

INFLUENCE OF THE PEDOT-PSS LAYER ON THE PERFORMANCE OF THE PHOTOVOLTAIC DEVICES

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Abstract. An analysis of any peculiarities of the I–V characteristic of the glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4) organic photovoltaic cell, that are absent in the same characteristic of the glass/ITO/MEH-PPV:PCBM(1:4) cell, shows that the conducting PEDOT:PSS polymer layer contributes to the decreases of both the cell serie resistance (R_S) and global dielectric constant (ϵ_{cell}) as photodevice main electrical parameters. The R_S decrease with increasing of the forward voltage can be associated with the field-assisted emission (Poole-Frenkel effect) of electrons from the coulombic traps in p-doped PEDOT component of the PEDOT:PSS polymer layer. On the other hand, in light conditions, the PEDOT:PSS/MEH-PPV:PCBM(1:4) interface region generated by the interdiffusion of the two polymer layers chains, having the constanta dielectrica lower that than of each isolated polymer layers, improves an increase of the exciton diffusion efficiency by the FRET mechanisms predominantly intrachain in the active MEH-PPV polymer layer. The disposition of the PEDOT chains in their interface region favors also the transport of the photocarriers generated by exciton dissociation *via* intrachain hopping mechanism, improving the cell transport efficiency. The presence of PEDOT:PSS as buffer layer in the structure of the organic solar cell using the conjugated polymer MEH-PPV:PCBM(1:4) as active layer, improves the conversion performance by enhancement of its components, as hole collection, exciton diffusion, photocarrier mobility.

Key words: organic photovoltaic cell, I–V characteristic, equivalent electric circuit, series resistance, dielectric constant.

1. INTRODUCTION

The discovery of conductive polymer materials has revolutionized the technology of electronic and optoelectronic devices by using them as electrodes or as the photoactive film in photoluminescence and photoconversion devices. Due to their mechanical properties, such as flexibility, maneuverability and low cost prices, they have successfully replaced expensive traditional materials such as silicon, $A_{II}B_{VI}$ compounds, as the active film.

Initially, the conversion efficiency increase of solar cells using a single conjugated polymer as the active film, was achieved by designing them as multilayer systems, in which an important component is the heterojunction of the active polymer with an electron acceptor material, which controls the exciton dissociation processes generated by lighting the active polymer and rapid charge transfer at the interface of the two materials. Subsequently, extending the area of heterojunctions was achieved by using a material made from a mixture of two conjugated polymers, electron donor – acceptor [1]. Thus, the active polymer blend is itself a bulk heterojunctions distribution and for efficient electron transfer in solar cell, the active layer is in contact with a conductive layer, hole collector (for example the conjugated polymer poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate), PEDOT:PSS) [2].

Conversion efficiency performance of the solar cells based on conjugated polymer blends, depends on many factors, such as: photon absorption followed of exciton generation efficiency, large exciton diffusion length so that they can reach the donor-acceptor interface, decreasing the exciton quenching by fixing them at trap charge, separation, transfer and collector efficiency at the electrode, decreasing charge recombination loss such that to predominate free charge. All these factors can be controlled by the active film choice and the layered structure cell [3].

The most studied photoactive material used in solar energy conversion is the conjugated polymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV). This is photoactive by generating a large number of excitons in PPV and electron donor.

In order to achieve a bulk heterojunctions active layer, it is mixed with other conjugated polymer as acceptor, such as fullerenes ([6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and derivatives) [1–4]. The performance of the solar cell depends on both the nature of the acceptor and stoichiometry of the blend. It is known, that the fullerenes doping level induces changes of the interchain interactions in blended conjugated polymer. Highest doping levels (*e.g.*, 75 wt % PCBM or [1:4] stoichiometry) induce the segregation of the conducting emitter polymer (MEH-PPV) and low- dielectric fullerene matrix (PCBM) [5].

In this article, we present an analysis of the influence of PEDOT:PSS buffer layer, on the performance of the bulk heterojunctions photovoltaic cells based on emitting conjugated polymer MEH-PPV:PCBM(1:4). The analysis aims to process the I-V characteristic experimental data in order to evaluate the R_s of the cell with PEDOT-PSS as hole-collector layer, compared to the cell without PEDOT:PSS, as well as the ϵ_{cell} of this multilayer system compared with those of the equivalent series capacity of a system consisting from the same successive isolated layers. The observed difference is related to the properties of the both PEDOT:PSS layer and PEDOT:PSS/MEH-PPV:PCBM(1:4) interface region.

