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The performance of new polymer solar cells based on thiophene and thienyl-quinoxaline with the post treatments

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ABSTRACT

A new low band gap (optical band gap=1.62 eV) polymer (TTQ) based on thiophene and thienyl-quinoxaline by substituting phenyl in quinoxaline unit for thiophene rings was synthesized and characterized for application in polymer solar cells (PSCs). The optical band gap (E_g^{opt}) deduced from the onset (765 nm) of the polymer absorption spectrum in the films was 1.62 eV, which was less than those of the polymers TQ and FTQ and was closer to the ideal band gap of a donor for BHJ polymer solar cell applications. For the optimized polymer solar cell of TTQ:PC₇₁BM, 1:1 w/w, in DCB solution, a PCE over 1.41% with V_{oc} of 0.70 V, J_{sc} of 3.89 mA/cm², and fill factor (FF) of 55% under AM1.5 conditions was achieved by solvent annealing in comparing with those of solvent surface treatment devices (PCE of 1.34%) and thermal annealing devices (PCE of 1.10%).

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1. Introduction

Organic bulk heterojunction (BHJ) solar cells with a bicontinuous interpenetrating network between the polymer donor and the fullerene acceptor exhibited potential advantages as lightweight, flexible, large area devices and in the low cost roll to roll fabrication methods [1,2]. Multidisciplinary efforts had been taken to pursue high power conversion efficiency (PCE) of polymer solar cells, such as rational designs of low band gap conjugated polymers [3–5], optimization of film morphology [6–8], and developing of new device architectures [9–11]. These efforts led to BHJ solar cells with PCEs close to 9% [12–15]. In recent years, a vast number of conjugated polymers have been developed and various chemical modifications have been used to optimize the physical and photovoltaic properties. A promising conjugated polymer was poly[2,3-bis(3-(octyloxy)phenyl)quinoxaline-alt-thiophene] (TQ), which offered good photovoltaic performance as well as ease of synthesis [16]. Moreover, a novel fluorinated copolymer (FTQ) showed a significantly higher open circuit voltage (V_{oc} =0.95), which resulted from the lowering of the polymer HOMO level from –5.36 eV to –5.51 eV in bulk heterojunction solar cells in

comparison with that of the polymer TQ [17]. Nevertheless, the optical band gaps (E_g^{opt}) of TQ and TTQ were about 1.7 eV which was much larger than optimal optical band gap (less than 1.4 eV). Moreover, quinoxaline-based D–A copolymers contained two pendant substituted benzene groups on the quinoxaline rings, which could freely rotate and potentially hinder the intermolecular packing of the copolymers and further influence charge carrier mobility [18].

In present work, a low band gap (optical band gap=1.62 eV) polymer (TTQ) with broad absorption from 300 nm to 760 nm by using thiophene as an electron-donating unit and thienyl-quinoxaline as an electron-accepting unit was designed and synthesized for photovoltaic application. The effect of the post treatments such as solvent annealing, thermal annealing and solvent surface treatment on the morphology and interface engineering of the TTQ:PC₇₁BM blend films were demonstrated. Polymer solar cells based on TTQ:PC₇₁BM show simultaneous enhancement in short-circuit current (J_{sc}) and fill factor (FF) after solvent post treatments of the active layer.

2. Materials and methods

All chemicals and reagents were obtained from Aldrich and Alfa Aesar. THF was dried over Na/benzophenone ketyl and freshly distilled prior to use. The synthetic routes of monomers and copolymer are shown in Scheme 1 (see Figs. S1–S3).

