ORIGINAL ARTICLE

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Bulk heterojunction solar cells of three polythienothiophenes

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Abstract: Semiconducting conjugated copolymers poly(3-phenyl-2-(thiophen-2-yl)thieno[3,2-b]thiophene) (PTTPh), poly(3-(4-methoxyphenyl)-2-(thiophen-2-yl)thieno[3,2-b]thiophene) (PTTPh-OMe) and poly(3-(4-N,N-dimethylaminophenyl)-2-(thiophen-2-yl)thieno[3,2-b]thiophene) (PTTPh-N$(CH_3)_2$), which were synthesized previously through Suzuki coupling method, were fabricated for solar cell applications. The devices had a structure of glass/ITO/PEDOT:PSS/polymer:PC61BM/Al. Bulk heterojunction photovoltaic cells were prepared as blends of PTTPh, PTTPh-OMe, PTTPh-N$(CH_3)_2$ and PC61BM in a 1:1 ratio, which delivered power conversion efficiencies of 0.43%, 0.039% and 0.027%, respectively, without addition of additives or device optimization.

Keywords: Thienothiophene; polythienothiophene; organic solar cell.

1. Introduction

Blends obtained from π-conjugated polymers have been the focus of intense research in development of organic photovoltaic (OPV) devices, for which the conjugated polymers are usually blended with an electron acceptor ($PC_{61}BM$), for converting the exciton into free charge carriers. Nano-morphology of the blend is an important factor for efficiencies of charge generation and transport. In order for electrode to collect electrons, the electron and hole must not recombine after the electron transfer from a donor to an acceptor [1].

Polythiophenes are among the most interesting polymer systems as they are rich in electrons and could be well engineered [2-4]. Thienothiophenes (TT), made of fused two thiophenes, are emerging thiophene based materials for solar cell applications [5-9], although they have potential of being applied in various areas such as electroluminescence, fluorescence, photochromism, optical chromophors and thin-film transistors [10]. These two fused rigid thiophene rings limit the rotational disorders between thiophene rings in favor of creating better conjuation [11,12]. Although TTs have four isomers,

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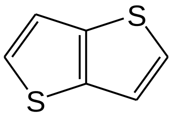
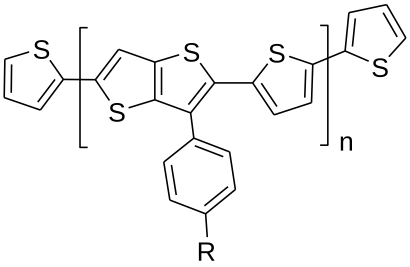
thieno[3,2-*b*]thiophene **1** has the lowest band gap and ionization potential, which is the result of the orientation of the fused rings, leading to a better conjugation in TT [13].

Copolymer of **1** with thiophene had a lower HOMO energy level compared with poly(3-hexylthiophene), which was explained to be due to a larger resonance stabilization energy of TT than thiophene [13,14]. Moreover, it is known that an extended, rigid π- conjugation with quinoidal character in the polymer backbone facilitates inter-molecular interactions between the polymer chains, and increases the charge mobility [15]. As a fused rigid thiophene ring system, TTs stabilize the quinoidal structure, reduce the band gap, and enhance $\pi \rightarrow \pi$ stacking [15-17]. Consequently, incorporation of fused thiophene-based units into a polymer backbone assists to enhance the conjugation and optimize the solid-state properties [18].



1 Thieno[3,2-*b*]thiophene

In this work, thiophene and 3-arylthieno[3,2-*b*]thiophene copolymers, which were successfully synthesized previously, applying Suzuki cross coupling conditions [19], were constructed as solar cells, having a structure of glass/ITO/PEDOT:PSS/polymer:$PC_{61}BM$/Al. Bulk heterojunction photovoltaic cells were fabricated from a blend of PTTPh, PTTPh-OMe, PTTPh-$N(CH_3)_2$ and $PC_{61}BM$ in a 1:1 ratio, power conversion efficiencies of which were determined and surface morphologies of the films were investigated.