2. EXPERIMENTAL RESULTS

Evaluation of both the R_s and $\varepsilon_{\text{cell}}$ parameters was performing by processing the dark I - V characteristic of the multilayer organic solar cell with the structure glass/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al, shown in Fig.1a. By hatch are highlighted the ITO/PEDOT:PSS and PEDOT:PSS/MEH-PPV:PCBM(1:4) interface regions. In Fig.1b is presented the flat band energy-level diagram of ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al cell (adapted from [6]).

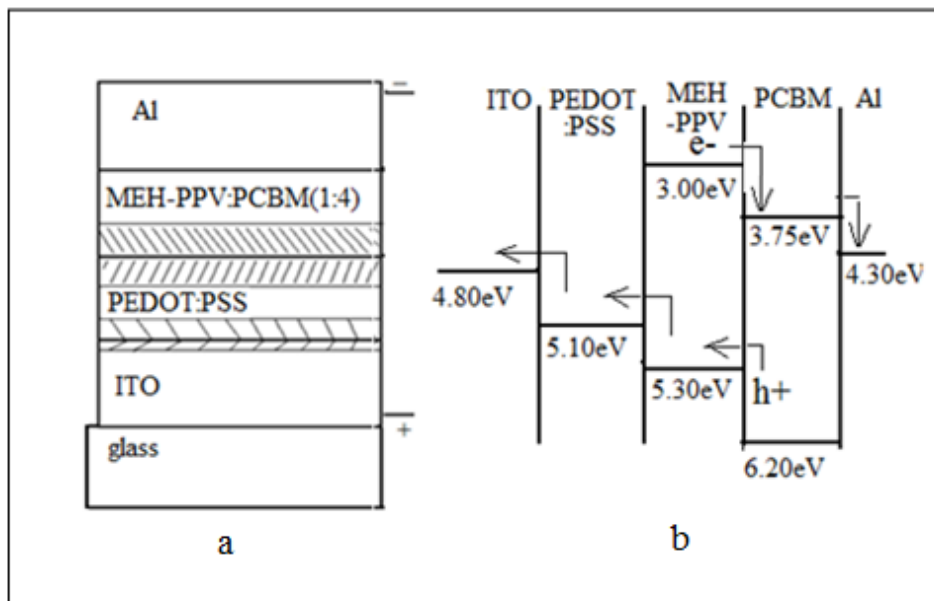


Fig. 1 – a) The layered structure of glass/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al; b) the flat band energy-level diagram of ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al cell (adapted from [6]).

Molecular structure of the conjugated polymers PEDOT:PSS, MEH-PPV and PCBM is shown in Fig. 2. It is known that the conductive PEDOT:PSS polymer layer controls the hole transport conditions, which he collects at the electron donor positions (Fig. 2a) of PEDOT component [7]. In PEDOT:PSS structure, PEDOT (conductor) and PSS (dielectric) chains are electrostatically bounds, so that using a solvent with highest dielectric constant enhances increase conductivity [7, 8]. At the contact with glass/ITO substrate, by the interdiffusion is generated an interface region with greater extension in the polymer layer, in which, by steric interactions, the flexible polymer chains attenuates the substrate

roughness, while at the contact with blended polymer MEH-PPV:PCBM (Fig. 2b,c) generates an interface region with considerable extension in both polymers layers and with specific properties. By interdiffusion PEDOT and MEH-PPV conductive chains, increases the proportion of the conductor phase, and their interface gets ohmic properties. Increasing of the conductive chains concentration favors the intrachain exciton transport mechanism [9].

