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For the Bright Future—Bulk Heterojunction Polymer Solar Cells with Power Conversion Efficiency of 7.4%

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Sun is the largest carbon-neutral energy source that has not been fully utilized. Although there are solar cell devices based on inorganic semiconductor to efficiently harvest solar energy, the cost of these conventional devices is too high to be economically viable. This is the major motivation for the development of organic photovoltaic (OPV) materials and devices, which are envisioned to exhibit advantages such as low cost, flexibility, and abundant availability.[1] The past success in organic light-emitting diodes provides scientists with confidence that organic photovoltaic devices will be a vital alternate to the inorganic counterpart.

At the heart of the OPV technology advantage is the easiness of the fabrication, which holds the promise of very low-cost manufacturing process. A simple, yet successful technique is the solution-processed bulk heterojunction (BHJ) solar cell composed of electron-donating semiconducting polymers and electron-withdrawing fullerides as active layers.[2] The composite active layer can be prepared as a large area in a single step by using techniques such as spin-coating, inkjet-printing, spray-coating, gravure-coating, roller-casting etc.[3] In the last fifteen years, a significant progress has been made on the improvement of the power-conversion efficiency (PCE) of polymer BHJ solar cells, and the achieved efficiencies have evolved from less than 1% in the poly(phenylene vinylene) (PPV) system in 1995,[2] to 4–5% in the poly(3-hexylthiphene) (P3HT) system in 2005,[4] to around 6%, as reported recently.[5] However, the efficiency of polymer solar cells is still significantly lower than their inorganic counterparts, such as silicon, CdTe and CIGS, which prevents practical applications in large scale.

There are many factors limiting the performance of the BHJ solar cells.[6] Among them, the properties of materials of the active layer are the most determining factor in the overall performances of polymer solar cells.[7] Ideally, the polymers should have a broad absorption in the solar spectrum to ensure effective harvesting of the solar photons and a high charge-carriers mobility for charge transport. Further, suitable energy levels of the polymer are required that match those of the fullerides. The polymer should have a low-lying highest occupied molecular orbital (HOMO) energy level to provide a large open-circuit voltage (V_{oc}) and a suitable lowest unoccupied molecular orbital (LUMO) energy level to provide enough offset for charge separation. In addition, morphology of the active composite layer plays a very important role. It is imperative that a bicontinuous network with a domain width approximately twice that of the exciton diffusion length and a high donor/acceptor interfaces is formed, which favors the exciton dissociation and transport of the separated charges to the respective electrode.[8] Most of the polymers reported to date are far from ideal to fulfill all these requirements.[9]

We have developed a series of novel semiconducting polymers based on alternating ester substituted thieno[3,4-*b*]thiophene and benzodithiophene units.[10] These polymers exhibit a synergistic combination of properties that lead to an excellent photovoltaic effect. The stabilization of quinoidal structure from thieno-[3,4-*b*]thiophene results in a low bandgap of the polymer of about 1.6 eV, showing efficient absorption around the region with the highest photon flux of the solar spectrum (about 700 nm). The rigid backbone results in a good hole mobility of the polymer, and the side chains on the ester and benzodithiophene enable good solubility in organic solution and suitable miscibility with the fulleride acceptor. The introduction of fluorine into the thieno[3,4-*b*]thiophene provides the polymer with a relatively low-lying highest occupied molecular orbital (HOMO) energy level, which offers enhanced V_{oc}. The polymer chain is found to be stacked on the substrate in the face-down conformation from grazing-incidence wide-angle X-ray scattering studies.[11] This is very different from the polymer alignment in well-studied P3HT solar cell system and favors charge transport.[11] All these advantages of thieno[3,4-*b*]thiophene and benzodithiophene polymers (PTBs) make them good candidates for BHJ polymer/fullerides solar cell application and a PCE up to 6.1% has been achieved from PTB4/PC$_{61}$BM prototype devices.[5a]

After an extensive structural optimization we further developed a new polymer from the PTB family, PTB7, which exhibited an excellent photovoltaic effect. A PCE of about 7.4% has been achieved from PTB7/PC$_{71}$BM (see Fig. 1a PC$_{71}$BM = phenyl-C$_{71}$-butyric acid methyl ester) solar cell devices, which is the first polymer solar cell showing a PCE over 7%. Herein, we described our systematic studies on the photovoltaic performance of this new polymer. The results indicated a great potential and bright future for polymer solar cells.

