

## PHOTOVOLTAIC STRUCTURES BASED ON BIOLOGIC/POLYMERIC SEMICONDUCTING THIN FILMS

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Photovoltaic cells based on biologic (Chlorophyll-a, Chl-a) and polymeric (poly(3-hexylthiophene-2,5-diyl), P3HT, and [6,6]-phenyl-C61 butyric acid methyl ester, PCBM) thin films were prepared and characterized. Two types of structures were fabricated, either with a bi-layer Chl-a/P3HT:PCBM(1:1, wt.%) or a single layer Chl-a:P3HT:PCBM(10:1:1, wt. %) design, the photoactive layers being deposited by spin coating technique. Their optical and photovoltaic properties were analyzed and compared with those of a bulk heterojunction P3HT:PCBM(1:1, wt.%) cell. Similar values were found for fill factor and open circuit voltage but an enlarged region of spectral response was observed in the case of the cells containing Chl-a. The short-circuit current measured in the case of Chl-a/P3HT:PCBM(1:1, wt.%) and Chl-a:P3HT:PCBM(10:1:1, wt.%) based cells was smaller than in the case of P3HT:PCBM(1:1, wt.%) cell.

(Received September 21, 2015; Accepted November 6, 2015)

*Keywords:* Organic photovoltaic cells, Chlorophyll-a, Polymeric blend

### 1. Introduction

The synthesis of conductive polymers [1] opened new perspectives in the field of organic-based photovoltaic cells. An important step was made at the beginning of the 1990s by introducing the bulk-heterojunction concept [2-3] that refers to a mixture between two organic materials with different energetic parameters (ionization energy or electronic affinity) tuning their behavior as donor or electron acceptor. Three important steps are required to convert solar energy into electricity: (a) absorption of incident photons, (b) charge carriers separation and (c) collection to electrodes. Organic materials can absorb solar light in the range of 400 – 700 nm, which represent about 60% of the whole solar energy range [4]. In organic molecules the exciton diffusion length is usually smaller than 100 nm and donor domains must have similar characteristic lengths to maximize the charge carrier's collection and to stop recombination processes. Thus, the morphology of the structure becomes important, since it affects the carrier's transport from acceptor and donor domains to electrodes [5-8].

Experimental [9-10] and theoretical [5] studies on photovoltaic cells based on polymeric thin films proved that good photovoltaic performances are obtained for a mixture between poly(3-hexylthiophene-2,5-diyl) (P3HT), as donor, and [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) as acceptor. P3HT is one of the most stable organic polymers, with relatively low ionization energy, behaving as good donor of electrons. The difference between HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) is 2.10 eV [11-

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12], making it a good absorber in the visible range. PCBM is a fullerene derivative with relatively high electron affinity, behaving as good acceptor of electrons, with the HOMO-LUMO energy difference of 2.4 eV [9], [13].

Plants are suitable, low-cost and abundant sources for natural dyes which act as sunlight harvesters. A natural photo-active molecule of particular interest is chlorophyll-a (Chl-a), a natural porphyrin, the key molecule in the photo-synthesis process, which has a great potential for solar cell applications [14-21]. Despite the power conversion efficiencies of Chl-a based photovoltaic cells still being small [22] as compared to other similar structures [23], this type of devices can be good candidates for cheap, environmentally friendly and easy to fabricate photovoltaic cells. Here we report our results on fabrication and characterization of hybrid biological/polymeric photovoltaic structures based on Chl-a and P3HT:PCBM(1:1, wt.%) polymeric blend, in the configuration glass/ITO/PEDOT:PSS/Chl-a:P3HT:PCBM(10:1:1, wt.%) /Al and glass/ITO/PEDOT:PSS/Chl-a/P3HT:PCBM(1:1, wt.%) /Al. Their performances are compared with those obtained for conventional bulk heterojunction P3HT:PCBM(1:1, wt.%) cells, in the configuration glass/ITO/PEDOT:PSS/P3HT:PCBM(1:1, wt.%) /Al. This study was motivated by our previous results demonstrating that by using materials with a tetrapyrrole ring [20], [25] the photovoltaic performances and stability in time of P3HT:PCBM based cells were improved [19], [24].

## 2. Experimental procedures

### 2.1. Materials

Biologic and organic thin film based photovoltaic cells were prepared by spin coating onto optical glass substrates covered with a thin indium tin oxide (ITO) layer. Spin coating, as a technique for thin film deposition, has many advantages related with homogeneity and easy processing of the films, but is deficient in terms of thickness control.

