

Development of New Semiconducting Polymers for High Performance Solar Cells

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Solar energy harvesting using the photovoltaic effect requires active semiconducting materials to convert light into electricity. Currently, solar cells based on silicon are the dominant technology, which exhibit high conversion efficiency. The drawback of these devices is their high cost.¹ Organic semiconducting materials, and more specifically semiconducting polymers, are expected to provide for the facile manufacture of low cost, flexible, and market compliant devices.² Since the discovery of the photovoltaic effect in bulk heterojunction (BHJ) devices, there has been a considerable development in polymer solar cells.³ So far, after extensive optimization, a power conversion efficiency of $\sim 4\text{--}5\%$ has been achieved and confirmed in solar cells using regio-regular poly(3-hexylthiophene) (P3HT) as an electron-donor material and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) as an acceptor.⁴ However, a bottleneck in conversion efficiency seems to be reached by using P3HT because it harvests photons with wavelengths below ~ 650 nm, which is a small portion of the whole solar spectrum.² Therefore, organic materials with low band gaps, which can efficiently harvest solar energy over a broader spectrum, are needed to push these types of solar cells into practical applications.⁵ The structure and synthesis of these materials require judicious design.⁶ Most recently, low band gap polymer PV system showed over 4–5% efficiency with extensive device engineering efforts.⁷ In this paper, we describe a new low band gap semiconducting polymer for high performance polymer solar cells, which exhibits a power conversion efficiency of 5.6% under the AM1.5G one-sun condition.

The new polymer, PTB1 (Figure 1a), is synthesized via the Stille polycondensation between an ester substituted 2,5-dibromothiophene and dialkoxyl benzodithiophene distannane monomers.⁸ The thieno[3,4-*b*]thiophene repeating units are known to stabilize the quinoidal structure of the backbone that narrows the energy gap of resulting polymers.⁹ The ester substituted thieno[3,4-*b*]thiophene in this new polymer renders it both soluble and oxidative stable.

Gel permeation chromatography (GPC) studies showed a number averaged molecular weight of 18.3 kg/mol and weight averaged molecular weight of 22.9 kg/mol with a polydispersity of 1.25. The polymer solution in *o*-dichlorobenzene showed an absorption maximum at 682 nm with the onset at 774 nm (Figure 1b). The solid film of the polymer exhibits slightly red-shifted absorption around 690 nm with the onset at 784 nm, which coincides with the corresponding maximum photon flux region in solar spectrum (~ 700 nm). The absorption coefficient of the polymer film at 690 nm is $7.5 \times 10^{-3} \text{ nm}^{-1}$. The optical band gap calculated from the onset of the film absorption is ~ 1.62 eV. The cyclic voltammetry (CV) studies on polymer thin films coated on a glass carbon electrode indicated that the oxidation onset is -0.22 eV to a Ag/

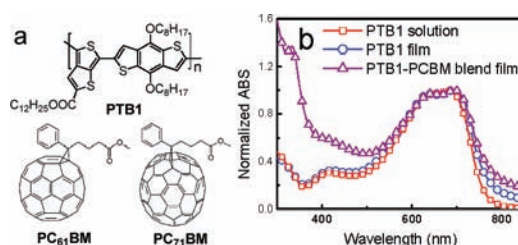


Figure 1. (a) Molecular structures of the PTB1 polymer and fullerene derivatives. (b) Normalized absorption spectra of the polymer PTB1 in dichlorobenzene, PTB1 film, and PTB1–PC₆₁BM blend film.

Ag⁺ electrode, while the reduction occurs at 1.48 eV. The redox potential of ferrocene/ferrocenium under the same conditions is located at 0.12 eV, which is assumed to have an absolute energy level of -4.80 eV to vacuum.¹⁰ So the energy levels of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are determined to be -4.90 and -3.20 eV, respectively.

The photovoltaic properties of PTB1 were studied in two composites (with either PC₆₁BM or PC₇₁BM) in structures of ITO/PEDOT:PSS/polymer:fullerides/Ca/Al. Figure 2a shows the photo *J*–*V* curves of the polymer solar cells with a PTB1:PC₆₁BM 1:1 weight ratio. The active layer thickness is $\sim 100\text{--}110$ nm. A short circuit current, *J*_{sc}, of 12.5 mA/cm² is achieved, with an open circuit voltage, *V*_{oc}, of 0.58 V, and a fill factor of 65.4%. The resulting power conversion efficiency is thus 4.76%.

It has been reported that PC₇₁BM has similar electronic properties as PC₆₁BM, but a higher absorption coefficient in the visible region.¹¹ The active layer was then further modified with the weight ratio of PTB1:PC₇₁BM at 1:1.2 and identical thickness around 100–110 nm. A higher *J*_{sc} of 15.0 mA/cm² was obtained. The device exhibits a *V*_{oc} of 0.56 V and a fill factor of 63.3%, which yields an impressive PCE of 5.30%. (Figure 2a) The change of donor/acceptor weight ratio to achieve optimal performance is hard to understand at first glance. However, by considering the difference in molecule weights, the molar ratios of donor and acceptor for the two optimized systems are very close, which happens to be the same ratio as that in the optimized model P3HT:PCBM system. The device absorbs light in almost the whole visible range in spectrum and shows high external quantum efficiencies (EQEs) for both PTB1/PC₆₁BM and PTB1/PC₇₁BM solar cells (Figure 2b). For the PTB1/PC₆₁BM solar cell, the maximum EQE is over 60% at 650 nm and is $\sim 50\%$ in the range from 550 to 750 nm. When the PC₇₁BM was used, the PTB1/PC₇₁BM solar cell exhibits a higher EQE, almost all over 60% in the range from 400 to 750 nm, with a maximum of 67% at 650 nm.

