Creation of a gradient polymer-fullerene interface in photovoltaic devices by thermally controlled interdiffusion

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Efficient polymer-fullerene photovoltaic devices require close proximity of the two materials to ensure photoexcited electron transfer from the semiconducting polymer to the fullerene acceptor. We describe studies in which a bilayer system consisting of spin-cast 2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene copolymer (MEH-PPV) and sublimed C_{60} is heated above the MEH-PPV glass transition temperature in an inert environment, inducing an interdiffusion of the polymer and the fullerene layers. With this process, a controlled, bulk, gradient heterojunction is created bringing the fullerene molecules within the exciton diffusion radius of the MEH-PPV throughout the film to achieve highly efficient charge separation. The interdiffused devices show a dramatic decrease in photoluminescence and concomitant increase in short circuit currents, demonstrating the improved interface. © *2002 American Institute of Physics.*
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Organic photovoltaic materials are heavily studied because of the potential for lightweight, flexible, inexpensive, efficient solar cells. A major advance in polymeric photovoltaic devices was achieved with the observation of photogenerated charge separation in poly(para-phenylenevinylene) (PPV)-C_{60} composites.[1] Upon photoexcitation, rapid electron transfer occurs from the polymer to the high electron affinity C_{60}.[2] However, photoexcited electron-hole pairs at distances larger than ∼10 nm from the fullerene acceptor recombine before charge separation occurs, yielding photoluminescence (PL).[3,4] Significant improvements of the photovoltaic efficiency have been achieved by providing improved donor/acceptor proximity throughout the device using interpenetrating polymer networks[5,6] and polymer/fullerene blends,[7–9] resulting in "bulk heterojunctions." Nanoscale compositional control of the electron donor and acceptor species is clearly important to optimizing the performance of polymeric photovoltaics.

Here, we demonstrate an approach for controlling the nanoscale composition of a polymer/fullerene film. Starting from a standard bilayer system of 90 nm of spin-cast 2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene copolymer (MEH-PPV) followed by 100 nm of sublimed C_{60}, the film is then heated at temperatures in the vicinity of the MEH-PPV glass transition temperature to enhance the diffusion of the fullerene into the polymer, resulting in a concentration gradient structure. Because the fullerene acceptor is thus distributed throughout the film, exciton recombination is dramatically reduced. This is observed as a decrease in the

photoluminescence by an order of magnitude and an increase in the photocurrent by an order of magnitude throughout much of the visible spectrum. We also observe that a valley in the spectral photoresponsivity of the MEH-PPV/C_{60} bilayer system, ascribed to the short optical penetration depth at the peak of the MEH-PPV absorbance, is eliminated following the interdiffusion process. The resultant photoresponsivity is thus quite uniform for wavelengths from 340 to 560 nm. The improvement in the photovoltaic efficiency of these devices is achieved by the rearrangement of the spatial locations of the MEH-PPV and fullerene components on the nanometer length scale.

Devices were prepared by first spin coating a poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) complex (PEDOT) (Bayer Corp.) from an aqueous solution onto an indium tin oxide (ITO)-coated glass substrate to yield a layer of approximately 50 nm to improve the interface between the ITO and photovoltaic polymer film. Subsequently, MEH-PPV (M.W. ∼85 000, H.W. Sands Corp.) was spin coated from a 1% wt/vol chlorobenzene solution to give a film thickness of 90 nm. After annealing the film in vacuum at 150 °C for 1 h, a C_{60} (MER Corp.) film with a thickness of 100 nm was sublimed onto the MEH-PPV. Interdiffusion of the MEH-PPV and C_{60} layers was induced by heating the film on a hot plate inside a N_2 glovebox for five minutes at 150 or 250 °C. After the interdiffusion process was completed, 200 nm of Al were evaporated as a top electrode. Each film consisted of eight devices, each with an active area of 12 mm^2.

Film thicknesses were determined from the optical density (OD) values which were calculated from transmission and reflection data measured with a Filmetrics F20-UV thin-film spectrometer system using

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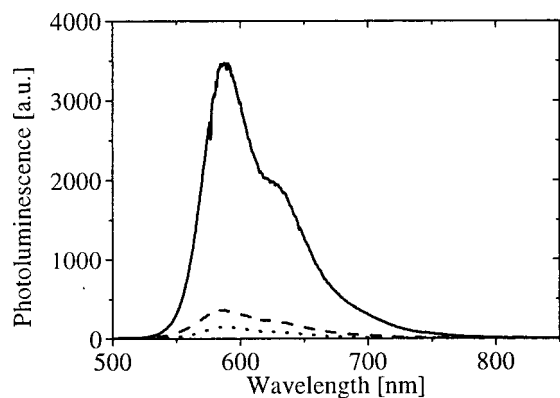[b]Author to whom correspondence should be addressed; electronic mail: rheflin@vt.edu

FIG. 1. Photoluminescence of an unheated MEH-PPV/C_{60} bilayer device (solid) and two heated MEH-PPV/C_{60} devices [5 min at 150 °C (dotted) and 5 min at 250 °C (dashed)].

$$OD = -\log \frac{T}{1-R}. \tag{1}$$

Through measurement of interference fringes in much thicker films, optical density calibrations of 7.80×10^{-3} nm^{-1} for MEH-PPV at a wavelength of 490 nm and 2.67×10^{-3} nm^{-1} for C_{60} at 435 nm were obtained.

