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Two wide-bandgap fluorine-substituted benzotriazole based terpolymers for efficient polymer solar cells

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ABSTRACT

In this work, the fluorine substituted benzotriazole (FBTz) unit is introduced into terpolymers for the first time. FBTz as an acceptor unit was added to the terpolymers of PTT-FBTz and PTTz-FBTz, in which the bithiophene (biTh) unit is used as the donor unit and thieno[3,2-*b*]thiophene (TT) or thiazolo[5,4-*d*]thiazole (TTz) is adopted as a third component, respectively. Compared to PTT-FBTz with TT as the third component, PTTz-FBTz with TTz showed pronounced aggregated shoulder peaks both in solution and film absorption spectra. Electrochemical cyclic voltammetry (CV) shows PTTz-FBTz possesses both lower HOMO/LUMO level than PTT-FBTz due to the higher electronegativity of nitrogen atoms in TTz unit. Subsequently, the bulk-heterojunction polymer solar cells (PSCs) based on PTTz-FBTz show a higher power conversion efficiency of 7.03%, which is much higher than those of PTT-FBTz based devices (PCE = 2.63%). The enhancement of photovoltaic performance based on PTTz-FBTz is mainly attributed to the deeper highest occupied molecular orbital (HOMO) level, higher carrier transport and better molecular packing.

1. Introduction

There has been a tremendous development of solution-processed polymer solar cells (PSCs) in the last few decades on account of their potential advantages of low cost, light weight, solution processability and flexibility [1–7]. In order to promote the photovoltaic performance, the new conjugated polymer donor comprising electron-rich (D) and electron-deficient (A) units has become one of the most attractive research fields [8–16].Recently, the high power conversion efficiencies (PCEs) has made a great breakthrough due to the development of new copolymers, for which power conversion efficiencies (PCEs) above 13% have been reported [17–20].

To date, the copolymers are the most promising donor materials in the field of PSCs, which have a series of good properties, such as broad absorption spectra, tunable energy levels and bandgaps through a variety of D and A units by intramolecular charge transfer (ICT). At the same time, the solubility and molecular packing can also be changed [21–25]. Enormous efforts have been made to optimize the device performance by designing the novel copolymer, however, because of the difficulty of exploiting new D and A units, only a few new units have successfully achieved a high PCE, such as benzothiadiazole (BT), thienopyrroledione (TPD), diketopyrrolopyrrole (DPP), thieno[3,2-*b*]thiophene (TT), benzodithiophene (BDT) and dithieno[2,3-d;2′,3′- *d*’]benzo[1,2-b;4,5-b’]dithiophene (DBT) et al. [26–32].

From the foregoing perspective, it is interesting to design a polymer with three or more building blocks in one polymer backbone. Terpolymers composed of three different units in the backbone are good examples to make use of the properties of various donor and acceptor units [33,34]. Normally, terpolymers have two structures, one is of the type of D–D–A using two donor units and one acceptor unit, another is D–A–A using one donor unit and two acceptor units. Adding a third component to the D–A copolymers can show synergetic effects in the electrical, optical, and structural properties of the polymers, such as obtaining a broad light absorption by a new ICT peak or π–π*, balancing the influence between solubility and molecular packing, tuning the energy levels and mobility [6,35–40]. Recently, the PCE values based on terpolymers over 9% have been reported [41–47].

Among the reported copolymers, fluorine substituted benzotriazole (FBTz) has been a popular electron-accepting building block due to its stronger electron-withdrawing property, which can obtain a low highest occupied molecular orbital (HOMO) energy level, a high open-circuit voltage (V_{oc}) and a high fill factor (FF).·In addition, FBTz unit with soluble alkyl chain shows a good processibility of the polymer [48–54]. Li and co-workers have reported a series of copolymers composed of bithienyl-benzodithiophene (BDTT) donor unit and FBTz acceptor unit, leading to a PCE of 9.53% [55]. Yan and co-workers have

