

# Improvement in performance of P3HT/PCBM solar cell by using dithiafulvalene-based $\pi$ -conjugated oligomer

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## Abstract

We investigated the effect of the amount of dithiafulvalene (DTF) derivative as a conjugated oligomer on performance of organic solar cell composed from poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C<sub>61</sub>butyric acid methyl ester (PCBM) blend films. A new  $\pi$ -conjugated oligomer, PTBT, containing DTF unit act as the electron-rich donors and benzothiazole group act as the electron-deficient acceptor in the main chain, was synthesized using Suzuki coupling polymerization. The incorporation of the conjugated DTF inside P3HT:PCBM blend improved the power conversion efficiencies (PCEs) with approximately 1.78 %. By adding specific amounts of the PTBT into P3HT:PCBM blend, the solar cell performance parameters, i.e., open circuit potential, fill factor, and power conversion efficiency improved as a result of improvement in the charge carrier transfer taking place between P3HT and PCBM through the conjugated PTBT oligomers. Compared to the binary blend devices, the devices doped PTBT exhibited relatively better stability under ambient atmosphere conditions.

本研究利用 Suzuki 耦合聚合法合成一種新穎性含有四硫富瓦烯基團的共軛寡聚合物(PTBT)，探討其摻混於 P3HT:PCBM 異質界面太陽能電池提升光伏打性質之研究。此 PTBT 寡聚合物的分子結構以四硫富瓦烯基團當作電子予體，並以苯并噻二唑單元當作電子接受體。摻混 PTBT 寡聚合物於 P3HT:PCBM 系統提升光電轉換效率為 1.78 %，此外，開路電壓、填充因子和光電轉換效率的提升，乃歸因為添加 PTBT 寡聚合物改善了 P3HT 和 PCBM 之間的載子移動速率。此摻混系統在一般環境中，呈現非常高的穩定性。本研究所開發的共軛寡聚合物可有效提升太陽能電池的光電轉換效率，可作為未來 BHJ 太陽能電池的摻混材料。

**Keywords:** bulk-heterojunction solar cells; dithiafulvalene; P3HT/PCBM blends

## INTRODUCTION

Organic photovoltaic devices (OPVs) have received much attention because of their promising effective ability to convert light energy into electrical energy. Moreover, OPVs have the advantages of low-cost, flexible and light-weight [1-4]. In the past decade, BHJ polymer solar cells have made significant progress and their power conversion efficiency (PCE) has been up to 10 % [5]. The photoactive layer of BHJ solar cells is commonly composed of a blend film of a conjugated polymer and soluble fullerene derivatives. In such blend systems, the efficiency of the BHJ solar cells is affected by many factors, for example the light absorption of the solar cells, the mobility of the charge carriers and the morphology of the blend film [6]. In other words, improving these factors can increase the efficiency of BHJ solar cells. Besides the efficiency, OPVs' stability also limits their practical application. Several studies have shown that the degradation of BHJ solar cells is originated from the reaction with oxygen, water, etc. There have been some studies reporting the stability of devices under ambient conditions without encapsulation or with simple mechanical protection of the active layer with no barrier properties [7-9].

In this work, we have synthesized a conjugated dithiafulvalene-based oligomer, **PTBT** (Fig. 1), consisting of the  $\pi$ -conjugated dithiafulvalene unit as the electron-rich donors and the benzothiazodazole as the electron-deficient acceptor in the main chain. We described the concentration effect of **PTBT** on light harvesting and performance of BHJ solar cells made from blend of P3HT and PCBM (1:1 weight ratio). The optical absorption spectroscopy and current-voltage (I-V) characteristic measurements of devices under AM 1.5G illumination were carried out. The experimental processes and the data analyses are given below. The solar cell doping 5 wt % of **PTBT** exhibited the best PCE of 1.78 % under ambient atmosphere conditions, while the device without **PTBT** shown 1.41 %. Furthermore, the former decreased to 1.22 % after 24 h, but the latter only 0.35 %.