Photoluminescence was measured with an Ocean Optics S2000 fiber optics spectrometer. The sample was illuminated through the glass and ITO with light from a Xe lamp that was passed through a CVI CM110 monochromator to select a wavelength of 470 nm with an intensity of 3.8 mW/cm^2. The luminescence signal was collected by the fiber at an angle of 45° with respect to the incident light. The same illumination source in combination with a Keithley 485 picoammeter was used to measure the photoresponsivity spectra. Identical spectral photoresponsivity measurements were made on a calibrated Si photodiode to correct for the light intensity spectrum of the Xe lamp/monochromator. $I-V$ curves were recorded with a Keithley 236 Source Measure Unit both in the dark and under 470 nm illumination. All of the above measurements were made in an argon environment to inhibit oxidation of the polymer. The illuminated area on the samples was in all cases 2 mm^2.

The optical absorption spectrum of a pure MEH-PPV film between 300 and 850 nm has an absorption edge at 590 nm and an absorption maximum at 490 nm in the visible portion of the spectrum. For a C_{60} film, the absorption starts a slow rise around 700 nm, followed by a peak at 435 nm and a stronger maximum at 338 nm. Correcting for reflection effects, the optical density of a bilayer system of MEH-PPV/C_{60} is the superposition of the two single layer films. The heating of the films for the interdiffusion does not lead to any measurable changes in the absorption spectrum, confirming that there is no degradation in the film constituents due to the heat treatment.

The photoluminescence (PL) of the devices can be used as a measure of the exciton dissociation in the films. If the photogenerated excitons are not dissociated, they can recombine radiatively leading to photoluminescence. The well-known effect of ultrafast electron transfer from the polymer to C_{60} is used to increase the exciton dissociation efficiency in photovoltaic devices. Figure 1 shows the photoluminescence of a sequence of samples. The unheated
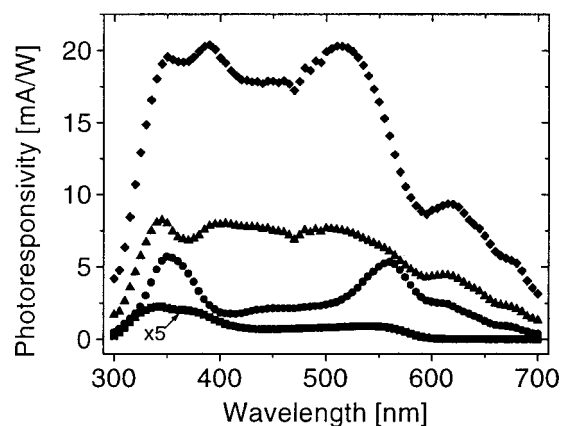

FIG. 2. Photoresponsivity (magnified by 5×) of a MEH-PPV device (squares), an unheated MEH-PPV/C_{60} bilayer device (circles), a MEH-PPV/C_{60} bilayer device that was heated at 150 °C for 5 min (triangles) and a MEH-PPV/C_{60} bilayer device that was heated at 250 °C for 5 min (diamonds).

MEH-PPV/C_{60} bilayer shows a strong PL signal which is not significantly reduced compared to a MEH-PPV single layer device. This is because effective exciton dissociation is only possible for excitons that are created within ~ 10 nm of a fullerene. Thus, the PL is quenched only within a small volume at the interface of MEH-PPV and C_{60}. In the MEH-PPV bulk, radiative recombination of the excitons remains efficient. The devices heated at 150 and 250 °C show a decrease of an order of magnitude in the PL, indicating that the heat treatment induced interdiffusion of the polymer and fullerene layers. The interdiffusion of C_{60} molecules into the polymer provides electron acceptors throughout the bulk, therefore strongly quenching the PL. The number of MEH-PPV photoexcitation sites that do not undergo exciton dissociation is thus reduced by 90%.

