

## ON THE ELECTRICAL AND PHOTO-ELECTRICAL BEHAVIOR OF THE PHOTOVOLTAIC CELLS BASED ON POLYMERIC AND CHLOROPHYLL-A THIN FILMS

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**Abstract.** Photovoltaic cells based on conductive polymers, such as poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PC<sub>61</sub>BM), and chlorophyll-a (Chl-a) were fabricated and characterized, in ambient atmosphere. The architecture of prepared samples has been completed by deposition of buffer layers facilitating the charge carriers' collection to electrodes. To improve the holes collection, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and Chl-a were used, and lithium fluoride (LiF) for the electrons' collection, respectively. Both, the active layer and the holes selective layer (HSL) were customized as P3HT:PC<sub>61</sub>BM + Chl-a (1:1:1), and PEDOT:PSS + Chl-a (4:1) or the bi-layer structure Chl-a/PEDOT:PSS. Indium thin oxide (ITO) was preferred as anode, while aluminum as back electrode. The obtained devices were electrical and photo-electrical characterized, and their performances were discussed in terms of ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al conventional structures. We demonstrated that a customized PEDOT:PSS + Chl-a (4:1) HSL improved with more than 50% the external quantum efficiency of fabricated photovoltaic cells, compared with the results of conventional structures. Modest values of open circuit voltage and fill factor were calculated in the case of Chl-a/PEDOT:PSS HSL based photovoltaic cells, most likely due to a non-optimized interface between Chl-a and PEDOT:PSS which lead to the creation of a great number of defects acting as recombination centers.

**Key words:** P3HT, PCBM, Chl-a, organic photovoltaic cell.

### 1. INTRODUCTION

Due to their unique electrical and optical properties, conductive polymers are more and more used in the architecture of electronic and optoelectronic devices, such as organic field effect transistors, organic light emitting diodes, and organic photovoltaic cells (OPV) [1-6]. In the field of OPV, a particular configuration denoted bulk-heterojunction (BHJ) and defined as a mixture between two organic semiconductors (one donor and one acceptor) had attracted special attention from scientific community. BHJs can be seen as a 3D interpenetrating network, build from donor and acceptor domains, providing a good interfacial contact between its constitutive, and facilitating the excitons diffusion and photo-generated charge carriers separation before their recombination [7,8]. Being the active layer in photovoltaic cells, particular interest was paid to the BHJ morphology, especially after was demonstrated the great influence onto the photovoltaic performances. In this moment, we may say without making a mistake that the blend between P3HT, as donor, and PC<sub>61</sub>BM, as acceptor, in 1:1 ratio, can be considered conventional structure. Thus, the link between morphology of the active layer and performances was investigated by modifying the ratio between P3HT and PC<sub>61</sub>BM [9], adding different nanoparticles [10], synthesizing new types of polymers [11, 12] or using various solvents [13–15].

Deeply analyzing the standard configuration of a photovoltaic cell, fabricated as anode/holes selective layer/active layer/electrons selective layer (ESL)/cathode was observed that the photovoltaic performances

are strongly influenced by the quality of both HSL/active layer and active layer/ESL interfaces. One of the most used holes selective layer is PEDOT:PSS, or customized configurations based on PEDOT:PSS [16–19], while LiF is frequently preferred as ESL [20].

The search of the appropriate active layer of OPV was conducted to the use of natural pigments [21–23], and a special attention was given to chlorophyll (Chl), the most widespread photosynthetic light harvester on Earth [24–26]. The interest in the usage of chlorophyll, particularly Chl-a, is due to the presence of the photosynthetic reaction centers that have diode-like behavior [27], and thereby can be easily integrated in photovoltaic and photochemical devices [28, 29] and biomolecular electronics [27, 30, 31].

In this work, we prepared photovoltaic cells based on conductive polymers and Chl-a by customizing either HSL or the active layer. In terms of active layer, this study can be considered a sequel of [32] but taking into account a different ratio between constitutive, while the novelty is related with the fabrication of an improved HSL structure involving either a 4:1 ratio mixture between PEDOT:PSS and Chl-a or a layer-by-layer deposition of Chl-a and PEDOT:PSS. The performance of the obtained photovoltaic cells were discussed in terms of ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al conventional structure (CS).

