Solution Processed p-i-n solar cells based on P3HT:PCBM bulk heterojunctions

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Abstract

An opening study on p-i-n structure formation by electrochemical doping with ionic liquids, IL, namely 1-butyl-3-methylimidazolium hexafluorophosphate and tetra-n-butylammonium tetraphenylborate, in the P3HT:PCBM system was carried out. We demonstrate the possibility to increase the power conversion efficiency, PCE, of the photovoltaic cells based on P3HT:PCBM, even though a decrease of performance is also shown before the formation of the p-i-n structure. The IL addition produces large changes in the morphology of the film. Upon formation of a p-i-n structure, a reduction of the non-geminate recombination and an increase of the charge carriers mobilities are observed.

Introduction

Crystalline and polycrystalline solar cells are the dominant technology of the photovoltaic market, representing nearly 90% of it (1). This strong position was possible thanks to the high boost given by the public subsidies (2). However, even if their price keeps lowering around 50% per year, they are not yet competitive with other energy sources. Organic photovoltaic cells, OPVs, represent an alternative technology and they are produced using low cost production techniques. OPVs could replace the inorganic counterpart, at least in some applications, and create new implementation of the photovoltaic technology. The discovery of conductive and semiconductive organic materials has led to the possibility to built electronic devices with features not achievable by the inorganic counterparts. In the last 30 years, this has given rise to the development of devices such as organic batteries (3), organic light emitting diodes, OLEDs, (4) (5), organic field effect transistors, OFETs, (6), light-emitting electrochemical cells, LECs, (7), and OPVs (8). At the moment, the highest efficiency of a polymeric solar cell in laboratory scale is 10%. This is considered a high value compared with, poly(3-hexylthiophene) and [6,6]-phenyl-C61 butyric acid methylester blend, P3HT:PCBM, the most extensively studied polymer-fullerene system, whose PCE reaches about 5% (9). A further improvement, coming from the inorganic semiconductors' world and which some groups successfully realized also with organic materials, is the introduction of the *p-i-n structure*. The idea is to produce a series of stacked layers which have different carriers transport properties, through a doping process:

- a highly doped material with hole transporting ability, indicated as p-doped, in contact with the anode of the cell
- an intrinsic layer in the middle, without a net doping effect which is responsible for light absorption

- a highly doped material with electron transporting ability, indicated as n-doped, in contact with the cathode of the cell

Differently from inorganic, the concept of enhancing the ability of a layer to transport just one kind of charge carrier (doping process) is not crucial in organic materials (10). The process of doping can be obtained in several ways, for example co-evaporating molecules with high hole, or electron, transporting properties, respectively, with the donor or acceptor (11) (12). Further improvement is the realization of a dynamic p-i-n structure by in situ electrochemical doping, as already demonstrated (13) (14). The displacement of ions inside the active layer produced by the application of a bias is able to induce the formation of a p- and a n-region. The approach used in previous works was to add a metal triflate salt and polyethylene oxide, PEO, which exerts the role of a solid state electrolyte, to a poly(*p*-phenylene vinylene), PPV, system. Our aim was to produce in situ electrochemical doping of a P3HT:PCBM based cell by the addition of an ionic liquid, IL. Ionic liquids are extensively used in the preparation of LECs, being soluble in most organic solutions, chemically and electrochemically stable at temperatures lower than 200°C and within large potential range and presenting high ionic conductivity (reaching 0.1 S cm^{-1}). The ILs used here are 1-butyl-3-methylimidazolium hexafluorophosphate and tetra-n-butylammonium tetraphenylborate.

Results and Discussion

In the next discussion, the blend containing 1-butyl-3-methylimidazolium hexafluorophosphate is identified as P3HT:PCBM:mIm, and the blend containing tetra-n-butylammonium tetraphenylborate is identified as P3HT:PCBM:bAm. The amount of IL added to the blend is specified as the percentage of its mass with respect to the mass of the P3HT.

