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EFFECT OF CNTS AND METAL-PHTHALOCYANINES ADDING ON THE PHOTO-ELECTRICAL BEHAVIOR OF THE PHOTOVOLTAIC STRUCTURES BASED ON POLYMERIC BLENDS

L. BASCHIR[a,b], S. ANTOHE[b], A.RADU[b], R. CONSTANTINEANU[b],
S. IFTIMIE[b,d*], I. D. SIMANDAN[b,c], M. POPESCU[c]
[a]*National Institute of Optoelectronics, INOE-2000 Bucharest-Magurele*
[b]*University of Bucharest, Faculty of Physics, Magurele-Ilfov, Romania*
[c]*National Institute for Material Physic,Magurele, Romania*
[d]*LPHIA Laboratory, LUNAM - Angers University, France*

Photovoltaic structures based on P3HT:PCBM(1:0.8) mixed with barium stearate (BS), carbon nanotubes (CNT) and different phtalocyanines (Coperphthalocyanine (CuPc), Zincphthalocyanine (ZnPc) and Magnesiumphthalocyanine (MgPc) were successfully prepared by spin-coating technique onto optical glass substrates covered with ITO and PEDOT:PSS. The goal of this study was to investigate the influence of barium stearate, carbon nanotubes and different small molecules of dyes mixed with the P3HT:PCBM ”conventional” blend on the photovoltaic response of the ”custom” obtained structures. The current-voltage characteristics were drawn in the dark and illumination and the external quantum efficiency was determined for each from the prepared samples.

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1. Introduction

In the last twenty years the organic photovoltaic cells (OPVs) were intensively studied because they present some important advantages like: low cost materials, non-toxic precursors, low mass and very cheap techniques to prepare large area of thin films and a good mechanical flexibility [1,2]. Even thought the start in the field of OPV was done on single and multiple layered structures based on small molecules of different dyes, the best results obtained in the last two decades were from the bulk heterojunction (BHJ) photovoltaic devices for which the power conversion efficiency (PCE) was in the range of 6-8% [3,4]. The most common mixture as active layer is related with poly(3-hexylthiophene-2,3diyl), a regioregular polymer, (P3HT) and [6,6]-phenyl C_{61} butyric acid methyl ester, a fullerene derivative (PCBM) [5-7]. Two important challenges are still in work for many research groups: the increase of power conversion efficiency and time stability [8]. To improve the photovoltaic cells PCE many methods were tried like the development of new materials which have a larger optical absorption than P3HT [3], morphology induced changes by thermal and chemical treatments [9-11] or the use of different electrodes and ”buffer” layers [12-15]. To obtain good performances for these kinds of devices a good correlation between the active layer thickness and the diffusion exciton length is required otherwise the charge carriers mobility decreases and the power conversion efficiency too [16]. Metallic nanoparticles or ZnO nanoparticles, mixed in the ”buffer” layers contributes to the increase of photovoltaic performances and also, improves the time stability [8,17,18]. On the other hand, metallic phtalocyanines and porphyrines have important properties like: a very good mechanical and chemical stability, high molar extinction coefficients for a very large part of solar spectrum, electron-donating or electron-accepting materials, and near IR optical absorption, that recommend

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[*] Corresponding author: sorina.iftimie@fizica.unibuc.ro

them for photovoltaic applications [19-26]. In turn, the carbon nanotubes having electron-accepting properties [27-29] can be incorporated in the OPVs architecture helping to improve the photovoltaic performances.

Taking into account these, in this paper barium stearate, carbon nanotubes and different phtalocyanines (ZnPc, MgPc and CuPc) were mixed with P3HT:PCBM ”conventional” solutions. The influence of metallic phtalocyanines on the current intensity in dark was studied and the external quantum efficiency (EQE) values were determined and compared. The carbon nanotubes and barium stearate addition also influenced the EQE values for the ”customized” devices.

