

## Improved morphology of polymer-fullerene photovoltaic devices with thermally induced concentration gradients

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Gradient concentration profiles for efficient charge transfer and transport can be created in polymer-fullerene organic photovoltaics by thermally induced interdiffusion of an initial bilayer. Prior demonstrations with poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and C<sub>60</sub> have been limited by the low miscibility of the two component materials. The morphology of the interdiffused films and resultant photovoltaic efficiency are improved by the use of the more miscible electron donor/electron acceptor pair of poly(3-octylthiophene) and C<sub>60</sub>. The resultant concentration gradient profile is demonstrated by Auger spectroscopy and ion-beam milling. Increases in the short-circuit currents and fill factors relative to interdiffused MEH-PPV/C<sub>60</sub> devices lead to monochromatic power conversion efficiencies of 1.5% at 470 nm. © 2005 American Institute of Physics. [DOI: 10.1063/1.1845574]

Organic photovoltaic devices have been intensely studied over the past decade as an alternative to inorganic solar cells due to the potential for inexpensive, light-weight, flexible devices.<sup>1-4</sup> Solar illumination conversion efficiencies of 2.5% and beyond have been demonstrated.<sup>5,6</sup> Organic solar cells are typically based on an electron donor-acceptor system. In one class of devices, the electron donor is a conjugated polymer and the acceptor is a fullerene. Upon absorption of a photon, an exciton is created on the electron donor. Ultrafast charge transfer of the electron from the conjugated polymer onto the fullerene acceptor<sup>7</sup> leads to an efficient separation of charges. This charge transfer can only occur, however, if the donor and acceptor are in close proximity, typically less than 10 nm.<sup>8-10</sup> This close proximity of donor and acceptor can be achieved by using a blend of the two materials as the active layer of the solar cell, a so-called bulk heterojunction. A further improvement in terms of charge transport can be made by creating a concentration gradient of donor and acceptor within the active layer having a donor-rich phase at the anode and an acceptor-rich phase at the cathode.<sup>11</sup>

We have recently demonstrated that thermally induced interdiffusion can be used to create a bulk heterojunction with a concentration gradient of donor and acceptor from anode to cathode starting from a bilayer of a conjugated polymer and C<sub>60</sub>.<sup>12</sup> The interdiffused devices exhibited an order of magnitude decrease in photoluminescence and order of magnitude increase in photoresponsivity over most of the

visible spectrum relative to the bilayer system. In the specific case of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and C<sub>60</sub>, it was found that the strong phase separation of the polymer and fullerene put a restriction on the interdiffusion leading to relatively modest monochromatic conversion efficiencies of 0.3%.<sup>13</sup> It was concluded that a proper choice of miscible donor and acceptor is essential for a successful interdiffusion.

Here, we present studies using the conjugated polymer poly(3-octylthiophene) (P3OT) as the donor and C<sub>60</sub> as the acceptor. Starting from a bilayer of P3OT and C<sub>60</sub>, devices were heated to induce an interdiffusion of the two layers. Improved photocurrents and *I*-*V* characteristics demonstrate the successful interdiffusion process. In addition, the morphology of the films was studied by recording the polymer concentration from anode to cathode with Auger spectroscopy in combination with ion-beam milling. The results show that in the heated bilayers the polymer concentration varies throughout most of the active layer, confirming that the interdiffusion leads to a concentration gradient of donor and acceptor material in the device. Compared to the previous studies on MEH-PPV/C<sub>60</sub>, P3OT/C<sub>60</sub> bilayers show improved interdiffusion behavior leading to monochromatic power conversion efficiencies of 1.5%.

Devices were prepared by first spin coating a poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) complex (PEDOT:PSS) (Bayer Corp.) onto indium tin oxide (ITO)-covered glass substrates. After drying the PEDOT film, regioregular poly(3-octylthiophene) (Sigma-Aldrich Corp.) was spin cast from a 1.5% wt/vol chloroform solution. Devices were then annealed for 1 h at 120 °C under vacuum ( $3 \times 10^{-6}$  Torr) to remove residual water and solvents before a 100-nm layer of C<sub>60</sub> (MER Corp.) was sublimed on the P3OT layer. Finally, a 200-nm aluminum layer was evapo-

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rated as a top electrode. The typical film thicknesses of the P3OT and fullerene layers were each  $\sim 100$  nm as determined from the absorption measurements with a Filmetrics F20-UV thin-film spectrometer system. Absorption coefficients of  $14 \times 10^4 \text{ cm}^{-1}$  at 512 nm and  $6 \times 10^4 \text{ cm}^{-1}$  at 435 nm were determined for P3OT and  $\text{C}_{60}$ , respectively, from interference fringes in much thicker films. The interdiffusion heating was carried out for 5 min at 130 or 210 °C inside an Ar flowbox prior to deposition of the Al electrode.