## EXPERIMENTAL

### Synthesis of the polymer

The synthesis of **PTBT** was carried out using a nickel-catalyzed Yamamoto coupling reaction. The general synthetic procedures for **PTBT** are described as follows: To a 100 ml round-bottom flask, Ni(COD)<sub>2</sub> (1.0 g, 3.55 mmol), 2,2-dipyridyl (0.55 g, 4.55 mmol), and 1,5-cyclooctadiene (0.348 g, 3.5 mmol) were dissolved in 10 ml of DMF under a nitrogen atmosphere. The solution was heated to 80 °C for half an hour to form a purple complex.

2-(2,7-dibromo-9H-fluoren-9-ylidene)-4,5-bis(hexylthio)-1,3-dithiole (0.92 g, 1.40 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.41 g, 1.40 mmol), in a mixture of 30 ml of toluene and 5 ml of DMF, were added to the solution, and heated at 80 °C for another 3 days. After being cooled to room temperature, the reaction mixture was poured into a mixture of 200 ml of HCl, 200 ml of acetone, and 200 ml of methanol, which was stirred for 2 h. The solid was filtered, and redissolved in chloroform. Then it was precipitated in a large amount of methanol. The solid was purified by a Soxhlet extractor for 24 h using acetone as the solvent. The polymer was obtained after drying in vacuum at 80 °C. Yield: 45.6 %. <sup>1</sup>H NMR: (CDCl<sub>3</sub>, ppm): 7.38-7.84 (br, ArH), 2.96-2.98 (br, CH<sub>2</sub>), 1.25-1.86 (m, CH<sub>2</sub>), 0.85-0.90 (br, CH<sub>3</sub>). *M<sub>w</sub>* = 2.3 kg/mol, *M<sub>w</sub>*/*M<sub>n</sub>* = 1.42. *T<sub>d5</sub>* = 267.6 °C. *T<sub>g</sub>* = 69.2 °C.

## Device Fabrication

The fabricated BHJ device has a configuration of ITO/PEDOT:PSS/active layer/Al. Devices were prepared on cleaned indium tin oxide (ITO)-coated glass substrates (8Ω/sq). ITO substrates were sequentially patterned by the mixed solution (*V<sub>H2O</sub>*:*V<sub>HCl</sub>*:*V<sub>HNO3</sub>* = 10:9:1), followed by cleaning with deionized water, acetone and isopropyl alcohol, dried. PEDOT:PSS was passed through a 0.45 μm filter before being deposited on ITO through spin-coating at 5000 rpm in air. A blend of P3HT:PCBM:**PTBT** with weight ratios of 1:1:*x*, where *x* is the weight ratio of **PTBT** to P3HT, ranging from 2 to 10 wt % (10 mg/ml in *o*-dichlorobenzene (*o*-DCB)). The solution was then filtered through a 0.22 μm poly(tetrafluoroethylene) filter, and then spin-coated with 5000 rpm for 45 s on top of the PEDOT:PSS layer. Subsequently, the devices were dried at room temperature for 2 h. Then, the device was completed by depositing a 120 nm thick layer of Al at pressures of less than 5 × 10<sup>-5</sup> torr. Effective light absorption surface area of the resulting organic solar cell device was 0.15 cm<sup>2</sup>. All photovoltaic data were measured under air atmosphere.

## RESULTS AND DISCUSSION

### Photovoltaic performance

We have measured the current-voltage characteristics of the ITO/PEDOT:PSS/P3HT:PCBM/Al and ITO/PEDOT:PSS/P3HT:PCBM:**PTBT**/Al devices under AM 1.5G white light illumination with intensity of 100 mW/cm<sup>2</sup> as a function of **PTBT** amount in the blend under ambient atmosphere condition. P3HT:PCBM device shows a typical PCE of 1.41 %, with a short-circuit current density (*J<sub>sc</sub>*) of 5.73 mA/cm<sup>2</sup>, an open-circuit voltage (*V<sub>oc</sub>*) of 0.51 V and a fill factor (FF) of 48.3 %. Incorporating **PTBT** in quantities of 2 wt %, 5 wt % and 10 wt % in the P3HT:PCBM film led to significant enhancements in the *J<sub>sc</sub>* and FF values compared to the P3HT:PCBM