## 2. EXPERIMENTAL PROCEDURES

Exploiting the advantage that chlorophyll-a can be used as constitutive of both active layer and holes selective layer, photovoltaic cells with different architectures were fabricated by spin-coating, in ambient atmosphere. The electrical and photo-electrical behavior of ITO/PEDOT:PSS + Chl-a (4:1)/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al denoted here as **S1**, ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM + Chl-a (1:1:1)/LiF/Al denoted here as **S2**, and ITO/Chl-a/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al denoted here as **S3** were analyzed and discussed in terms of ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al conventional structures. For all prepared samples, optical glass substrates were used. In the case of holes selective layer of **S1**, four volumes of PEDOT:PSS based water solution and one volume of Chl-a based methanol solution were mixed, while for **S3** the Chl-a thin layer was deposited from a 1,2-dichlorobenzene based solution. The active layer in both P3HT:PC<sub>61</sub>BM (1:1) and P3HT:PC<sub>61</sub>BM + Chl-a (1:1:1) configurations was obtained by physically mixing equal amounts of their components, and using 1,2-dichlorobenzene solvent. For all fabricated samples an active area of 0.4 cm<sup>2</sup> had been taken into account.

Working routine of samples' fabrication as well as the involved characterization procedures were detailed in a previous paper [32].

## 3. RESULTS AND DISCUSSIONS

Schematic representation of fabricated photovoltaic structures is shown in Figure 1 (Fig. 1a), together with the band offset diagram of component materials (Fig. 1b).

The current-voltage (I-V) characteristics in dark of **S1**, **S2**, and **S3** fabricated photovoltaic structures are shown in Fig. 2, compared to the results obtained for ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al CS.

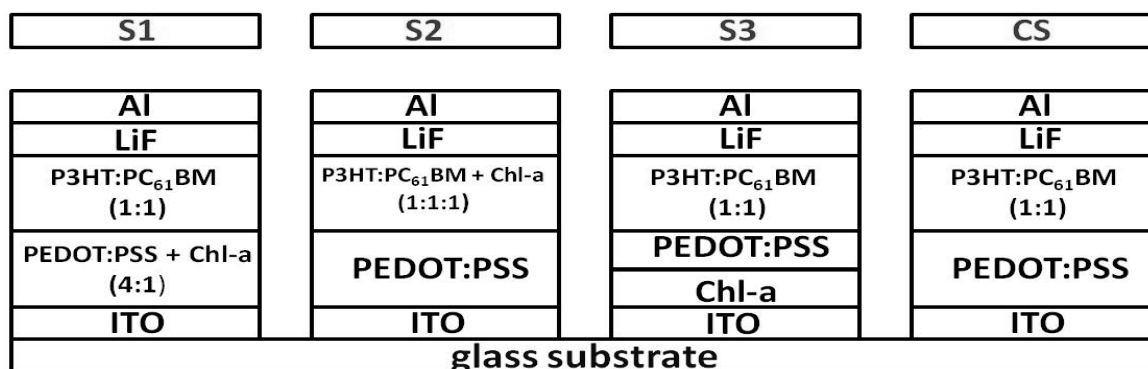


Fig. 1a – Schematic configurations of fabricated photovoltaic structures.

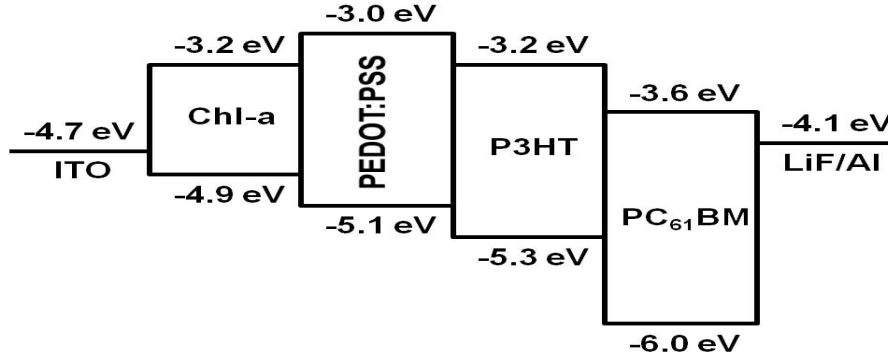


Fig. 1b – Band offset diagram of constitutive of fabricated photovoltaic cells.