ITO covered glass substrates, 8-12  $\Omega$ /sq, commercially available from Sigma-Aldrich Co. were ultrasonically cleaned in acetone, isopropyl alcohol and deionized water, 15 minutes each procedure. The band offset diagram of materials used in this study is presented in figure 1. A poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) thin film was used as buffer layer at the front transparent ITO electrode.

The configuration of the layers in the fabricated devices is presented in figure 2. Chl-a was prepared from spinach leaves as described in [25] and deposited as thin film from a stock solution (90 mg Chl-a in 1 mL chloroform), by spin coating technique in two steps: 500 rpm/10 seconds and 1000 rpm/15 seconds. P3HT and PCBM (Sigma Aldrich Co.) were mixed in dichlorobenzene (1:1, wt.%) and deposited by the same technique, in two steps: 650 rpm/60 seconds and 1500 rpm/5 seconds. Chl-a:P3HT:PCBM(10:1:1, wt.%) layer was deposited from a solution of Chl-a, P3HT and PCBM in dichlorobenzene. To complete the photovoltaic cells, a thin aluminum back electrode layer was deposited by thermal vacuum evaporation (TVE).

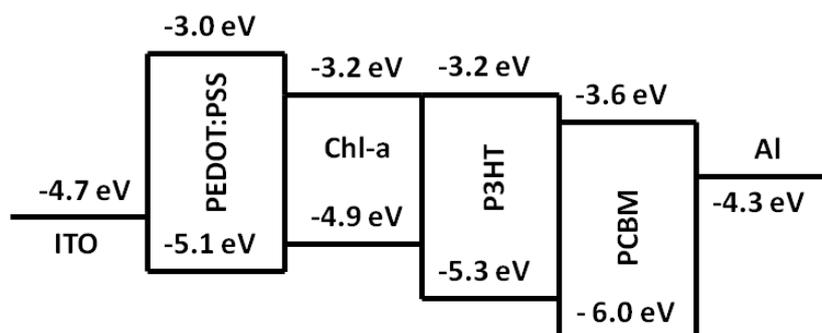


Fig.1 Band offset diagram for materials used in our cells [26].

|           |                 |           |
|-----------|-----------------|-----------|
| Al        | Al              | Al        |
| P3HT:PCBM | Chl-a:P3HT:PCBM | P3HT:PCBM |
| PEDOT:PSS | PEDOT:PSS       | Chl-a     |
| Glass/ITO | Glass/ITO       | PEDOT:PSS |
|           |                 | Glass/ITO |

Fig.2 Layer configurations of fabricated cells

## 2.2. Characterization techniques

The surface morphology of the films was characterized by atomic force microscopy (AFM, MDT Ntegra) in semicontact (intermittent contact) mode, and scanning electron microscopy (SEM, Tescan Vega XM). Absorption spectra of the thin films used as active layers were recorded in the 300 – 900 nm spectral range, at room temperature. Current-voltage (I-V) characteristics, in dark and AM 1.5 conditions, were recorded using a Keithley 2400 sourcemeter and a Newport Oriel solar simulator, at room temperature.

## 3. Results and discussions

### 3.1. Morphological features

Fig. 3 shows SEM micrographs of the deposited layers, while AFM images of the same samples are shown in figure 4.

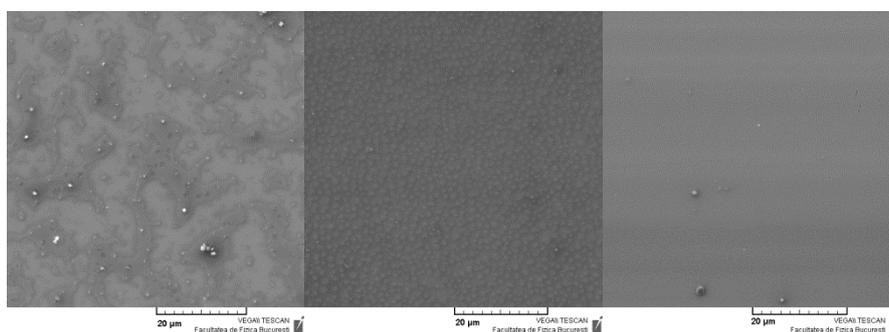


Fig.3 SEM images of the surfaces of glass/ITO/Chl-a/P3HT:PCBM(1:1, wt.%), left side, glass/ITO/Chl-a:P3HT:PCBM(10:1:1, wt.%), middle, and glass/ITO/P3HT:PCBM(1:1, wt.%), right side, thin films

