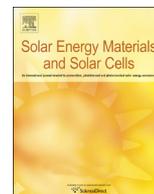




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Photovoltaic analysis of the effects of PEDOT:PSS-additives hole selective contacts on the efficiency and lifetime performance of inverted organic solar cells



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ABSTRACT

Solution processed inverted organic photovoltaics (OPVs) usually use (Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) PEDOT:PSS derivatives as hole selective contact. In this study the effect of different PEDOT:PSS formulations, Al4083, PH and PH500 in inverted structured OPVs is investigated. Through detailed device physics analysis PEDOT:PSS PH is proposed as most suitable hole selective contact for inverted OPVs device function. Furthermore, PEDOT:PSS PH hole selective contact is treated with 3 different wetting agents, Zonyl FS-300 fluorosurfactant (Zonyl), 2,5,8,11-tetramethyl-6-dodecyn-5,8-diol ethoxylate (Dynol) and Zonyl:Dynol mixture and the corresponding non-encapsulated inverted OPVs investigated under accelerated humidity lifetime conditions. The inverted OPVs incorporating PEDOT:PSS:Zonyl hole selective contact shown limitations on humidity lifetime performance due to the poorest adhesion properties of Zonyl-treated PEDOT:PSS PH compared with Dynol and Zonyl/Dynol mixture treated PEDOT:PSS PH.

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1. Introduction

Solution processed inverted organic photovoltaics OPVs could allow more flexibility on designing the production process of OPVs and thus provide technological opportunities [1–3]. In the inverted structure the electrons are extracted at the bottom electrode (ITO/*n*-type metal oxide) and the holes are extracted at the top electrode (Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS/Metal) [3]. Recent studies demonstrated inverted OPVs with power conversion efficiencies (PCE) between 8–12% (single and multi-junction cells), by using newly synthesized conjugated polymers and by incorporating novel buffer layers to form the top selective contact [4,5]. Although device efficiency continues to improve, the molecular scale function of many materials used is still not fully understood. In addition, the interfaces formed between solution processed materials and their impact on device performance is in most cases a complicated matter of study [6].

The solution processed top electrode is a major challenge in designing economically viable inverted OPVs. Despite the recent

progress in employing solution-based metal oxide hole selective contacts in inverted OPVs [7–9], PEDOT:PSS is still the most common solution-based hole selective contact for the top electrode of inverted OPVs, because of its tuneable electronic properties and compatibility with various printing processes [10]. On the other hand, PEDOT:PSS has been suggested as a primary degradation source under accelerated lifetime conditions of inverted OPVs [11]. We have recently used reverse engineering to prove that the PEDOT:PSS hole selective contact is the main limiting factor for long OPV lifetime performance under accelerated humidity lifetime conditions [12]. The exact mechanism of degradation still remains unclear. Barrier formation at the critical active layer/PEDOT:PSS interface as well as PEDOT:PSS bulk properties degradation due to its hygroscopic nature have been suggested [13].

The study of this material over the last years resulted in PEDOT:PSS formulations varying significantly in electronic properties, such as electrical conductivity, work function, wetting properties, acidity etc. Many reports have demonstrated the incorporation of additives in PEDOT:PSS, such as high boiling point solvents, in order to regulate the aforementioned properties for the desired application [14]. Yan and Okuzaki demonstrated that ethylene glycol used in PEDOT:PSS PH500 can significantly increase electrical conductivity of the layer, by removing PSS content from the film [15]. Dimethyl sulfoxide (DMSO)

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[16], sorbitol [17], and many others [18–20] have also been used for electrical conductivity enhancement in PEDOT:PSS thin films.

A major processing issue of PEDOT:PSS hole selective contact in inverted OPVs is its hydrophilic nature and thus the high surface tension of its solutions. Despite the aforementioned additives drastically enhancing the electronic properties of PEDOT:PSS, they are not able to reduce the surface tension of PEDOT:PSS solutions in order to lead to improved wettability of the active layer surface. Based on that, processing additives have been extensively used in PEDOT:PSS as wetting agents, resulting in reduced surface tension and addressing the problem of wettability of PEDOT:PSS buffer layer coated on top of hydrophobic polymer:fullerene active layers in inverted OPVs [21]. Isopropanol [22], 2,5,8,11-tetramethyl-6-dodecyn-5,8-diol ethoxylate (Dynol 604) [23], Zonyl FS fluorosurfactant (Zonyl) [24] other fluorosurfactants [25] are such examples. We recently demonstrated that an optimum mixture of Zonyl and Dynol wetting agents of PEDOT:PSS could cause synergetic effects on the initial performance of inverted OPVs, resulting in enhanced hole selectivity, reliability and power conversion efficiency [26]. Thus, we proved that the choice of wetting agents, which necessarily have to be used in PEDOT:PSS hole selective contacts, has a significant impact on inverted OPVs initial performance.

