

2.5% efficient organic plastic solar cells

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We show that the power conversion efficiency of organic photovoltaic devices based on a conjugated polymer/methanofullerene blend is dramatically affected by molecular morphology. By structuring the blend to be a more intimate mixture that contains less phase segregation of methanofullerenes, and simultaneously increasing the degree of interactions between conjugated polymer chains, we have fabricated a device with a power conversion efficiency of 2.5% under AM1.5 illumination. This is a nearly threefold enhancement over previously reported values for such a device, and it approaches what is needed for the practical use of these devices for harvesting energy from sunlight. © 2001 American Institute of Physics. [DOI: 10.1063/1.1345834]

The discovery of ultrafast, photoinduced charge transfer from a conjugated polymer to C₆₀ (buckminsterfullerene) has fueled research on semiconducting-polymer based photovoltaic devices.¹ Early devices, fabricated from conjugated polymer/C₆₀ bilayers,^{2,3} yielded low power-conversion efficiencies (<0.1%) due to insufficient interfacial contact area between the donor and acceptor layers. This efficiency was improved by blending a soluble methanofullerene directly into the conjugated polymer film.⁴ Thus far, the efficiency of these devices under AM1.5 illumination has been limited to approximately <1%. Among the several geometries for organic photovoltaic devices investigated to date, including conjugated polymer blends,⁵ layers of low molecular weight organic molecules,^{6,7} and also the recently reported halogen-doped organic single crystals,⁸ the polymer based devices were mostly attractive due to their easy production technology. These “plastic” photovoltaic devices offer the possibility of low-cost fabrication of large-area solar cells for harvesting energy from sunlight. Aside from possible economic advantages, organic materials also possess low specific weight and are mechanically flexible—properties that are desirable for a solar cell.

In the following we will demonstrate that the mechanical and electrical properties of the photoactive layer in plastic solar cells can be favorably determined by the casting conditions. In detail, the choice of the proper casting solvent, in our case chlorobenzene, allows us to nearly threefold the efficiency of these devices reported up to now. The results for the devices produced from chlorobenzene are compared to devices produced from toluene, which is, with respect to device efficiency, an excellent representative for all the other solvents reported in literature up to now. Figure 1 shows atomic force microscopy (AFM) images of the surfaces of MDMO-PPV(poly)[2-methyl,5-(3*,7** dimethyl-

octyloxy)]-p-phenylene vinylene):PCBM ([6,6]-phenyl C61 butyric acid methyl ester) blend films spin coated using either toluene or chlorobenzene. The molecular structures of the compounds are shown in Fig. 2. The images clearly show different surface morphologies. The surface of the toluene-cast film contains features with horizontal dimensions on the order of 0.5 μm. Measurements of the mechanical stiffness and adhesion properties of the surface (performed simultaneously as the topographic imaging) indicate that these vertical features have a chemical composition different than the surrounding valleys. Since such features are not observed in films of pristine MDMO-PPV spin coated from toluene, we assign them to be phase-segregated regions that contain

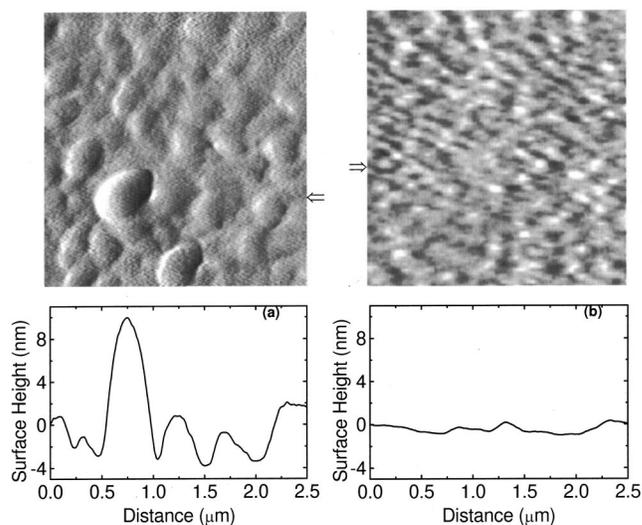


FIG. 1. AFM images showing the surface morphology of MDMO-PPV:PCBM (1:4 by wt.) blend films with a thickness of approximately 100 nm and the corresponding cross sections. (a) Film spin coated from a toluene solution. (b) Film spin coated from a chlorobenzene solution. The images show the first derivative of the actual surface heights. The cross sections of the true surface heights for the films were taken horizontally from the points indicated by the arrow.