1. Influence of ionic liquid addition on blend morphology

In order to test the IL effect on the morphology of the blend, a series of AFM measurements was performed. Fig.1 shows the AFM 3D images, obtained on a 5 μm x 5 μm area in tapping mode. Tab.1 contains the roughness of the AFM images, specified as the root mean square value, rms. The rms value of the P3HT:PCBM film was taken from Li et al. (15). Pure PCBM forms film with a flatter surface than P3HT. The addition of 5% of 1-butyl-3-methylimidazolium hexafluorophosphate does not affect PCBM morphology, while the addition to P3HT gives rise to the formation of high and isolated peaks. These experimental results seem to indicate a better chemical compatibility of the IL with PCBM than with P3HT. The effect of addition of 5% of 1-butyl-3-methylimidazolium hexafluorophosphate on the P3HT:PCBM blend surface morphology is quite strong too. High peaks surrounded by flat regions can be observed, Fig.1(e), and an almost 6 times larger rms value was calculated. The observed change in morphology is expected to have a significant impact on cell performance and should affect the movement of excitons, free charges and maybe also of ions. In order to conclude if the observed behavior is dependent on the nature of the ionic liquid, a device with 1% of tetra-n-butylammonium tetraphenylborate was also tested (see Fig.1.(f)). Tetra-n-butylammonium tetraphenylborate shows smaller surface changes, which actually does not

mean that it has less influence on the overall morphology, and the rms value is quite close to that of P3HT:PCBM. Tetra-n-butylammonium tetraphenylborate seems to be more compatible with P3HT:PCBM, even though this conclusion is certainly influenced by its lower concentration.

Tab.1 Roughness rms values extracted from AFM measurements in several blends.

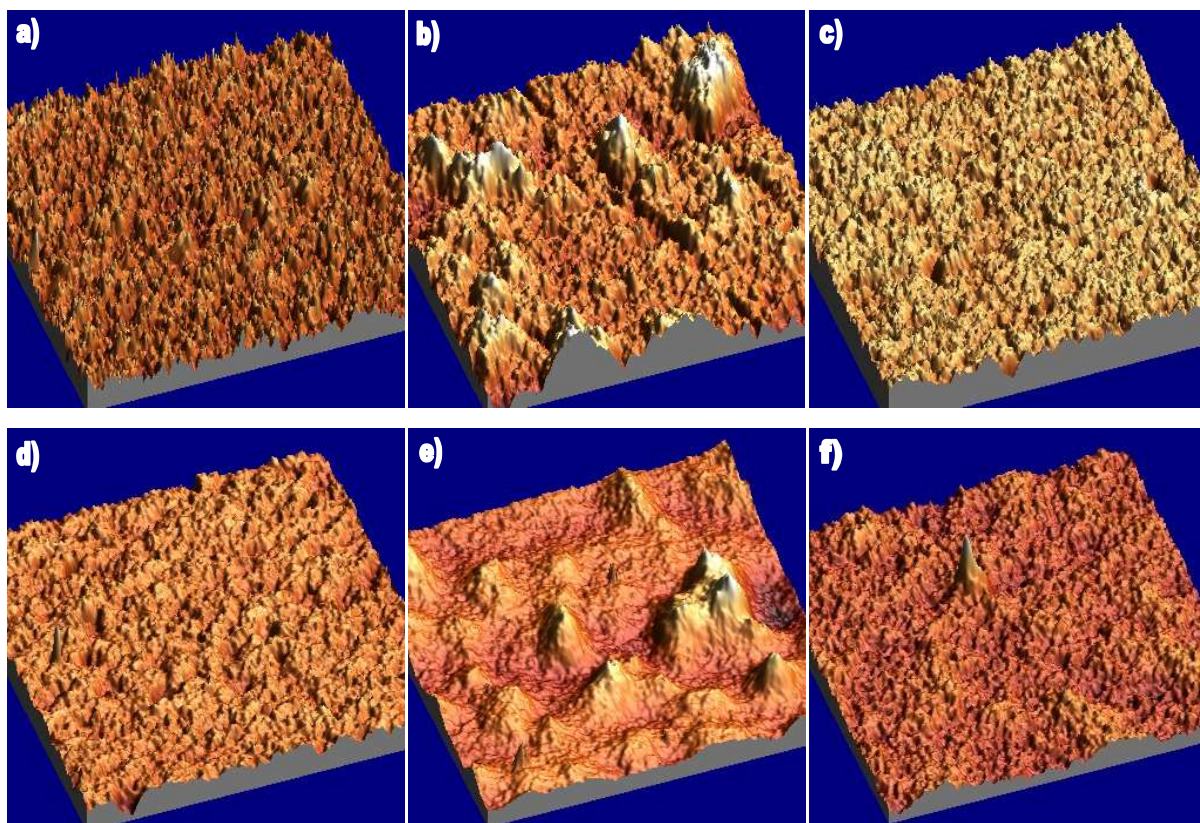|	Rms value [nm]
P3HT	1.25
P3HT:5%mIm	6.53
PCBM	0.54
PCBM:5%mIm	0.52
P3HT:PCBM	0.75 (Ref. (15))
P3HT:PCBM:5%mIm	4.38
P3HT:PCBM:1%bAm	0.94