PTTPh R= H
PTTPh-OMe R= MeO
PTTPh-$N(CH_3)_2$ R= $N(CH_3)_2$

2. Results and discussion

2.1. Syntheses of the polymers

Syntheses of the polymers **PTTPh**, **PTTPh-OMe** and **PTTPh-$N(NCH_3)_2$**, which were summarized in Figure 1, were conducted according to the literature data.[19]

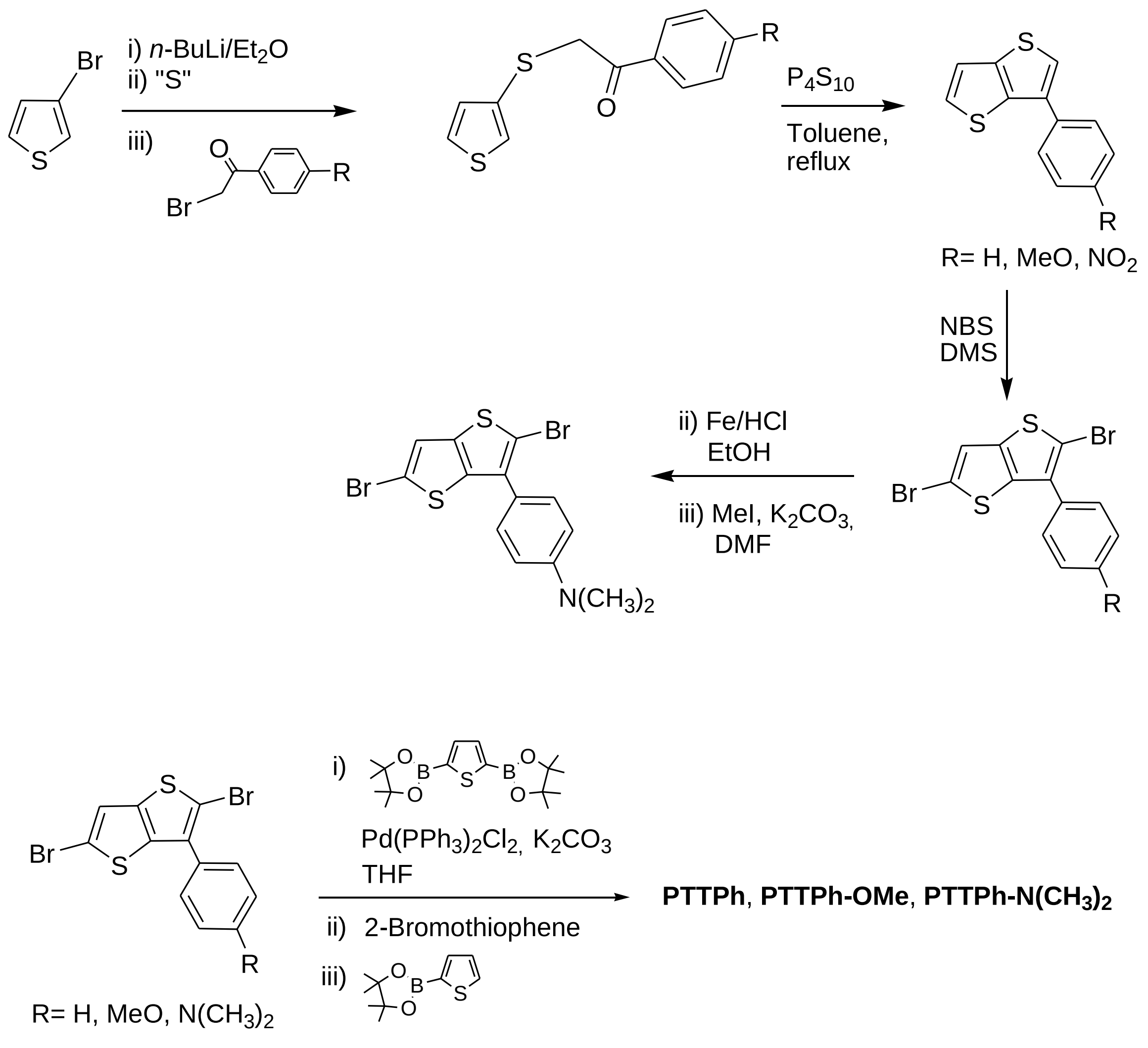


Figure 1. Syntheses of the polymers.

2.2. Device performance under illumination

Organic solar cells, having a structure of glass/ITO/PEDOT:PSS/polymer:$PC_{61}BM$/Al, were fabricated on ITO-coated glass substrates. J&V characteristics of the polymers in dark and under illuminated conditions at AM 1.5G (100mW/cm^2) were depicted in Fig. 2. Photovoltaic parameters such as short circuit current (Jsc), open circuit voltage (Voc), fill factor (FF), and power conversion efficiency (PCE) were summarized in Table 1. For each polymer, five devices were fabricated to obtain more reliable PV data, which indicated that among the solar cells, PTTPh had the highest Voc, j_{sc}, FF and efficiency values of 0.74 V, 2.19 mA/cm^2, 0.27 and 0.43, respectively. PTTPh-OMe and PTTPh-$N(CH_3)_2$ solar cells displayed very poor PV behavior, which could be due to the presence of side groups, i. e. methoxy and dimethylamine, on the phenyl moiety. Although these side groups have electron donating properties, which are expected to enrich the TTs in electron density and improve the device performances, as the experimental results indicated, rather than such a positive contribution they had a negative effect. Thus, as they do not provide any steric hindrance to destroy the conjugation, only the possible explanation could be that they may prevent good intermolecular interactions and stacking.