Photocurrent spectra were measured using a 300-W Xe lamp in combination with a CVI CM 100 monochromator as the illumination source and a Keithley 485 picoammeter to record the short circuit currents  $I_{\text{SC}}$ . The power spectrum  $P(\lambda)$  of the lamp was determined with a calibrated Si diode. The external quantum efficiency (EQE) was then calculated using

$$\text{EQE} = \frac{hc I_{\text{SC}}(\lambda)}{e \lambda P(\lambda)}. \quad (1)$$

$I$ - $V$  curves were measured with a Keithley 236 source measure unit in the dark or using the 470-nm monochromatic light of the above described Xe lamp.

To study the morphology of the interdiffused films, we used a 610 Perkin-Elmer scanning auger spectroscopy system in combination with Ar-ion-beam milling. In this system, the surface layer of a film can be tested for its atomic constituents. After the Auger scan, the surface layer is milled off with an Ar-ion beam and the new surface layer can be tested. For these experiments, P3OT films were spin coated directly onto ITO-covered glass slides and  $\text{C}_{60}$  was subsequently sublimed. During the measurement, the ITO film was grounded to prevent charging of the films and substrate caused by the electron beam.

Regioregular P3OT is a microcrystalline polymer that shows a melting transition.<sup>14</sup> The melting temperature  $T_m$  of P3OT was determined to be 187 °C by differential scanning calorimetry (DSC). The glass transition temperature  $T_g$  of the polymer could not be observed but is believed to be below 100 °C. To test whether the melting transition has any influence on the interdiffusion process, the temperatures chosen for the interdiffusion were 130 °C, which is below  $T_m$  but above  $T_g$ , and 210 °C, which is above  $T_m$ .

The photocurrent spectra of the unheated and heated devices are shown in Fig. 1. Upon heating, the EQE improves by an order of magnitude. Little difference is observed in the EQE whether the interdiffusion heating is done below or above  $T_m$ . For the photocurrent, there is no advantage in performing the interdiffusion heating above the melting transition of the P3OT. The sharp cutoff of the photocurrents below 350 nm is due to the strong absorption of the glass substrate and the ITO/PEDOT electrode, which prevents any light below 350 nm to penetrate into the active layer.

Figure 2 shows the  $I$ - $V$  characteristics of the devices in the fourth quadrant.  $I$ - $V$  curves were measured under monochromatic illumination at 470 nm ( $3.8 \text{ mW/cm}^2$ ). Upon heat treatment, the  $I$ - $V$  characteristics dramatically improve. The open circuit voltage and short circuit current of devices heated at 130 or 210 °C increase compared to the unheated films. However, the fill factor only improves for devices

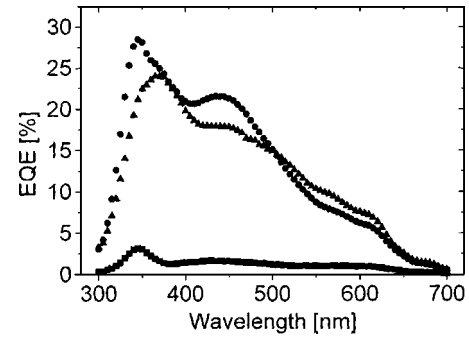


FIG. 1. EQE spectrum of an unheated P3OT/ $\text{C}_{60}$  bilayer device (squares), a P3OT/ $\text{C}_{60}$  bilayer device heated at 130 °C for 5 min (circles), and a P3OT/ $\text{C}_{60}$  bilayer device heated at 210 °C for 5 min (triangles). The EQE spectra of the two heat-treated devices are comparable and are an order of magnitude larger than the unheated bilayer device.

heated below  $T_m$  and decreases for devices heated above  $T_m$ . A summary of the device parameters is given in Table I. The monochromatic conversion efficiency calculated for devices heated at 130 °C is found to be 1.5%. The  $I$ - $V$  curves of the various devices clearly show that it is advantageous to perform interdiffusion below  $T_m$ .