In this study we firstly investigate inverted OPVs initial performance comparing 3 different PEDOT:PSS types, Al4083, PH and PH500, treated with the aforementioned mixture of 0.5 wt% mixture of Zonyl/Dynol (5/2) wetting agents. The aforementioned PEDOT:PSS formulations have been chosen to be used in this study because their different optoelectronic properties. This difference in optoelectronic properties, such as work function, electrical conductivity and PSS is strongly related with the hole selectivity of inverted OPVs. In addition those 3 PEDOT:PSS formulations are the commonly used PEDOT:PSS formulations for inverted OPVs hole selective contacts. Incorporating these layers as hole selective contacts in inverted OPVs, we observed a strong correlation of the hole selectivity of inverted OPVs with the aforementioned measured optoelectronic properties of PEDOT:PSS types. Despite the ~ 4 orders of magnitude higher electrical conductivity of PEDOT:PSS PH500, compare with the other two types of PEDOT:PSS, inverted OPVs using PEDOT:PSS PH exhibits the best initial inverted OPVs performance and reliability. The origin of these findings it is analyzed by a series of measurements based on device physics as described in details within Section 3.1 of this study. Furthermore, 3 series of non-encapsulated inverted OPVs using PEDOT:PSS PH treated with 3 different wetting agents, Zonyl 0.5 wt% (Zonyl-based inverted OPVs), Dynol 0.2 wt% (Dynol-based inverted OPVs) and 0.5 wt% mixture of Zonyl/Dynol (5/2) (Mixture-based inverted OPVs) as hole selective contact, have been tested under accelerated humidity conditions (RH=85% - $T=30^\circ\text{C}$ - Dark). Interestingly, we observed that Zonyl-based inverted OPVs exhibit almost half T80 (time to reach 80% of the initial power conversion efficiency) compared to the other two series of inverted OPVs under study. The origin of the faster degradation of Zonyl-based compared to the other two series of inverted OPVs it is attempted to be analyzed using, current density vs voltage (J/V), electrical conductivity, atomic force microscopy and contact angle studies, over time of exposure under harsh humidity environment. The paper highlights the importance of PEDOT:PSS/Additives interfacial interactions during processing. Based on those studies we proposed a PEDOT:PSS/Additives hole selective contact suitable for high performance solution processed inverted OPVs.

2. Experimental

All PEDOT:PSS types used in this study, Al4083, PH and PH500 were purchased from HC Stark. In all cases the processing

additives, Ethylene glycol (EG) (Sigma Aldrich), Zonyl FS-300 (Sigma Aldrich) and Dynol 604 (Air Products and Chemicals Inc.) were added in the corresponding PEDOT:PSS formulation and stirred 30 min before deposition. In order to regulate the thickness of each film during the doctor blading deposition the blade speed was changing accordingly and all the other processing parameters, such as blade height, solution volume and substrate temperature, were kept constant. For inverted solar cells fabrication, ITO substrates (sheet resistance $4\ \Omega/\text{sq}$, Psiotec Ltd Uk) were sonicated in acetone and subsequently in isopropanol for 10 min. ZnO electron transporting layer was prepared using a sol-gel process as described in details elsewhere [27]. The photo-active layer, a blend of P3HT:PCBM (1:0.8 wt%) 36 mg/ml in chlorobenzene, was doctor bladed on top of ZnO resulting in a thickness of $\sim 180\ \text{nm}$ as measured with a Veeco Dektak 150 profilometer. All of the aforementioned active layer solution processing parameters were established after a detailed optimization process of inverted OPVs performance. All PEDOT:PSS hole selective contacts investigated in this work have been doctor bladed on top of active layers. Then devices were transferred in a nitrogen filled glovebox and annealed at 140°C for 20 min followed by thermal evaporation of a silver layer with a thickness of 100 nm. The current density-voltage (J/V) characteristics were measured with a Keithley source measurement unit (SMU 2420). For illumination a calibrated Newport Solar simulator equipped with a Xe lamp was used, providing an AM1.5G spectrum at $100\ \text{mW}/\text{cm}^2$ as measured by an oriel 91,150 V calibration cell equipped with a KG5 filter. Net photocurrent vs voltage characteristics were obtained by extracting the dark from the illuminated J/V characteristics. Contact angle measurements have been performed using a KRUSS DSA 100E drop analysis system. Tapping mode AFM measurements have been applied a Veeco Nano-surf 2 setup. The material was doctor bladed on glass identical to device fabrication for electrical conductivity and work function measurements, which were carried out using a four point probe setup from Jandel engineering Ltd and Kelvin Probe setup from Besocke GmbH respectively. More details about the Kelvin Probe technique could be found elsewhere [28].