Table1. Photovoltaic parameters of solar cells of the polymers

Polymer	**Voc, V**	**Jsc, mA/cm^2**	**FF**	**η**
PTTPh Solar Cell	0.74	2.19	0.27	0.430
PTTPh-N(CH_3)$_2$ Solar Cell	0.58	0.34	0.23	0.039
PTTPh-OMe Solar Cell	0.50	0.23	0.23	0.027

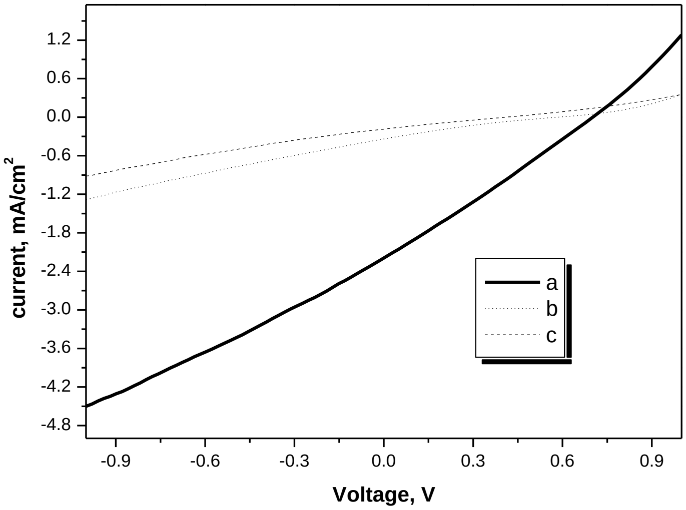


Figure 2. J&V characteristics plots of a) PTTPh; b) PTTPh-N(CH_3)$_2$;c) PTTPh-OMe solar cells under illumination of 100 mW/cm^2 (AM1.5).

2.3. Optical Properties

Absorption and electronic band gaps of the polymers, PTTPh, PTTPh-N(CH_3) and PTTPh-OMe, were reported previously,[19] which disclosed that they had absorption band gaps of 2.28, 2.29 and 2.42 eV and electronic band gaps of 2.43, 2.07 and 2.31 eV, respectively. Absorption spectra of the polymers were measured in dichloromethane and the optical band gaps were calculated from their absorption onsets. Concerning their electronic band gap calculations, the polymers were drop-coated onto Pt disc electrode and Pt and Ag wires were applied as counter and reference electrodes. Tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile was used as electrolyte. The polymers were scanned between (-2)-(+2) V, under nitrogen atmosphere, and their electronic band gaps were calculated from the differences between the onsets of oxidation and reduction peaks.

UV-Vis spectra of the three polymer:$PC_{61}BM$ films on ITO showed absorption maxima at around 380 and 470 nm, and they all had tails up to 700 nm (Fig. 3).

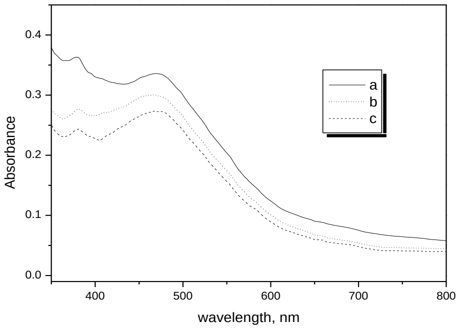
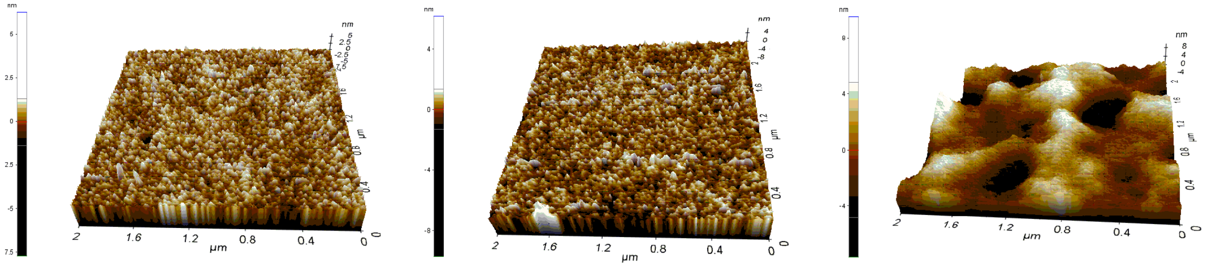


Figure 3. UV spectra of a) PTTPh-N(CH$_3$)$_2$; b) PTTPh; c) PTTPh-OMe with PCBM films on glass substrates.