2. Experimental

Barium stearate (BS) with carbon nanotubes (CNT) and different phtalocyanines (CuPc, ZnPc, MgPc) solutions were prepared using benzene as solvent, and stirred at 37 kHz for 1 hour to obtain a good homogeneity. These solutions were mixed with poly(3-hexylthiophene-2,3diyl) (P3HT, Aldrich Co.) and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM, Aldrich Co, 99.9% purity), 1:0.8 ratio, organic ones. The new solutions were deposited onto optical glass substrates covered with indium tin oxide (ITO, 40 nm), and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Aldrich Co.) thin films, 30 nm thickness. The ITO covered glass substrates were cleaned using acetone and isopropyl acid, for 15 minutes each. All the prepared solutions were deposited by spin-coating technique. Before the deposition of the active layer, the PEDOT:PSS thin film was dried for 24 hours at room temperature, in air, and after the active layer deposition a thermal annealing was performed, for 30 minutes at 70°C.

To complete the photovoltaic cells, in superstrate configuration, Figure 1, an aluminum (Al) back electrode (100 nm thick) was deposited over the active layer, by thermal vacuum evaporation (TVE). The residual pressure was constant during the process, 10^{-5} mbar.

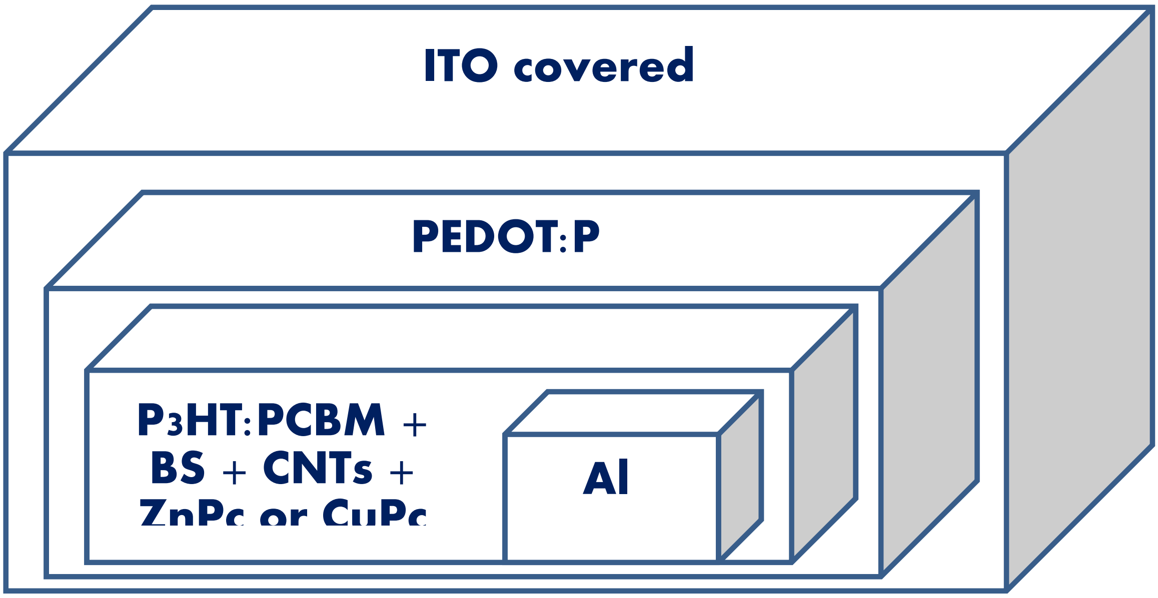

Fig.1. Schematic representation of the prepared samples.

The Glass/ITO/PEDOT:PSS/P3HT:PCBM(1:0.8)+BS+CNTs+Phtalocyanines (ZnPc, CuPc, MgPc)/Al obtained samples were electrical and photoelectrical characterized using an experimental setup, containing a Cornerstone 130 monochromator and a Keithley 2400 Source Meter, controlled by a computer. The current-voltage characteristics were drawn in dark and the external quantum efficiency (EQE) values were determined for all the prepared structures.

