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Organic bulk heterojunction solar cells using poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene)

Jack E. Parmer,¹ Alex C. Mayer,¹ Brian E. Hardin,¹ Shawn R. Scully,¹ Michael D. McGehee,^{1,a)} Martin Heeney,² and Iain McCulloch²

¹Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, USA

²Merck Chemicals, Chilworth Science Park, Southampton SO16 7QD, United Kingdom

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By transitioning to semicrystalline polymers, the performance of polymer-based solar cells has recently increased to over 5% [W. Ma *et al.*, *Adv. Fund. Mater.* **15**, 1665 (2005); G. Li *et al.*, *Nat. Mater.* **4**, 864 (2005); M. Reyes-Reyes *et al.*, *Org. Lett.* **7**, 5749 (2005); J. Y. Kim *et al.*, *Adv. Mater. (Weinheim, Ger.)* **18**, 572 (2005); J. Peet *et al.*, *Nat. Mater.* **6**, 497 (2007)]. Poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene) (pBTTT) has caused recent excitement in the organic electronics community because of its high reported hole mobility ($0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) that was measured in field effect transistors and its ability to form large crystals. In this letter, we investigate the potential of pBTTT as light absorber and hole transporter in a bulk heterojunction solar cell. We find that the highest efficiency of 2.3% is achieved by using a 1:4 blend of pBTTT and [6,6]-phenyl C₆₁-butyric acid methyl ester. The hole mobility as measured by space charge limited current modeling was found to be $3.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in this blend. © 2008 American Institute of Physics. [DOI: 10.1063/1.2899996]

Amid rising energy costs and international concern for climate change, the need for a change in energy technology and infrastructure has been widely recognized. While the cost per watt of solar cell technology has steadily decreased in the past decade, an estimated factor-of-five cost reduction is still needed before widespread adoption. One approach to lowering the cost is to make solar cells with low-cost organic materials that can be processed from solution in an inexpensive roll-to-roll manner. The efficiency of solar cells based on a blend of a semiconducting polymer and either of the fullerene derivatives [6,6]-phenyl C₆₁-butyric acid methyl ester (PC_[61]BM) and [6,6]-phenyl C₇₁-butyric acid methyl ester (PC_[71]BM) (both hereafter referred to generally as PCBM) has improved steadily since their inception and is now at 5%.^{1–5}

In organic bulk heterojunction solar cells, a mismatch between the mobilities of donor and acceptor materials causes asymmetric carrier extraction, thus causing a buildup of charge in the film. Such buildup creates a counter-electric-field that places a maximum on the photocurrent near the maximum power point of the cell and, thus, limits the overall efficiency.⁶ This problem, which is known as space charge limited photocurrent (SCLP), has been greatly alleviated by switching from amorphous to semicrystalline materials with higher hole mobility, such as poly-3-hexylthiophene, but it remains a significant challenge in the development of polymer:fullerene solar cells.^{7,8} A high hole mobility is also important for reducing geminate and bimolecular recombination.⁹ By incorporating poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene) (pBTTT) as the donor material, we anticipated that its high degree of crystallization would yield high mobility in the desired direction of charge transport.^{10,11} As we will show in this letter, the hole mobility of our most efficient pBTTT:PCBM cells as measured by space charge limited current (SCLC) modeling was found to be $3.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which was still

more than an order of magnitude less than the typical reported out-of-plane mobility of PCBM. We varied the polymer:fullerene blend ratio, the choice of fullerene, and annealing conditions. We found a maximum efficiency of 2.3% for a 1:4 blend ratio having a short-circuit current density (J_{sc}) of 9.37 mA/cm^2 , an open circuit voltage (V_{oc}) of 0.525 V, and a fill factor (FF) of 0.48. These initial results show the potential of pBTTT as a light absorbing, hole transporting material for use in high efficiency polymer:PCBM bulk heterojunction solar cells.