For all prepared devices, both forward and reverse biases were drawn in ambient atmosphere, considering positive voltage to ITO electrode. The series and shunt resistances were determined using the modified form of Shockley equation, depicted in Eq. (1):

$$I = I_0 \{ \exp[\beta(V - IR_s)] - 1 \} + \frac{V - IR_s}{R_{sh}}, \tag{1}$$

where  $I_0$  is the reverse saturation current,  $R_s$  is the series resistance, and  $R_{sh}$  is the shunt resistance. Here,  $\beta = \frac{q}{nkT}$ , for which  $q$  is the electronic charge,  $n$  is the quality diode factor,  $K$  is the Boltzmann constant, and  $T$  is the absolute temperature in Kelvin.

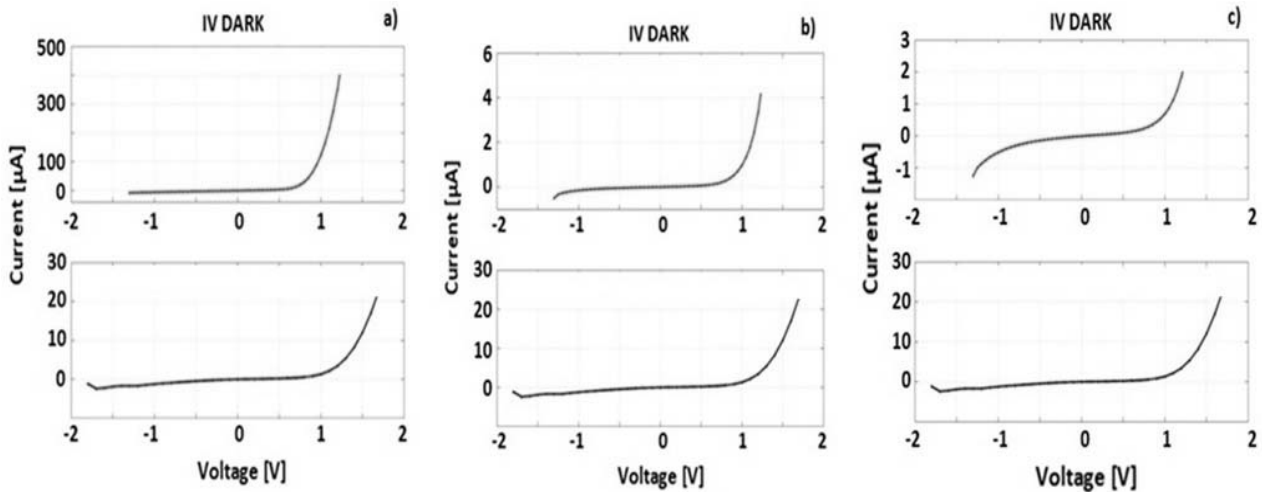


Fig. 2 – The I-V dark characteristics of: a) ITO/PEDOT:PSS + Chl-a (4:1)/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al; b) ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM + Chl-a (1:1:1)/LiF/Al; c) ITO/Chl-a/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al fabricated photovoltaic cells (red curves). The obtained results were compared with those for ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al samples (blue curves).

Table 1

Series and shunt resistances of the fabricated samples

Structure	$R_s$ ( $\Omega$ )	$R_{sh}$ ( $\Omega$ )
S1 - ITO/PEDOT:PSS + Chl-a (4:1)/P3HT:PC <sub>61</sub> BM(1:1)/LiF/Al	250	$200 \times 10^3$
S2 - ITO/PEDOT:PSS/P3HT:PC <sub>61</sub> BM + Chl-a (1:1:1)/LiF/Al	400	$11 \times 10^6$
S3 - ITO/Chl-a/PEDOT:PSS/P3HT:PC <sub>61</sub> BM (1:1)/LiF/Al	$10 \times 10^3$	$5.1 \times 10^6$
CS - ITO/PEDOT:PSS/P3HT:PC <sub>61</sub> BM/LiF/Al	$7 \times 10^3$	$2.5 \times 10^6$