Fig.1 3D reconstruction of the AFM measurements of a)P3HT, b) P3HT:5%mIm, c) PCBM, d) PCBM:5%mIm, e) P3HT:PCBM:5%mIm, f) P3HT:PCBM:1%bAm.

2. Effect of IL addition on cell performance

It was not possible to directly demonstrate the formation of the p-i-n structure. Instead we tried to collect data that would allow us to deduce its formation. We tested several OPVs with and without ionic liquid in several conditions. No direct measurements of ions localization or displacement were made. The study of cell's behavior was carried out for two different device conditions:

- the cell after production, which include an annealing process, indicated as *fresh cell*,
- the cell after the application of a bias.

Fig.2 shows a characterization of a 120 nm thick P3HT:PCBM device (in purple) and of a 190 nm thick device with 5% of 1-butyl-3-methylimidazolium hexafluorophosphate (in black). Tab.2 contains the parameters characterizing the two devices. We observed that the addition of IL decreases the PCE. The IL containing device shown has a higher thickness than the P3HT:PCBM device used as reference, but the performance reduction was verified to be a common feature in all the produced cells. For the P3HT:PCBM:5%mIm system, the device performance was better for a film thickness of 190 nm while the best performance for a P3HT:PCBM system was obtained with an active layer thickness of 120 nm.

Upon addition of the IL, we observe also a reduction of the open circuit voltage, V_{oc}, of about 20 mV, whose origin is not clear yet, and a reduction of the current density. This can be partially explained by a reduction in the absorption of the incident light due to the addition of IL, which is not absorbing. Obviously, the phenomenon should get more important increasing the IL concentration. The variation of absorption is shown in Fig.3. For the same thickness, around 120 nm, a reduction in the absorbance spectrum is reported, with a decrease of the absorption peaks of the P3HT at 520 nm and of PCBM at 330 nm. The absorption of a 190 nm active layer thickness containing 5% of 1-butyl-3-methylimidazolium hexafluorophosphate is also shown.
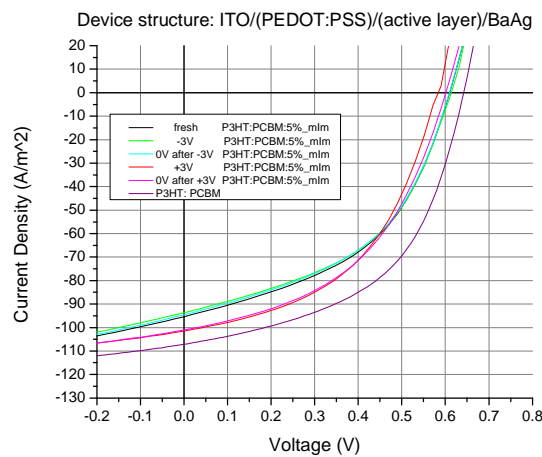

Fig.2 IV curves of fresh and biased P3HT:PCBM:5%mIm cell, firstly biased with -3V.

