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Polymer Photovoltaic Devices from Stratified Multilayers of Donor–Acceptor Blends**

By Lichun Chen, Dimitri Godovsky, Olle Inganas,* Jan C. Hummelen, René A. J. Janssens, Mattias Svensson, and Mats R. Andersson

The possibility that fully plastic flexible photovoltaic devices made of conjugated polymers and fullerene derivatives may be manufactured has recently been explored by a number of groups[1–5] in Europe and United States. Methods such as solvent casting, and inclusion in polymer matrices were applied to make large-area flexible devices.[6] Spin-coating from solution has been successfully applied to produce blend-based devices with the formation of so-called bulk heterojunctions in polymer/fullerene blends[5,6] as well as in polymer/polymer blends,[7,8] and lamination techniques have been used to obtain layered devices.[9] The conversion efficiency of these devices was substantially improved due to the enhanced interface area. Photoluminescence quenching due to photoinduced charge transfer is close to complete, but highly efficient collection of the photoinduced charges requires the ratio of the fullerene derivatives to conjugated polymer as high as 3:1.[1] The observation that photocurrent also originates by absorption of the two types of charge carriers from anode to cathode. While we have not yet obtained experimental and microscopic proof of this assertion, it is a plausible interpretation of a wealth of observations.

To prevent this problem, we could make a very large interface between donor and acceptor, while inducing direct contact of these phases with only one electrode; for the donor phase the anode and for the acceptor phase the cathode. This is not quite compatible with the more-or-less sharp interfaces found in bilayer photodiodes where a fullerene or other acceptor is evaporated on top of a polymer layer. If we wanted to make stratified but inter-diffused structures, a common solvent would hinder the utilization of these preparation methods for the fabrication of sharp multilayers. The application of special conditions during the spin-coating, however, makes it possible to obtain diffuse bilayer structures from soluble organic molecules and polymers. In this letter we present our attempts to combine the advantages of the interpenetrating network morphology in blends with the advantages of the bilayer structures, in order to obtain high fill-factor values in devices. This reflects the good conditions for charge collection and transport, which are essential for the realization of efficient polymer photovoltaic devices.

The MDMO-PPV is only slightly soluble in xylene at room temperature, but dissolves fully at 90 °C. The MDMO-PPV film spin-coated onto ITO glass substrate could not be dissolved by treatment in xylene at room temperature, and the thickness of MDMO-PPV film after this treatment was found to be the same as before, within experimental error. Thus the temperature-dependent solubility of MDMO-PPV and PCBM in xylene should allow us to make bilayer structures, by controlling the temperature of the [6,6]-PCBM-xylene solution used for the spin-coating on top of the MDMO-PPV layer. The side-groups of PCBM make it soluble in organic solvents (chloroform, xylene) and make it compatible with the conjugated polymer[1,12] in the nanoscale range. Since we prepare the photodiode structures by means of spin-coating PCBM dissolved in xylene on top of the MDMO-PPV layer at room temperature, a small amount of low molecular weight MDMO-PPV was dissolved in the xylene. This should lead to the formation of a diffuse interface, as the PCBM molecules penetrate the MDMO-PPV layer to some extent. This can be deduced from luminescence studies. The neat MDMO-PPV films have a strong luminescence if irradiated by monochromatic light (400 nm). The luminescence is totally quenched after deposition of a PCBM layer on top. As the thickness of the MDMO-PPV film was ca. 60 nm and the estimated exciton diffusion length in MDMO-PPV is ca. 10 nm,[13] if the interface between PCBM and MDMO-PPV is then sharp, then ca. 5/6 of the radiation caused by luminescence from MDMO-PPV layer should still be observed after the acceptor layer is deposited. The complete quenching of the luminescence shows that some of the PCBM molecules diffuse into the MDMO-PPV film and form an intermixed layer, similar in morphology to the interpenetrating donor–acceptor networks. This leads to a significant increase in the interface area between PCBM and MDMO-PPV. The embedded PCBM in the MDMO-PPV film can be partially removed if the bilayer sample is soaked in xylene; the luminescence from the MDMO-PPV film reappears, but its intensity is 5 times less than that from the untreated MDMO-PPV film. Thus we conclude that a fraction of the PCBM is left dissolved in the MDMO-PPV film, which is enough to still efficiently quench most of the lu-
minescence. The thickness measurement shows that the PCBM layer on top of the polymer can be taken away completely, while the thickness of MDMO-PPV layer remains the same, within experimental limits.