The calculated values of  $R_s$  and  $R_{sh}$ , together with the obtained qualitative results indicate a decrease of the energetic barrier at the anode/PEDOT:PSS + Chl-a (4:1) interface due to the contribution of Chl-a

acting as *p*-type semiconductor, taking into account a similar behavior at LiF/cathode interface. On the other hand, the presence of Chl-a as constitutive in the active layer leads to a partially decrease of the energetic barrier at anode/PEDOT:PSS interface, and to an opposite behavior at LiF/cathode interface. An architecture such as Chl-a/PEDOT:PSS that implies two distinct thin layers of same type semiconductor can be a solution to decrease the energetic barrier at anode/HSL interface and to facilitate the holes collection to electrode. For this, two conditions should be simultaneously met; the first one is an optimized interface between the two semiconductors and the second one is a very good match of the energetic levels of them. In the case of **S3**, we assume that the large values obtained for both series and shunt resistances are the result of a non-optimized interface between Chl-a and PEDOT:PSS. We consider that a great number of defects is created at Chl-a/PEDOT:PSS interface, and thus the series and shunt resistances of the device are increased. A similar behavior was also observed by F. Otieno and co-workers [7], in the case of PEDOT:PSS mixed with gold nanoparticles, as holes selective layer.

The obtained photo-electrical results are presented in Fig. 3, while the specific photovoltaic parameters are summarized in Table 2. The short-circuit current density ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor ( $FF$ ), and external quantum efficiency ( $EQE$ ) values were calculated for all fabricated samples and were discussed in the frame of conventional structures. The  $EQE$  was considered as the average value in the 450 – 850 nm range. Standard AM 1.5G conditions were used for the fourth quadrant measurements, in ambient atmosphere.

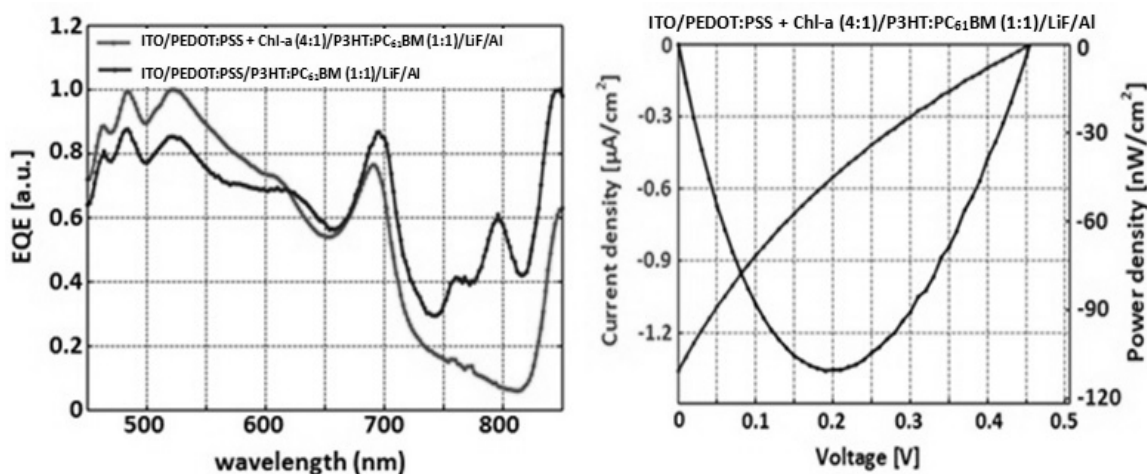


Fig. 3a – Normalized external quantum efficiency spectrum (EQE, left side) and the fourth quadrant (right side) of ITO/PEDOT:PSS + Chl-a (4:1)/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al fabricated photovoltaic structures. For comparison purpose the normalized EQE spectrum of ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al samples is given.