Tab.2 Parameters of P3HT:PCBM cell used as reference and P3HT:PCBM:5%mIm cell. V_{oc} is the open circuit voltage, I_{sc} is the short circuit current, FF is the fill factor and η is the power conversion efficiency.

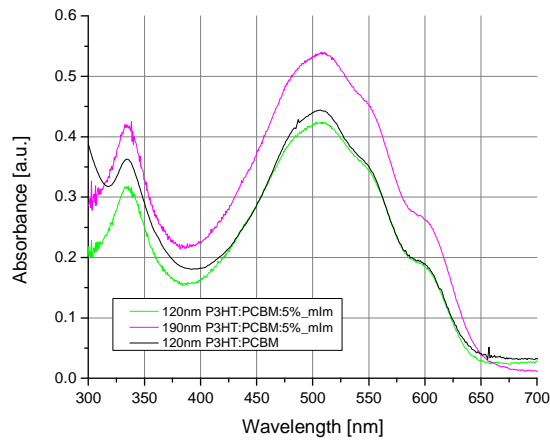|		V_{oc} [mV]	I_{sc} [A m^{-2}]	FF [%]	η
P3HT:PCBM		642	-107	52	3.55
P3HT:PCBM:5%mIm	Fresh	610	-95	47	2.74
	-3V	613	-93	48	2.71
	0V after -3V	610	-95	47	2.71
	+3V	584	-101	48	2.85
	0V after +3V	601	-101	47	2.86

Fig.3 Comparison of the absorption spectra of P3HT:PCBM and P3HT:PCBM:5%mIm.

We note that annealing improves the film efficiency of both types of devices (with or without IL).

3. Effect of biasing of the cell and formation of the p-i-n structure

The following step in the characterization of the cells was the application of a constant voltage, referred to as bias, for 2 minutes (other curves in Fig.2). A negative bias was applied first, followed by a positive bias. Time of biasing was not completely arbitrarily chosen: a constant I_{sc} value is reached after almost 60 seconds of biasing.

A 2 minute negative bias of the cell seems not to have an appreciable effect on the performance. On the other hand, the application of a positive bias leads to a small improvement of the power conversion efficiency. After a positive bias, V_{oc} is reduced by about 20 mV whereas the current density increases. The cell was characterized again few minutes after the bias application. The IV curve now shows that the improvement in I_{sc} is maintained and that there is a partial recovery of the open circuit voltage.

The influence of the sequence of bias application was also investigated. It was observed that a negative biasing applied after a positive one does not affect the cell behavior.

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A zoom of the curves around V=0 is depicted in Fig.4 on the left. The addition of the ionic liquid to the blend increases the slope of the curve when comparing with the P3HT:PCBM reference device. This indicates a decrease of the shunt resistance which is usually related with an increase of charge carrier recombination. Interestingly, after the application of the positive bias, the slope of the curve decreases, indicating that the recombination of charge carriers decreases. Thus, the application of a positive bias permits to improve charge extraction, thereby reducing the disadvantageous features of these cells.