The structure of PTB7 is shown in Figure 1a. The branched side chains in ester and benzodithiophene render the polymer good solubility in organic solvents. The weight average molecular weight (M_w) of PTB7 is 97.5 kDa with polydispersity index (PDI)

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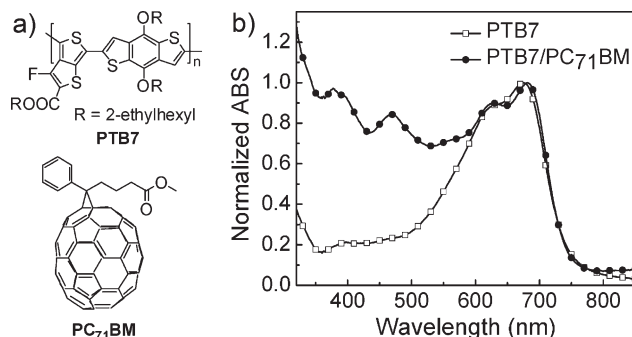3445 Fletcher Ave., El Monte, CA, 91731(USA)
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Figure 1. a) Structures of PTB7 and PC$_{71}$BM. b) Absorption spectra of PTB7 pure polymer film and blend film PTB7/PC$_{71}$BM in 1:1.5 weight ratio.
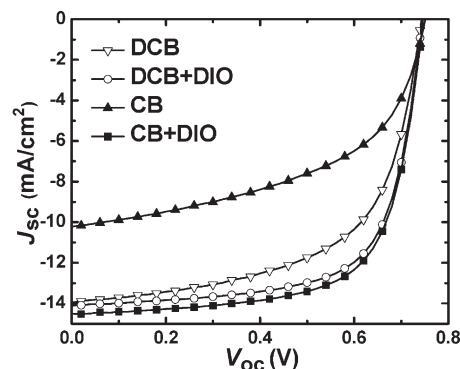

Figure 2. J–V curves of PTB7/PC$_{71}$BM devices using (i) DCB only, (ii) DCB with 3% DIO, (iii) CB, and (iv) CB with 3% DIO as solvents.

of 2.1. The HOMO and LUMO energy levels of PTB7 were determined by cyclic voltammetry (CV), which are −5.15 eV and −3.31 eV under calibration to ferrocene (see the Supporting Information). Although the side chains are branched, the PTB7 has a relatively high hole mobility, which is about 5.8×10^{-4} cm^2 V^{-1} s^{-1} measured from the space–charge limited current (SCLC) model (Supporting Information). The absorption spectrum of pure PTB7 film is showed in Figure 1b. The polymer shows strong absorption from 550 to 750 nm. However the absorption from 300 to 500 nm is relatively weak. To compensate the absorption of PTB7, PC$_{71}$BM, which has strong absorption in the visible range, is used as the acceptor. The resulting PTB7/PC$_{71}$BM-blend film exhibits a strong absorption covering a range from 300 to about 800 nm.

The solar cell performance is a function of composition. The PTB7/PC$_{71}$BM system spin-coated from o-dichlorobenzene (DCB) was first investigated to optimize the donor/acceptor (D/A) ratio. Table 1 shows the effect of the D/A weight ratio on the performance of solar cells under the same spin-coating condition (optimized), which lead to film thickness of ~100 nm. The initial test results indicated that the device with a 1:1.5 wt-ratio exhibits the best performance with an average short-circuit current (J_{sc}) of 13.56 mA cm^{-2} and a fill factor (FF) of 59.23%, leading to a PCE of 6.02%. V_{oc} has increased to 0.75 V as expected during molecule design, which represents a 34% increase from our original PTB1 (0.58 V) system reported before.[10] The average PCE was typically derived from 12 devices. The best efficiencies of these three D/A wt-ratios are 5.74% (1:1), 6.22% (1:1.5), and 5.58% (1:2), respectively.

