Enhanced efficiency of plastic photovoltaic devices by blending with ionic solid electrolytes

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One of the major technology bottlenecks of polymer photovoltaic cells is the low photoinduced current, due to the low carrier mobility and short exciton migration distance. In this letter we demonstrated that the electric current for polymer PV cells can be significantly enhanced by adding a small amount of ionic solid electrolyte. Heterojunction polymer photovoltaic devices, consisting of poly[2-methoxy-5-($2'$-ethyl-hexyoxy)-1,4-phenylene vinylene] (MEH-PPV) C_{60} and/or methanofullerene([6,6]-phenyl C61-butyric acid methyl ester) (PCBM) as the active materials, were fabricated. It has been found that the power efficiency of the organic was enhanced by blending ionic solid electrolyte, such as polyethylene oxide into the active layer. It is believed that the optimized polymer morphology, the improved electrical conductivity, and the *in situ* photodoping of MEH-PPV contribute to this enhancement of photovoltaic efficiency. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1710712]

Since the discovery of photoinduced charge transfer between organic donors and acceptors, great effort has been devoted to explore these materials for photovoltaic applications.[1–3] Plastic photovoltaic devices are now considered as promising and renewable energy source as the alternative of the inorganic counterparts,[3] for example, silicon photovoltaic cells.[4] It is anticipated that plastic solar cells have the advantage of mechanical flexibility, lightweight and lower fabrication cost for larger area devices.[3] However, the efficiency of current organic solar cells is still low for practical application. The performance of polymer solar cells is limited by several factors, such as the short exciton migration length, wide band gap of conjugated polymers, and low carrier mobility. For example, typical exciton diffusion length is in the range of 5 nm, which is far shorter than the device thickness (~ 50 nm).[5] The wide energy band gap of the polymers also misses the infrared portion of sunlight. Finally, the charge carrier mobility of organic materials is low, and as a result, the poor conductivity of organic thin films significantly cuts down the power efficiency. In the letter, we will present a way to improve the power efficiency of polymer solar cells by adding a very small amount of polymer electrolyte to the active polymer layer. It has been found in our laboratory that the power efficiency of organic photovoltaic devices was enhanced by blending ionic solid electrolyte, such as polyethylene oxide (PEO) and $LiCF_3SO_3$ into the active layer. The proposed mechanism of this observation is also discussed.

The highest power conversion efficiency of polymer photovoltaic devices reported so far is based on the heterogeneous p-n junction.[6] The bulk heterojunction not only provides high surface contacts for charge separation, but also an interpenetrating network for efficient charge separation and transport.[6] The polymer photovoltaic device in this study consists of a layer of polymer thin film sandwiched between a transparent anode [indium–tin–oxide (ITO)] and a metal cathode. The active material is an admixture of poly[2-methoxy-5-($2'$-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV, a p-type polymer), and C_{60} (an n-type electron acceptor) or methanofullerene (phenyl C61-butyric acid methyl ester) (PCBM). The chemical structures of the materials used in this work are shown in Fig. 1. The ITO glass substrates were cleaned by ultrasonic cleaner with the sequential treatments using detergent, deionized water, acetone, and isopropanol, respectively. The cleaned ITO surface was then modified by spin coating of 80 nm PEDOT:PSS (Baytron® P VP Al 4083). A MEH-PPV and C_{60} (or PCBM) premixing solution was then spin coated from 1,2-dichlorobenzene on the prepared substrates. The cathodes of devices, consisting of 500 Å of Ca and 1000 Å of Al, were thermally deposited on the top of films at $\sim 10^{-6}$ Torr. The active area of the device is 0.12 cm^2. The current–voltage (I–V) curves were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under illumination by a solar simulator [Thermo-Oriel 150 W solar simulator (AM1.5G)]. All devices were fabricated and tested in a nitrogen environment. Other experimental details could be found in Ref. 7.