From these studies, we conclude that PCBM is included in the PPV layer upon spin-coating, and that a graded layer must be expected. The concentration as well as concentration gradient cannot be determined; however, the concentration is large enough to completely suppress photoluminescence, which is expected to occur at very low values.[1]

The external quantum efficiency (EQE) curves of the devices A–D (ITO/PEDOT-PSS/MDMO-PPV/PCBM/Al) and their individual film absorption were measured (Fig. 1). MDMO-PPV has a strong absorption in the region 400–600 nm with a peak at 510 nm, along with a small absorption peak at 340 nm. The absorption spectra of PCBM[12] is similar to that of C60, with the absorption peak at 340 nm and smaller peaks located at 420–500 nm and 550–720 nm, respectively. The EQE peak at 340 nm in the spectra of the bilayer films comes from the absorption by PCBM, while the broadened peaks at 450 nm–550 nm originate from combination of PCBM at 460 nm and MDMO-PPV at 510 nm. A small shoulder in the range 600–720 nm comes from PCBM absorption. At 650 nm, the EQE is 1.29 %, 0.47 %, 0.29 %, and 0.19 % for device A, B, C, and D respectively, thus giving the relative measure of the PCBM contribution to the EQE in different devices. By decomposition of the EQE peak located at 450–550 nm into the one at 480 nm from PCBM and 510 nm from MDMO-PPV, we can also say that the contribution of PCBM to photocurrent decreases in a row from device A to device D.

The same trend can also be seen from dark current plots of devices. The rectification ratio for the dark current at ±1.5 V is 35, 230, 450, 245, and 12 in a row from devices A to E (Fig. 2). At 1.5 V forward-bias dark current is $6.3 \times 10^{-6}$, $6.5 \times 10^{-5}$, $2.1 \times 10^{-4}$, $3.2 \times 10^{-3}$, and $9.4 \times 10^{-2}$ A/cm$^2$ for device A, B, C, D, and E, respectively. This dramatic change of transport conditions by four orders of magnitude under forward bias is correlated to the thickness of the PCBM layer, varying among device A–E. We consider that the diffusion of PCBM into the MDMO-PPV layer should be rather similar under these deposition conditions, and that the concentration gradient as well as concentration will not vary much between devices A–E. We therefore attribute the decrease in current to the formation of layers of PCBM on top of a PCBM-soaked polymer layer. The characteristics of the dark current show the bulk limitation at forward current, decreasing in devices A–C and disappearing completely in device D and E. This suggests that the bulk transport limitation is due to the PCBM layer, which is decreasing in thickness in devices A–E: the higher the amount of solid in the spin-coating solution, the thicker the layer. The presence of a layer on top is also verified by removal of that layer during solvent soaking of samples (vide supra). The pure PCBM layer limits electron transport.

The fill-factor ($\eta$) is another parameter that determines device performance and influences energy conversion efficiency:

$$\eta = \frac{FF I_{sc}V_{oc}}{W}, \quad FF = \frac{IV_{max}}{I_{sc}V_{oc}}$$

(1)

where $W$ is the flow of solar energy and $FF$ is the fill-factor, which is defined as the maximal value of the product of photocurrent ($I$) and photo-voltage ($V$), normalized to the product of the short-circuit current ($I_{sc}$), and open-circuit voltage ($V_{oc}$). The $FF$ decreases by about 0.15–0.20 for devices A, B, and C, with an increase in irradiation intensity from $10^{-6}$ to $10^{-4}$ W/cm$^2$, but it decreases by less than 0.05 for device D (Fig. 3).
The linearity of the photocurrent-dependence on the light intensity may provide information about the recombination mechanism of the separated charge carriers. The irradiation wavelength was 500 nm with the intensity range $10^{-7}$ to $10^{-4}$ W/cm². The slope of the photocurrent–illumination relation in a logarithmic plot was 0.96, close to a linear relation. The linear relationship suggests small recombination effects.

There does exist, however, an interplay between rectification and harvested photocurrent. If a continuous pathway is formed by polymers touching both the cathode and the anode, they could conceivably lead to recombination of charge carriers throughout the whole device. Therefore there exists an optimal balance of thickness between the pure MDMO-PPV layer, MDMO-PPV/PCBM diffused layer, and pure PCBM layer, which maximizes the efficiency, balancing the tendency towards recombination, separation, and collection of charges at electrodes.

A further development of the diffuse interface idea is to use the acceptor PCBM with the addition of a small amount of polymer to provide hole pathways in the acceptor layer. We choose the POPT as such an addition with the ratio PCBM/POPT ca 5:1 by weight. This ratio was found to be optimal, and provides, as we assume, the interconnected hole pathways in the acceptor layer in consistence with predictions of the percolation theory. At the same time, from other studies, we expect during spin-coating from such bi-component solutions that we obtain self-stratified layers, with the higher polymer concentration at the bottom of the layer and higher acceptor-molecule concentration at the top of the film. In addition, if the two different polymers used here have highest occupied molecular orbitals (HOMOs) of sufficiently different energy, hole barriers might prevent recombination from occurring throughout the whole volume.