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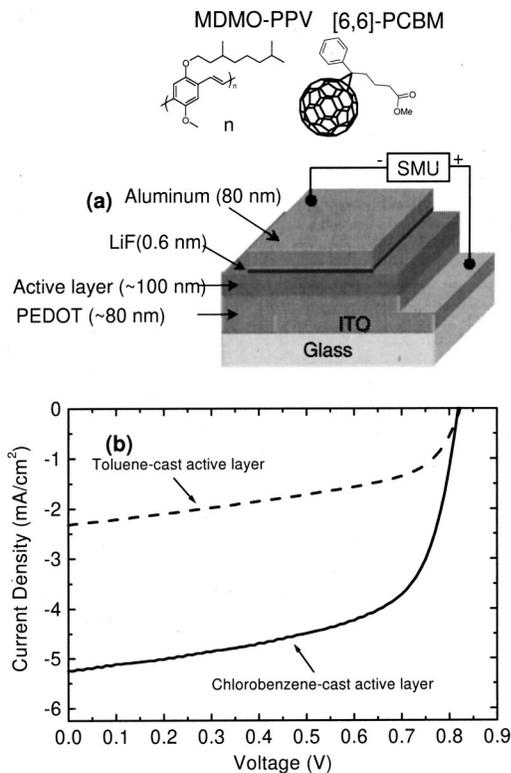


FIG. 2. Device structure, chemical structure, and characterization. (a) Device structure of the plastic solar cell and the chemical structure of the used compounds. The active area of the devices was typically $\sim 10 \text{ mm}^2$. (b) Characteristics for devices with an active layer that is spin coated from a toluene solution (dashed line): $J_{SC} = 2.33 \text{ mA/cm}^2$, $V_{OC} = 0.82 \text{ V}$, $FF = 0.50$, $\eta_{AM1.5} = 0.9\%$, and from a chlorobenzene solution (full line): $J_{SC} = 5.25 \text{ mA/cm}^2$, $V_{OC} = 0.82 \text{ V}$, $FF = 0.61$, $\eta_{AM1.5} = 2.5\%$. Data are for devices illuminated with an intensity of 80 mW/cm^2 with an AM1.5 spectral mismatch factor of 0.753. The temperature of the samples during measurement was 50°C .

different fullerene concentration. In contrast, the chlorobenzene-cast film contains structures with horizontal dimensions on the order of only $0.1 \mu\text{m}$. This indicates a much more uniform mixing of the constituents. Furthermore, the toluene-cast film has height variations on the order of 10 nm, whereas the chlorobenzene-cast film is extremely smooth, with height variations on the order of 1 nm. We attribute this contrast in film morphologies mainly to the fact that the solubility of PCBM in chlorobenzene is more than twice that in toluene.

To compare the impact of these different morphologies on the photovoltaic device performance, devices [see Fig. 2(a)] were fabricated in an identical manner except for the choice of solvent (either toluene or chlorobenzene) used for spin coating the active layer (MDMO-PPV:PCBM, 1:4 by wt.). The detailed production of these devices, which consisted in all cases of an indium tin oxide/PEDOT[poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)]/MDMO-PPV:PCBM/LiF/Al layered structure, is described elsewhere.⁹ A LiF/Al electrode was chosen instead of a pristine Al electrode in order to guarantee a good ohmic contact between the metal and the organic layer.^{10,11} Characterization of the devices was performed under illumination by a solar simulator. The AM1.5 conversion power efficiency $\eta_{AM1.5}$ of a photovoltaic device is given by

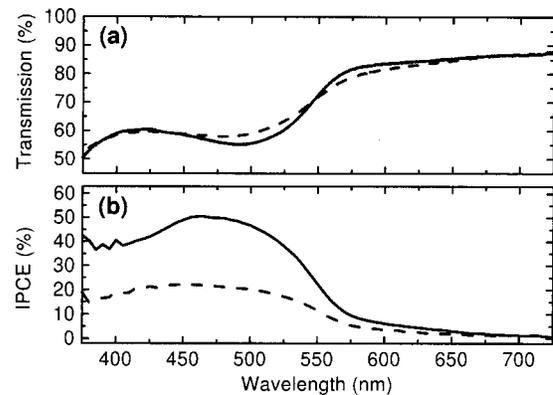


FIG. 3. (a) Optical transmission spectra of 100-nm-thick MDMO-PPV:PCBM (1:4 by wt.) films spin coated onto glass substrates from either toluene (dashed line) or chlorobenzene (solid line) solutions. (b) IPCE spectra for photovoltaic devices using these films as the active layer.

$$\eta_{AM1.5} = \frac{P_{out}}{P_{in}} m = FF \frac{V_{OC} J_{SC}}{P_{in}} m \quad (1a)$$

$$\text{with } FF = \frac{V_{mpp} J_{mpp}}{V_{OC} J_{SC}}, \quad (1b)$$

where P_{out} is the output electrical power of the device under illumination, P_{in} is the light intensity incident on the device as measured by a calibrated reference cell, V_{OC} is the open-circuit voltage, and J_{SC} is the short-circuit current density; m is the spectral mismatch factor that accounts for deviations in the spectral output of the solar simulator with respect to the standard AM1.5 spectrum and deviations in the spectral response of the device under measure with respect to that of the reference cell;¹² FF is the fill factor. For our measurements, $P_{in} = 80 \text{ mW/cm}^2$ and $m = 0.753$.