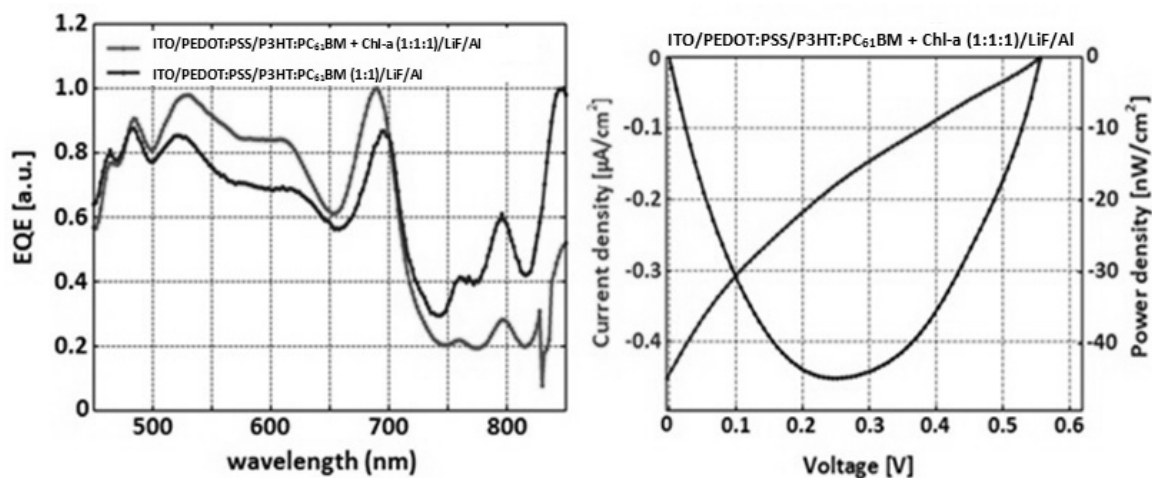


Fig. 3b – Normalized external quantum efficiency spectrum (EQE, left side) and the fourth quadrant (right side) of ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM + Chl-a (1:1:1)/LiF/Al fabricated photovoltaic structures. For comparison purpose the normalized EQE spectrum of ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al samples is given.

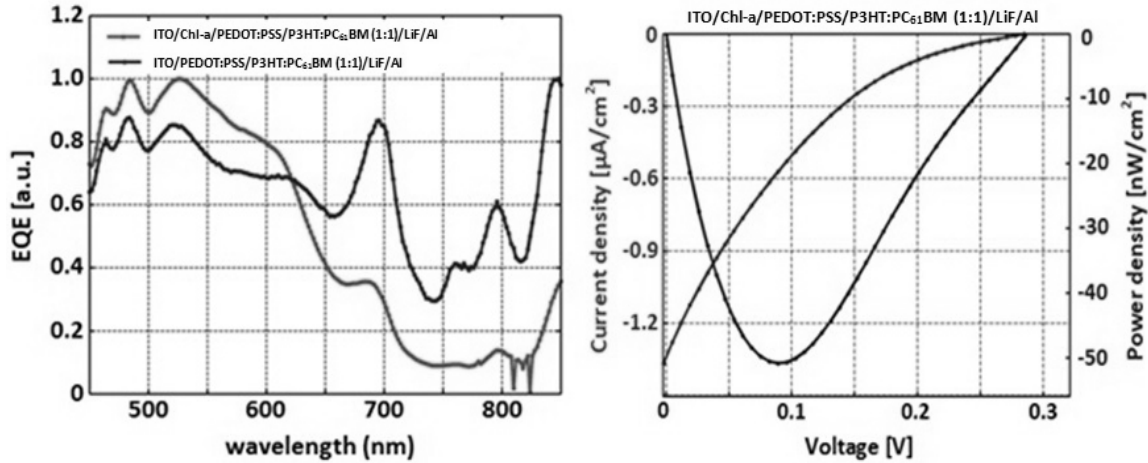


Fig. 3c – Normalized external quantum efficiency spectrum (EQE, left side) and the fourth quadrant (right side) of ITO/Chl-a/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al fabricated photovoltaic structures. For comparison purpose the normalized EQE spectrum of ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al samples is given.

Table 2

Calculated photovoltaic parameters of the fabricated structures

Structure	$J_{sc}$ ( $\mu\text{A}/\text{cm}^2$ )	$V_{oc}$ (V)	FF (%)	EQE (%)
S1	1.4	0.5	19	35
S2	0.5	0.6	18	16
S3	1.4	0.3	13	18
CS	1.0	0.5	16	17

The presence of the chlorophyll-a in the architecture of the active layer of **S2** fabricated photovoltaic structures leads to an enlargement of the spectral response, in the 500 – 650 nm range, compared to **S1** and **S3** samples. Despite this behavior, no significant increase of specific photovoltaic parameters was noticed, compared to the results of the structures based on P3HT:PC<sub>61</sub>BM mixture, as active layer. We assume that the obtained poor values of  $J_{sc}$ ,  $V_{oc}$ ,  $FF$ , and  $EQE$  are due to the fact that no chemical interaction took place between P3HT:PC<sub>61</sub>BM and Chl-a.

