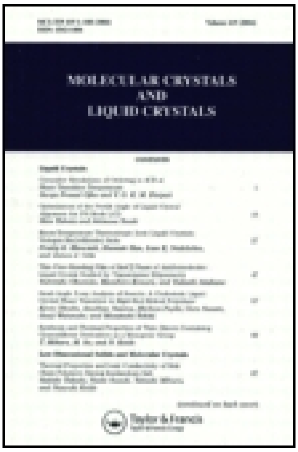

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Improvement of Poly(3-phenylthiophene)-Based Bulk Heterojunction Organic Solar Cells

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This paper describes the synthesis and photovoltaic studies of Poly(3-Phenylthiophene) (P3PhT). P3PhT was synthesized by the chemically oxidized polymerization in the presence of $FeCl_3$. Bulk heterojunction solar cells based on polymer were fabricated by using chloroform, chlorobenzene, and dichlorobenzene at different weight ratios of P3PhT. The different ratios of P3PhT as the electron donor blended with [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) as the electron acceptor were investigated. A maximum power conversion efficiency was achieved at a 2:3 (wt:wt) P3PhT:$PC_{61}BM$ blend ratio in dichlorbenzene.

Keywords Bulk heterojunction solar cells; chemical oxidative polymerization; conjugated polymer

Introduction

Nowadays, bulk heterojunction (BHJ) organic solar cells based on polymer:fullerene composites have attracted much attention as a low-cost, printable, light weight and flexible potential sources of renewable electrical energy [1–3]. The BHJ is the self-assembly of nanoscale heterojunctions by spontaneous phase separation of the polymer acts as a donor and the fullerene acts as an acceptor. For an efficient transfer of electrons from a donor to an acceptor, charge-separating is formed throughout the bulk of the materials [3,4].

Conducting polymer can produce electricity from sunlight using delocalized π-electron system. For example, Poly(3-Phenylthiophene) (P3PhT) with phenyl group at the 3 position of thiophene ring is an interesting material, their electro-optical properties were investigated [5,6].

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In this work we studied BHJ composites P3PhT/[6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) photoelectric properties with different ratios and solvents.

Methods

3-phenylthiophene (95%), and $FeCl_3$ (97%) were purchased from Aldrich Chemical Co., Inc.

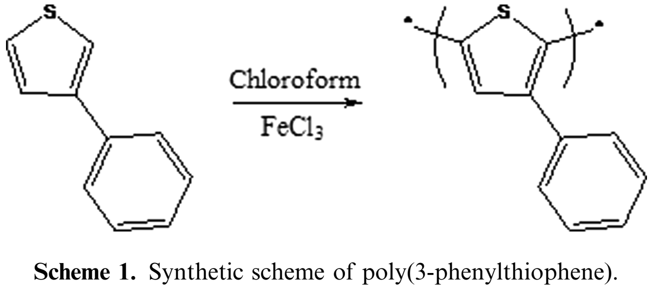
Synthesis of Poly(3-phenylthiophene) (P3PhT)

P3PhT was synthesized by oxidative polymerization using ferric chloride, as shown in Scheme 1. The procedure was similar to that described in the literature [7].

A three-neck round bottom flask was charged with $FeCl_3$ 2.7656 g (16 mmol) in 35 ml of chloroform under an argon atmosphere. The mixture was stirred at room temperature for 30 min; then 3-Phenylthiophene 0.6757 g (4 mmol) in 15 ml of chloroform was added. The mixture was stirred for 24 h, precipitated in methanol and filtered. The precipitate was dissolved in 30 ml of chloroform with 0.1 M EDTA solution, the mixture was stirred at 65°C for 45 min. The chloroform layer was collected and concentrated to 10 ml. The solution was poured into 300 ml of methanol. The polymer was collected and washed 3 times with methanol, yield 85%. ^{1}H-NMR ($CDCl_3$): 7.19 (s, 1H), 7.44 (d, 2H), 7.34–7.37 (m, 2H), 7.28 (d, 1H). UV-Vis; the λ_{max} at 428 nm.