3. Results and discussion

All the inverted OPVs used in that study has the following structure: ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag. Initially we performed a comparative study of the three most commonly used PEDOT:PSS formulations as hole selective contacts. Al4083, PH and PH500 have been treated with 0.5% mixture of wetting agents Zonyl/Dynol(5/2) and their optoelectronic properties have been measured. Note that 5 vol% of ethylene glycol has been added to PH500 together with the proposed additive mixture. This treatment has been used before and found to drastically enhance the electrical conductivity of PEDOT:PSS PH500 about 2 orders of magnitude [15,19]. The increased electrical conductivity PEDOT:PSS PH500 after the ethylene glycol treatment has been attributed to reduced PSS content from $\sim 1:2.5$ to $\sim 1:1.6$ (PEDOT to PSS ratio) [15]. Table 1 summarizes the measured work function and electrical conductivity of all PEDOT:PSS formulations used in this study. PSS content for each PEDOT:PSS formulation has been provided either by the manufacturer or the literature.

It is well known that the three aforementioned optoelectronic properties of PEDOT:PSS are crucial for the hole selectivity of inverted OPVs. An increase in electrical conductivity may be assigned to a reduced series resistance (R_s) of inverted OPVs due to efficient transportation of charges from the active layers to the terminals of the device [29]. Suitable work function it is expected to provide ohmic contact with the active layer of inverted OPVs and thus reduce the parallel resistance (R_p) of inverted OPVs by

reducing the interface recombination [30]. Finally, sufficient PSS content is necessary, in order to provide the desired hole selectivity within the inverted OPV [31].

Work function measurements have been performed on the samples using a Kelvin Probe setup. All of the studied PEDOT:PSS formulations exhibit similar work function values. On the other hand, electrical conductivity values, measured with a four point probe setup, exhibit a significant variation. Al4083 exhibit electrical conductivity in the order of 10^{-4} S/cm. All PEDOT:PSS PH formulations measured exhibit electrical conductivity from 7×10^{-3} S/cm to 1×10^{-2} S/cm. PH500 treated with the mixture of wetting agents and ethylene glycol exhibit electrical conductivity in the order of 2×10^2 , which is at least 4 orders of magnitude higher compared to the other two PEDOT:PSS formulations under investigation. Finally, the PSS content of Al4083 and PH is given from the manufacture at 1:6 and 1:2.5, compared to 1:1.6 for PH500 treated with EG as it has been reported before [15].

3.1. The effect of various PEDOT:PSS formulations on inverted OPVs initial performance

Three different PEDOT:PSS formulations mentioned in Table 1 have been used as hole selective contacts in inverted OPVs. The device architectures studied based on the initial inverted OPV performance and summarized as follows: Our control devices based PEDOT:PSS PH hole selective contact (ITO/ZnO/P3HT:PCBM/PEDOT:PSS PH:Zonyl/Dynol (5/2) 0.5 wt%/Ag-“PH-based inverted OPVs”) are compared with inverted OPVs that use PEDOT:PSS Al4083 hole selective contact (ITO/ZnO/P3HT:PCBM/PEDOT:PSS Al4083:Zonyl/Dynol (5/2) 0.5 wt%/Ag-“Al4083-based inverted OPVs”) and inverted OPVs that use PEDOT:PSS PH500 hole selective contact (ITO/ZnO/

P3HT:PCBM/PEDOT:PSS PH500:Zonyl/Dynol (5/2) 0.5 wt%:Ethylene glycol 5 vol%/Ag-“PH500-based inverted OPVs”). Fig. 1 demonstrates the illuminated and dark current density characteristics of the compared inverted OPVs.