Analyzing the photo-electrical behavior, for those fabricated structures that include a customized holes selective layer,  $I_{sc}$  has slightly great values compared to **S2** and **CS**, but the non-optimized interface between Chl-a and PEDOT:PSS leads to modest values of open circuit voltage and fill factor, in the case of **S3**. This behavior was already predicted by the electrical measurements (I-V characteristics in dark). An external quantum efficiency of 35% in the case of **S1**, almost double than the values for **S2**, **S3**, **S4**, and **CS**, was measured. Correlating the photo-electrical results with the electrical ones, we assume that an optimized holes selective layer such as PEDOT:PSS + Chl-a (4:1) can improve the charge carriers collection to anode. The 4:1 specific ratio between PEDOT:PSS and Chl-a was established taking into account electrical and photo-electrical results for different configurations of the holes selective layer, e.g. PEDOT:PSS + Chl-a (3:2), 2:3 and 1:4 (not shown here). Despite the fact that same P3HT:PC<sub>61</sub>BM (1:1) mixture was considered as active layer, for these configurations the photovoltaic performances were poor compared to conventional structures. We assume that such behavior can be attributed to the weak interactions taking place between PEDOT:PSS, which is a heavily doped *p*-type semiconductor [33,34], and Chl-a, which is a natural porphyrins, with *p*-type semiconductor features too, and thus an unhappy head-to-head diodes arrangement appeared.

#### 4. CONCLUSIONS

Polymeric/chlorophyll-a thin films based photovoltaic cells were fabricated by spin-coating, in ambient atmosphere. Different configurations were taken into account, either by customizing the holes selective layer such as PEDOT:PSS + Chl-a (4:1) and Chl-a/PEDOT:PSS, or the active layer, as P3HT:PC<sub>61</sub>BM + Chl-a

(1:1:1). The electrical and photo-electrical properties of the fabricated samples were analyzed and compared to the results obtained for ITO/PEDOT:PSS/P3HT:PC<sub>61</sub>BM (1:1)/LiF/Al conventional structures.

Building the holes selective layer as a mixture between PEDOT:PSS and Chl-a leads to a decrease of the energetic barrier, corresponding to a more efficient charge collection to anode, while a layer-by-layer deposition of Chl-a and PEDOT:PSS increases the energetic barrier at anode/holes selective layer interface.

By using Chl-a as constitutive in the active layer, except of the enlargement of the spectral response in the 500 – 650 nm range, the calculated specific photovoltaic parameters had smaller values than those obtained for conventional structures, and we believe this can be attributed to a strongly non-homogeneous active layer.

Even though the measured values of the specific parameters of the fabricated samples were modest, we demonstrated that using a customized PEDOT:PSS + Chl-a (4:1) holes selective layer, both the electrical and photo-electrical behaviors were improved, compared to conventional structures.