pBTTT:PCBM solar cells were prepared by spin coating from solution in a nitrogen environment. Indium tin oxide (ITO) coated glass substrates (Thin Film Devices) were scrubbed with a 10% Extran™ solution, sonicated in acetone and isopropyl alcohol for 10 min, rinsed in de-ionized water, and then placed in a UV-ozone chamber for 30 min. After cleaning, the substrates were coated in air with ~50 nm of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) purchased from Bayer with a resistivity of $1 \text{ k}\Omega \text{ cm}$. All subsequent processing occurred in a nitrogen glove box maintained at less than 2 ppm oxygen. The active layer solutions were prepared by dissolving pBTTT and PCBM in 1,2-*ortho*-dichlorobenzene. For complete dissolution, the solutions were heated at 90 °C and stirred for several hours. Before spin coating, the solutions were cooled to 60 °C. Both PC_[61]BM and PC_[71]BM (Nano-C) were both used as acceptor species; however, cells blended with PC_[71]BM consistently gave higher currents and power conversion efficiencies (PCEs) because of increased absorption in the ultraviolet region of the spectrum.^{12,13} pBTTT was synthesized as reported earlier in Ref. 14. After spin coating, the still wet films were placed in a closed Petri dish and allowed to dry overnight as described by Li *et al.*² The films were then transferred to a high vacuum ($\sim 10^{-6}$ torr) chamber for metal electrode deposition. Electrode areas ranged from 0.035 to 0.07 cm². An argon laser with a beam wavelength of 514 nm was used for photoluminescence (PL) measurements. Samples were kept in a nitrogen environment

^{a)}Electronic mail: mmcgehee@stanford.edu.

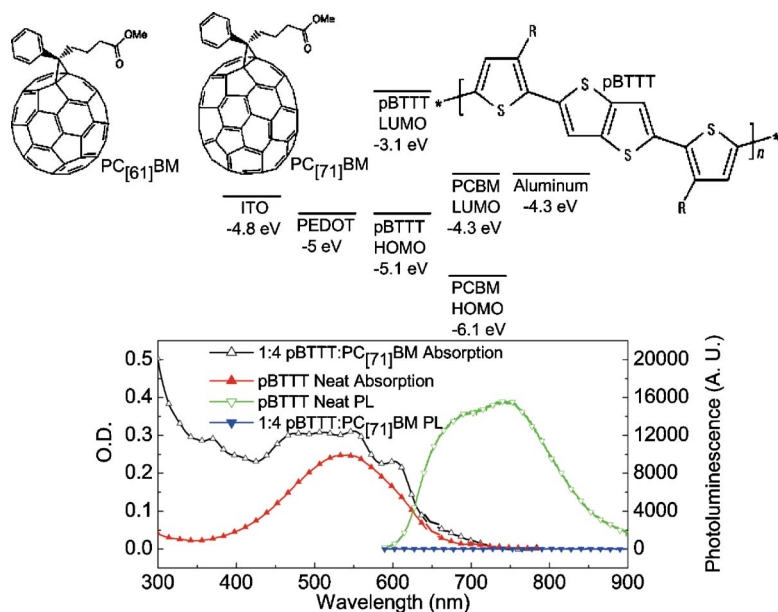


FIG. 1. (Color online) Molecular structures, energy levels, and absorption and PL spectra. PCBM, ITO, and aluminum energy levels were obtained from common literature values. The pBTTT HOMO level was obtained from Ref. 10. The pBTTT lowest unoccupied molecular orbital was estimated from the absorption maximum. Perfect exciton quenching and 55% light absorption at the maximum are demonstrated in the PL and absorption spectra. The absorption spectrum does not account for reflection from the aluminum electrode.

throughout these measurements. Current density–voltage (J - V) measurements were carried out with a Keithley 2400 source meter and a 91160 300 W Oriel solar simulator equipped with a 6258 ozone-free Xe lamp and an air mass (AM) 1.5 G filter. The lamp intensity was measured with an NREL calibrated Si photodiode. Spectral mismatch was minimized by tuning the lamp intensity, such that the integrated absorbed photon flux was the same for pBTTT as it would be under the 100 mW/cm² integrated AM 1.5 G spectrum. We have also cross calibrated our simulator by following Ref. 15, and we find good agreement. Furthermore, we find good agreement between external quantum efficiency data (measured without bias light under low intensity) integrated with the AM 1.5 G spectrum and the low intensity J_{sc} measured with our calibrated simulator. Cells were annealed by directly placing them on a hot plate in nitrogen atmosphere. They were cooled on a metal surface at room temperature for 5 min before testing. Quantum efficiency measurements were performed by low-frequency chopping of monochromatic light incident on the cell and using lock-in detection to measure current as a function of wavelength relative to a calibrated silicon photodiode with known response.