The dark current and photocurrent of the diode with the structure ITO/PEDOT/MDMO-PPV/PCBM:POPT(1:0.2)/Al under 780 W/m² are shown in Figure 4. The dark current is around one magnitude higher than that of device D without POPT. Under solar illumination conditions, the fill-factor is as high as 0.5. In this structure, the increased interface area is mainly in between POPT and PCBM, and thus the excitons formed in PCBM may be dissociated at the interface between PCBM/POPT, and separated holes are transferred to the anode by continuous pathways formed by POPT. An increase of POPT in the blend layer is expected to increase the interface between POPT and PCBM, but to dramatically reduce the rectification of dark current and also the open-circuit voltage. The energy-conversion efficiency drops to 0.024 % in the device with POPT:PCBM (1:0.5). The increased concentration of POPT may isolate the PCBM phases from the cathode and reduce the efficiency of charge collection.

The increased contribution of PCBM in the EQE dependencies, in comparison with the devices without POPT, can be clearly observed in the EQE spectra as shown in Figure 1. The EQE at 650 nm is about 10 times higher than those of devices C and D. The enhanced EQE and extended spectral coverage lead to the increase of the short circuit photocurrent reaching $9.6 \times 10^{-4}$ A/cm² under 780 W/m² irradiation conditions. The open-circuit voltage is 0.78 V and the energy conversion efficiency is 0.5 %.

Thus by means of the use of special conditions during spin-coating of PCBM on top of the MDMO-PPV, as well as by adding a small amount of POPT to the PCBM–xylene solution, we succeeded in improving the energy conversion efficiencies by a factor of 4–5 in comparison with the homogeneous blends of the same materials. We attribute this improvement to the peculiar morphology of our structures; in particular, the diffuse interface, which combines a large donor–acceptor interface area with the conductive-pathways ge-
ommunity suitable for proper charge collection under solar illumination conditions.

In the long road towards producing organic-based devices useful for photovoltaic energy conversion, far beyond landmarks such as sensitized TiO₂ cells, polymers offer easy manufacturing but so far low conversion efficiencies. We have fabricated polymer photovoltaic devices based on stratified spin-coated films of acceptor (PCBM) on top of a donor (MDMO-PPV), thus forming a diffuse junction due to the partial dissolution of the bottom layer and intermixing during the spin-coating of the upper layer. External quantum efficiencies as high as 25–30% between 400 and 550 nm were obtained, and the energy-conversion efficiency is 0.5% with a fill-factor equal to 0.5. The high energy-conversion efficiency and the high fill-factors are attributed to the morphology of the diffuse donor–acceptor interface, where PCBM is distributed throughout the MDMO-PPV, and POPT forms a continuous hole pathway in the PCBM layer.

**Experimental**

Poly[2-methoxy-5-(3,7′-dimethyloctyloxy)-1,4-phenylenevinylene], MDMO-PPV [14,17] was used as a donor, and a soluble methanofullerene [6,6]-phenylbutadiene (Poly[2-methoxy-5-(3,7′-dimethyloctyloxy)-1,4-phenylenevinylene], MDMO-PPV has molecular weight $M_w = 344,000$ g/mol, $M_n = 118,000$ g/mol, $D = 3.44$ as determined by size-exclusion chromatography against polystyrene standards using tetrahydrofuran (THF) as a solvent. A PEDOT:PSS (poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonic acid) (Baytron P, Bayer AG) layer was used as a polymer anode on top of indium tin oxide (ITO), and the MDMO-PPV layer was deposited on top of PEDOT:PSS by spin-coating from a hot solution of xylene.

## References


**A Sol–Gel-Derived Glass as a Fuel Cell Electrolyte**

By Masayuki Nomgami,* Hiromi Matsushita, Yoichi Goto, and Toshihiro Kasuga

Fuel cells produce a direct electric current by the reverse chemical reaction of water electrolysis, and they have attracted significant attention because of their ability to produce high energy without the emission of harmful pollutants. The hydrogen is dissociated into hydrogen ions (protons) and electrons in the anode of the electrolyte, and the electrons flow out through an external circuit to the cathode. This electron flow, that is, the direct current, can be used as energy when a load is connected. On the other hand, the protons move through the electrolyte to the cathode, where they react with electrons and oxygen to form water. There are a number of fuel cell design parameters with various objectives, usually distinguished by the electrolytes employed. A series of perfluorinated ionomers such as Nafion have received much consideration as possible electrolyte separators, as they have high protonic conductivities at low temperatures, if developed. Despite this, these compounds still have problems for practical use, because of their chemical and mechanical degradation during prolonged usage. Stable inorganic membranes with high protonic conductivities at low temperatures, if developed, would extend functionality beyond the limitation of organic films and have potential for various applications, but few reports are available on the preparation of these inorganic materials.5–7 We have been conducting a study of the prepa...