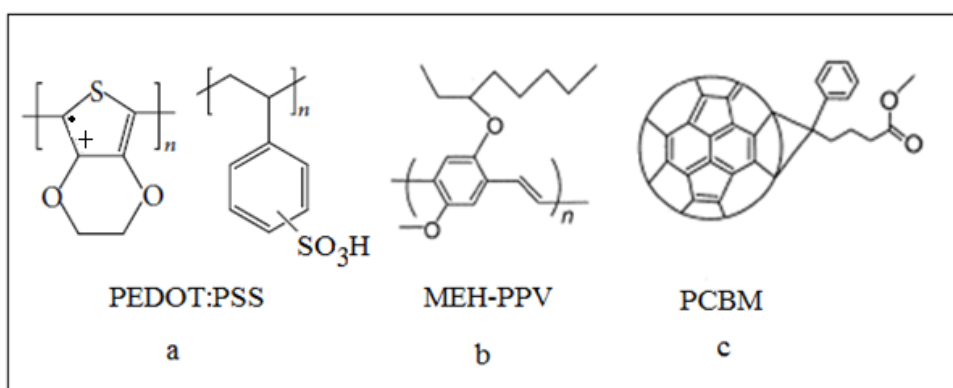
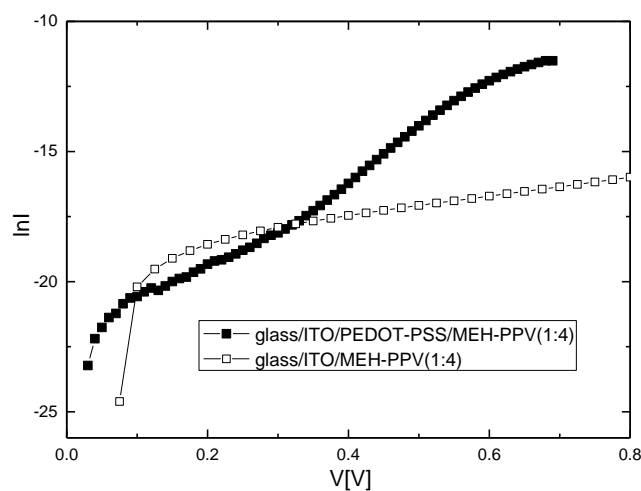


Fig. 2 – Molecular structure: a) conjugated polymer PEDOT:PSS;
b) conjugated polymer MEH-PPV;
c) fullerene PCBM.



a)