3. Results and discussion

The current-voltage (I-V) characteristics in dark for the prepared samples are presented in figures 2a, 2b and 2c. In figure 2a the I-V curves in dark for Glass/ITO/PEDOT:PSS/P3HT:PCBM(1:0.8) + BS + CNT + ZnPc/Al photovoltaic cells and for those having as active layer only the P3HT:PCBM(1:0.8) mixture were compared. All data were recorded at room temperature. The results obtained for the customized samples with barium stearate, carbon nanotubes and ZnPc show that the current intensity is two or three order of magnitude higher than the value obtained for the ”conventional” ones.

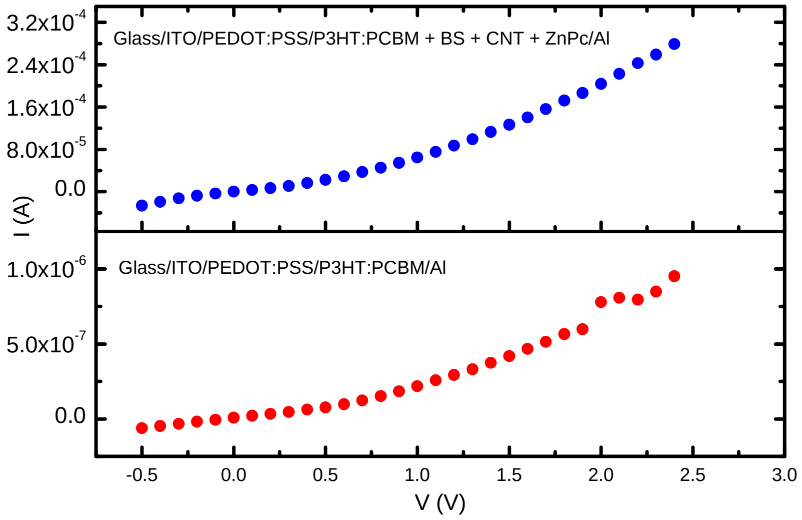

Fig.2a. I-V characteristics in dark for Glass/ITO/PEDOT:PSS/P3HT:PCBM + BS + CNT + ZnPc/Al and Glass/ITO/PEDOT:PSS/P3HT:PCBM/Al

The same behavior can be noticed also in the case of Glass/ITO/PEDOT:PSS/P3HT:PCBM + BS + CNT + CuPc/Al cells, Fig. 2c, but not for those with MgPc present in the mixture, Fig.2b. For Glass/ITO/PEDOT:PSS/P3HT:PCBM + BS + CNT + MgPc samples the current intensity in dark have similar values as for the ”conventional” ones photovoltaic cells, and the current-voltage characteristics is practically linear, without any asymmetry. The diagram band present in figure 3 confirms that the energy levels for ZnPc, MgPc and CuPc are relatively appropriate with LUMO (Lowest Unoccupied Molecular Orbital) and HOMO (Highest Occupied Molecular Orbital) orbitals of the P3HT and PCBM. This fact can be related with the increases of the current intensity in dark for samples having ZnPc and CuPc in the active layer mixture, because, on a hand, the ZnPc and CuPc have the HOMO very closely with that of PEDOT:PSS, than clearly improving the holes collection at ITO electrode, and on the other hand their LUMO are above the LUMO of PCBM assuring also a good collection of the electrons to Al electrode. Judging in these energetical terms (see figure 3), it is easy to observe that MgPc adding will have not a similar effect on the electrical behavior of the Glass/ITO/PEDOT:PSS/P3HT:PCBM + BS + CNT + MgPc samples.