Fabrication of BHJ Solar Cells Devices

Two sets of BHJ devices were fabricated similar to the literature [8]. Glass/indium tin oxide substrates were deposited with poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS) by spin coating at 4000 rpm and dried at 100°C for 25 min. For device Set 1, with 5.62 mg, 7.50 mg, and 11.25 mg of P3PhT were designated to be P3PhT1, P3PhT2, and P3PhT3 respectively which were blended with PCBM in the ratio of 1:1 and 2:3 polymer to PCBM by weight in dichlorobenzene. Each composite material was spin coated onto the PEDOT:PSS layer at 1200 rpm. Finally device Set 2, with 5.62 mg, 7.50 mg, and 11.25 mg of P3PhT were designated to be P3PhT1, P3PhT2, and P3PhT3 respectively which were blended with PCBM in ratio of 1:1 polymer to PCBM by weight in different solvents which are chloroform, chlorobenzene, and dichlorobenzene. Each composite material was spin coated onto the PEDOT:PSS layer at 1200 rpm. Lithium fluoride and aluminum electrode were deposited via thermal evaporation at approximately



Scheme 1. Synthetic scheme of poly(3-phenylthiophene).

3–4 Å and 100 nm thick, respectively. All devices were tested using an AM 1.5 standard operating with an illumination intensity of 100 mW/cm^2.

Characterization

^{1}H-NMR spectra were recorded using a Bruker 300 UltraShield (300 MHz).

Cyclic voltammetry (CV), the experiment was performed in a solution of n-Bu_4NPF_6 (0.1 M) and P3PhT (10 mg) in dried CH_2Cl_2 at scan rate of 50 mV/s. A glassy carbon electrode, a platinum electrode and an Ag/Ag$^+$ electrode were used as the working electrode, the counter electrode and the guasi-reference electrode respectively.

Results and Discussion

Electrochemical and Optical Properties

The HOMO and LUMO energy levels of the P3PhT was determined by cyclic voltammetry (CV), the onset potential corresponding to oxidations is 0.83 V. The UV-vis spectrum was shown in Figure 1, with $\lambda_{onset} = 548$ nm. The band gap energy was determined by Planck's equation.

The onset oxidation potential (E_{onset}), E_{HOMO}, band gap energy (E_{gap}), and E_{LUMO} were summarized in Table 1.

The E_{HOMO} was calculated according to an empirical equation [9] as follows:

$$E_{HOMO} = -(4.44 + E_{onset})(eV)$$

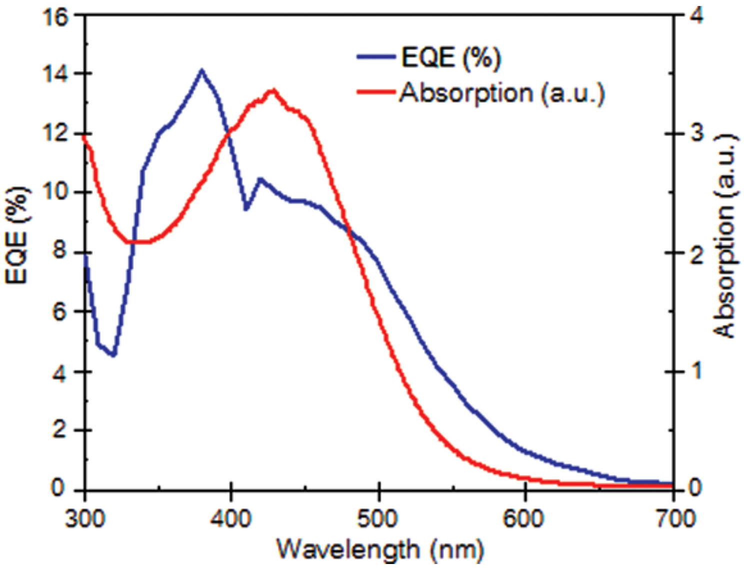


Figure 1. UV-vis absorption spectrum of polymer in dichlorobenzene solution and external quantum efficiency (EQE) spectra of 11.25 mg of P3PhT blended with 2:3 PCBM by weight ratio in dichlorobenzene BHJ solar cells.

Table 1. The onset oxidation potential (E_{onset}), E_{HOMO}, band gap energy (E_{gap}), and E_{LUMO} of P3PhT

Polymer	E_{onset} (V)	E_{HOMO} (eV)	E_{gap} (eV)	E_{LUMO} (eV)
P3PhT	0.83	−3.61	2.26	−1.35

E_{onset} and the E_{gap} was estimated from absorption onset of the P3PhT, thus, E_{LUMO} was calculated using the equation:

$$E_{LUMO} = E_{HOMO} + E_{gap}$$

From Figure 1, UV-vis absorption of P3PhT in solution without PCBM-blend was compared with the external quantum efficiency (EQE) spectra of P3PhT film with PCBM-blend. The absorption maxima of P3PhT and PCBM were around 428 nm and 350 nm respectively, so the EQE spectra showed P3PhT absorption at 428 nm and PCBM absorption around 350–390 nm.

