

Electrical and Photoelectrical Properties of Organic Photovoltaic Cells Based on poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C₆₁

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Abstract

Bulk-heterojunction photovoltaic structures based on P3HT-PCBM polymer blends were prepared by spin coating technique, using optical glass substrates covered with 30 nm thick ITO. The dark Current-Voltage characteristics of the ITO/P3HT/Al, ITO/PCBM/Al and ITO/P3HT:PCBM(1:1)/Al structures were measured. Their non-linearity and asymmetry were explain on the base of electro/organic semiconductor interface behavior. The measured spectral response of the cells revealed the features also observed in absorption spectra of the blends. A quantum efficiency of 28% was measured experimentally. The power conversion efficiency of the blend structures was higher than those of the single layer structures based on the ordinary P3HT and PCBM layer respectively .

Keywords: polymer blends, P3HT, PCBM, bulk-heterojunction

Introduction

Since Tang[1] first presented a thin film organic solar cell based on a donor-acceptor heterojunction two decades ago, tremendous effort has been invested in improving the power conversion efficiency (η) of organic photovoltaic devices. The first organic

photovoltaic cells were on Schottky type M_1 /Organic layer/ M_2 (M_1 and M_2 metals with different work functions, in such a way that one contact should be ohmic and the other one a blocking contact). In these structures the organic dye was the monomeric phthalocyanines, merocyanines, porphyrins, e.a, and the photovoltaic response is due to the separation of the photogenerated charge carriers in the built electric field present at the rectifying metal/semiconductor interface. The power conversion efficiency was small of the order of 10^{-2} % [2]. Using two-layered structures in which the photoactive region is the heterojunction between two organic layers, with complementary absorption spectra, the power conversion efficiency was increased with approximately two orders of degree [3]. Trying to enlarge the photoactive region three-layered structures were reported with an increased efficiency due to the number of sites for exciton dissociation [4]. Following the photovoltaic mechanism, an excitonic one, which takes place in this kind of cells, the structures based on polymeric blends, seem to be more promising for photovoltaic cells with relatively high efficiency about 4-5 %, but more cheap than the organic monomeric thin films [5]. Among the large range of polymeric materials tested as active layers, polymer-fullerene bulk heterojunction solar cells have shown promising perspectives because of the high quality of these materials in terms of mobility and thermal stability [6-10].

Here we present electrical and photoelectrical properties of organic photovoltaic cell based on poly(3-hexylthiophene) [P3HT], 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C_{60} [PCBM]. We stress the differences observed for the devices based on single components and those fabricated from blend of the above polymers.

Sample Preparation and Experimental Procedures

The anode has been patterned on ITO-coated glass, commercially available from Praezisions Glass und Optik (CEC020P). The cleaning of the substrates, prior to the deposition of the active layers, consisted in ultrasonication in acetone and rinsing in isopropanol and deionized water. Deposition of a buffer PEDOT layer (100 nm thick) by spin coating was done. Regio-regular P3HT and PCBM were purchased from Aldrich and used as received. The thicknesses of the fabricated devices were: 100 nm (P3HT), (PCBM), (P3HT:PCBM ,1:1 blend).

An Al top contact was deposited by vacuum thermal evaporation to complete the photovoltaic structures. The residual pressure in the chamber was 10^{-5} Torr and the

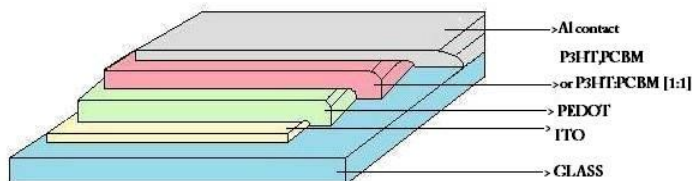


Fig.1 Structure of the photovoltaic cells based on P3HT, PCBM and P3HT: PCBM blend, respectively.

samples were maintained at room temperature during deposition. Across section through the

prepared samples is shown in figure 1.