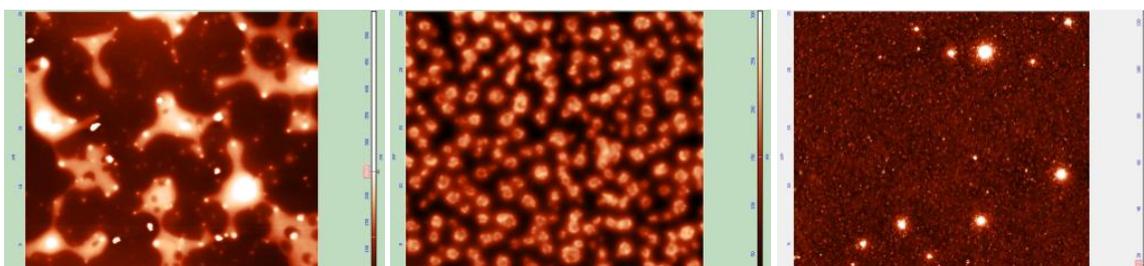


Fig.4 AFM images of the surface of glass/ITO/Chl-a/P3HT:PCBM(1:1, wt.%), left side, glass/ITO/Chl-a:P3HT:PCBM(10:1:1, wt.%), middle, and glass/ITO/P3HT:PCBM(1:1, wt.%) thin films. The scanned area was  $25 \times 25 \mu\text{m}^2$ .

Table1. Thickness and parameters characterizing the surface morphology of the analyzed samples. The values of the thickness were determined by X-ray reflectivity for all active layers.

| Active layer                  | Thickness (nm) | R <sub>a</sub> (nm) | R <sub>RMS</sub> (nm) |
|-------------------------------|----------------|---------------------|-----------------------|
| Chl-a/P3HT:PCBM(1:1, wt.%)    | 206            | 43                  | 54                    |
| Chl-a:P3HT:PCBM(10:1:1, wt.%) | 277            | 47                  | 56                    |
| P3HT:PCBM(1:1, wt.%)          | 175            | 1.1                 | 2.4                   |

Roughness average, R<sub>a</sub>, and root-mean-square roughness, R<sub>RMS</sub>, values were determined from AFM scans and are summarized in Table1.

In the case of P3HT:PCBM(1:1, wt.%) AFM surface morphology parameters confirm the good miscibility between components. In the case of samples containing chlorophyll-a the surface is much more rough. Similar roughness values were obtained for Chl-a films deposited by spin coating on optical glass (not shown here). One can notice distinct domains on the surface of glass/ITO/Chl-a/P3HT:PCBM(1:1, wt.%), while the surface of Chl-a:P3HT:PCBM(10:1:1, wt.%) is more homogeneous.

### 3.2. Optical properties

For optical characterization, Chl-a/glass, P3HT:PCBM(1:1, wt.%) and Chl-a:P3HT:PCBM(10:1:1, wt.%) /glass thin films were prepared, following the procedures indicated above. Their absorption spectra, recorded at ambient temperature, are shown in figure 5. Typical absorption peaks of Chl-a can be easily seen at 670 nm (Q<sub>y</sub> band) and 435 nm (Soret band). For the blend P3HT:PCBM(1:1, wt.%) a large absorption band, from 500 to 700 nm, is observed, with a shoulder at 600 nm and a peak around 550 nm attributed to P3HT [27]. The absorption maximum corresponding to PCBM occurs at 500 – 530 nm [28]. The main feature of the absorption spectrum of the Chl-a:P3HT:PCBM(10:1:1, wt.%) mixture is the extension of the absorption band, covering almost entire visible region from 300 to 700 nm. This is important for photovoltaic applications.

### 3.3. Photovoltaic response

The action spectra of the external quantum efficiency (EQE) of the analyzed photovoltaic cells are shown in figure 6.