The depth profile of the polymer/fullerene layer was acquired with Auger spectroscopy in combination with ion-beam milling. Here, we used the fact that the thiophene backbone contains sulfur that can be detected with Auger spectroscopy. In contrast,  $\text{C}_{60}$  is made up entirely of carbon. From the strength of the sulfur signal, we can therefore make a qualitative statement about the polymer content in the surface layer. The limitations of this technique are the penetration depth of the electron beam, which is about 5 nm, and the fact that the ion-beam milling does not remove a perfectly smooth layer. Furthermore, the technique cannot distinguish

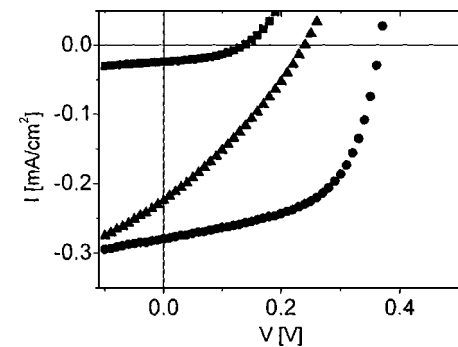


FIG. 2. Current-voltage characteristics (470 nm,  $3.8 \text{ mW/cm}^2$ ) for an unheated P3OT/ $\text{C}_{60}$  bilayer device (squares), a P3OT/ $\text{C}_{60}$  bilayer device heated at 130 °C for 5 min (circles), and a P3OT/ $\text{C}_{60}$  bilayer device heated at 210 °C for 5 min (triangles).

TABLE I.  $I$ - $V$  characteristics of unheated and heated P3OT/ $\text{C}_{60}$  devices under monochromatic illumination (470 nm,  $3.8 \text{ mW/cm}^2$ ).

Interdiffusion temperature	$V_{\text{OC}}$ (V)	$I_{\text{SC}}$ (mA/cm <sup>2</sup> )	FF
Unheated	0.14	$16 \times 10^{-3}$	0.41
130 °C	0.36	$277 \times 10^{-3}$	0.57
210 °C	0.23	$226 \times 10^{-3}$	0.32

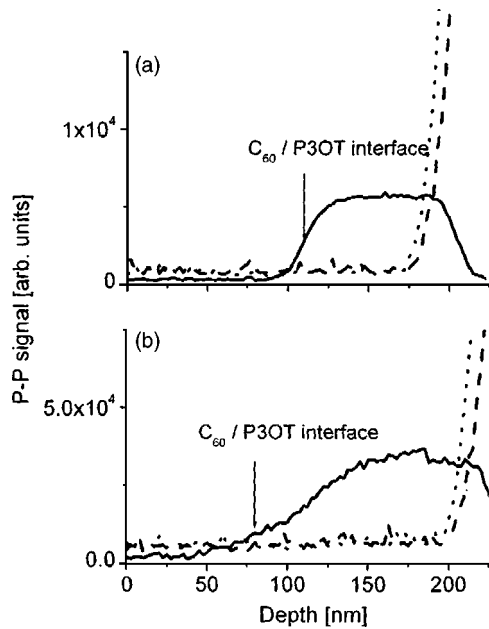


FIG. 3. Depth profiles of (a) an unheated P3OT/C<sub>60</sub> bilayer device and (b) a P3OT/C<sub>60</sub> bilayer device heated at 130 °C. The concentration of sulfur (solid), indium (dotted), and oxygen (dashed) was monitored. The arrow indicates the position of the P3OT/C<sub>60</sub> interface as determined from absorption measurements. The unheated bilayer shows a rather sharp interface between P3OT and C<sub>60</sub>. For the interdiffused film, the P3OT concentration rises slowly throughout more than 100 nm (from 35 to 150 nm) of the bulk of the film.

between carbon from the polymer and carbon from the C<sub>60</sub>. Therefore, no determination can be made whether a layer is free of C<sub>60</sub>.

Figure 3(a) shows the peak-to-peak (P-P) Auger signal of an unheated bilayer of C<sub>60</sub> and P3OT as a function of depth in the film. The P-P signal is directly related to the concentration of the element in the surface layer and therefore provides information about the composition of the tested surface. The P3OT and C<sub>60</sub> layers each had a thickness of 110 nm as determined from the absorption measurements. The sulfur signal is zero while the tested surface is within the C<sub>60</sub> layer and then shows a sharp increase in the vicinity of the interface between the P3OT and C<sub>60</sub>. In the P3OT layer, the sulfur signal remains constant, indicating a constant concentration of the polymer throughout the layer. Finally, the sulfur signal drops and the indium and oxygen signals appear when the scan hits the P3OT/ITO interface. This depth scan shows that the unheated bilayer is a rather distinct two-layer system. It should be mentioned here that the Auger scan does not rule out small amounts of C<sub>60</sub> in the P3OT layer. As a matter of fact, photoluminescence studies (not presented here) indicate that small amounts of C<sub>60</sub> already diffuse into the P3OT bulk during sublimation of the C<sub>60</sub>, leading to photoluminescence quenching. This is in agreement with the observations by Schlebusch *et al.*<sup>15</sup>