The reference cell used in the measurements, a KG5 filter covered silicon detector, could eliminate the spectral mismatch in the P3HT:

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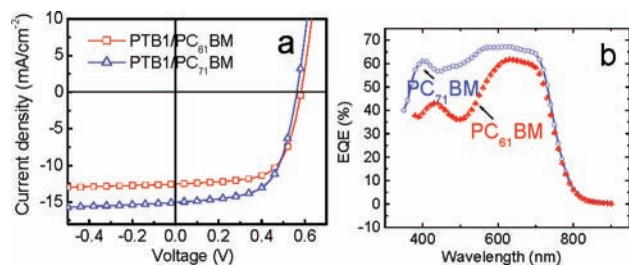


Figure 2. (a) Current–voltage characteristics of polymer solar cells under AM 1.5 condition (100 mW/cm^2). (b) External quantum efficiency of PTB1/ PC_{61}BM and PTB1/ PC_{71}BM .

PC_{61}BM system.¹² However, the spectral response of the new polymer is extended more into the red region and the spectral mismatch needs to be considered. By inserting an AM1.5G standard spectrum, Oriel solar simulator (with 1.5G filter) spectrum, and EQE data, we calculated the spectral mismatch factor to be 0.95 using a program provided by NREL, which results in the corrected photocurrent ca. 15.6 mA/cm^2 , a value clearly among the best in the polymer solar cells reported. The corrected power conversion efficiency is thus 5.6%. Further integration on the spectral response of the cell with an AM1.5G standard solar spectrum yielded a J_{sc} of 15.1 mA/cm^2 , which agrees well (within 4% error) with the photocurrent obtained by J – V measurement and spectral mismatch correction.

Several factors contribute to the high power conversion efficiency of polymer solar cells based on PTB1. First of all, PTB1 has a close to optimal band gap of 1.6 eV as well as a preferred energy level.¹³ The high hole mobility and the capability of forming balanced carrier mobility in the blend lead to the high fill factor. The high EQE is the direct result of the proper match of energy levels. Although the band gap of PTB1 is lower by 0.3 eV than that of P3HT, a sufficient D/A energy difference was maintained to provide enough driving force for exciton dissociation in the donor–acceptor interfaces. Second, the thieno-thiophene unit can stabilize the quinoidal structure in the polymer chain and thus enhance the planarity along the aromatic polymer backbone.¹⁴ The benzodithiophene unit makes the backbone of PTB1 more rigid than P3HT. As a result, the planarity and conjugation length of the polymer show a little change with the introduction of PC_{61}BM , which is illustrated by the small change in the absorption of the blend film at a longer wavelength (Figure 1b). In the absorption region above 600 nm, the absorption of the blend film is almost the same as that for the polymer film. The rigidity and planarity of the polymer backbone are directly responsible for the high SCLC mobility of PTB1, $\sim 4.5 \times 10^{-4} \text{ cm}^2/\text{v}\cdot\text{s}$ as measured by using the space charge limited current (SCLC) method (S-Figure 2). For comparison, the hole mobility of regioregular P3HT (synthesized from McCullough's method¹⁵ with $M_n = 90\text{k}$ and $\text{PDI} = 1.31$, and regioregularity $>95\%$), measured under the same conditions, is $2.7 \times 10^{-4} \text{ cm}^2/\text{v}\cdot\text{s}$. Third, the polymer blend system has a preferred interpenetrating network morphology that can benefit not only the charge separation but also the charge transport, which lead to the high fill factors. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) studies revealed that the morphology of the PTB1/ PC_{61}BM blend film exhibited very fine domains and no large phases can be found (S-Figure 3). Small nanofibers ($\sim 5 \text{ nm}$ width) are observed in TEM images and are distributed in the entire image field, indicating a more effective

donor–acceptor interaction.¹⁶ Ultrafast photoluminescence studies revealed that the PTB1/ PC_{61}BM blend film exhibited a higher degree of PL quenching due to the photoinduced charge transfer from the polymer to PC_{61}BM (S-Figure 1) than the corresponding P3HT: PC_{61}BM system. All of these results indicated that the polymer and PCBM formed an effective interpenetrating network in the blend film, which favors exciton dissociation in the interfacial area and transport in the corresponding domains.

In conclusion, a highly processible and stable, new semiconducting polymer, PTB1, based on alternating thieno-[3,4-*b*]thiophene and benzodithiophene units has been synthesized. The simple solar cells prepared from the blend of this polymer and fullerene derivatives exhibit a high solar energy conversion efficiency of 5.6% and high fill factor of over 65% without special treatments. Considering the significant improvement in polymer solar cells through device engineering in numerous polymer/fullerene systems, such as the P3HT/PCBM blend, this polymer system exhibits a very promising potential as a candidate for further exploration in solar cells with real applications.

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Supporting Information Available: Synthesis and hole mobility measurement, device preparation and characterization, photoluminescent spectra of the polymer film and blend film and TEM, AFM images. This material is available free of charge at <http://pubs.acs.org>.

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