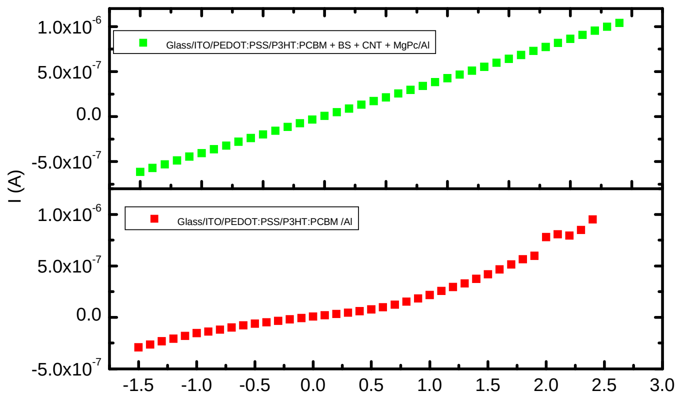

Fig.2b. I-V characteristics in dark for Glass/ITO/PEDOT:PSS/P3HT:PCBM + BS + CNT + MgPc/Al and Glass/ITO/PEDOT:PSS/P3HT:PCBM/Al

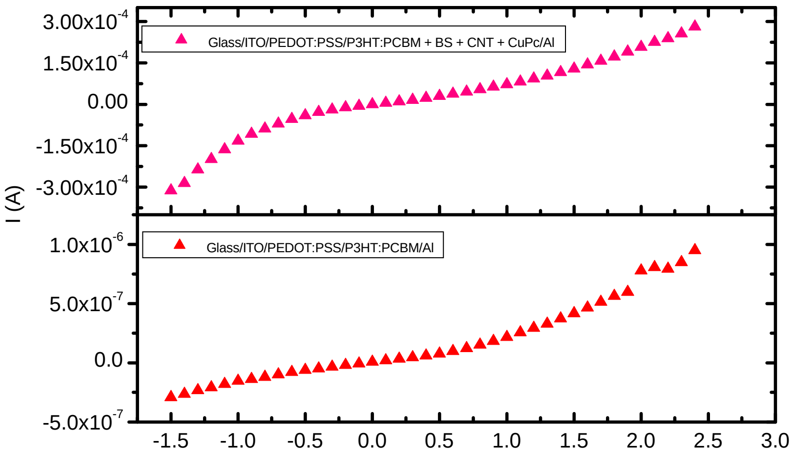

Fig.2c. I-V characteristics in dark for Glass/ITO/PEDOT:PSS/P3HT:PCBM + BS + CNT + CuPc/Al and Glass/ITO/PEDOT:PSS/P3HT:PCBM/Al

Concerning the presence of carbon nanotubes in the active layer, its effect cannot be neglected because of their strong donor properties and the easy way to associate with conducting polymers [30]. Practically the carbon nanotubes adding, distributed in the whole volume of the active layer, if their distribution will be ordered, should improve the transport of the photogenerated electrons trough the blend, then their collection to the Al electrodes too.

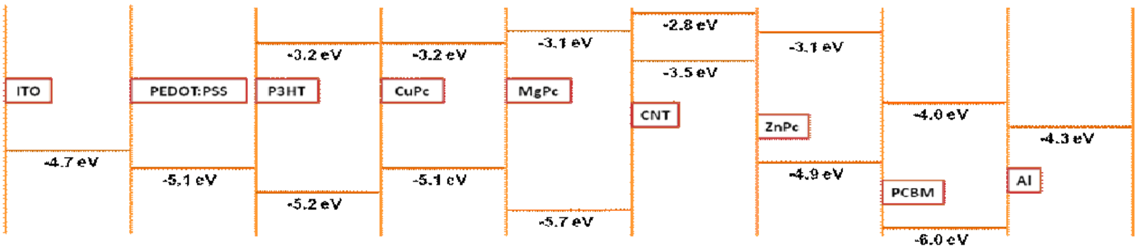

Fig.3. Diagram band for P3HT, PCBM, CNT and the used phtalocyanines

The external quantum efficiency (EQE) spectra for all the prepared samples are presented in figure 4.

The highest external quantum efficiency value, was obtained for Glass/ITO/PEDOT:PSS/P3HT:PCBM + BS + CNT + ZnPc/Al photovoltaic cells, around 18% at 430 nm, as comparing with the value of 3% obtained at the same wavelength, in the case of samples having just P3HT:PCBM blend as active layer. Also, the EQE maximum is slightly shifted to higher wavelength comparing with the values obtained for the others samples.