Absorption spectra were recorded at room temperature using a UV-VIS Perkin-Elmer Lambda 35 Spectrophotometer. Action spectra were performed with a set-up consisting of a Cornerstone130 monochromator and a Keithley 2400 Source Meter, controlled by a computer. The current-voltage I - V characteristics of the cells, both in dark and under illumination with monochromatic light, corresponding to the maximum in action spectrum for each sample, were measured at room temperature. Moreover, the fourth

quadrant I - V characteristics were recorded under air mass 1.5 simulated solar illumination (100 mW/cm^2) using a Solar Simulator AM 1.5.

3. Experimental Results and Discussion

3.1. Experimental results for the ITO/PEDOT/P3HT/Al cells

Figure 2 shows the I - V characteristic of a typical ITO/PEDOT/P3HT/Al cell in the dark, at room temperature, for both forward and reverse bias. The forward bias

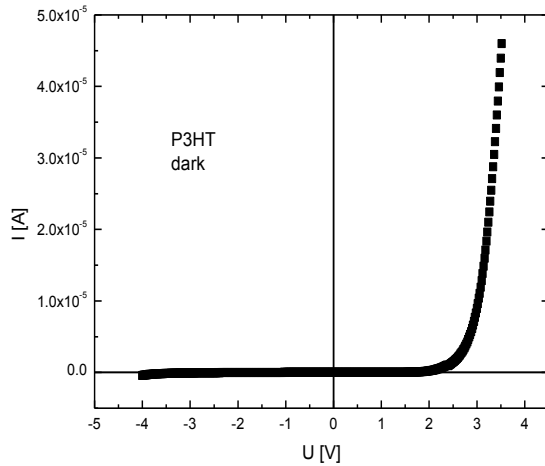


Fig.2 Dark I - V characteristic of a typical ITO/PEDOT/P3HT/Al cell.

conditions correspond to positive voltage on the ITO electrode with respect to the other one (Al). As seen in Fig. 2, the I - V dependence is highly asymmetric, with a rectifying factor ($R_R = I_f/I_r$ at the same voltage V), of about 500 at 3.5V.

We suppose that the asymmetry is due to the presence of a blocking contact (Schottky barrier) at the Al/P3HT interface, while the interface ITO/PEDOT/P3HT behaves like an ohmic contact.

Figure 3 shows the absorption spectrum of the P3HT layer together with the action spectrum of the short-circuit photocurrent of the ITO/PEDOT/P3HT/Al cell. Both spectra were obtained under illumination through ITO electrode. The maximum in the action spectrum (at 550 nm) is red-shifted as compared to the local maximum appearing at 512 nm in the optical absorption. A possible explanation is that at shorter wavelengths carriers' photogeneration is stronger near the PEDOT surface rather than deep in the bulk

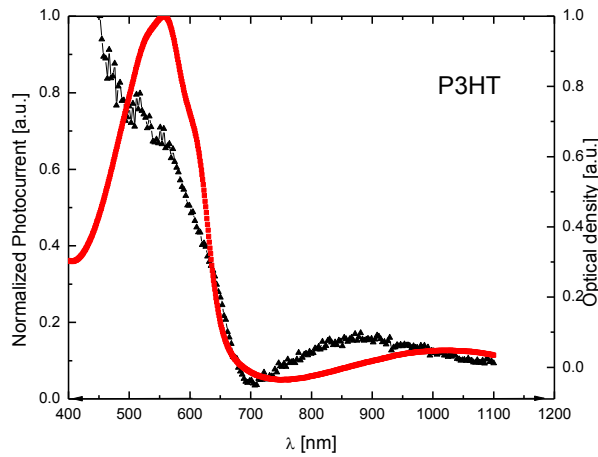


Fig.3 Photocurrent normalized to the power of the light source (black up-triangles) and the corresponding absorption spectrum of P3HT (red circles), in the case of ITO/PEDOT/P3HT/Al structure.

itself, through fundamental absorption mechanism, and the photovoltaic effect at ITO/PEDOT/P3HT junction is suppressed.