Information about the mobility of charge carriers is obtained from the IV curve around the V_{oc} voltage, e.g. looking at the series resistor R_s (Fig.4 on the right). The IL addition initially produces a decrease of the slope of the curve, corresponding to a decrease in the charge carriers mobility. When a positive bias is applied, the cell shows a lower R_s, indicating an increase of charge carriers mobility, as deduced from the increase of the slope of the IV curve at V_{oc}, being even slightly better than the P3HT:PCBM reference. Negative bias do not show any significant effects.
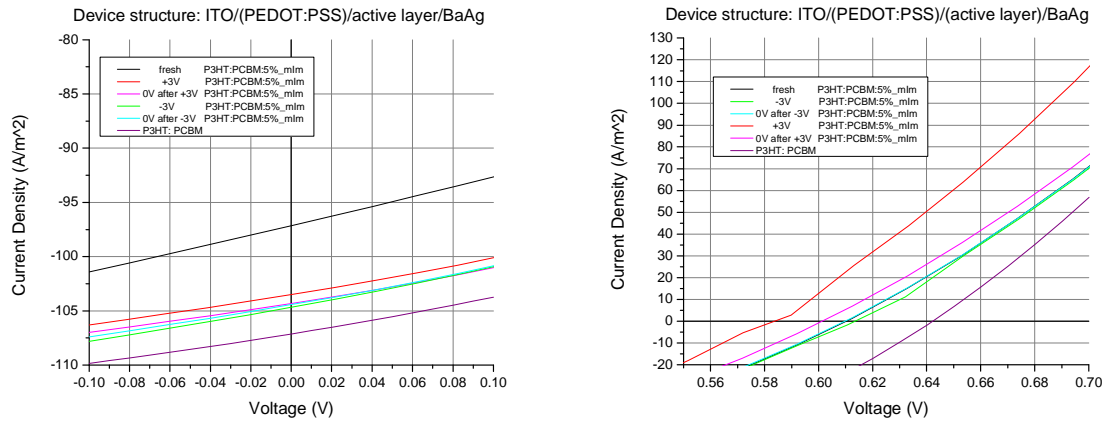

Fig.4 Zoom of IV curves at I_{sc}, on the left, and at V_{oc}, on the right.

Time is obviously an important variable in the movement of ions. Ionic liquids are composed by ions with high molecular weight, thus, it is relevant to study the effect of longer biasing time. To carry out this study a device containing 1% of tetra-n-butylammonium tetraphenylborate in a P3HT:PCBM blend with a 190 nm active layer thickness was fabricated. A +3V bias was applied for several hours, measuring the IV curve every 2h (Fig.5). The application for a long time gives the same kind of results described for the short time, but the increase of the carriers mobilities and the reduction of carriers recombination are stronger. The two effects combined give rise to an increase of FF, and thus a higher power conversion efficiency (see Tab.3 and Fig.5). It is possible to identify several interesting points:

- There is large increase of performance after 2h, due to the increase in current density,
- subsequent measurements of the cell, after 48 hours and 140 hours, give rise to higher performances in terms of both V_{oc} and I_{sc}. On the other hand, there is a systematic reduction in the FF. The comparison of

the two curves seems to show small degradation of performance after 140 hours, anyway the cell seems to have a good stability up to weeks.

In the end, it was possible to obtained a PCE of 3.64%, slightly better than the P3HT:PCBM used as reference. The improvement induced by the +3V bias is remarkable, with an increase in performance of almost 35% comparing with the fresh cell.

Tab.3 Parameters of a fresh and biased cell at different time.

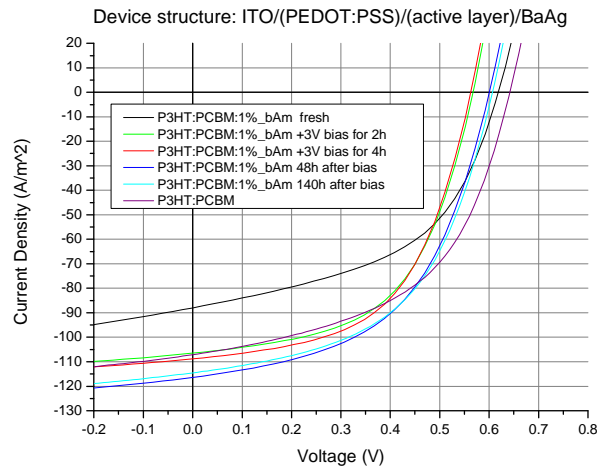|		V_{oc} [mV]	I_{sc} [A m^{-2}]	FF [%]	H
P3HT:PCBM:1%bAm	Fresh	619	-88	50	2.72
	+3V for 2h	567	-106	55	3.31
	+3V for 4h	563	-109	55	3.36
	0V after +3V for 4h measured 48h later	600	-117	52	3.63
	0V after +3V for 4h measured 140h later	607	-115	52	3.64

Fig.5 IV curves fresh and +3V biased of P3HT:PCBM:1%bAm cell, at different time.