Fig. 1(a) shows the illuminated J/V characteristics of the three compared inverted OPVs. All the inverted OPVs under study exhibit good diode behavior with similar open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) values. On the other hand Al4083-based inverted OPVs exhibit significantly increased series resistance (R_s) compared to the other two representative inverted OPVs something which is verified from the dark J/V characteristics as well (Fig. 1(b)). In addition, from Fig. 1(b) we observe a significantly decreased parallel resistance (R_p) of the PH500-based compared to the other two representative inverted OPVs under study. Thus, PH-based devices exhibits the best fill factor values due to better combination of device internal resistances, R_s and R_p .

These observations could be correlated with the measured optoelectronic properties of PEDOT:PSS formulations used in this experimental run (Table 1). Since all the compared inverted OPVs use the same device configuration, we assume that the differences between the three inverted OPVs on device internal resistances (R_s and R_p) arise from different the bulk electrical conductivity of the PEDOT:PSS formulations under comparison. Specifically, the increased R_s of the Al4083-based inverted OPVs could attributed to its lower electrical conductivity compared to the other two PEDOT:PSS formulations (Table 1). As it is has been suggested previously, the bulk electrical conductivity of the electrodes has an influence in R_s of an organic diode [32]. An increase in electrical conductivity may be assigned to a reduced series resistance (R_s) of inverted OPVs due to efficient transportation of charges from the active layers to the terminals of the device [29]. In contrast, despite the ~ 4 orders of magnitude higher electrical conductivity of PH500 compared to PH and Al4083 no further enhancement in R_s for the PH500-based inverted OPVs compared with PH-based and Al4083-based inverted OPVs is observed (0.9 Ω , 1.1 Ω , 3.4 Ω respectively -Fig. 1(b) Table 2). Similar observation have been observed in a normal device structures OPVs by Kim et al. [33]. Based on the above experimental results and device analysis studies, it is likely that the R_s of inverted OPVs could not be further reduced, if the bulk electrical conductivity of PEDOT:PSS is above a threshold value in the order of magnitude of about 10^{-2} S/cm. On the other hand, electrical conductivity less than 10^{-2} S/cm seems to lead in inverted OPVs with significantly increased R_s and thus lower FF and PCE.

Table 1

Work function, electrical conductivity and PSS content of all PEDOT:PSS formulations used in this study.

PEDOT:PSS Formulation	Work function [eV]	Electrical conductivity [S/cm]	PEDOT:PSS content
Al4083:Zonyl/Dynol (5/2) 0.5%	4.8	0.0009	1:6
PH500:Zonyl/Dynol (5/2) 0.5%: Ethylene Glycol 5%	4.9	207	1:1.6 [15]
PH:Zonyl/Dynol (5/2) 0.5%	4.8	0.01	1:2.5
PH:Zonyl 0.5%	4.9	0.007	1:2.5
PH:Dynol 0.2%	4.7	0.014	1:2.5