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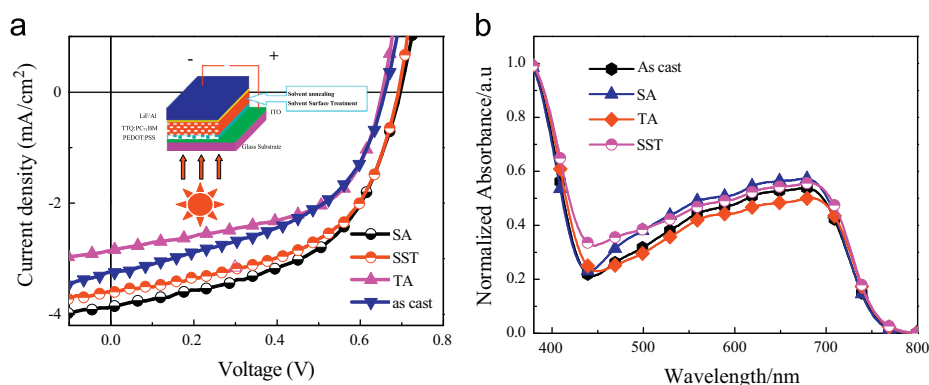
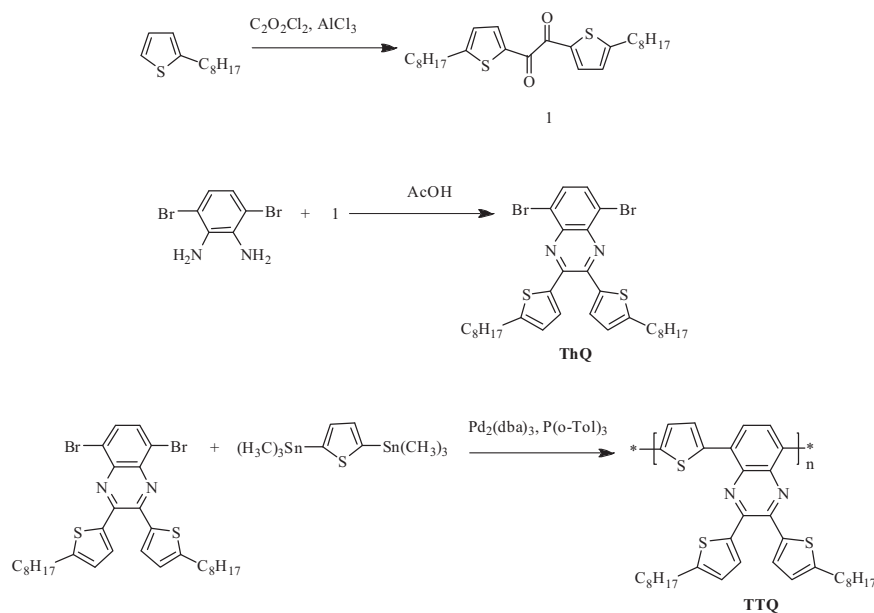


Fig. 1. J - V curves of PSCs (a) and absorption spectra (b) of the TTQ:PC₇₁BM blend films based on TTQ:PC₇₁BM (D/A ratio = 1:1) by using post treatments.

3. Results and discussion

Absorption properties and electrochemical properties: The absorption properties of the polymer TTQ were investigated both in CHCl₃ solution and in film state as shown in Fig. S4. The absorption bands in the film have two peaks at 390 nm and 690 nm which were broader than those in solution where three peaks were found to be 360 nm and 600 nm. The optical band gap (E_g^{opt}) of TTQ could be estimated to be 1.62 eV from the UV-vis spectra in solid film. The onset potentials ($E_{\text{ox}}/E_{\text{red}}$) of the synthesized TTQ were 0.34/−1.55 V. From the E_{ox} and E_{red} values of the polymers, the corresponding HOMO or LUMO energy levels and the electrochemical band gap (E_g^{ec}) of the polymers were calculated. It can be seen that a low HOMO energy level of −5.06 eV was obtained.

Photovoltaic properties: For the sake of investigation, the photovoltaic properties of the copolymers and the polymer solar cells were fabricated with a general device structure of ITO/PEDOT:PSS/TTQ:PC₇₁BM/LiF/Al. The active films were post processed by solvent annealing (SA), solvent surface treatment (SST) and thermal annealing. The TTQ:PC₇₁BM blend film was processed by thermal annealing (at 110 °C, 1 min) in a glove box or a solvent annealing overnight (~12 h) in a glove box. As well as the TTQ:PC₇₁BM film was post processed by ethanol with a wetting time of

2 min, then the ethanol was spin-coated at 2000 rpm on top of the active layer for 60 s. The film thickness of the active layers with different D/A ratios was optimized by controlling the speed of the spin-coating process. The photovoltaic characteristics of TTQ:PC₇₁BM-(1:1)-based device under solvent surface treatment (ethanol), solvent annealing (~12 h) and thermal annealing are compared in Fig. 1(a). The PSC device without any post treatments was defined as the as-cast device. When the morphology of the TTQ:PC₇₁BM (1:1) active layers was optimized by using solvent annealing and solvent surface treatment, the PSCs showed a significant enhancement in J_{sc} and FF in comparing with that of the as-cast device, which led to PCEs of 1.41% and 1.34%. A similar photovoltaic performance (PCE=1.10%) of the PSC devices under thermal annealing (at 110 °C, 10 min) could be obtained (see Table 1).

Furthermore, it was clear that the shunt resistances (R_{sh}) were calculated as $7.5 \times 10^2 \Omega \text{ cm}^2$, $7.3 \times 10^2 \Omega \text{ cm}^2$ and $5.0 \times 10^2 \Omega \text{ cm}^2$ for the solvent annealing, solvent surface treatment and thermal annealing devices, respectively, which were higher than that of a thermal annealing device ($300 \Omega \text{ cm}^2$) (see Table 1). Moreover, the series resistance (R_s) of the thermal annealing, ethanol-treated and solvent annealing devices were $100 \Omega \text{ cm}^2$, $50 \Omega \text{ cm}^2$ and $32 \Omega \text{ cm}^2$, respectively, which were lower than that of a thermal annealing device ($130 \Omega \text{ cm}^2$). These data were in agreement with the decreased leakage current and slightly increased FF in the

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