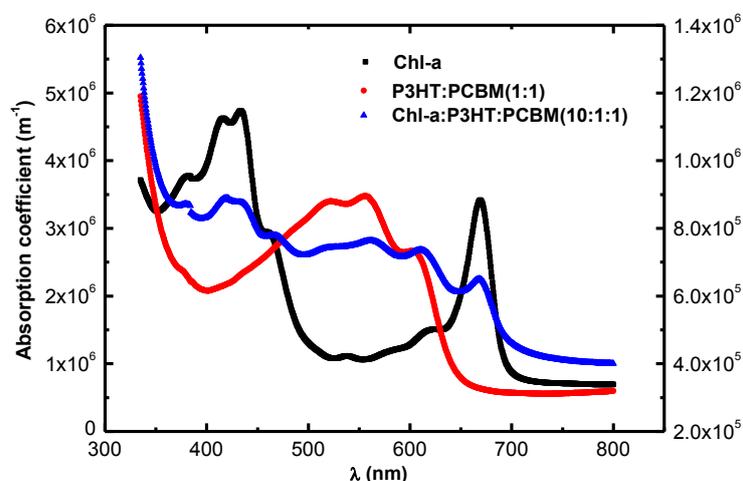


Fig.5 Absorption spectra of Chl-a, black squares, P3HT:PCBM(1:1, wt.%), blue triangles, and Chl-a:P3HT:PCBM(10:1:1, wt.%), red circles, thin films

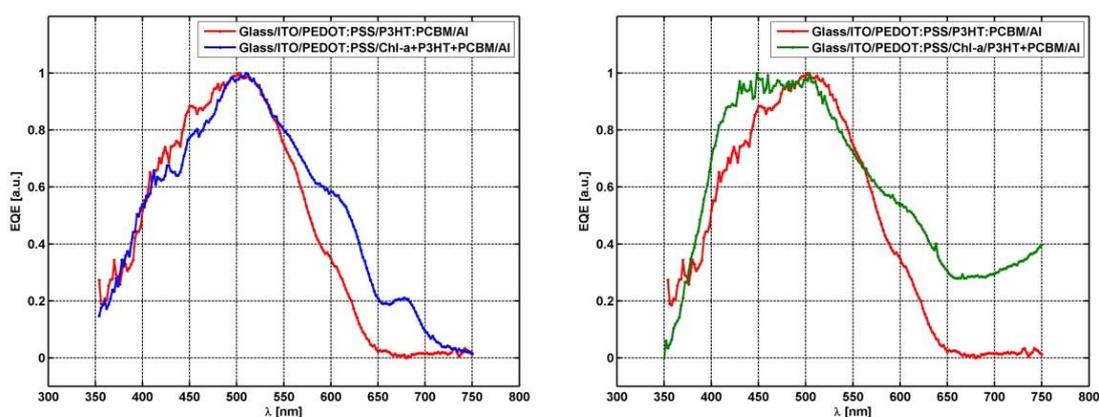


Fig.6 Normalized EQE spectra recorded for the cells having Chl-a:P3HT:PCBM(10:1:1, wt.%), blue curve – left side, and Chl-a/P3HT:PCBM(1:1, wt.%), green curve – right side, respectively, as active layers. For comparison purpose the normalized EQE spectrum of a cell based on P3HT:PCBM(1:1, wt.%) is also shown (red curve).

For both glass/ITO/PEDOT:PSS/Chl-a:P3HT:PCBM(10:1:1, wt.%) /Al and glass/ITO/PEDOT:PSS/Chl-a/P3HT:PCBM(1:1, wt.%) /Al structures the spectral response range was extended due to Chl-a absorption bands. The Chl-a peak at 680 nm is more visible in the EQE spectrum of the cell with the composite active layer, Chl-a:P3HT:PCBM(10:1:1, wt.%). It vanishes in the case of Chl-a/P3HT:PCBM(1:1, wt.%) structure, most likely due to recombination at Chl-a/P3HT:PCBM interface; the two layers are not well separated in this case and the films are not uniform, which may increase the density of recombination centers.

The fourth quadrant of current-voltage characteristics recorded in AM 1.5 conditions are shown in figure 7, and the photovoltaic parameters are summarized in Table2.

The cells have similar values for fill factor (FF) and open circuit voltage. However, the short-circuit current is significantly smaller in the case of the cells based on Chl-a:P3HT:PCBM(10:1:1, wt.%) and Chl-a/P3HT:PCBM(1:1, wt.%) active layers. This is mainly due to the non-optimized PEDOT:PSS/Chl-a interface which introduces an energy barrier for hole transport.