Figure 2 shows the spectral photoresponsivity of various MEH-PPV single layer and MEH-PPV/C_{60} bilayer films. MEH-PPV has a sharp increase in photoresponsivity at the absorption edge and a peak at 550 nm. The addition of a C_{60} layer increases the photoresponsivity by a factor of ~ 20 due to the electron-hole dissociation by the fullerene at the polymer/fullerene interface. In both films, a minimum of the photocurrent is observed in the region of maximum absorption of MEH-PPV (400–550 nm). We attribute this to the filter effect.[10,11] Because of the large MEH-PPV absorbance, the majority of excitons are created near the ITO/MEH-PPV interface. For the MEH-PPV single layer device, the electrons are not easily collected at the Al electrode since they are created far from it and are not transported well through the hole-transporting MEH-PPV. In the case of the MEH-PPV/C_{60} bilayer, most excitons are created far away from the C_{60} interface where efficient exciton dissociation occurs.

The heated MEH-PPV/C_{60} devices, one heated below the MEH-PPV T_g and one above, show several important distinct characteristics. The T_g of MEH-PPV was confirmed to be ~ 230 °C by differential scanning calorimetry analysis. The devices heated at 150 °C for 5 min no longer have a photocurrent minimum at the maximum MEH-PPV absorption. Instead, the photoresponsivity is nearly constant over the wavelength range between 340 and 560 nm. This indi-
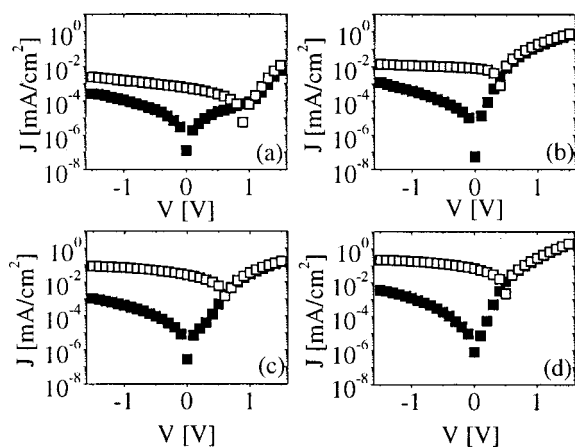
FIG. 3. Current–voltage characteristics for a MEH-PPV device (a), an unheated MEH-PPV/C_{60} bilayer device (b), a MEH-PPV/C_{60} bilayer device heated at 150 °C for 5 min (c) and a MEH-PPV/C_{60} bilayer device heated at 250 °C for 5 min (d). The filled symbols show the dark I–V curves, and the open show the illuminated (3.8 mW/cm^2 at 470 nm) I–Vs.

cates that, even at temperatures significantly below T_g of MEH-PPV, C_{60} can partially interdiffuse into the polymer bulk and therefore reduce the filter effect observed in unheated bilayer systems. This result is supported by the reduction of PL observed in the devices. On the other hand, no significant increase in the maximum photoresponsivity is observed. Even though fullerenes have diffused into the polymer bulk and enhanced the charge separation, the charge transport out of the device is not optimized for these conditions. Heating at 250 °C for 5 min increases the photoresponsivity by an order of magnitude throughout most of the visible range. This shows that heating above T_g improves the interdiffusion of the fullerenes into the polymer bulk such that charge separation and charge transport out of the devices are enhanced.

The corresponding dark and illuminated current density J versus voltage plots for the devices described above are shown in Fig. 3. All devices have more than two orders of magnitude rectification in the dark and more than one order of magnitude when illuminated at 470 nm. The open circuit voltage (V_{OC}) is reduced from 0.95 V in a single MEH-PPV layer device to 0.39 V in the unheated MEH-PPV/C_{60} bilayer device. Upon heating, V_{OC} improves to 0.64 V for the device heated at 150 °C and 0.47 V for the device heated at 250 °C.

We have made similar observations for the PL and the photoresponsivity in devices fabricated without the PEDOT layer on the ITO, thus demonstrating that the observed improvements are not related to interdiffusion of the PEDOT into the MEH-PPV bulk. The primary advantages of the PEDOT layer are less variation in the photoresponsivity from one device to the next on each film and improvements in the I–V characteristics of the devices. The measurements reported here were reproduced on at least two films of each type (eight devices per film) with less than a 20% variation between equivalent devices.

In conclusion, we have fabricated polymer-fullerene bilayer systems in which the charge transfer and charge transport have been improved by thermally controlled interdiffusion. This leads to increased proximity of C_{60} molecules to optical excitations throughout the bulk of the film as demonstrated by luminescence quenching of one order of magnitude. The corresponding order of magnitude increase in photocurrent in the region of maximum absorption of the MEH-PPV indicates the formation of a bulk heterojunction due to thermally controlled interdiffusion. The optical absorption spectra of the MEH-PPV/C_{60} composite films before and after the interdiffusion process are indistinguishable, demonstrating that the enhanced photovoltaic efficiency is due solely to nanoscale control of the spatial locations of the two components.

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