrast, the optimized geometry of BDT-BT-HTH (Fig. 3d) shows that the hexyl groups linked to BDT unit and thiophene ring can arrange orderly.

3.5. Photovoltaic properties

OSCs devices were fabricated with BDT-HTH-BT and BDT-BT-HTH as donor materials, $PC_{71}BM$ as acceptor material [30,31] and the device was in the structure of ITO/PEDOT:PSS/Active layer/Al as the same as the reference [23]. Fig. 4 shows the current density-voltage (*J-V*) curves of the OSCs with best PCE values. The photovoltaic data of the OSCs