Current-Voltage Measurement

For devices Set 1, the different amount of P3PhT blended with 1:1 and 2:3 PCBM ratios in dichlorobenzene were observed. The result was shown in Figure 2, when the amount of P3PhT increased the power conversion efficiency (% Eff) also

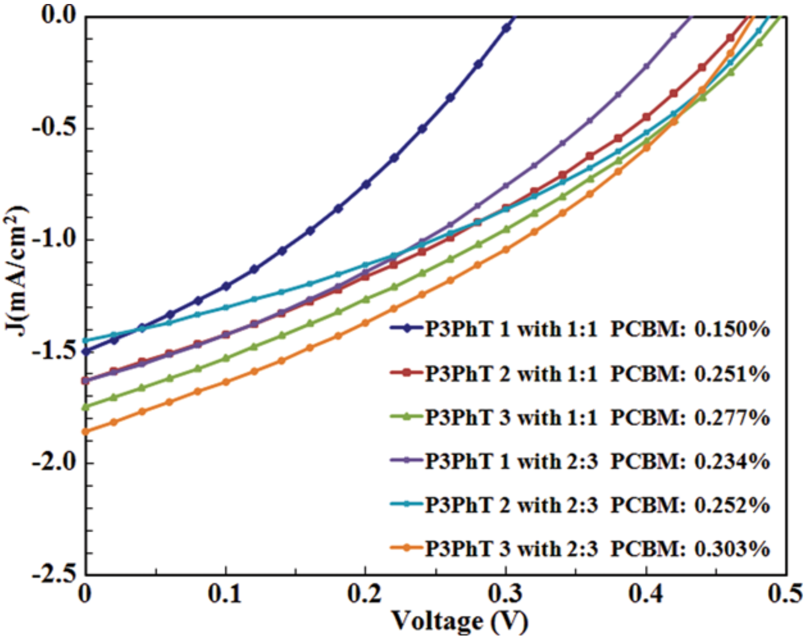


Figure 2. *I–V* characteristics of P3PhT:PCBM BHJ solar cells with different amount of P3PhT and P3PhT:PCBM ratios.

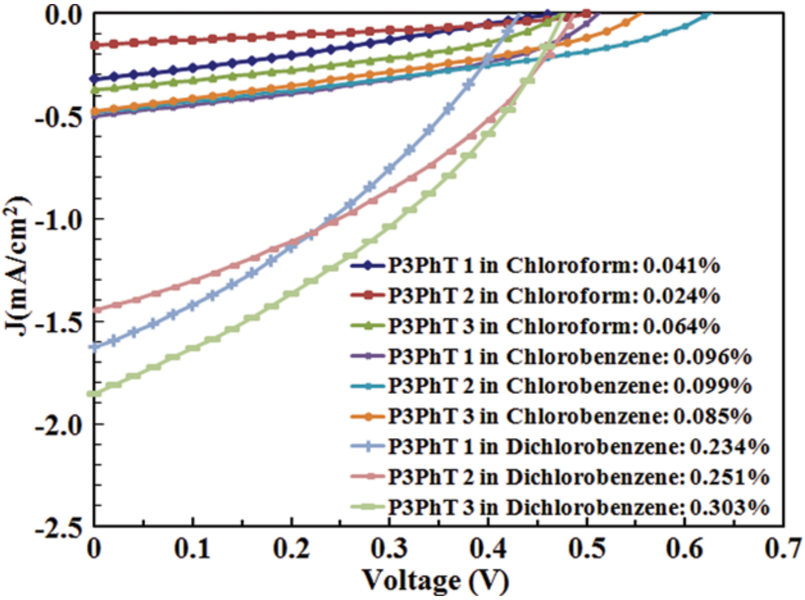


Figure 3. *I-V* characteristics of P3PhT:PCBM BHJ solar cells with different amount of P3PhT and solvents at 2:3 P3PhT:PCBM ratio.

increased, and at 2:3 P3PhT:PCBM ratio the power conversion efficiency was higher than that of 1:1 ratio. The result from Figure 2 showed that P3PhT acted as a donor and PCBM acted as an acceptor. When the amount of P3PhT and PCBM increased, electron donor and acceptor also increased which cause the higher current density and voltage.

The results of devices Set 2 are shown in Figure 3, the different amount of P3PhT blended with 2:3 PCBM ratio in different solvents that is chloroform, chlorobenzene, and dichlorobenzene. The best power conversion efficiency was found in dichlorobenzene, and the worst result was found in chloroform. The results from Figure 3 showed that the boiling point of solvents should have an effect on devices. The higher boiling point of the solvent got the better result, possibly affect the smoothness of P3PhT film. The external quantum efficiency (% EQE) of 14.1 was observed from the best device, as shown in Figure 1.

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