device. Blends with 5 wt % PTBT in the ternary blend resulted in the highest PCE of 1.78 %. The increasing in  $V_{oc}$  with doping PTBT could be observed, and the best value of  $V_{oc}$  was 0.57 V when doping 2 wt % or 5 wt % PTBT. We found that the  $V_{oc}$  values of the solar cell correlates with the HOMO-LUMO energy gaps of the materials in the active layer. These results suggest that introducing PTBT into P3HT polymer chains enhances the donating strength of molecules, and is the cause of the raise in the  $V_{oc}$  values. The electrochemical data show that the energy bandgap of PTBT (2.64 eV) was larger than P3HT (1.90 eV). The addition of PTBT onto P3HT:PCBM blend affect the energy bandgaps of the active layer. FF and charge-carrier mobility ( $\mu$ ) were found to increase with a PTBT doping concentration above 2 wt%; the maximum values of which are 55.6 % and  $4.59 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ , respectively, with the doping 2 wt % of PTBT. We attributed the increasing  $\mu$  to the stronger intermolecular interactions of PTBT, leading to the improvement of charge transfer of molecules. Generally, the charge transfer might be the main reason for increasing  $J_{sc}$ . However, the experimental results of  $J_{sc}$  were not identical to that. We found that the maximal value of  $J_{sc}$  was approximately  $6.08 \text{ mA/cm}^2$  when we doped 5 wt % PTBT into P3HT:PCBM blend. It indicates that the increase in  $J_{sc}$  might correspond to enhancements in the external quantum efficiency. However, the  $J_{sc}$  of the devices with doping 2 wt % and 10 wt % PTBT were smaller than that without doping. It indicates that the decrease in  $J_{sc}$  when adding PTBT might be attributable to the poor morphology of the blends. The aggregates inside the blends hinder the polymer chains from charge carriers to transfer through the bulk and reach the contacts. The PCE increased from 1.41 % of the pristine blend to 1.72 %, 1.78 %, and 1.50 % of doping 2 wt %, 5 wt %, and 10 wt % PTBT, respectively. The results suggest that a small amount of PTBT in the active layer was responsible for increasing the PCE because of the improvement of the charge-carrier mobility and the absorption intensity. However, adding extra amounts of PTBT led to the formation of poor phase separation, which limited the generation of electron-hole pairs, and hence, the PCE decreased. We compared the series resistances ( $R_s$ , defined from the J-V curves near 1.5 V under light illumination) and shunt resistances ( $R_{SH}$ , defined from the J-V curves near 0 V under light illumination) as a function of PTBT concentration. The  $R_s$  decreased from  $29.2 \text{ }\Omega\text{cm}^2$  to  $22.5 \text{ }\Omega\text{cm}^2$  at 2 wt % PTBT loading, and then increased to  $28.7 \text{ }\Omega\text{cm}^2$  and  $30.3 \text{ }\Omega\text{cm}^2$  at 5 wt % and 10 wt %, respectively. In all cases the  $R_s$  was lower in devices with PTBT below 5 wt % loading compared to P3HT:PCBM device. In contrast, the  $R_{SH}$  reached a maximum of  $684.8 \text{ }\Omega\text{cm}^2$  at 5 wt % PTBT, while that in the 0 wt % was  $956.4 \text{ }\Omega\text{cm}^2$ . The results suggests that the improved FF could also be attributed to a lower  $R_s$ , implying better nanoscale crystallinity and improved nanomorphology in the BHJ blends with PTBT.