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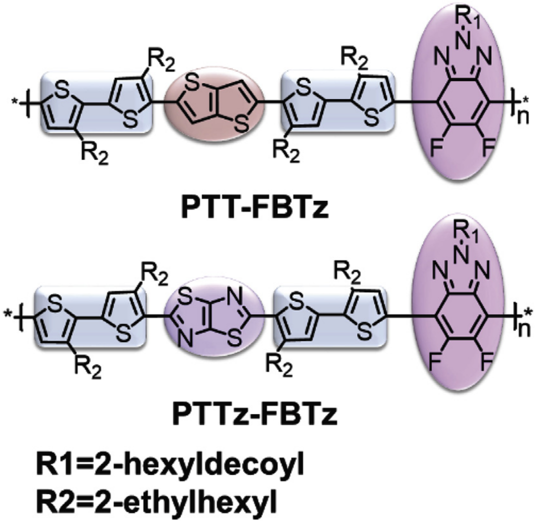

Fig. 1. Structures of PTT-FBTz and PTTz-FBTz.

reported a novel donor polymer, PvBDTTAZ, containing BDT donor and FBTz acceptor units, which obtained a PCE 11.2% [56].

Inspired by the above results, we adopt the FBTz unit to construct terpolymers for the first time. In this work, we have synthesized two terpolymers named PTT-FBTz and PTTz-FBTz based on bithiophene (biTh) as the donor unit and FBTz as the acceptor unit, respectively. In order to improve the coplanarity, we introduced thieno[3,2-*b*]thiophene (TT) and thiazolo[5,4-*d*]thiazole (TTz) as a third component to the polymers, respectively. After adding the electron-rich TT unit, PTT-FBTz is a D1–D2–D1–A1 structure. At the same time, PTTZ-FBTZ exhibits a typical D1–A1–D1–A2 structure due to the electron-withdrawing properties of TTz unit (Fig. 1). The electrochemical properties, UV–vis absorption, film morphology and photovoltaic performances of the two terpolymers were investigated. According to a conventional device structure, PTTz-FBTz-based solar cells show a high PCE of 7.03%, which is higher than those of PTT-FBTz devices (PCE = 2.63%). The results indicate that PTTz-FBTz is a potential photovoltaic material which has a structure of one donor and two acceptor units.

2. Experimental section

2.1. Materials

All the chemicals and solvents were purchased from commercial resources and without any further purification. 3-Bromothiophene (1) and 4,7-dibromo-5,6-difluoro-2-(2-hexyldecyl)-2*H*-benzo[*d*] [1–3]triazole (4) was purchased from commercial company. Tributyl(4-(2-ethylhexyl)thiophen-2-yl)stannane (3) was synthesized by the reported literature [57–59]. The synthesis of the monomer 2,5-bis(3-(2-ethylhexyl)-5-(trimethylstannyl)thiophen-2-yl)thieno[3,2-*b*]thiophene (7a) and 2,5-bis(3-(2-ethylhexyl)-5-(trimethylstannyl)thiophen-2-yl)thiazolo[5,4-*d*]thiazole (7b) were illustrated in our previous work [34].

2.2. Synthesis of compounds and terpolymers

2.2.1. Synthesis of 4,7-bis(4-(2-ethylhexyl)thiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2H benzo[d][1,2,3]triazole (5)

A mixture of Tributyl[4-(2-ethylhexyl)thiophen-2-yl]stannane (3) (2.43 g, 5 mmol) and 4,7-dibromo-5,6-difluoro-2-(2-hexyldecyl)-2*H*-benzo[*d*] [1–3]triazole (4) (1.07 g, 2 mmol) were added into in a flask (100 mL) and were dissolved in toluene (30 mL). The solution was purged with nitrogen for 10 min, after the $Pd(PPh_3)_4$ (345 mg, 0.3 mmol) was added into the solution. The reaction was refluxed at 110 °C under nitrogen atmosphere overnight. Then the solvent was evaporated and the crude product was purified by silica gel column chromatography with petroleum ether/dichloromethane (10:1) as the eluent to afford yellow-green oil (1.07 g, 70% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 8.12 (s, 2H), 7.12 (s, 2H), 4.72 (d, *J* = 6.6 Hz, 2H), 2.66 (d, *J* = 6.9 Hz, 4H), 2.28 (m, 1H), 1.68 (m, 2H), 1.40–1.28 (m, 40H), 0.97–0.86 (m, 18H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 149.00, 148.73, 145.65, 145.39, 142.20, 137.57, 131.91, 131.79, 123.77, 109.87, 59.94, 40.40, 39.07, 34.47, 32.57, 31.94, 31.86, 31.55, 29.90, 29.62, 29.57, 29.36, 28.97, 26.40, 26.36, 25.68, 23.11, 22.70, 22.69, 14.20, 14.12, 14.10, 10.92. IR (KBr) 2959, 2927, 2855, 1600, 1511, 1459, 1377, 1288, 995, 856, 746, 723 cm^{-1}. HRMS (MALDI-FTICR) *m/z* calcd for $C_{46}H_{71}F_2N_3S_2$, 767.5057; found: 767.5048. The ^1H NMR and ^{13}C NMR spectrum are provided in Fig. S1-2.