The energy levels and molecular structures of pBTTT, PC_[61]BM, and PC_[71]BM are shown in Fig. 1. As can be seen from the energy levels, there is an adequate energy offset for electron transfer from pBTTT to the fullerenes. Absorption and PL spectra of both pure pBTTT and a 1:4 pBTTT:PC_[71]BM blend are shown in Fig. 1(b). From the absorption, we see that a film with a 115 nm thick active layer and no reflecting electrode absorbs about 55% of the light at the maximum. The vibronic peaks in the blend film absorption suggest that PCBM enhances the crystallinity of pBTTT. This unusual result is being explored using synchrotron radiation and will be discussed further in a subsequent publication. The absence of PL from the blend suggests that virtually all of the excitons are dissociated by electron transfer, as expected based on the energy offsets.

To see if the crystallinity of pBTTT resulted in a high charge carrier mobility and to investigate the dependence on pBTTT:PCBM blending ratio, we measured the hole

mobility of the blends using the SPLC method. Mobility was determined by fitting current-voltage curves of hole-only diodes to the SPLC equation, as described in Refs. 7 and 8. Hole-only diodes were prepared by replacing aluminum with palladium as the top metal contact because its work function (5.1 eV) is close to the highest occupied molecular orbital (HOMO) of pBTTT. The mobilities of these diodes, shown in Fig. 2, with 1:1, 1:3, and 1:4 blending ratios were determined to be 2.4×10^{-5} , 1.35×10^{-4} , and 3.8×10^{-4} cm² V⁻¹ s⁻¹, respectively. The diodes with a 1:5 ratio of pBTTT to PC_[71]BM and annealed diodes of all blending ratios consistently shorted, thus, no mobility data were obtained for these devices. The mobility of a pure pBTTT film was 10^{-4} cm² V⁻¹ s⁻¹, which was much lower than the value reported in an field effect transistor geometry,¹⁰ and the addition of PCBM had a negative effect on hole mobility up to a 1:3 pBTTT:PCBM ratio. The maximum measured hole mobility in the 1:4 blend was nearly four times higher than that in a neat film but still an order of magnitude lower than the electron mobility of PCBM. The reason for the low mobility

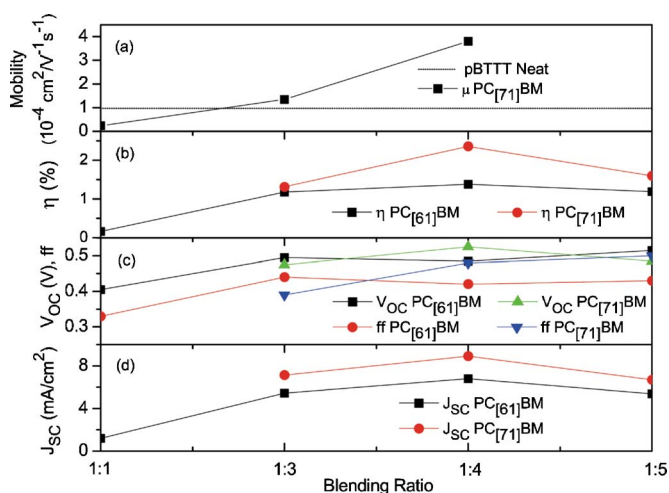


FIG. 2. (Color online) Mobility (a), η (b), V_{oc} and FF (c), and J_{sc} (d) as a function of blending ratio. Cells blended with PC_[61]BM were spun at 900 rpm and cells blended with PC_[71]BM were spun at 700 rpm; all other parameters were kept the same. The line in (a) is for pristine pBTTT film.