A plot of the current density versus voltage for the two devices is shown in Fig. 2(b). The open-circuit voltages of the cells are identical (0.82 V). However, the chlorobenzene-based device exhibits a more than twofold increase in the short-circuit current density as compared to the toluene-based device ($5.25 \text{ vs } 2.33 \text{ mA/cm}^2$). As shown in Fig. 3(a), the optical transmission spectra of the active layer films are nearly identical, except for a small redshift in the MDMO-PPV absorption (425–575 nm) in the chlorobenzene-cast film, as expected for the case of increased interchain interactions. Thus, the chlorobenzene-based device is much more efficient at converting photons to electrons. This is explicitly demonstrated in Fig. 3(b) in the plot of external quantum efficiency, or incident photon to converted electron (IPCE) ratio, as a function of wavelength. The fill factor also increases (0.50 vs 0.61) upon changing the solvent from toluene to chlorobenzene. The increased short-circuit current density and fill factor combine to yield a nearly threefold increase in the AM1.5 power conversion efficiency (0.9% vs 2.5%).

These enhancements seen in the short-circuit current density and the IPCE can be explained by an increased charge carrier mobility for both holes and electrons in the chlorobenzene-cast active layer. As illustrated above with the AFM images, the tendency of the PCBM molecules to phase segregate into clusters is suppressed when chlorobenzene is used as the solvent. Clustering of the PCBM molecules is

expected to decrease the charge carrier mobility for electrons, since the voids between the clusters present large barriers to the hopping process. Monte Carlo simulations of transport in a disordered medium have shown that the charge carrier mobility is very sensitive to inhomogeneous density variations of the hopping sites.¹³ The charge carrier mobility for holes is also affected by the morphology of the film, since the relative orientation of the conjugated polymer chains determines the degree of interchain interactions. This has been evidenced recently by theoretical studies on interchain interactions in conjugation polymers¹⁴ and experimental studies on conjugated polymer-based organic light-emitting diodes.¹⁵ The ability of the solvent to affect the degree of interchain interactions has been shown using light-scattering and spectroscopy experiments.¹⁶ It was determined for MEH-PPV, a conjugated polymer similar in structure to MDMO-PPV (poly[2-methoxy, 5-(2'-ethyl-hexyloxy-p-phenylene vinylene)]), that the polymer chains assume an open conformation, leading to a high degree of interchain interactions, in films spin coated using chlorobenzene. Recent results from field-effect mobility measurements (S.E.S., W. Geens, C.J.B., J. Poortmans, and N.S.S.) are in agreement with this. We find that the charge carrier mobility for holes in pristine MDMO-PPV is approximately one order-of-magnitude greater in films spin coated from chlorobenzene as opposed to toluene. The increase in the fill factor of the devices can also be explained by an increased charge carrier mobility, as well as the much smoother surface of the chlorobenzene-cast active layer that leads to better interfacial contact with the cathode. Taken all together, these results indicate that spin coating the active layer blend from a chlorobenzene solution has the fortuitous effect of simultaneously enhancing the morphological microstructures of both components that form the interpenetrating networks.

The IPCE plot in Fig. 3(b) shows a maximum value of 50% in the wavelength range of 460–480 nm. The efficiency for the conversion of absorbed photons to electrons in this device is extremely high. The light absorption of the device was measured (using a reflection geometry) to be less than 60% at 460 nm. This yields an internal quantum efficiency, or absorbed photon to converted electron, larger than 85%. Since the J_{SC} of the devices was measured to have a linear dependence on the incident light intensity for values up to 80 mW/cm², monochromatic power conversion efficiencies can be calculated from the IPCE data. Assuming $V_{OC}=0.82$ V and $FF=0.61$, this yields a power conversion efficiency of 9.5% at 488 nm for the chlorobenzene-based device.

In conclusion, we emphasize that the highly efficient photovoltaic device presented here is a synthetic, organic

light-harvesting system that converts absorbed photons to electrons with an efficiency approaching 100% at peak wavelength. Further work is needed to increase the open-circuit voltage, the fill factor, and the overlap of the spectral response with the sun's spectrum to achieve a power conversion efficiency that is approaching that of inorganic solar cells. However, these results demonstrate that organic photovoltaic devices can be a viable technology for future power generation.

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