2.2.2. Synthesis of 4,7-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-2H-benzo[d][1,2,3]triazole (6)

Compound 5 (0.77 g, 1 mmol) was dissolved in chloroform (20 mL) in a flask (100 mL), *N*-bromosuccinimide (0.374 g, 2.1 mmol) was added slowly at room temperature. The solution was stirred for 2 h. After the reaction was complete, the ice water (20 mL) was added into the mixture, the organic layer was extracted by dichloromethane (3 × 50 mL) and dried over with $MgSO_4$. The solvent was evaporated and the crude product was further purified by silica gel column with petroleum ether/dichloromethane (20:1) as the eluent to obtain a yellow oil (0.66 g, 71% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 7.90 (s, 2H), 4.69 (d, *J* = 6.3 Hz, 2H), 2.58 (d, *J* = 6.9 Hz, 4H), 2.23 (m, 1H), 1.69 (m, 2H), 1.42–1.26 (m, 40H), 0.96–0.84 (m, 18H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 148.91, 148.64, 145.54, 145.29, 141.61, 137.21, 131.70, 131.41, 113.67, 109.30, 59.97, 39.99, 39.10, 33.71, 32.53, 31.92, 31.86, 31.53, 29.90, 29.62, 29.57, 29.35, 28.82, 26.39, 26.34, 25.71, 23.09, 22.69, 14.16, 14.11, 14.09, 10.88. IR (KBr) 2959, 2927, 2857, 1648, 1513, 1459, 1379, 1259, 1099, 1026, 1000, 801 cm^{-1}. HRMS (MALDI-FTICR) *m/z* calcd for $C_{46}H_{69}Br_2F_2N_3S_2$, 925.3247; found: 925.3236. The ^1H NMR and ^{13}C NMR spectrum are provided in Fig. S3-4.

2.2.3. Synthesis of PTT-FBTz

Compound 6 (138 mg, 0.15 mmol) and 7a (128 mg, 0.15 mmol) were added into a flask (50 mL) and were dissolved in toluene (8 mL). The solution was flushed with nitrogen for 10 min, after $Pd(PPh_3)_4$ (8 mg) was added into the flask. The solution was flushed with nitrogen for another 10 min. The reaction was heated to 110 °C gradually and stirred for 33 h at 110 °C under nitrogen atmosphere. After the reaction was complete, the solution was cooled to room temperature, the mixture was precipitated into methanol (60 mL) and filtered. After drying, the crude product was purified by column chromatography using chloroform as eluent to obtain pure product (102 mg, 53% yield). The molecular weights (M_w) = 35.0 KDa, polydispersity index (PDI) = 2.0, the decomposition temperature T (5% weight loss) = 433 °C. Elem. anal. for $C_{76}H_{107}F_2N_3S_6$: C 70.42, H 8.31, N 3.24; found: C 69.76, H 8.40, N 3.31.

2.2.4. Synthesis of PTTz-FBTz

Compound 6 (138 mg, 0.15 mmol) and 7b (128 mg, 0.15 mmol) were added into a flask (50 mL) and were dissolved in toluene (8 mL). The solution was flushed with nitrogen for 10 min, after $Pd(PPh_3)_4$ (8 mg) was added into the flask. The solution was flushed with nitrogen for another 10 min. The reaction was heated to 110 °C gradually and stirred for 25 h at 110 °C under nitrogen atmosphere. After the reaction was complete, the solution was cooled to room temperature, the mixture was precipitated into methanol (60 mL) and filtered. After drying, the crude product was purified by column chromatography using chloroform as eluent to obtain pure product (125 mg, 65% yield). M_w = 33.5 KDa, PDI = 1.8, T (5% weight loss) = 418 °C. Elem. anal. for $C_{74}H_{105}F_2N_5S_6$: C 68.46, H 8.32, N 5.40; found: C 67.80, H 8.16, N 5.35.