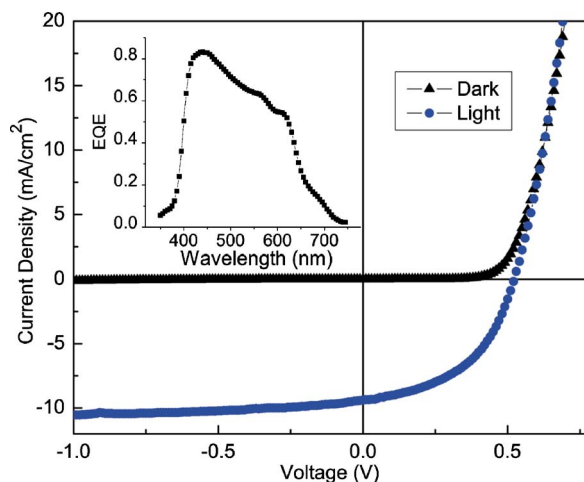


FIG. 3. (Color online) The I - V curves of the optimized pBTTT:PC_[71]BM cell in the dark and under calibrated 1 sun illumination (PCE=2.34%, J_{sc} =9.37 mA/cm², V_{oc} =0.525 V, FF=0.48). The inset shows the quantum efficiency as a function of wavelength for this high efficiency cell. This curve when integrated with the AM 1.5 G solar spectrum gives 10.8 mA/cm².

of all pBTTT films is still being explored, but we speculate that it is due to a high edge-on orientation, as has been observed previously in annealed pBTTT films.¹⁰

Efficiency increase with PCBM loading has been observed in many polymer:PCBM systems.^{8,16,17} Figure 2 shows that all measures of cell performance improve with the addition of either PC_[61]BM or PC_[71]BM up to a 1:5 ratio of pBTTT:PCBM. Studies that have observed this trend and have measured hole mobility at various blending ratios have found that the hole mobility measured by SCLC modeling increases with PCBM loading.⁸ The ratio that yielded the highest efficiency was found to be 1:4 pBTTT:PCBM, the same ratio which gave the highest hole mobility. Cells with PC_[71]BM in place of PC_[61]BM as the acceptor material had consistently higher currents and efficiencies due to the stronger absorption of PC_[71]BM.^{12,13} Annealing (not shown) lead to a lower current and, hence, a lower device efficiency. The reason for this decrease in performance is still being investigated. The highest device efficiency was achieved by using 1:4 pBTTT:PC_[71]BM with an active layer thickness of 115 nm spun at 700 rpm from 1,2-*ortho*-dichlorobenzene at 60 °C. The J - V curves of this optimized cell are shown in Fig. 3. This cell had a J_{sc} of 9.37 mA/cm², a V_{oc} of 0.525 V, and a FF of 0.48 for an overall PCE of 2.3%. The inset shows the quantum efficiency as a function of wavelength. Integrating this with the solar AM 1.5 G spectrum gives ~10.8 mA/cm². This is slightly larger than the 1 sun J_{sc} we measure because J_{sc} is sublinear with light intensity and the quantum efficiency was measured at low intensity with no bias light. We find it surprising that the highest efficiency was found for a 1:4 pBTTT:PCBM ratio. This ratio has been found to be optimum for amorphous polymer^{8,16,17}—rather than for semicrystalline polythiophene:PCBM blends, the optimum of which has been reported to be near 1:1 polymer:PCBM.^{1–5}

An increase in the cell thickness beyond 115 nm yielded a lower J_{sc} and FF. As mentioned, initial measurements indicate a sublinear dependence of J_{sc} on light intensity. Furthermore, decreasing the light intensity, and, thus, the photocur-

rent, improved the FF of all devices. For example, decreasing the light intensity from 1 sun to 0.1 sun improved the FF from 0.42–0.46 to 0.50–0.54 for the 1:4 pBTTT:PC_[71]BM devices. A sublinear dependence of J_{sc} on light intensity and decreasing FF with increasing light intensity are indicative of SCLP or bimolecular recombination.¹⁸ SCLP at this thickness is consistent with the results of Mihailetchi *et al.*,⁷ who found 100 nm to be the maximum thickness for cells with mobility near 10^{–4} cm² V^{–1} s^{–1} to be free from a space charge limited regime.

Bulk heterojunction solar cells with PCEs of 2.3% were fabricated with pBTTT. The high mobility needed to make devices with active layers thicker than 115 nm was not achieved due to relatively low mobility in the direction normal to the substrate. When the hole and electron mobilities are matched in the vertical direction, it will be possible to make thick cells that absorb higher fractions of incident radiation and extract carriers in regimes not limited by SCLP. If the absorption and quantum efficiency were 90% between 400 and 650 nm, the short-circuit current density would approach 14 mA/cm². Because of this and the high hole mobility previously reported for pBTTT in the planar direction,¹⁰ we are optimistic that the pBTTT:PCBM combination is a promising photovoltaic system and that higher efficiencies may be achieved with more optimized processing and a better understanding of what limits the hole mobility, and consequently, efficiency.

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