of the P3HT layer. Due to the inherent presence of defect states at the PEDOT/P3HT interface, this could lead to the recombination of the photogenerated carriers. Also at wavelengths shorter than 400 nm, incident photons are highly absorbed in the ITO/PEDOT electrode

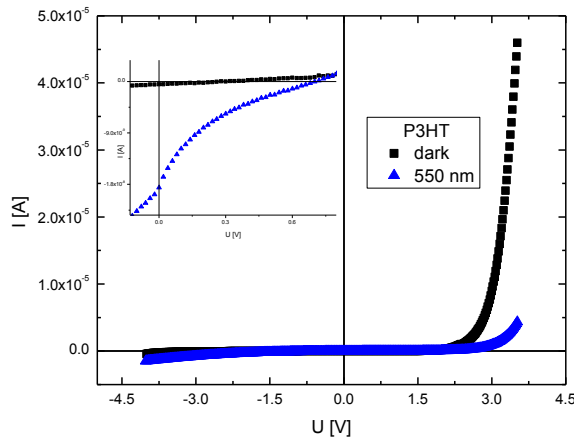


Fig.4 I-V characteristics of an ITO/PEDOT/P3HT/Al cell, in dark (black squares) and under 550 nm monochromatic light illumination (blue up-triangles). A detail of the fourth quadrant is shown in the inset.

of the parameters characterizing the photovoltaic response of the cell are $I_{sc} = 1.36 \times 10^{-7}$ A (the short-circuit current), $U_{oc} = 0.9$ V (the open-circuit voltage) and $FF = U_m I_m / I_{sc} U_{oc} = 16.7\%$ (the fill-factor).

3.2 Experimental results for the ITO/PEDOT/PCBM/Al cells

The dark I-V characteristics, at room temperature, for both forward and reverse

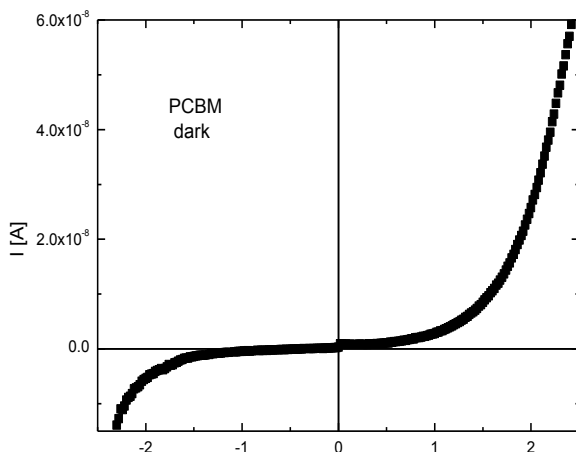


Fig.5 Dark I-V characteristics of a typical ITO/PEDOT/PCBM/Al cell

The fourth quadrant of I-V characteristic of the ITO/PEDOT/P3HT/Al cell, measured under illumination through ITO with monochromatic light at wavelength $\lambda = 550$ nm, corresponding to the maximum in the action spectrum is shown in figure 4. The values

bias, obtained for this sample are shown in figure 5. The forward bias conditions correspond to positive voltage on the Al contact with respect to the other one (ITO electrode). The I-V

dependence is asymmetric, with a rectifying factor R_R , of about 10 at 2 V. We suppose that the asymmetry is due to the presence of a blocking contact (Schottky barrier) at the ITO/PEDOT/PCBM interface, while the Al/P3HT interface behaves like an ohmic contact.