Fig. 3

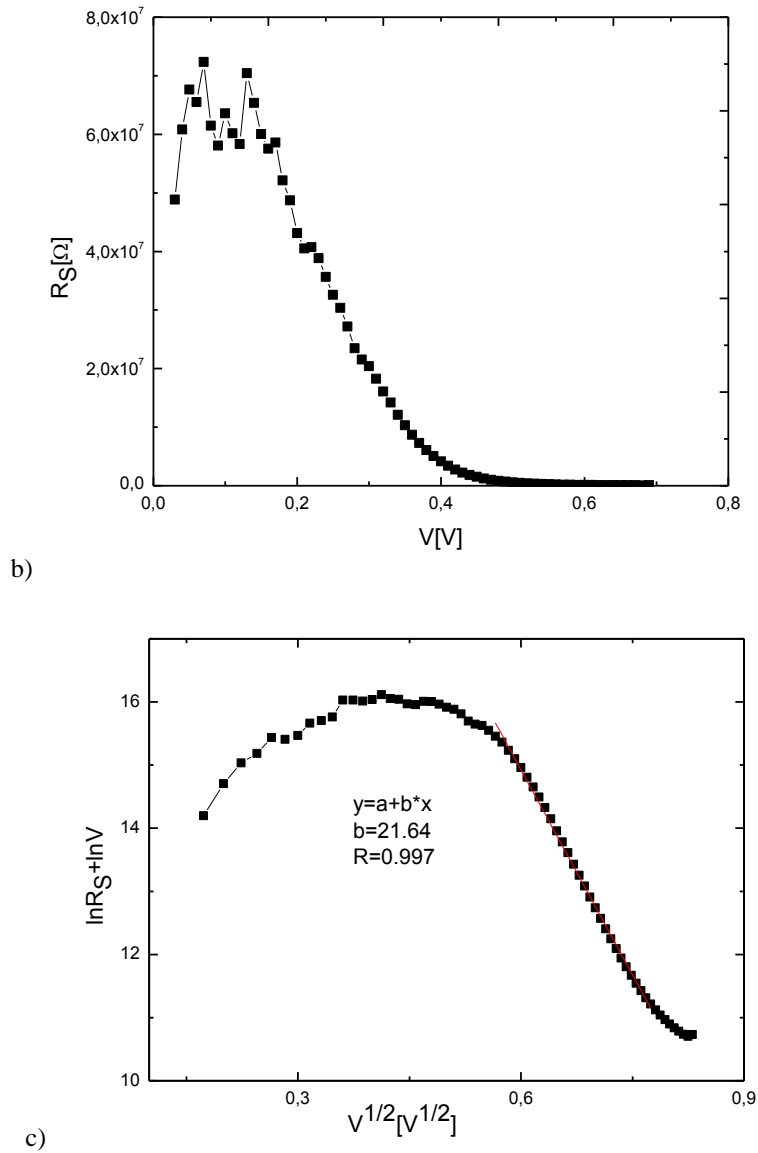


Fig. 3 (continued) – a) The forward bias $\ln I = f(V)$ plot of the glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al and glass/ITO/ MEH-PPV:PCBM(1:4)/Al cells; b) the evaluated $R_s(V)$ plot for the cell with PEDOT-PSS; c) Poole-Frenkel as $(\ln R_s + \ln V) = f(V^{1/2})$ plot.

Usually, the R_s parameter of the solar cell is determined from the deviation of the $\ln I = f(V)$ curve for the cell, from that of the ideal junction ($R_s = 0$) with the same components, for the same current, at forward bias. Figure 3a illustrates the

dependence of $\ln I = f(V)$ for both: the glass/ITO/PEDOT:PSS/MEH-PPV:PCBM(1:4)/Al and glass/ITO/MEH-PPV:PCBM (1:4)/Al solar cells, in dark conditions (experimental data I represents the current in A). For the cell without PEDOT:PSS, this dependence is uniform, nearly linear with a single slope, while for the cell with PEDOT:PSS the current has greater values and the same dependence is non-uniform, with a slope that changes with the increasing of applied voltage, suggesting that the R_s depends themselves on the applied voltage.

3. DISCUSSIONS

The usual procedure to characterize the current mechanism in the material system of the solar cell is to evaluate the discrete elements of the equivalent electric circuit that fits the measured current. It is known that the dependence of the current through the cell it is described by the equation:

$$I(V) = I_0 \exp \left[\frac{q(V - IR_s)}{nk_B T} \right] - I_{sc}, \quad (1)$$

where I_0 is the saturation current, n is the ideality factor characterizing the current mechanisms through the junction barrier, R_s is the series resistance defined as the bulk electrical resistance of the photoactiv medium plus the resistences of contacts on electrodes, I_{sc} is the short-circuit current, q is the electron charge, k_B is Boltzmann's constant and T is the temperature. If in equation (1) is taken in consideration the dependence $R_s(V)$, then we can obtain an expression of this dependency [10], which allows the determination $R_s(V)$ using the $I-V$ characteristic experimental data from Fig. 3a:

$$R_s(V) = \frac{1}{I} \left[V - V_0 - \frac{1}{\alpha} (\ln I - \ln I_0) \right], \quad (2)$$

where (V_0, I_0) is working point determined so that $R_s(V_0, I_0) \approx 0$ and $\alpha = \frac{q}{k_B T}$. Adaptation of the method proposed in [10] is possible if the injection of carriers can be neglected and $I_{sc} \approx 0$. The obtained $R_s(V)$ curve using $V_0 = 0.026$ V and $I_0 = 1.668 \times 10^{-11}$ A determined from Fig. 3a, is presented in Fig. 3b. This behaviour reflects the dependence of the cell conductivity on the applied field intensity, so that can be processed in the Poole-Frenkel effect formalism frame [11], namely an applied electric

field enhances an exponential current growth due to the diminution of the ionization energy of the electron traps,

$$I \sim Fe^{\left(\frac{-q(E_i - \sqrt{\frac{qF}{\pi\epsilon_0\epsilon_{cell}}})}{k_B T} \right)} \quad (3)$$