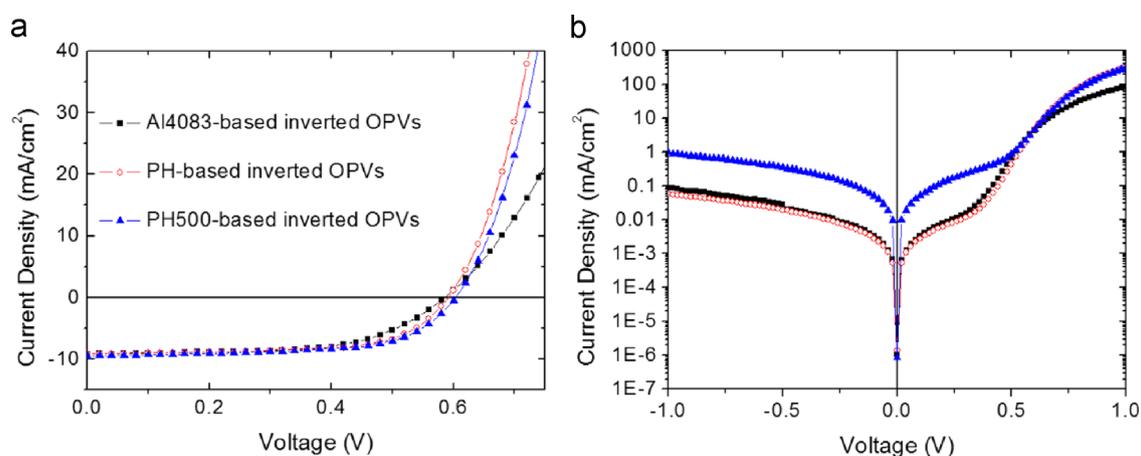


Fig. 1. (a) Illuminated and (b) dark current density vs voltage (J/V) characteristics of 3 inverted OPVs using different PEDOT:PSS formulations as hole selective contact, Al4083:Zonyl/Dynol (5/2) 0.5 wt% (black closed squares), PH:Zonyl/Dynol (5/2) 0.2 wt% (red open circles), PH500:Zonyl/Dynol (5/2) 0.5 wt% (blue filled triangles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Concerning the R_p behavior of the 3 inverted OPVs under comparison, we observe significantly lower R_p for PH500-based devices compared to the other two inverted OPVs. On the other hand, PH and Al4083-based devices exhibits similar leakage current. Since the work function between the 3 PEDOT:PSS formulations under comparison is similar, the increased leakage current (reduced R_p) of the PH500-based inverted OPVs could be attributed to the lower PSS content (higher conductivity) compared to the other two representative inverted OPVs. As it has been suggested before the concentration of PSS in bulk PEDOT:PSS is crucial for the electron blocking properties (hole selectivity) of inverted OPVs [31]. In contrast, despite that Al4083 contains almost ~ 2.5 times more PSS compared to PH, the leakage current of the corresponding devices is similar. Again, based on these observations it could be suggested that the R_p of inverted OPVs using PEDOT:PSS hole selective contacts, could not be further enhanced over a threshold value of PSS content in PEDOT:PSS of about 1:2.5. On the other hand, PSS content less than 1:2.5 seems

Table 2
Device efficiency parameters of the three representative inverted OPVs under study.

Inverted OPV	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	V_{bi} (V)	R_s (ohm)	R_p (ohm)
Al4083-based	59	9.07	60	3.19	66	3.4	1005
PH-based	59	9.09	65	3.49	66	1.1	920
PH500-based	59	9.41	62	3.44	67	0.9	780

to lead in inverted OPVs with significantly decreased R_p and thus reduced hole selectivity, lower FF and PCE.

Table 1 summarizes the efficiency parameters of each inverted OPV under study. The devices internal resistances have been calculated using a simulation model described previously by Waldauf et al. [34]. The built-in voltage (V_{bi}) has been calculated using net photocurrent vs voltage measurements. These measurements can be used to measure the built-in potential (V_{bi}) and thus the changes in the energy barriers at the interfaces between the active layer and the electrodes [35]. The V_{bi} was found to be 0.66 V, 0.66 V and 0.67 V for the Al4083, PH and PH500-based inverted OPVs device respectively.

Fig. 2 demonstrates the average results in box plots of the 12 devices for each series of inverted OPVs under study. Similar trends have been observed in other experimental runs.

Though the V_{oc} of the 3 series of inverted OPVs under study is similar, Al4083-based exhibit more dispersed values compared with the other two inverted OPVs under study. On the other hand, the J_{sc} of the PH-based is averagely lower compared with the other two inverted OPVs. Finally, the fill factor of PH-based is averagely higher compared with the other two inverted OPVs. The latter is a result of better combination of R_s and R_p of PH-based inverted OPVs compared with the other two series of inverted OPVs under study, as analyzed above (Fig. 1). As a result, the PCE values are averagely similar between the 3 compared series of inverted OPVs. Though, PH-based devices exhibiting slightly averagely higher PCE compared to the other two series of inverted OPVs under study with increase reproducibility, an important factor for commercialization of solution processed OPVs. The above studies indicate that PEDOT:PSS PH is most suitable PEDOT:PSS derivative for hole