The optical absorption spectrum of PCBM film and the action-spectrum of I_{sc} of a typical ITO/PEDOT/PCBM/Al cell are plotted in figure 6. One can easily notice the anti-

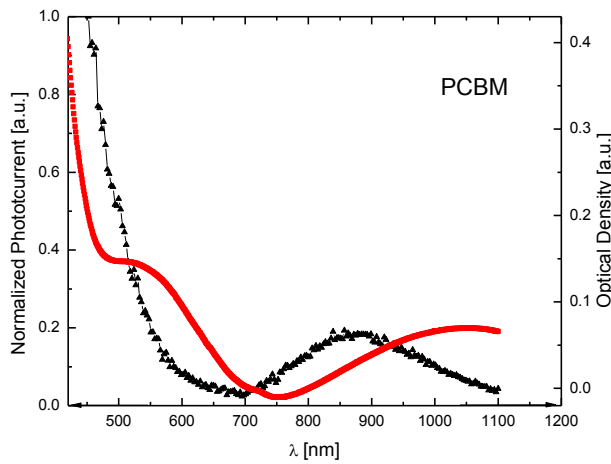


Fig.6 Photocurrent normalized to the power of the light source (black) and the corresponding absorption spectrum of PCBM (red), in the case of ITO/PEDOT/PCBM/Al structure.

far away from the PCBM/Al interface (photoactive region). Only photons slightly absorbed in the volume of organic layer will generate photocarriers in the region of the internal electric field (photoactive region), then participating to the photovoltaic response.

batic response of the PCBM layer, i.e., maximum photocurrent is obtained for photon energies where the absorption is at its minimum. This is due to the filtering effect of the PCBM film. The photons strongly absorbed in PCBM give rise to charge carriers

3.3 Experimental results for the ITO/PEDOT/P3HT:PCBM[1:1]/Al cells

The photovoltaic properties for the blend cells are by far better than those observed for single-layer cells. An asymmetric behavior was observed as well as in the case of the structures where P3HT and PCBM were the only active layers.

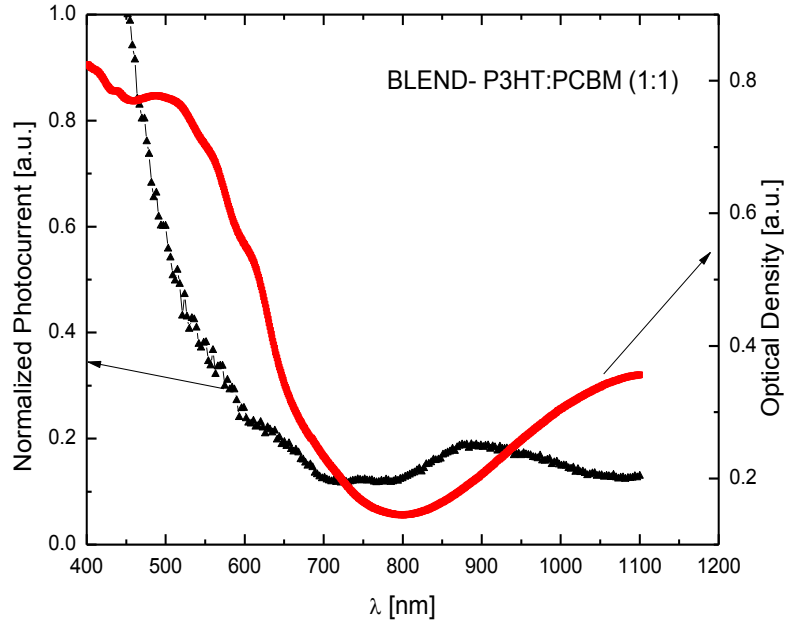


Fig.7 Photocurrent normalized to the power of the light source (black) and the corresponding absorption spectrum of P3HT: PCBM (1:1)(red), in the case of ITO/PEDOT/P3HT:PCBM(1:1)/Al structure.

The absorption spectrum of the P3HT:PCBM [1:1] layer together with the action spectrum of the short-circuit photocurrent of the ITO/P3HT:PCBM/Al cell is represented in figure 7. The maximum in the action spectrum (at 485 nm) is slightly red-shifted as compared to the local maximum at 455 nm in the optical absorption. Both spectra were obtained under illumination through ITO electrode.