The effect of biasing with different positive voltage values was also investigated on P3HT:PCBM:1%bAm cell with Al cathode (Fig.6 and Tab.4). The cells were biased for 2 min at +3 or +5V. An increase in cell PCE is observed after the application of +3V, yet a strong decrease of PCE occurs upon application of +5V bias. At the +3V bias, I_{sc} is lower than in the fresh device and this may be related with the use of Al as anode. It leads to a different build-in voltage across the cell. Yet the overall gain in power conversion efficiency is due to the increase in mobility by the formation of p- and n- regions, and the decrease of non geminate recombination. In this study, here, a P3HT:PCBM cell with Al cathode and an active layer of 180 nm was used as reference.

Tab.4 Parameters of fresh and biased cell, at different bias voltages.

		V_{oc} [mV]	I_{sc} [A m^{-2}]	FF [%]	η
P3HT:PCBM		643	-100	53	3.41
P3HT:PCBM:1%bAm	Fresh	647	-94	42	2.58
	+3V	606	-88	59	3.17
	+5V	610	-53	54	1.76

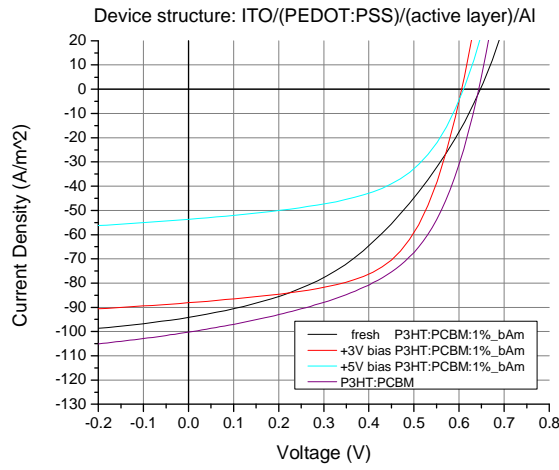Device structure: ITO/(PEDOT:PSS)/(active layer)/Al

Fig.6 Fresh and biased IV curves of P3HT:PCBM:1%bAm cell, at different bias voltages.

The apparently controversial effect of a positive bias can be explained considering the phenomena acting in the photocurrent generation and carriers extraction, and their different strength at different voltage values:

- Excitons are neutral species, bound electron and hole pairs, but, due to spatial distance between the two charges, an electric field is influencing their separation. The higher the external electric field the more probable will be the excitons dissociation,

- The p- and n- regions, produced by the applied external electric field, present high conductivity of one kind of charge carrier but also present large quenching effects. Quenching is stronger with increasing size of the p- and n- regions.

The behavior of the cell biased at +5V is different from the one biased at +3V. If indeed doping occurs, it is possible that at +5V the doped regions extend much further into the active layer and exciton quenching within these doped regions can compete with the exciton dissociation process. Hence, with wide p- and n- regions exciton quenching would increase leading to a strong decrease of extractable current and thus of PCE. We consider that this experimental evidence is another hint of the formation of a p-i-n structure. Besides, a similar behavior was also reported using PPV and metal triflate salts, providing additional confirmation to our hypothesis (14).