The performances of solar cells based on a PTB7/PC$_{71}$BM-blend film are further enhanced by using mixed solvent in preparing films. A mixed-solvents approach has been shown to

be effective in several polymer solar cell systems, including classical P3HT[12] as well as several high-efficiency low-bandgap polymers.[13] Preliminary study in the PTB7 system showed that the PTB7/PC$_{71}$BM-blend film prepared from mixed solvent of dichlorobenzene (DCB)/1,8-diiodoctane (DIO) (97%:3% by volume) increases the fill factor from 60.25% to 68.9%. Figure 2 showes the effect of mixed solvent on the polymer solar cell performance and data are summarized in Table 2. The J_{sc} enhancement is relatively small, only a 0.14 mA cm^{-2} increment. The PCE increases from 6.22% to 7.18%. However, if chlorobenzene (CB) is used as the solvent, a low current density of 10.2 mA cm^{-2}, as well as a low fill factor of 50.52% was observed, which corresponds to a PCE of 3.92%. This phenomenon indicates that the solvents affect the polymer packing.[14] Upon mixing of 3% DIO to the solvent, the solar cell J_{sc} of the resulting blend film was significantly increased to 14.5 mA cm^{-2}. The fill factor, at the same time, increases to 69%. The combined effect leads to the power-conversion efficiency of 7.40%. This is the best results in a polymeric solar cell reported so far.

The dramatic enhancement of the photovoltaic performances is caused by the change in the morphology of the blend film. The transmission electron microscopy (TEM) images (Fig. 3) clearly showe that there are large domains (about 100–200 nm in diameter) in the blend film prepared from CB, which will diminish exciton migration to the donor/acceptor interface and is not favorable for charge separation. The morphology of blend film prepared from CB/DIO is much more uniform and there is no large phase separation, showing good miscibility between PTB7

Table 1. Photovoltaic parameters of devices with various PTB7/PC$_{71}$BM weight ratios.

PTB7/PC$_{71}$BM (weight ratio)	Voc [V]	J_{sc} [mA cm^{-2}] (average)	PCE [%] (average)	FF [%] (average)	PCE [%] (maximum)
1:1	0.76	13.58	5.63	54.51	5.74
1:1.5	0.75	13.56	6.02	59.23	6.22
1:2	0.75	11.40	5.31	62.16	5.58

Table 2. Device photovoltaic parameters of (i) DCB only, (ii) DCB with 3% DIO, (iii) CB, and (iv) CB with 3% DIO as solvent(s). The J_{sc} calculated from EQE spectrum and the error between calculated (calc.) and measured J_{sc} is also shown.

	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	J_{sc} (calc.) [mA cm^{-2}]	Error [%]
DCB	0.74	13.95	60.25	6.22		
DCB+DIO	0.74	14.09	68.85	7.18	13.99	0.74
CB	0.76	10.20	50.52	3.92		
CB+DIO	0.74	14.50	68.97	7.40	14.16	2.34

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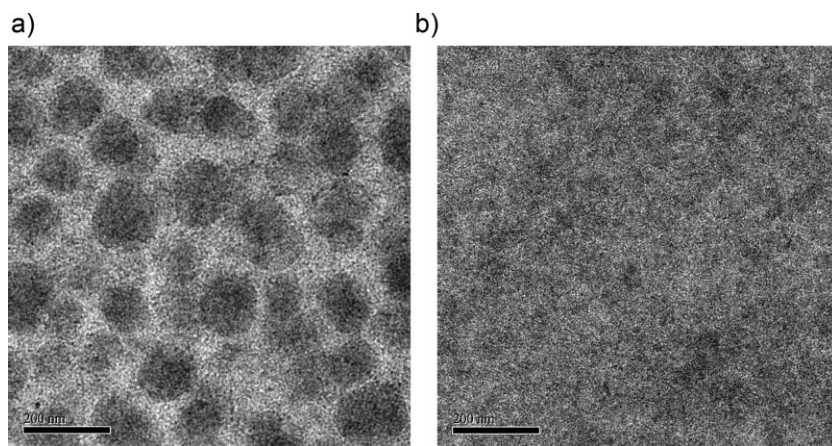COMMUNICATION