and consequently increases of their mobility by hopping transport activation,

$$\mu(F) = \mu_0 e^{\left(\frac{\beta_{PF}\sqrt{F}}{k_B T} \right)} \quad (4)$$

where E_i is the ionization energy in the electric field absence case, $F = \frac{V}{d_{cell}}$ is the electric field intensity, q is the electron charge, ϵ_{cell} is the dielectric constant of the whole cell, d_{cell} is the thickness of the cell, μ is carriers's mobility, ϵ_0 is the vacuum permittivity, q , k_B and T have the same above significance. The Poole-Frenkel coefficient β_{PF} has the expression:

$$\beta_{PF} = \sqrt{\frac{q^3}{\pi\epsilon_0\epsilon_{cell}}} \quad (5)$$

and can be evaluated from experimental data. Thus, taking into account that $R_s \sim \frac{1}{\mu(F)}$, for a given sample (traps concentration is constant), at constant temperature (here $T = 300K$), we obtain $\ln R_s = \ln Q - \ln V + \alpha\sqrt{V}$, where

$$\alpha = \beta_{PF} \frac{1}{d_{cell}} \frac{1}{k_B T} \quad (6)$$

and $\ln Q$ assembles all constants. Using the value of the slope $\alpha = \frac{\Delta(\ln R_s + \ln V)}{\Delta(\sqrt{V})}$ on linear decreasing portion of the curve from Fig. 3c, we obtain $\beta_{PF} = \alpha d_{cell} k_B T$.

Previous studies have shown that the conduction mechanism in PEDOT:PSS is thermally activated both in PEDOT:PSS [12] and in MEH-PPV:PCBM(1:4) [6], so that is plausible hypothesis about the existence of a

localized states distribution. For the used cell, the anode is ITO layer, and the cathode is Al film, so that the propagation region consists from PEDOT:PSS and MEH-PPV:PCBM(1:4) layers, Fig. 1b. Using (5) in (6) we can extract the experimental value for ϵ_{cell} . Taking into account the cell geometry ($S = 2 \text{ cm}^2$ and each layer has the same size $d \sim 50 \text{ nm}$), with $d_{cell} \sim 100 \text{ nm}$, we obtain $\beta_{PF} = 22 \times 10^{-5} \text{ eV} \cdot \text{V}^{1/2} \cdot \text{m}^{1/2}$ and $\epsilon_{cell} \sim 0.2$. These values characterize high conductive materials. For comparison, for metal, *e.g.* Al, $\epsilon_{Al} = n_{Al}^2 = 0.587^2 = 0.345$, while for semiconductor, *e.g.*, for wide band gap nano-SnO₂ polycrystalline film [11], $\beta_{PF} = 3.76 \times 10^{-5} \text{ eV} \cdot \text{V}^{1/2} \cdot \text{m}^{1/2}$.

To highlight the influence of PEDOT: PSS polymer layer and of its interfaces on the dielectric properties of the cell, it is useful to compare the experimental value with the calculated dielectric constant, for the same dielectric consisting from PEDOT-PSS and MEH-PPV:PCBM(1:4) layers, starting from the equivalent series capacity of the isolated layers (neglecting the interfaces) capacities [13], so that:

$$\frac{1}{C_{cell}^{calc}} = \frac{1}{C_{PEDOT:PSS}} + \frac{1}{C_{MEH-PPV:PCBM}}. \quad (7)$$

Because all capacitors have the same surface, and the layers have approximately the same thickness, we can write:

$$\frac{2}{\epsilon_{cell}^{calc}} = \frac{1}{\epsilon_{PEDOT:PSS}} + \frac{1}{\epsilon_{MEH-PPV:PCBM}}. \quad (8)$$

where we have considered $\epsilon_{PEDOT:PSS} = n_{PEDOT:PSS}^2 = 1.5^2$ [14], and $\epsilon_{MEH-PPV:PCBM(1:4)} = n_{MEH-PPV:PCBM(1:4)}^2 = 1.81^2$ [6]. We obtain $\epsilon_{cell}^{calc} = 1.98$. Considering ϵ_{cell} and ϵ_{cell}^{calc} respectively, we can compare the equalities:

$$\left(\frac{1}{\epsilon_{PEDOT:PSS}} + \frac{1}{\epsilon_{MEH-PPV:PCBM}} \right)_{\epsilon_{cell}^{calc}=1.98} \cong 1, \quad (9)$$

$$\left(\frac{1}{\epsilon_{PEDOT:PSS}} + \frac{1}{\epsilon_{MEH-PPV:PCBM}} \right)_{\epsilon_{cell} \approx 0.2} \cong 10. \quad (10)$$