The depth profile of a heated bilayer system is shown in Fig. 3(b). Here, the C<sub>60</sub> layer was 80 nm and the P3OT was 160 nm thick. The bilayer was heated at 130 °C for 5 min. After etching through 35 nm of C<sub>60</sub> with no sign of sulfur,

the sulfur signal starts increasing steadily throughout most of the film. After more than 100 nm of increasing sulfur concentration, the signal levels off and stays constant until it drops off when the etching hits the ITO layer. The jump in signal at a depth of 185 nm is due to a readjustment in the electronics of the system during the experiment. This scan shows that, in fact, the heat treatment has created a concentration gradient of the P3OT throughout most of the bulk of the active layer. The Auger signal cannot give an exact description of the nanoscale morphology of the layer since the detected sulfur signal is an average of the exposed area during the measurement. But it can give a trend in the polymer concentration, which is clearly changing throughout the bulk.

In conclusion, we have successfully created a polymer/fullerene bulk heterojunction with a concentration gradient of donor and acceptor throughout the bulk of the active layer. In the interdiffused devices, the photocurrents were improved by an order of magnitude compared to the unheated devices. In addition, *I*-*V* curves showed improved *V*<sub>OC</sub> and fill factor (FF) in the interdiffused devices. In the case of regioregular P3OT, our studies show that the best results are obtained by heating at temperatures below *T*<sub>m</sub> of the polymer. Heating above *T*<sub>m</sub> results in lower open circuit voltages and fill factors than heating below *T*<sub>m</sub>. Auger spectroscopy in combination with ion-beam milling revealed a morphology of the film where the unheated films have a clear bilayer structure and the heated films show a concentration gradient of the polymer throughout most of the active layer. This study shows that the heat treatment indeed results in the intended concentration gradient of donor and acceptor.

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- <sup>1</sup>G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* **270**, 1789 (1995).
- <sup>2</sup>D. Gebeyehu, C. J. Brabec, F. Padinger, T. Fromherz, J. C. Hummelen, D. Badt, H. Schindler, and N. S. Sariciftci, *Synth. Met.* **118**, 1 (2001).
- <sup>3</sup>M. Granstrom, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson, and R. H. Friend, *Nature (London)* **395**, 257 (1998).
- <sup>4</sup>L. Chen, D. Godovsky, O. Inganäs, J. C. Hummelen, R. A. J. Janssens, M. Svensson, and M. R. Andersson, *Adv. Mater. (Weinheim, Ger.)* **12**, 1367 (2000).
- <sup>5</sup>S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen, *Appl. Phys. Lett.* **78**, 841 (2001).
- <sup>6</sup>F. Padinger, R. S. Rittberger, and N. S. Sariciftci, *Adv. Funct. Mater.* **13**, 1 (2003).
- <sup>7</sup>N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, *Science* **258**, 1474 (1992).
- <sup>8</sup>D. Vacar, E. S. Maniloff, D. W. McBranch, and A. J. Heeger, *Phys. Rev. B* **56**, 4573 (1997).
- <sup>9</sup>J. J. M. Halls, K. Pichler, R. H. Friend, S. C. Moratti, and A. B. Holmes, *Appl. Phys. Lett.* **68**, 3120 (1996).
- <sup>10</sup>A. Haugeneder *et al.*, *Phys. Rev. B* **59**, 15346 (1999).
- <sup>11</sup>K. O. Sylvester-Hvid, S. Rettrup, and M. A. Ratner, *J. Phys. Chem. B* **108**, 4296 (2004).
- <sup>12</sup>M. Drees, K. Premaratne, W. Graupner, J. R. Heflin, R. M. Davis, D. Marciu, and M. Miller, *Appl. Phys. Lett.* **81**, 4607 (2002).
- <sup>13</sup>M. Drees, R. M. Davis, and J. R. Heflin, *Phys. Rev. B* **69**, 165320 (2004).
- <sup>14</sup>T. A. Chen, X. Wu, and R. D. Rieke, *J. Am. Chem. Soc.* **117**, 233 (1995).
- <sup>15</sup>C. Schlebusch, B. Kessler, S. Cramm, and W. Eberhardt, *Synth. Met.* **177**, 151 (1996).