a)

b)

Figure 3. TEM images of PTB7/PC$_{71}$BM-blend film prepared from CB without (a) and with (b) DIO (the scale bar is 200 nm).

and PC$_{71}$BM and formation of interpenetrating networks. Based on current understanding of OPV, the improved morphology should result in the increase of FF and J_{sc}.

The external quantum efficiency (EQE) curves of champion cells using CB:DIO and DCB:CIO as solvent are shown in Figure 4a. Both devices show rather efficient photoconversion efficiency in the range between 400 and 700 nm with EQE values over 50%. In the CB:DIO device, the maximum EQE is 68.1% at 630 nm. This represents one of the highest EQE values in organic solar cells from a low-band-gap polymer system disclosed in literature. The maximum EQE in DCB:DIO device is also high, it reached to 66.6% at 620 nm. These measurements are rather
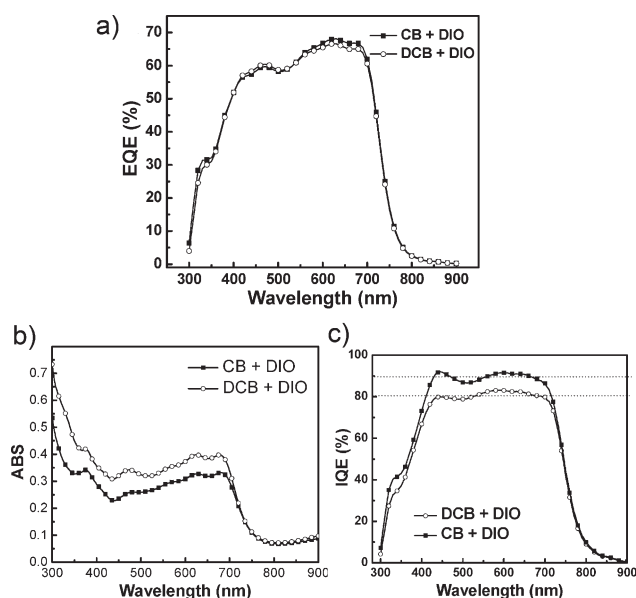

Figure 4. a) EQE spectra of champion cells from DCB with 3% DIO and CB with 3% DIO. b) UV–vis absorption spectra (single pass) of the active layers champion cells (DCB with 3% DIO and CB with 3% DIO). c) IQE derived from the EQE and absorption spectra in the same champion cells.

accurate as further examined by integrating the EQE data with the AM1.5G solar spectrum. The calculated J_{sc} is 14.16 mA cm^{-2} in the champion CB:DIO device. Comparing to the measured J_{sc} of 14.5 mA cm^{-2}, it represents an error of 2.3%. The same procedure was conducted for the DCB:DIO device, the calculated J_{sc} value of 13.99 mA cm^{-2} is within 1% error compared to the measured one. Table 2 shows the device parameters as well as the comparison of calculated and measured J_{sc} values and their errors.