The blend cell shows an improved (wider) spectral response as compared to the case of single layer cells (figure

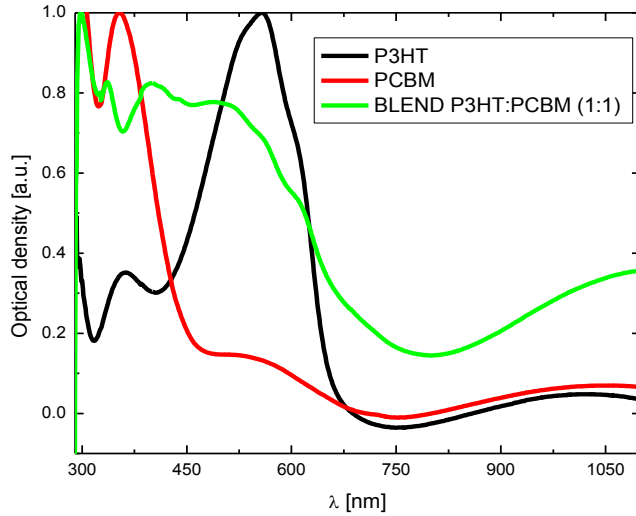


Fig.8 Action spectra of the 3 samples:P3HT(black line), PCBM(red line) and P3HT:PCBM[1:1] (green line)

8). The action spectrum of the blend P3HT:PCBM [1:1] has an absorption peak wide from 300 nm until 700 nm, containing the P3HT spectrum(450-700nm) and the PCBM spectrum (300-450 nm).

The fourth quadrant of I-V characteristics of ITO/PEDOT/P3HT:PCBM[1:1]/Al cell

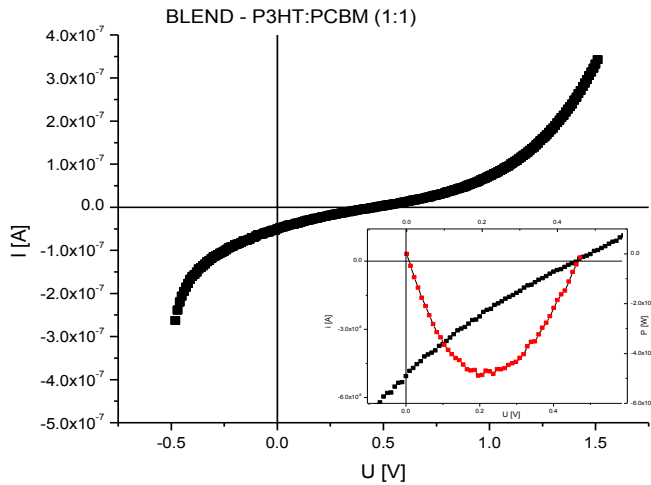


Fig.9 I-V characteristics of ITO/PEDOT/P3HT:PCBM(1:1)/Al measured by using a solar simulator AM 1.5. A detail of the fourth quadrant is shown in the inset-the incident power(red squares).

measured under illumination by using a solar simulator AM 1.5 and incident power P_{in} is showed in figure 9.

A value of 0.46 V was measured for the open-circuit voltage, while the short-circuit current was 2.24×10^{-8} A and the fill-factor was $FF=20.6\%$.

Conclusions

Polymer (P3HT, PCBM and their blend) based photovoltaic cells were produced by spin-coating technique. Their I-V characteristics were measured in dark and under monochromatic light and AM1.5 conditions. Junction parameters were extracted as well as the parameters characterizing the photovoltaic response. A good rectification ratio was obtained for all analyzed samples .

The sample containing P3HT only as active layer shows a photovoltaic response due, probably, to the Schottky barrier at Al back contact. A value of 0.9 V was measured for the open-circuit voltage, while the short-circuit current was 1.36×10^{-7} A; FF=16,7%.

Al/PCBM/PEDOT/ITO sample shows no photovoltaic response, acting simply as a photoresistance .

P3HT:PCBM (1:1) sample shows a promising photovoltaic response.

A value of 0.46 V was measured for the open-circuit voltage, while the short-circuit current was 2.24×10^{-8} A. A fill-factor of FF=20.6% was measured in this case. Currently, work is in progress, to improve the performance of the cells.

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