2.4. Investigation of blend morphology

The surface morphologies of the blend films were investigated by AFM, which indicated that while PTTPh and PTTPh-OMe had more homogenous structure, and had roughness values of 0.6 and 0.54 nm, respectively, PTTPh-N(CH)$_3$ (2 nm) exhibited a phase separation (Fig. 4), which could be due to not enough compatibilities of the blend film components. Moreover, while PTTPh and PTTPh-OMe had a very close blend grain sizes, approximately 60 nm, such grains were not detectable for PTTPh-N(CH$_3$):PCBM blend, although some clusters were observed to be approximately 300 nm. Such a quite different morphology of PTTPh-N(CH$_3$)$_2$ solar cell could be another reason for the lower efficiency of PTTPh-N(CH$_3$):PCBM blend. On the other hand, as both PTTPh-OMe and PTTPh-N(CH$_3$)$_2$ blends had lower efficiencies, compared with the PTTPh blend, the main reason for lower efficiencies could be bad intermolecular interactions and stacking caused by methoxy and dimethyamine groups on the phenyl moiety.



a **b** **c**

Figure 4. AFM 3D topography images of PTT:PCBM blends a) PTTPh; b) PTTPh-OMe; c) PTTPh-N(CH$_3$)$_2$.

3. Experimental

3.1. Materials and Solutions

PTTPh, PTTPh-OMe, and PTTPh-N(CH$_3$)$_2$ were synthesized according to the literature method [19]. Hole transport layer, poly(3,4-ethylenedioxythiophene) (PEDOT), doped with poly(styrene sulfonic acid) (PSS) (PEDOT:PSS Clevios P), and n-type semiconductor phenyl C$_{61}$ butyric acid methyl ester (PC$_{61}$BM) were purchased from Heraeus and Sigma-Aldrich, respectively. Blend solutions were prepared by PCBM in 1,2-dichlorobenzene (Alfa Aesar) in 1:1 ratio.

3.2. Measurements

The current density-voltage (J-V) characteristics of the devices were obtained under light illumination, using as a standard solar irradiation of 100 mW/cm^2 (AM1.5) with Xenon lamp as a light source and computer-controlled voltage-current Keithley 2600 source meter at 25 ^{o}C under ambient atmosphere. Morphology of the blend films were investigated using Atomic force microscopy (Park Systems).

3.3. Film and device fabrication

All the cells were fabricated on indium tin oxide (ITO) coated glass substrates, having a sheet resistance of 25 **Ω**/cm. The substrates were cleaned in an ultrasonic bath with acetone, isopropyl alcohol and deionized-water successively for 5 min and then dried with nitrogen gas. The PEDOT:PSS were spin coated on glass substrates and annealed at 100 ^{o}C for 10 minutes. The blended solutions of the polymer:PCBM (1:1) were spin-coated on PEDOT-PSS coated substrates. Finally, the Al cathode was coated by thermal evaporation and the devices were encapsulated.

4. Conclusion

We have successfully fabricated three new semiconducting polythienothiophenes, i. e. poly(3-phenyl-2-(thiophen-2-yl)thieno[3,2-b]thiophene) (PTTPh), poly(3-(4-methoxyphenyl)-2-(thiophen-2-yl)thieno[3,2-b]thiophene) (PTTPh-OMe) and poly(3-(4-*N*,*N*-dimethylaminophenyl)-2-(thiophen-2-yl)thieno[3,2-b]thiophene) (PTTPh-N$(CH_3)_2$), devices for solar cell applications with PCE, in which the ratio of the polymers and PCE was kept as 1:1. PTTPh, PTTPh-N$(CH_3)_2$,PTTPh-OMe solar cells delivered a power conversion efficiencies of 0.43 %, 0.039 % and 0.027 %, respectively, without addition of additives or device optimization. These results indicated that the TT based polymeric materials are promising candidates for efficient and stable polymer solar cells. Currently, our studies have been directed to the improvement of the efficiencies of the polymers and the preparation of new thienothiophene materials for solar cell applications.

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