More than 24 polymer PV cells have been fabricated and tested, and the results are very reproducible with typical I–V curves shown in Fig. 2. Figure 2 shows the I–V character of the device with MEH-PPV and C_{60} (MEH-PPV:C_{60}=3:1

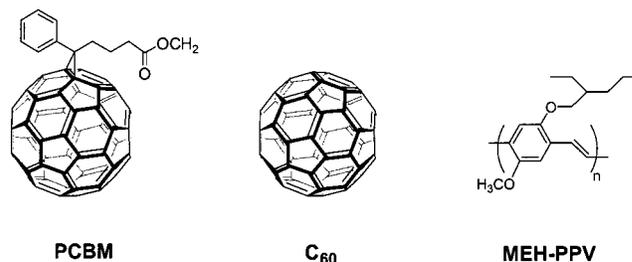**PCBM**   **C_{60}**   **MEH-PPV**

FIG. 1. Chemical structure of the materials used in this study.

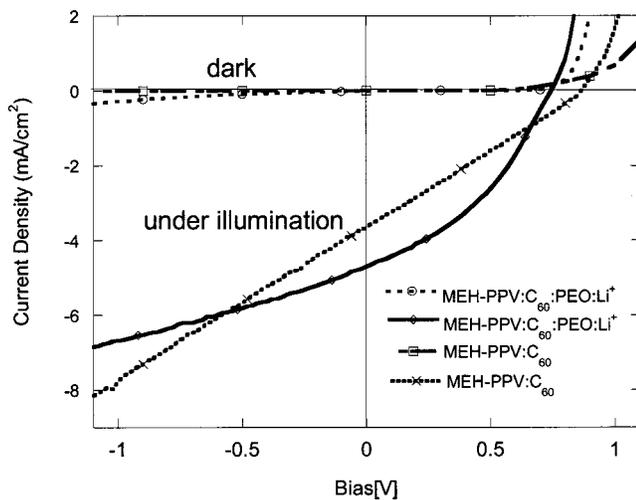[a]Electronic mail: yangy@ucla.edu

FIG. 2. $I-V$ curves of PV devices. The photoactive layers consist (a) MEH-PPV:$C_{60}=3:1$, (b) MEH-PPV:C_{60}:PEO:LiCF$_3$SO$_3$ = 3:1:0.25:0.05. A 100 mW/cm^2 AM 1.5 G solar simulating light was illuminated from device anodes.

FIG. 3. $I-V$ curves of PV devices. The photoactive layers consist MEH-PPV:PCMB=1:4 (solid line) or MEH-PPV:PCMB:PEO:LiCF$_3$SO$_3$ = 1:4:0.08:0.02 (dashed line). A 100 mW/cm^2 AM 1.5 G solar simulating light was illuminated from device anodes.

weight ratio) as the active layer under 100 mW/cm^2 AM1.5G illumination. The open circuit voltage (V_{oc}) and short circuit current (I_{sc}) were 0.88 V and 3.7 mA/cm^2, respectively. The fill factor (FF), which is defined as $(V_{oc}^*I_{sc})/(V_m^*I_m)$, was 0.26 ($V_m$ and I_m are the voltage and the current density at the maximum power output, respectively). The power conversion efficiency was calculated as 0.8%. When PEO and LiCF$_3$SO$_3$ were added into this active layer, where the weight ratio of the active polymer layer is MEH-PPV:C_{60}:PEO:LiCF$_3$SO$_3$=3:1:0.25:0.05, it can be clearly seen that the I_{sc} increased to 4.7 mA/cm^2 (Fig. 2). Meanwhile, the FF increased to 0.38. Although the V_{oc} decreased to 0.75 V, the resulting power efficiency increased to 1.3%. However, when more polymer electrolyte was added, it was found that the performance decreased. This is probably due to the serious phase separation between MEH-PPV and polymer electrolyte, which has been suggested as the main reason which causes the deterioration of polymer devices.[8]

The dc $I-V$ measurement (Fig. 2) was examined both from +2 to −2 V and from −2 to +2 V. Both scans show the same $I-V$ characteristics, and no apparent hysteresis was observed. In the past, it has been reported that the low mobility of the ions in polymer thin film results in significant $I-V$ hysteresis.[9] Our $I-V$ scans rule out the contribution of the movement of ions to the photocurrent, hence the contribution of ionic current to our PV device is insignificant.

