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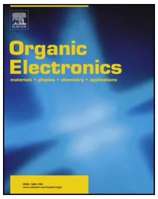

Effect of Thieno[3,2-*b*]thiophene π-bridge on photovoltaic performance of a D-A copolymer of alkoxy-benzodithiophene-alt-fluoro-benzotriazole

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ABSTRACT

A new J-series D-A copolymer **J41** based on alkoxy-benzodithiophene (BDT)-alt-fluorobenzotriazole (FBTA) was synthesized with thieno[3,2-*b*]thiophene (TT) as π-bridges. In comparison with its corresponding D-A copolymer J40 with thiophene π-bridges, **J41** shows a deeper HOMO energy level of −5.39 eV and slightly blue-shifted absorption. The polymer solar cells (PSCs) with **J41** as donor and a low bandgap *n*-type organic semiconductor (*n*-OS) ITIC as acceptor exhibited a maximum power conversion efficiency (PCE) of 8.74% with a higher V_{oc} of 0.93 V, which is significantly improved in comparison with the PCE of 6.48% with V_{oc} of 0.89 V for the corresponding PSCs with J40 as donor. The results indicate that the π-bridge engineering could further improve photovoltaic performance of the BDT-alt-FBTA-based D-A copolymers.

1. Introduction

Polymer solar cells (PSCs) have triggered extensive research interest during the last decades, because of their advantages of low-cost, light-weight, and flexibility, showing tremendous potential in fabricating colorful, semitransparent and flexible solar cell devices in the future [1–8]. The active layer of PSCs is composed of a blend of a *p*-type conjugated polymer as donor and a fullerene derivative (such as PCBM or $PC_{71}BM$) or an *n*-type organic semiconductor (*n*-OS, such as ITIC, IDIC etc.) as acceptor. Recently, the *n*-OS acceptors demonstrated excellent photovoltaic performance, and the power conversion efficiency (PCE) of the PSCs with narrow bandgap *n*-OS as acceptor and wide bandgap conjugated polymer as donor reached 9–13% [9–12].

For the PSCs with narrow bandgap *n*-OS as acceptor, the wide bandgap conjugated polymer donor, which possesses complementary absorption with the acceptor in the visible and NIR region, plays very important role for obtaining high power conversion efficiency [13–22]. For example, our group developed a series (J-series) of wide bandgap D–A copolymers based on benzodithiophene (BDT)-alt-fluorobenzotriazole (FBTA) [13–19]. By side chain engineering of attaching alkylthiophene, alkylthio-thiophene or alkylsilyl-thiophene conjugated side chains, the PCE of the PSCs with the polymers as donor and ITIC as acceptor reached over 11% [16–18].

For the D-A copolymer donor materials, the π-bridges between the donor and acceptor units also influence the physicochemical and photovoltaic properties of the D-A copolymers [19,23–27]. For example, Wang et al. studied the effect of π-bridges on the photovoltaic performance of the D-A copolymers based on benzodithiophene (BDT) and benzothiadiazole (BT) [24]. They used furan, thiophene and thieno[3,2-*b*]thiophene (TT) as the π-bridges in the D-A copolymers and found that the D-A copolymer with TT π-bridges showed the best photovoltaic performance. However, there is no report on the effect of the TT π-bridges for the J-series wide bandgap polymers.

In order to enlarge the family of the J-series D-A copolymers, here we introduced the TT π-bridges in the main chain of the J-series polymers, and take a low performance J-series polymer J40 [14] based on alkoxy-BDT-alt-FBTA with thiophene π-bridges as a control sample. The new D-A copolymer based on alkoxy-BDT-alt-FBTA with TT π-bridges, called as **J41**, shows a deeper the highest occupied molecular orbital (HOMO) energy level of −5.39 eV and slightly blue-shifted absorption probably owing to some main chain twist due to the bigger thieno[3,2-*b*]thiophene units. The PSCs with **J41** as donor and ITIC as acceptor demonstrated a PCE of 8.74% with a higher V_{oc} of 0.93 V, which is significantly improved in comparison with the PCE of 6.48%

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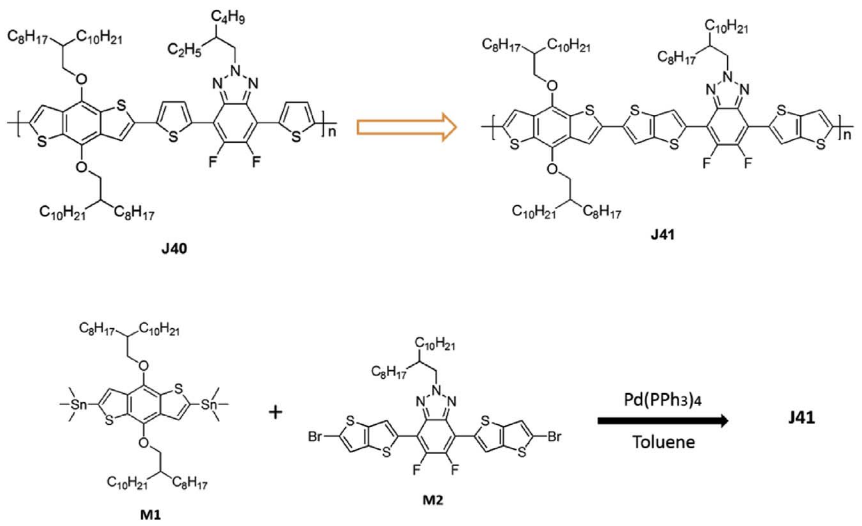

Scheme 1. Molecular structures of J40, **J41** and the synthetic route of **J41**.

with V_{oc} of 0.89 V for the corresponding PSCs with J40 as donor.