The Glass/ITO/PEDOT:PSS/P3HT:PCBM + BS + CNT + CuPc/Al photovoltaic cells have a small ”shoulder” around 430 nm and a large peak around 400 nm attributed to CuPc, then enlarging the action spectra with respect to those of single P3HT:PCBM blend cells.

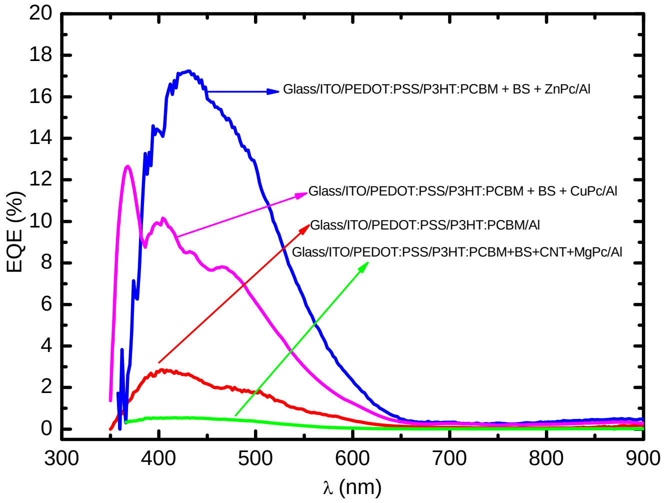

Fig.4. EQE spectra of the prepared photovoltaic cells

The smallest EQE values were obtained for the Glass/ITO/PEDOT:PSS/P3HT:PCBM + BS + CNT + MgPc/Al structures values even smaller than for those obtained for the photovoltaic cells having P3HT:PCBM as active layer.

This can be explained in a similar approach with that used above to explain the electrical behavior of these samples, but also we will try to add to those other relevant comments.

First, it is important to note that the diagram band from Fig.3, confirms that the magnesiumphtalocyanine band gap has a larger value (2.60 eV) comparing with the values for ZnPc (1.80 eV) and CuPc (1.90 eV). This fact shows that it is not so good absorber for the common range of the absorption of the other components from the structure. Also, it’s very high HOMO does not qualify it as good donor. All these factors can be responsible for the small value of EQE in the case of structures containing MgPc as adding in the whole organic absorber.

Second, the two pristine solutions, P3HT: PCBM in chlorobenzene and BS + CNT + Phtalocyanines in benzene, were mixed together and only stirred to obtain a good homogeneity, and in this case we must notice that the chemical affinity between components becomes important. In most of the cases the metal phtalocyanines simply mixed with P3HT:PCBM solutions decrease the P3HT crystallinity [31]. Taking into account also that the external quantum efficiency values for those samples having MgPc mixed in the active layer (see Fig.4) was smaller than for photovoltaic cells based on P3HT:PCBM, a possible explanation can be related with a poor chemical affinity between MgPc and the other components or the formation of big clusters that one a hand block the optical absorption, and on the other hand increases the scattering of the charge carriers, then decreasing their mobility.

4. Conclusions

Photovoltaic cells based on polymers blends customized with barium stearate, carbon nanotubes and different phtalocyanines were prepared onto optical glass substrates, using ITO as TCO. The electrical measurements showed that the ZnPc and CuPc dispersed uniformly in the active layer mixture improve the current intensity in dark and at illumination, increasing also the external quantum efficiency of the bulkheterojunction polymeric cells. The presence of carbon nanotubes should facilitate the charge carrier's transport in the polymeric blend, but just if the carbon nanotubes will be uniformly distributed in the whole volume of the blend. This is not possible using the spin coating technique for the thin films deposition. For Glass/ITO/PEDOT:PSS/P3HT + PCBM + BS + CNT + MgPc/Al samples, current intensity in dark has similar values as for P3HT:PCBM active layer ones, and, moreover, the EQE values are smaller than these "conventional" devices. In the paper the authors tried to explain from physical point of view the behavior of each prepared structure.

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