When C_{60} was replaced with PCBM as the electron acceptors, similar enhancement of device performance was observed. PCBM has much higher solubility in common organic solvent than that of C_{60}. When a much higher amount of PCBM respective to MEH-PPV was used, it is much easier to establish electron conduction channel in the organic thin films.[3] Consequently, the PCMB photovoltaic cells usually have higher efficiency than PV device using pure C_{60}. Figure 3 shows the $I-V$ curve of the device with MEH-PPV and PCBM (MEH-PPV:PCBM=1:4 weight ratio) as the active layer. The V_{oc} and I_{sc} are 0.87 V and 5.7 mA/cm^2, respectively. The FF is 0.44. Compared with the device based on C_{60}, the higher FF implies less internal power loss as a
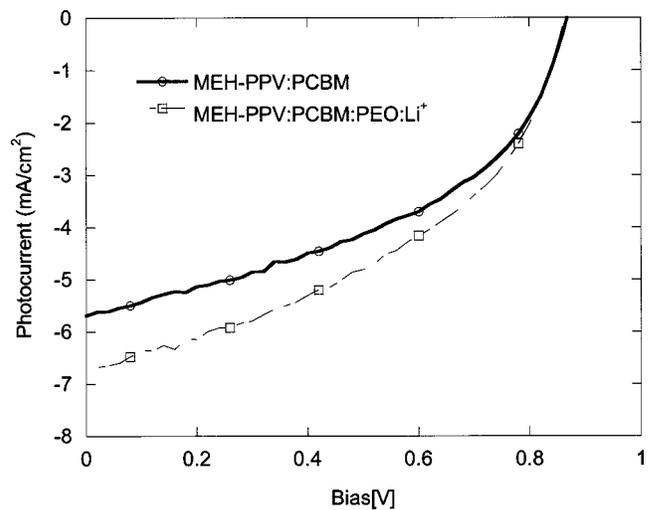
result of better electron transportation and collection efficiencies due to the much higher amount of C_{60} moieties in the active layer. The resulting power conversion efficiency is 2.2%. When PEO and LiCF$_3$SO$_3$ were added into this active layer, where the weight ratio of the active polymer layer is MEH-PPV:PCBM:PEO:LiCF$_3$SO$_3$ = 1:4:0.08:0.02, it can be clearly seen that the I_{sc} increased to 6.8 mA/cm^2 (Fig. 3). As a result, the output power conversion efficiency was improved to 2.5%.

Figure 4 shows the photocurrent response of the device under short circuit condition. The photocurrent was rather stable under the illumination. Hence, it is likely the electronic current, not the ionic current, is the dominant current of our PV device. It is known that the motions of ions are much slower than electrons in organic thin films.[9] If the ionic current contributes to the photocurrent, the response of the photocurrent should be slow and the current should decrease and reach equilibrium overtime.
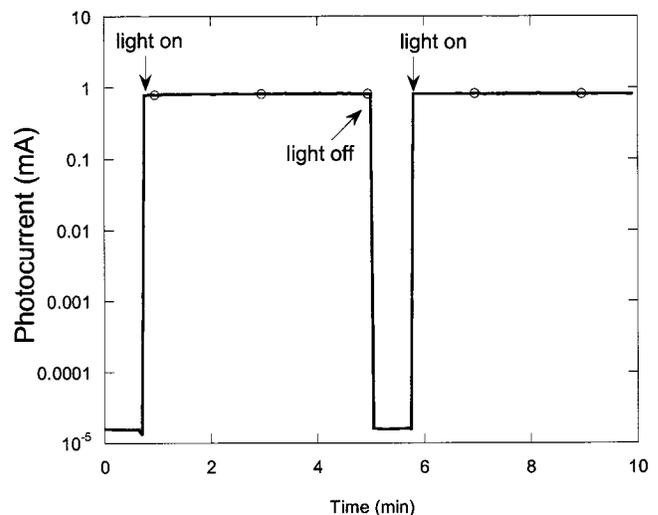