2. Results and discussion

2.1. Materials and synthesis

The chemical structure and synthetic route of the polymer **J41** are illustrated in Scheme 1. M1 and M2 were purchased from SunaTech, Inc. Polymer **J41** was synthesized by the Stille-coupling polymerization of M1 and M2 with high yield of 91%. **J41** can be easily dissolved in common organic solvents like chloroform, tetrahydrofuran (THF) and 1,2-dichlorobenzene at room temperature. The molecular weight and polydispersity index (PDI) of the polymer were evaluated by Gel permeation chromatography (GPC) method, showing that **J41** has a number-average molecular weight (M_n) of 44.8 kDa with a polydispersity index (PDI) of 2.06. Thermo-gravimetric analysis (TGA) was carried out to gauge the thermal stability of polymer **J41**, as shown in Fig. 1(a). The thermal decomposition temperature (T_d) of **J41** with 5% weight loss is *ca.* 326 °C, slightly higher than that of the corresponding polymer J40 with thiophene π-bridges, which indicates that polymer J41 has sufficient thermal stability for its application in PSCs. It should be mentioned that the alkyl side chains on FBTA unit of **J41** is longer than that of J40 for improving the solubility of J40 because of its larger thienothiophene fused ring π-bridges.

2.2. Photophysical properties

Fig. 1(b) shows film absorption spectra of polymer **J41**, ITIC and their blend. Both **J41** and ITIC possess absorption peaks with vibronic shoulder in the long wavelength range, indicating the ordered aggregation existence and strong $\pi-\pi$ stacking interaction in the films. **J41** film owns two well-defined absorption main peaks at 532 and 576 nm with absorption edge at 620 nm. It can be found that the absorption of **J41** is 10 nm blue shifted in comparison to that of **J40**, which could be owing to some main chain twist due to the bigger thieno[3,2-*b*]thiophene units. As shown in Fig. 1(b), Polymer **J41** and ITIC have well matched complementary absorption in the vis-NIR region, and the absorption of the blend films of **J41**: ITIC covers a broad wavelength range from 390 to 780 nm.

We employed cyclic voltammetry [28] to evaluate HOMO energy level (E_{HOMO}) and the lowest unoccupied molecular orbital (LUMO) energy level (E_{LUMO}) of the polymer **J41**. As shown in Fig. 2(a), the oxidation/reduction potentials ($\varphi_{\mathrm{ox}}/_{\mathrm{red}}$) of **J41** are 1.03/−1.67 V *vs.* Ag/AgCl. Based on the equations: $E_{\mathrm{HOMO/LUMO}} = -\mathrm{e}\,(\varphi_{\mathrm{ox}}/_{\mathrm{red}} + 4.36)$ (eV) [16], (Redox potential of Fc/Fc$^+$ is 0.44 V *vs* Ag/AgCl in our measurement system, and we take the energy level of Fc/Fc$^+$ as 4.8 eV below vacuum) we then calculated the $E_{\mathrm{HOMO/LUMO}}$ levels of **J41** to be −5.39/−3.69 eV. And the HOMO energy offset between **J41** and ITIC (−5.54 eV) (ΔE_{HOMO}) is 0.15 eV, which is much below the empirical threshold value (0.3 eV) of effective exciton dissociation in PSCs.

Photoluminescence (PL) quenching experiment was carried out to study photo-induced charge transfer behavior in the polymer **J41**, ITIC and their blend film. Based on their maximum absorptions (as seen in Fig. 1(b)), the excitation wavelength of 576 nm is set for **J41** donor and 700 nm for ITIC acceptor. For the blend films, both emission peaks of **J41** and ITIC were significantly quenched when excited at the wavelength of 576 nm and 700 nm, as shown in Fig. 2(b). Nevertheless, the quenching degree of the PL excited at 700 nm is slightly lower than that of the PL excited at 576 nm, indicating that the hole transfer efficiency from the acceptor to donor is slightly lower than that of the electron

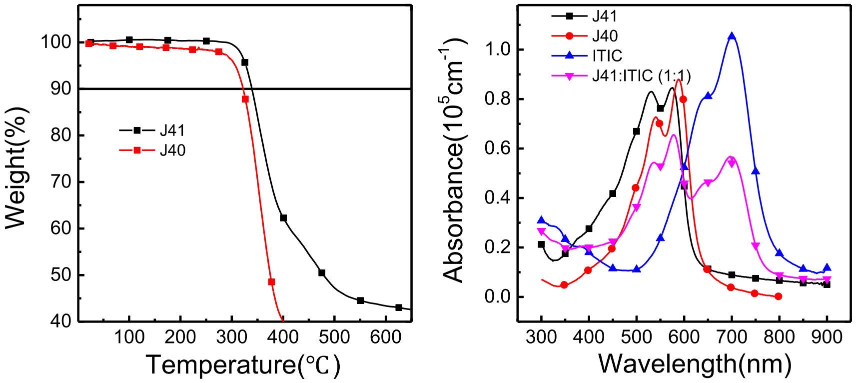

Fig. 1. (a) TGA plot of **J41** and J40; (b) Absorption spectra of **J41**, J40, ITIC and **J41**:ITIC blend films (1:1, w:w).