Table2. Photovoltaic parameters of the cells, measured in AM 1.5 conditions

| Active layer                  | $J_{sc}$ ( $\mu\text{A}/\text{cm}^2$ ) | $V_{oc}$ (V) | FF (%) |
|-------------------------------|--|--------------|--------|
| Chl-a/P3HT:PCBM(1:1, wt.%)    | 0.5                                    | 0.54         | 23     |
| Chl-a:P3HT:PCBM(10:1:1, wt.%) | 2.2                                    | 0.44         | 19     |
| P3HT:PCBM(1:1, wt.%)          | 631                                    | 0.54         | 25     |

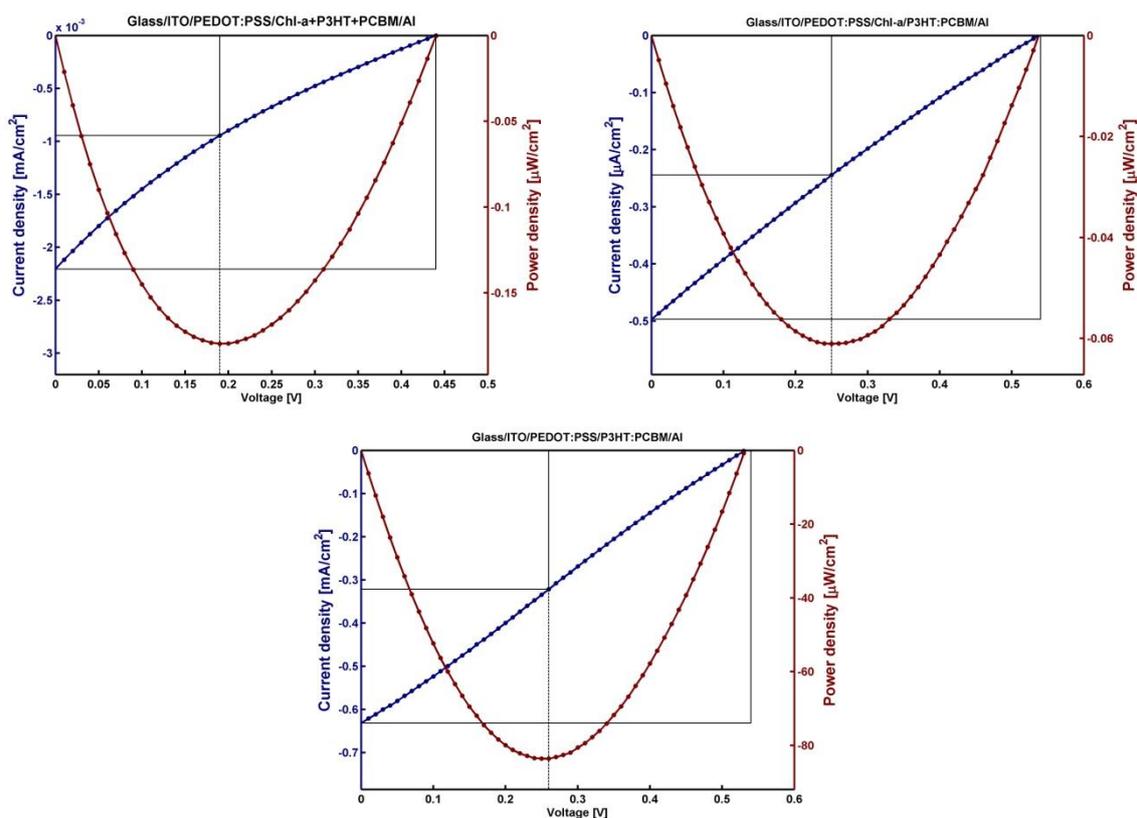


Fig.7 I-V characteristics measured in AM 1.5 conditions for glass/ITO/PEDOT:PSS/Chl-a:P3HT:PCBM(10:1:1, wt.)/Al, left side up, glass/ITO/PEDOT:PSS/Chl-a/P3HT:PCBM(1:1, wt.)/Al, right side up, and glass/ITO/PEDOT:PSS/P3HT:PCBM(1:1, wt.)/Al, center down, photovoltaic cells.

#### 4. Conclusions

Photovoltaic cells based on biologic (chlorophyll-a) and organic polymeric semiconductors (P3HT:PCBM mixture) were prepared by spin coating technique in different configurations and their performances were compared to that of standard prepared P3HT:PCBM based cells. Introduction of chlorophyll-a results in the extension of the spectral range of the photovoltaic response. The fill factors and open circuit voltages have similar values for all prepared samples; the short-circuit current is diminished in the case of the cells containing Chl-a. This last effect is most likely caused by the energy barrier for hole transport at PEDOT:PSS/Chl-a interface and could be corrected by introducing a buffer layer optimized for use with Chl-a; further work is required to optimize this type of devices.

#### Acknowledgements

The authors wish to thank Raluca Gavrilă from National Institute for Research and Development in Microtechnologies, Bucharest, Romania for performing AFM scans and AFM related discussion.

This work was supported by the Romanian Executive Unit for Financing Higher Education, Research and Innovation (UEFISCDI) under STAR program, grant no. 1/2012.

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