## REFERENCES

1. N.B. UKAH, J. GRANSTROM, R.R.S. GARI, G.M. KING, S. GUHA, *Low-operating voltage and stable organic field-effect transistors with poly (methyl methacrylate) gate dielectric solution deposited from a high dipole moment solvent*, Appl. Phys. Lett., **99**, 243302, 2011.
2. B. CANIMKURBEY, Z.A. KOSEMEN, C. CAKIRLAR, S.E. SAN, M. YASIN, S. BERBER, A. KOSEMEN, *Fabrication and investigation of P3HT:PCBM bulk heterojunction based organic field effect transistors using dielectric layers of PMMA:Ta2O5 nanocomposites*, Microelectron. Eng., **180**, 65, 2017.
3. S. JEONG, S.H. KIM, D.Y. KIM, C. KIM, H.W. LEE, S.E. LEE, Y.K. KIM, S.S. YOON, *Blue organic light-emitting diodes based on diphenylamino dibenzo[g,p] chrysene derivatives*, Thin Solid Films, **636**, 8, 2017.
4. B. JIA, H. LIAN, Z. CHEN, Y. CHEN, J.H. HUANG, Q.C. DONG, *Novel carbazole/thiazole-based host materials with high thermal stability for efficient phosphorescent organic light-emitting diodes*, Dyes Pigm., **147**, 552, 2017.
5. I. VAICIULIS, M. GIRTAN, A. STANCIULESCU, L. LEONTIE, F. HABELHAMES, S. ANTOHE, *On titanium oxide spray deposited thin films for solar cells applications* Proceedings of the Romanian Academy Series A-Mathematics Physics Technical Sciences Information Science **13**, 335, 2012.
6. L.J. ROZANSKI, C.T.G. SMITH, K.K. GANDHI, M.J. BELIATIS, G.D.M.R. DABERA, K.D.G.I. JAYAWARDENA, A.A.D.T. ADIKAARI, M.J. KEARNEY, S.R.P. SILVA, *A critical look at organic photovoltaic methodology: Defining performance enhancement parameters relative to active area*, Sol. Energy Mater. Sol. Cells, **130**, 513, 2014.
7. F. OTIENO, N.P. SHUMBULA, M. AIRO, M. MBUSO, N. MOLOTO, R.M. ERASMUS, A. QUANDT, D. WAMWANGI, *Improved efficiency of organic solar cells using Au NPs incorporated into PEDOT:PSS buffer layer*, AIP Adv., **7**, 085302, 2017.
8. S. ANTOHE, S. IFTIMIE, L. HROSTEA, V.A. ANTOHE, M. GIRTAN, *A critical review of photovoltaic cells based on organic monomeric and polymeric thin film heterojunctions*, Thin Solid Films, **642**, 219, 2017.
9. U. NEUPANE, B. BAHRAMI, M. BIESECKER, M.F. BAROUGH, Q. QIAO, *Kinetic Monte-Carlo modeling on organic solar cells: Domain size, donor acceptor ratio and thickness*, Nano Energy, **35**, 128, 2017.
10. W. ZHANG, N.A. NGUYEN, R. MURRAY, J. XIN, M.E. MACKAY, *A comparative study on the morphology of P3HT:PCBM solar cells with the addition of Fe3O4 nanoparticles by spin and rod coating methods*, J. Nanopart. Res., **19**, 315, 2017.
11. Y.Y. LIANG, Z. XU, J.B. XIA, S.T. TSAI, Y. WU, G. LI, C. RAY, L.P. YU, *For the bright future-bulk heterojunction polymer solar cells with power conversion efficiency of 7.4%*, Adv. Mater., **22**, E135+, 2010.
12. J.-D. CHEN, C. CUI, Y.-Q. LI, L. ZHOU, Q.-D. OU, C. LI, Y. LI, J.-X. TANG, *Single-junction polymer solar cells exceeding 10% power conversion efficiency*, Adv. Mater., **27**, 1035, 2015.
13. B. KADEM, M. AL-HASHIMI, A. HASSAN, *The effect of solution processing on the power conversion efficiency of P3HT-based organic solar cells*, Energy Procedia, **50**, 237, 2014.
14. B. KADEM, A. HASSAN, W. CRANTON, *The effects of organic solvents and their co-solvents on the optical, structural, morphological of P3HT:PCBM organic solar cells*, AIP Conf. Proc., **1758**, 020006, 2016.
15. G.A. NEMNES, S. IFTIMIE, A. PALICI, A. NICOLAEV, T.L. MITRAN, A. RADU, S. ANTOHE, *Optimization of the structural configuration of ICBA/P3HT photovoltaic cells*, Appl. Surf. Sci., **424**, 264, 2017.
16. P. SHAO, X. CHEN, X. GUO, W. ZHANG, F. CHANG, Q. LIU, Q. CHEN, J. LI, Y. LI, D. HE, *Facile embedding of SiO2 nanoparticles in organic solar cells for performance improvement*, Org. Electron., **50**, 77, 2017.
17. C. BESLEAGA, L. ION, V. GHENESCU, G. SOCOL, A. RADU, I. ARGHIR, C. FLORICA, S. ANTOHE, *Transparent indium zinc oxide thin films used in photovoltaic cells based on polymer blends*, Thin Solid Films, **520**, 6803, 2012.
18. E.L. LIM, C.C. YAP, M.A.M. TERIDI, C.H. TEH, A.R. BIN MOHD YUSOFF, M.H.H. JUMALI, *A review of recent plasmonic nanoparticles incorporated P3HT:PCBM organic thin film solar cells*, Org. Electron., **36**, 12, 2016.
19. Y.A.M. ISMAIL, N. KISHI, T. SOGA, *Improvement of organic solar cells using aluminum microstructures prepared in PEDOT:PSS buffer layer by using ultrasonic ablation technique*, Thin Solid Films, **616**, 73, 2016.
20. A. RADU, S. IFTIMIE, V. GHENESCU, C. BESLEAGA, V.A. ANTOHE, G. BRATINA, L. ION, S. CRACIUN, M. GIRTAN, S. ANTOHE, *The influence of LiF layer and ZnO nanoparticles additions on the performances of flexible photovoltaic cells based on polymer blends*, Dig. J. Nanomater. Biostruct., **6**, 1141, 2011.
21. X.-F. WANG, H. TAMIYAKI, *Cyclic tetrapyrrole based molecules for dye-sensitized solar cells*, Energy Environ. Sci., **3**, 94, 2010.