The stability in the photovoltaic response of P3HT:PCBM:PTBT (1:1:0.05 wt %)

ternary blend devices was investigated as compared with that of P3HT:PCBM solar cells. All photovoltaic data were measured under air atmosphere. Figures 3 (a), (b) and (c) show I-V plots of those devices measured under illumination after degraded in atmosphere condition with different time. The current density ( $J_{sc}$ ) and PCE values of P3HT:PCBM blend after 24 h decreased from 5.73 mA/cm<sup>2</sup> and 1.41 % to 1.54 mA/cm<sup>2</sup> and 0.35 %, respectively. However, the devices based on doping 5 wt% **PTBT** exhibited relatively slow degradation as compared to those without doping. The PCE values of doping **PTBT** degraded from 1.78 % to 1.22 % and the current density ( $J_{sc}$ ) decreased from 6.08 mA/cm<sup>2</sup> to 4.29 mA/cm<sup>2</sup> after 24 h. The results suggest that the enhanced stability in the photovoltaic response of the P3HT:PCBM:**PTBT** devices was attributable to the better shielding of the P3HT:PCBM blend by rather stable **PTBT** molecules. The **PTBT**, like TTFs, have two redox peaks, and both of them were nearly reversible, indicating that the excited states of **PTBT** are more stable than those of P3HT. Therefore **PTBT** reveals extreme stability in the redox processes. Electrons and holes of the radical species in the charge carrier transport processes are relatively more stable because of the enhanced stability of the materials in the devices.

## CONCLUSIONS

In summary, we have successfully constructed BHJ solar cells incorporating **PTBT** that show enhanced efficiency. **PTBT** possesses good redox feature and high charge-carrier mobility. The P3HT:PCBM:**PTBT** blends show enhanced performances of photovoltaic devices, which are attributed to the better charge-carrier mobility between **PTBT** and P3HT:PCBM. Adding a 5 wt % of **PTBT** induces the enhancement of the short circuit current ( $J_{sc}$ ) from 5.73 mA/cm<sup>2</sup> to 6.08 mA/cm<sup>2</sup>. In comparison to P3HT:PCBM device, the device with 5 wt% **PTBT** exhibited a significant increase of 26.2 % in PCE due to improved  $J_{sc}$  and FF. The doping of **PTBT** also affects the energy gap in the active layer, led to the increase of  $V_{oc}$ . Compared to the binary blend devices, the devices based on the ternary blend exhibits relatively better stability in all photovoltaic parameters. The addition of **PTBT** makes it more robust and stable in electrochemical and environmental stability as providing protection to the P3HT:PCBM system under ambient atmosphere condition. These results demonstrate that **PTBT** is a promising candidate for BHJ solar materials.

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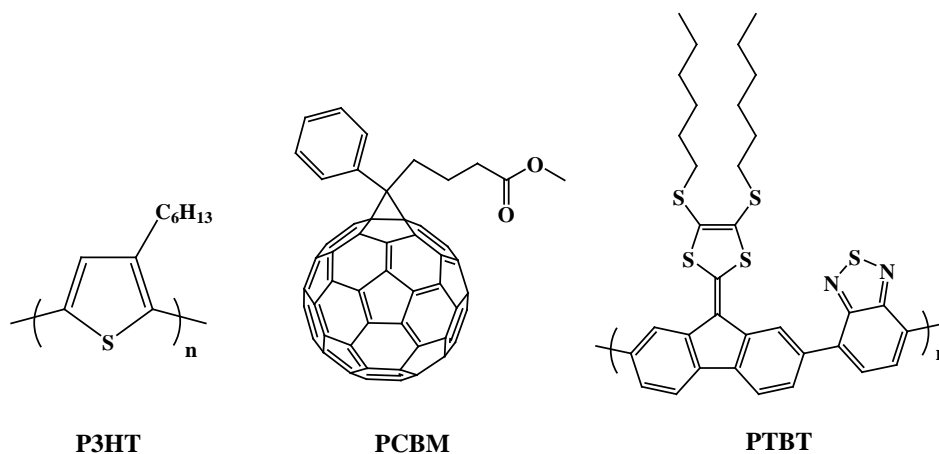


Figure 1. Chemical structures of PTBT, PCBM and **PTBT**.