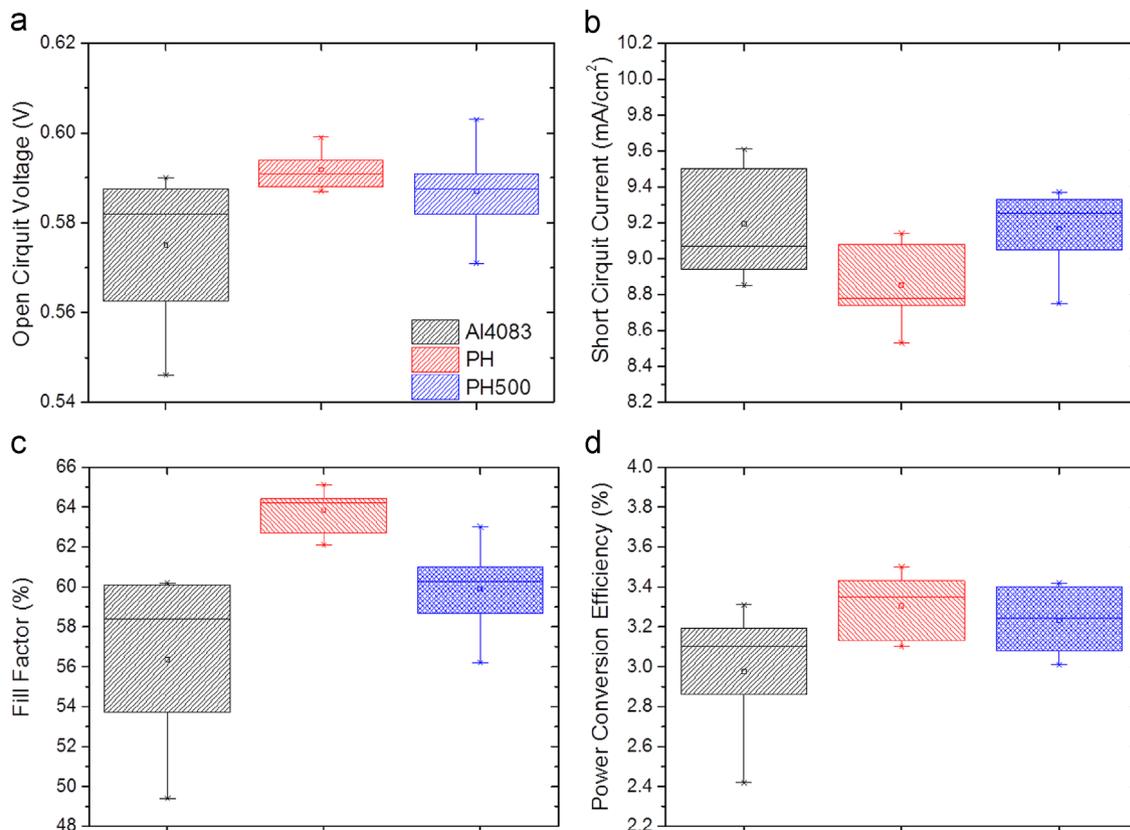


Fig. 2. (a) Open-circuit voltage (b) Short-circuit current density (c) Fill factor and (d) Power conversion efficiency results in box plots of 8 devices of each of the 3 series of inverted OPVs using different PEDOT:PSS formulations as hole selective contact, Al4083:Zonyl/Dynol (5/2) 0.5 wt% (black), PH:Zonyl/Dynol (5/2) 0.2 wt% (red), PH500:Zonyl/Dynol (5/2) 0.5 wt% (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