22. Y. AMAO, Y. YAMADA, K. AOKI, *Preparation and properties of dye-sensitized solar cell using chlorophyll derivative immobilized TiO<sub>2</sub> film electrode*, J. Photochem. Photobiol. A, **164**, 47, 2004.
23. A. KAY, R. HUMPHRY-BAKER, M. GRAETZEL, *Artificial photosynthesis. 2. Investigations of the mechanism of photosensitization of nanocrystalline TiO<sub>2</sub> solar cells by chlorophyll derivatives*, J. Phys. Chem., **98**, 952, 1994.
24. S. ANTOHE, LAURA TUGULEA, V. GHEORGHE, V. RUXANDRA, I. CĂPLANUS AND L.ION, , *Electrical and Photovoltaic Properties of ITO/Chlorophyll a/TpyP/Al p-n Junction Cells*, Phys. Stat. Sol. (a), **153**, 581, 1996.
25. M.E. BARBINTA-PATRASCU, N. BADEA, C. UNGUREANU, C. PIRVU, V. IFTIMIE, S. ANTOHE, *Photophysical studies on biocomposites based on carbon nanotubes and chlorophyll-loaded biomimetic membranes*, Rom. Rep. Phys., **69**, 604, 2017.
26. L.O. BJORN, G.C. PAPAGEORGIOU, R.E. BLANKENSHIP, GOVINDJEE, *A viewpoint: Why chlorophyll a?*, Photosynth. Res., **99**, 85, 2009.
27. M. KAMRAN, V. FRIEBE, J. DELGADO, T. AARTSMA, R. FRESE, M. JONES, *Demonstration of asymmetric electron conduction in pseudosymmetrical photosynthetic reaction centre proteins in an electrical circuit*, Nat. Commun., **6**, 6530, 2015.
28. O. YEHEZKELI, R. TEL-VERED, D. MICHAELI, I. WILLNER, R. NECHUSHTAI, *Photosynthetic reaction centre-functionalized electrodes for photo-bioelectrochemical cells*, Photosynth. Res., **120**, 71, 2014.
29. M. GRATZEL, *Photoelectrochemical cells*, Nature, **414**, 338, 2001.
30. B.D. REISS, D.K. HANSON, M.A. FIRESTONE, *Evaluation of the photosynthetic reaction centre protein for potential use as a bioelectronic circuit element*, Biotechnol. Prog., **23**, 985, 2007.
31. T. MIKAYAMA, T. MIYASHITA, K. IIDA, Y. SUEMORI, M. NANGO, *Electron transfer mediated by photosynthetic reaction centre proteins between two chemical-modified metal electrodes*, Mol. Cryst. Liq. Cryst., **445**, 291, 2006.
32. S. IFTIMIE, M.E. BARBINTA-PATRASCU, D. GAZDARU, A. RADU, B. BITA, D. STAIKU, N. KORGANCI, L. ION, S. ANTOHE, *Photovoltaic structures based on biologic/polymeric semiconducting thin films*, Dig. J. Nanomater. Biostruct., **10**, 1249, 2015.
33. D. KHODAGHOLY, J. RIVNAY, M. SESSOLO, M. GURFINKEL, P. LELEUX, L.H. JIMISON, E. STAVRINIDOU, T. HERVE, S. SANAU, R.M. OWENS, G.G. MALLIARAS, *High transconductance organic electrochemical transistors*, Nat. Commun., **4**, 2133, 2013.
34. S. ZHANG, P. KUMAR, A.S. NOUAS, L. FONTAINE, H. TANG, F. CICOIRA, *Solvent-induced changes in PEDOT:PSS films for organic electrochemical transistors*, APL Mater., **3**, 014911, 2015.

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