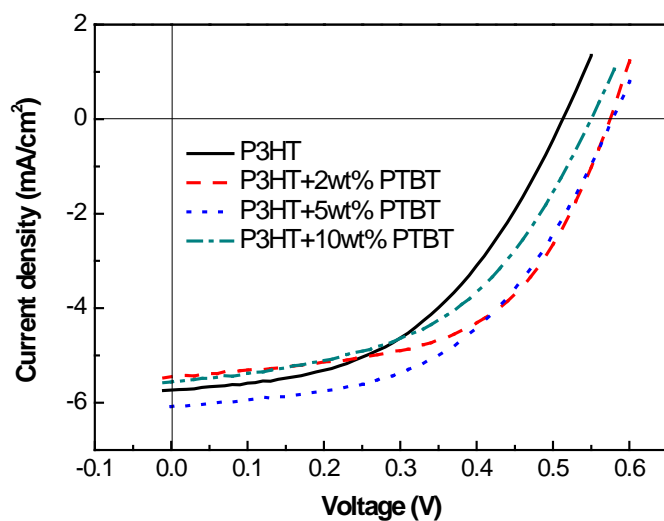


Figure 2. Current-voltage characteristics under illumination of the devices based on the blends of P3HT:PCBM:PTBT [1:1:0-0.1 w/w].

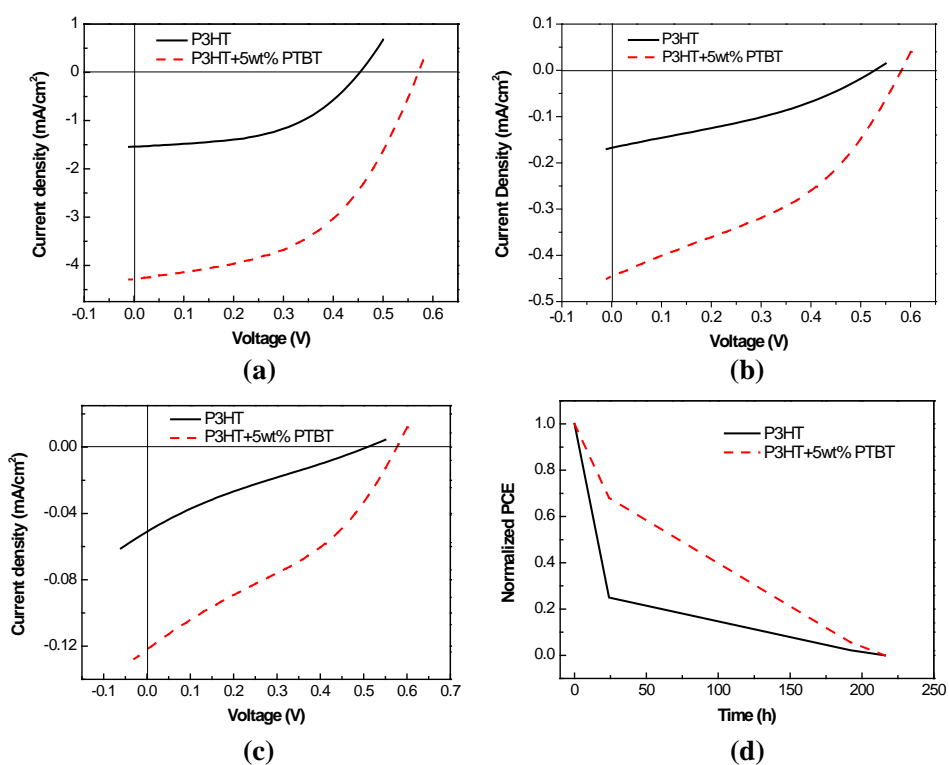


Figure 3. (a), (b) and (c) Illuminating current-voltage characteristics of the devices based on the blends of P3HT:PCBM [1:1 w/w] and P3HT:PCBM:PTBT [1:1:0.05 w/w] degraded under ambient atmosphere condition after 24 h, 192 h and 216 h, respectively; (d) degradation in normalized PCE of different devices.