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Conclusions

Using two chemically compatible ionic liquids it was possible to prepare ion containing bulk-heterojunction solar cells based on a blend of P3HT and PCBM. The performance of the devices deteriorates with the addition of the ionic liquids, proportionally with the amount added. Yet, an increase in the solar cell performance was obtained after applying a positive bias, while negative biases did not lead to a significant change in the performance of the solar cells. This increase is more pronounced for longer biasing times. Direct evidence of the formation of a p-doped, intrinsic and an n-doped region was not obtained. Yet several results can be explained in the framework of the p-i-n structure. The increase in current density and the improvement of the fill factor are some of them. Also the change in the slope of the curve close to V=0 and to the V_{oc} after positive biases indicate a reduction of the recombination and an increase in the charge carrier mobilities, respectively, which can be explained by the formation of highly conductive doped regions adjacent to the electrodes. Furthermore, when the applied bias is too high, no increase in current density and power conversion efficiency is obtained.

Therefore, it appears possible that a p-i-n junction is formed in the ion containing P3HT:PCBM solar cells. In the P3HT:PCBM solar cell to which 1% of tetra-n-butylammonium tetraphenylborate was added the PCE obtained after positive biasing at 3 volts increased by 35% over the unbiased cell. More importantly, perhaps, is that the PCE obtained was higher than the ion-free P3HT:PCBM reference cell.

Experimental Details

1-butyl-3-methylimidazolium hexafluorophosphate and tetra-n-butylammonium tetraphenylborate, received from Aldrich Chemistry, were dissolved in chlorobenzene at the concentration, respectively, of 4.6 mg/ml and 1.4 mg/ml, and mixed for at least one hour. 20 mg of regioregular P3HT at electronic grade received from Rieke Metal Inc., 16 mg of [60]PCBM at 99.5% by Solenne, 0.22ml of 1-butyl-3-methylimidazolium hexafluorophosphate solution (or 0.15 ml of tetra-n-butylammonium tetraphenylborate solution) and 0.78 ml (or respectively 0.85 for the other solution) of chlorobenzene were mixed in a magnetic stirrer. Mixing was performed for at least 36h at room temperature.

Prepatterned ITO-covered glass substrates were cleaned with soap and water, followed by a series of sonication processes in tap water, distilled water and isopropyl alcohol. Finally, a 30 minutes treatment under UV lamp was performed. A SUSS Delta80 RC spin coater was used to fabricated a 70 nm PEDOT:PSS layer, using PEDOT:PSS Clevios™ P VP AI 4083. The layer was then dried by heating on a hot plate at 150°C for 10 minutes.

Active layers are deposited by spin coating at a speed of 1000 rpm or 2000 rpm, with acceleration of 1000 rpm/second, for 20 seconds. Thicknesses around 120 nm and 190 nm were respectively fabricated. Thickness measurements were made with a Ambios-Technology profilometer model XP-1, placed on a vibration isolation table. After spin coating of the blend, substrates were placed inside an inert gas glove box (1 ppm of O_2 and <1 ppm of H_2O).

There, cathode thermal deposition was performed in a Edwards Auto 500 thermal evaporation system. The vacuum chamber is installed inside the glove box and it is able to achieved a pressure of the order of 10^{-6} mbar, using a rotative vane pump in series with a turbomolecular pump. A 5 nm of Ba/70 nm of Ag, or 70 nm of Al, are deposited according to the chosen device structure. After the top contact fabrication, an annealing treatment at 150°C for 5 min was performed on the devices inside the inert gas glovebox.

Electrical measurements on the devices were performed inside the glove box under a solar simulator by ECN (Energy research Centre of the Netherlands), which permits to obtained the characteristic IV curve of the cell under illumination and in the dark. Illumination is done by an halogen lamp, and measurements are taken after at least 10 minutes from its switching on. The

measurement of EQEs required a previous calibration step, performed with a certified reference silicon cell. The I_{sc} current was not corrected with the AM 1.5G spectrum. IV curves of the solar cells are recorded using a Keithley 2400 SourceMeter.

Absorbance measurements were performed in a Avaspec-2048 Avantes spectrophotometer and AFM measurements were made in a tapping mode with a Veeco Nanoscope IVa Multimode Scanning Probe Microscope. AFM raw data were analyzed with WSxM software (17).

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