We further estimated the internal quantum efficiency (IQE) of these cells. Figure 4b is the one-pass absorption curves of the films coated under the same condition as those used in the champion cells (CB:DIO and DCB:DIO). The absorption represents the film only. The estimation is based on the following simple facts and assumptions: i) 4% light loss at the air ($n = 1$)/glass ($n = 1.5$) interface, b) metal is considered a perfect mirror (i.e., the film absorbs twice), and c) the absorption in glass, indium tin oxide (ITO), and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) PEDOT:PSS in real devices is ignored. Thus the value of IQE is actually underestimated. The estimated IQE for both DCB:DIO and CB:DIO champion cells is shown is Figure 4c. In the CB:DIO champion cell, the IQE spectrum shows a very high value of over 90% in a wide range from 420 to 660 nm. The maximum IQE reaches 92%. The wide and high IQE data unambiguously prove the very high quality of the new polymer system. In this system the exciton dissociation, the charge transport in donor and acceptor networks, and the charge extraction in both organic/electrode interfaces are all very close to 100%. These facts imply that the morphology of blend films is close to the ideal donor and acceptor nanometer-scale interpenetrating network. Further investigation is underway to decode the morphology in the new system. The IQE in the DCB:DIO system is ~10% lower than the CB:DIO counterpart with a maximum value of 83.2%. However, we did observed a weak thickness dependence of the PCE in the DCB:DIO system, which may indicate higher IQE. Certification experiments will be performed in the near future and further results will be reported elsewhere.

In summary, we have successfully developed an excellent new semiconducting polymer, PTB7. BHJ solar cells based on the blend films of PTB7 with PC$_{71}$BM exhibited an efficiency up to 7.4%, which is the first polymer solar cell system showing a PCE over 7%. Both EQE and IQE obtained from such solar cells are very high, implying that the harvest of solar energy is very efficient. The results confirm that the thieno[3,4-*b*]thiophene-benzodithiophene polymers are a promising class of materials for developing high-performance polymer solar cells.

Experimental

The polymer PTB7 was synthesized according to a previously reported method [5a]. The photovoltaic property of PTB7 was studied in the

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structure of ITO/PEDOT:PSS/polymer (PC$_{71}$BM)/Ca/Al. ITO-coated glass substrates (15 $\Omega \square^{-1}$) were cleaned stepwise in detergent, water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried in an oven for several hours. A thin layer ($\sim$30 nm) of PEDOT:PSS (Baytron P VP A1 4083) was spin-coated onto a cleaned ITO surface, which was pretreated by ultraviolet ozone plasma for 15 min. Low-conductivity PEDOT:PSS was chosen to minimize the measurement error from device areas due to the lateral conductivity of PEDOT:PSS. After being baked at 120 °C for $\sim$20 min, the substrates were transferred into a nitrogen-filled glove box ($<$0.1 ppm O$_2$ and H$_2$O) for active layer coating and electrode formation. The device was then tested in air after the encapsulation in the glove box. The device area was determined to be ca. 10.0 mm^2 using microscopy. The thickness of the films was measured with a DekTek II profilometer. The current-density–voltage (J–V) curves were measured using a Keithley 2400 source measure unit. The photocurrent was measured under AM 1.5G illumination at 100 mW cm^{-2} under a Newport Thermal Oriel 91192 1000 W solar simulator (4 in. × 4 in. beam size). The light intensity was determined by a monosilicon detector (with KG-5 visible color filter) calibrated by National Renewable Energy Laboratory (NREL) to reduce spectral mismatch. After collecting EQE data, we used an AM1.5G standard spectrum, an Oriel solar simulator (with 1.5G filter) spectrum, and EQE data of both reference cell and tested polymer solar cells to calculate the spectral mismatch factor according to standard procedure [15]. The mismatch factor of 0.96 was then used to obtain correct J_{sc} and power conversion efficiency.

EQE measurements were conducted using an EQE system (Model QEX7) by PV Measurements Inc. (Boulder, Colorado). After collecting the EQE data, the software also integrates the date with the AM1.5G spectrum and reports the calculated J_{sc} value, which is helpful for checking the accuracy of the measurement. We have compared J_{sc} derived from EQE with spectral mismatch corrected J_{sc} from J–V testing for our champion cells. The details on experimental procedures to determine the device efficiency are given in the Supporting Information.

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