FIG. 4. Photocurrent responses of the PV device consisting a photoactive polymer layer with polymer blended with electrolyte (the weight ratio of each component in the polymer blend is MEH-PPV:PCMB:PEO:LiCF$_3$SO$_3$=1:4:0.08:0.02).
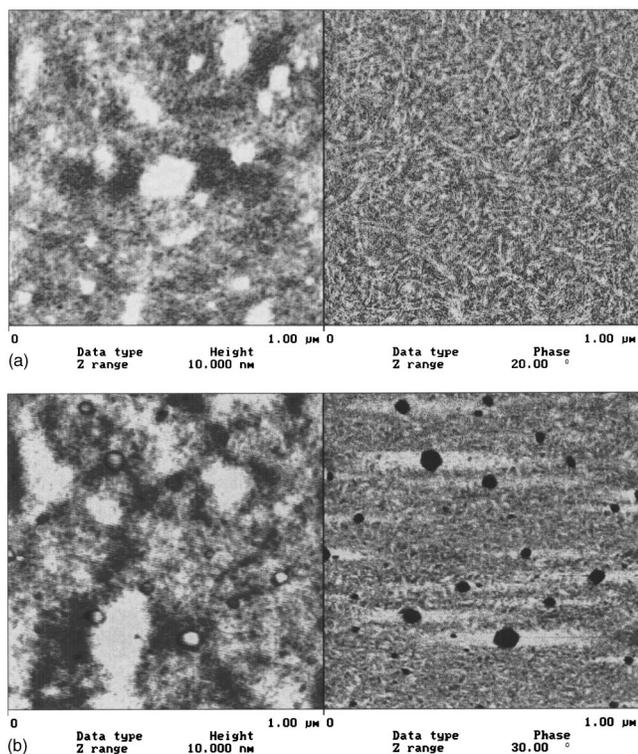
FIG. 5. AFM images of the photoactive layer of the photovoltaic devices. The films consist of (a) MEH-PPV:C_{60}=3:1; (b) MEH-PPV:C_{60}:PEO: LiCF$_3$SO$_3$=3:1:0.25:0.05. The left panels are height mode image; while the right panels are phase images. Nanosize domains were found in the thin film consists the polymer electrolyte.

The improvement of the device performance is also probably due to one or more of the three mechanisms: the improvement of morphology, the enhancement of material conductivity, and due to the "*in situ* photodoping" of the polymer.[3] It is known that the performance of polymer photovoltaic devices strongly depends on the thin-film morphology of the active layer.[3,6,7] The morphologies of the MEH-PPV:C_{60} films were investigated by atomic force microscopy (AFM). Figure 4(a) shows both the AFM height and phase images of the film consisting of the mixture of MEH-PPV and C_{60}. The film surface shows some polymer aggregates which are evident by the dark and bright regions of the phase image of Fig. 5(a), and the root-mean-square (rms) roughness is 0.53 nm. On the other hand, the rms roughness of the film consisting of MEH-PPV, C_{60}, and PEO and Li ion complexes is 0.64 nm, similar to that of the film, which only contains MEH-PPV and C_{60}. However, from the AFM image [Fig. 5(b)], some small different phase regions, which have the diameter up to 65 nm were observed. It is suspected these dark regions are the salts that are not fully dissolved in the polymer film. Despite these "giant" regions of undissolved salts, the rms value is similar to the one without the solid electrolyte. This observation suggests that the

film morphology of Fig. 5(b) is indeed smoother or have less polymer aggregates. We suspected that the nanosize morphology manipulation, caused by the additive, optimizes the device performance.

Alternatively, the improvement of the device performance is probably also due to the *in situ* photodoping of the polymer.[3] When a photo induces a charge transfer between MEH-PPV and C_{60}, because of the high concentration of free ions in the active layers, the "photo-oxidized" MEH-PPV will probably be doped by these ions. The doped polymer usually has much higher conductivity. Consequently, the increased thin film conductivity diminishes the power loss due to the decreased shunt resistance from the internal circuit. However, when much higher C_{60} moieties (PCBM) were used as the photoactive layer in the devices, because majority charge carriers can go through the conducting channel established by PCBM, the improvement of conductivity due to the doped MEH-PPV is not as significant as the C_{60} device. The power efficiency enhancement of the devices based on PCMB (Fig. 3) is thus not as apparent as that based on C_{60} (Fig. 2).

In conclusion, it has been shown that the power efficiency of organic photovoltaic devices was enhanced by blending ionic solid electrolyte, such as polyethylene oxide and LiCF$_3$SO$_3$ complexes into the active layer. It is believed that the optimized polymer morphology and/or the *in situ* photodoping of MEH-PPV contribute to this enhancement. This enhancement of photocurrent (and subsequently the power conversion efficiency) does not sacrifice the device open-circuit voltage, therefore, we believe this method provides an ideal approach to enhance the short-circuit current of polymer photovoltaic cells. The AFM image shows some electrolytes still do not fully dissolve and suggests that this device still has room for improvement, when a better electrolyte system is adopted.

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