We consider that the ITO layer capacity is not modified (or that the influence of their interface with PEDOT-PSS layer is insignificant). Results

that for the real cell, $\epsilon_{PEDOT:PSS}$ and $\epsilon_{MEH-PPV:PCBM(1:4)}$ have lower values than for corresponding isolated polymer layers.

In the real cell, the two layers are intertwined on a considerable length (like of polymer chains length), and have new dielectric properties. Lower values of the dielectric constant characterizes a high conductive material. This behaviour is possible if the interface region consists to large regions with high concentration of conductive chains of PEDOT and MEH-PPV. Another consequence of the lower dielectric constant of the PEDOT:PSS/MEH-PPV:PCBM(1:4) interface is the increase of the critical distance,

$$R_0 \sim \frac{1}{(\epsilon_{solv})^{\frac{1}{2}}}. \quad (11)$$

until the diffusion of the exciton generated in the active medium ($\epsilon_{solv} = \epsilon_{cell}$), it is possible through the fluorescence resonance energy transfer mechanism (FRET) [9]. On the other hand, considering the conductive properties [15], and polar character [8, 16] of both the PEDOT and MEH-PPV chains [17], it is possible that in the interface region, the dipole-dipole interaction to facilitate alignment of PEDOT and MEH-PPV chains. In these conditions, the diffusion of the exciton generated in MEH-PPV is predominantly intrachain and the transport of the photocarriers coming from the exciton dissociation is predominantly through intrachain hopping longways of PEDOT chains. Thus, both the exciton diffusion efficiency, and the transport of photocarriers to electrode, as factors of the cell conversion efficiency, can be improved if it can generate large regions with high concentration of PEDOT and MEH-PPV chains. In practice, this condition can be achieved by adding a polar organic solvent (sorbitol, ethylene glycol) during the deposition of PEDOT: PSS layer [16]. Dipole-dipole interaction with polar PEDOT layer, decreases the intensity of the electrostatic interaction between the PEDOT polar chains and the PSS hydrophilic chain [16,18]. The following aggregation of PEDOT chains generates regions with high concentration of PEDOT, in both the PEDOT-PSS layer and PEDOT-PS/ MEH-PPV:PCBM (1:4) interface.

4. CONCLUSIONS

Results of the analysis developed in this paper can be attributed to the influence of the PEDOT:PSS buffer layer on the electrical parameters of the glass/ITO/PEDOT: PSS/MEH-PPV:PCBM(1:4) solar cell, because it uses any peculiarities of the I - V characteristic, which do not occur for the same characteristic of the solar cell without the PEDOT: PSS layer. Decreasing of the series resistance with increasing of the forward voltage can be associated with the emission of the trapped electrons at p-doped PEDOT chain sites due to the diminution their ionization energy with Poole-Frenkel energy. Taking into account the conjugated polymer PEDOT:PSS structure (Fig. 2a), the released traps caused by electrons leaving, become acceptor traps for the holes, thus favoring the role of PEDOT: PSS layer as hole collector. On the other hand, the PEDOT:PSS/MEH-PPV:PCBM(1:4) interface region enhances the exciton diffusion efficiency in the emitting MEH-PPV:PCBM(1:4) layer. This interface is generated by the interdiffusion of the two polymer layers chains and has the dielectric constant lower than that of both the isolated polymer layers, so that improve the increase of the exciton diffusion efficiency by the FRET mechanisms predominantly intrachain in the active MEH-PPV layer. The disposition of the PEDOT chains in the interface region favors the transport of the photocarriers generated by exciton dissociation by intrachain hopping mechanism, improving the cell transport efficiency. The presence of PEDOT: PSS as buffer layer in the structure of the solar cell using the conjugated polymer MEH-PPV:PCBM(1:4) as active layer, improves the conversion performance by enhancement of its components as hole collection, exciton diffusion, photocarrier transport.

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