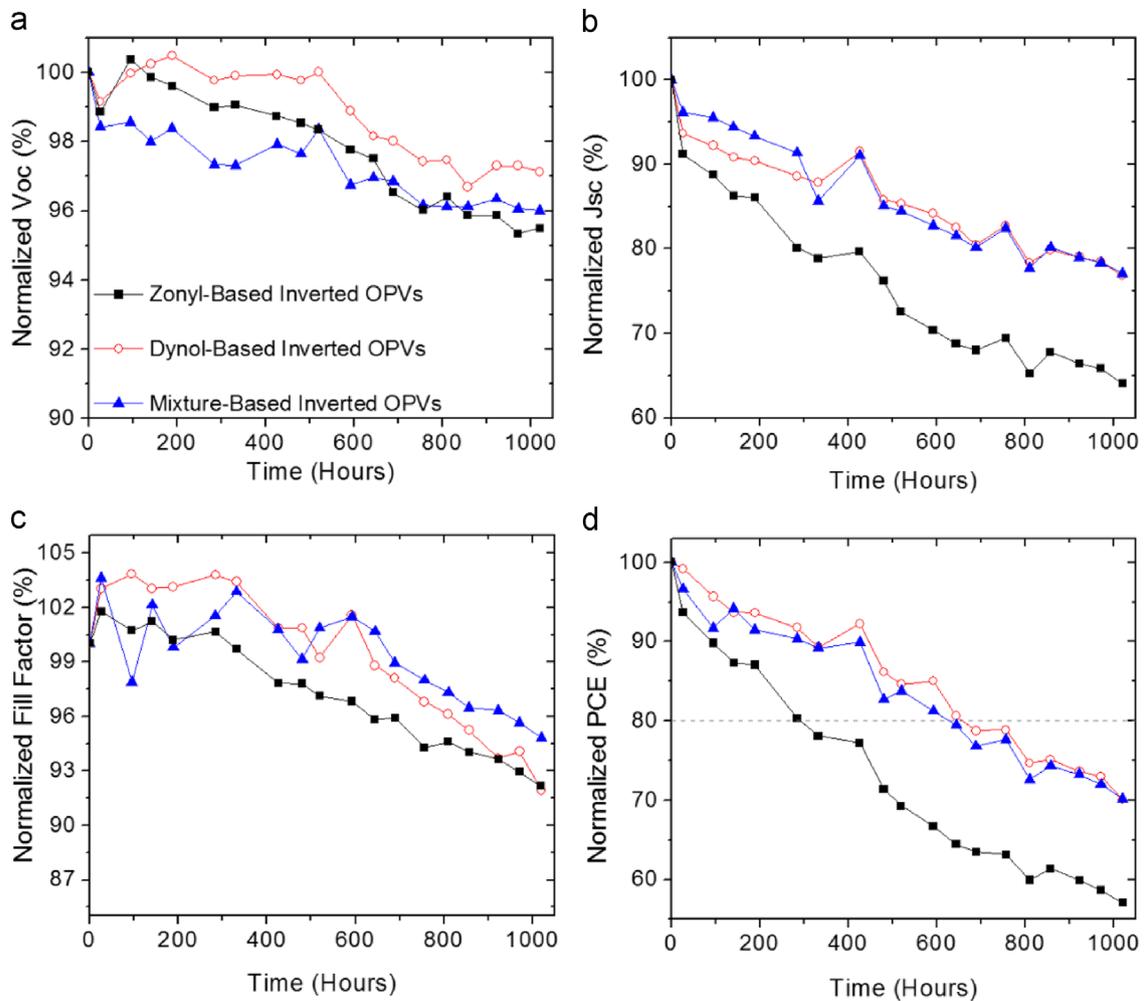


Fig. 3. Normalized (a) Open circuit Voltage (V_{oc}) (b) Short-circuit current (J_{sc}) (c) Fill Factor (FF) and (d) Power conversion efficiency (PCE) of the three non-encapsulated inverted OPVs under study as a function of time, under exposure in accelerated humidity lifetime conditions, RH=85% – $T=30^\circ\text{C}$ – Dark. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

selective contact in inverted OPVs compared to PEDOT:PSS Al4083 and PH500.

3.2. The effect of different wetting agent treatment on accelerated humidity lifetime performance of inverted OPVs

Lifetime performance is an equally important factor for cost efficient commercialization of OPVs. As mentioned before PEDOT:PSS has been identified as the major degradation mechanism of OPVs under harsh humidity conditions. This failure of the OPVs has been attributed to the hygroscopic nature of PEDOT:PSS [10] and/or its interfacial interactions with the active layer [36].

As also mentioned before PEDOT:PSS processing as hole selective contact in inverted OPVs requires wetting agents in order to overcome wettability limitations of the hydrophobic active layer by the hydrophilic PEDOT:PSS. Thus, we have recently reported the synergetic effects of zonyl:dynol PEDOT:PSS additives on the PCE and reliability of inverted OPVs [26].

In this paper, we examined the behavior under accelerated humidity lifetime performance of non-encapsulated inverted OPVs using PEDOT:PSS PH treated with the same 3 different wetting agents. Three series of inverted OPVs have been tested using differently treated PEDOT:PSS hole selective contacts as follows: PEDOT:PSS PH treated Zonyl 0.5 wt% (Zonyl-based device Inverted OPVs), Dynol 0.2 wt% (Dynol-based device Inverted OPVs), mixture of Zonyl: Dynol-5:2 0.5 wt% (Mixture-based Inverted OPVs). For the testing,

8 devices of each series have been fabricated. Fig. 3 presents the average normalized photovoltaic parameters of all the non-encapsulated inverted OPVs under study. Similar results have been observed in two others identically performed experimental runs.

Normalized V_{oc} vs time of exposure under accelerated humidity conditions graph (Fig. 3(a)) shows similar drop between the three non-encapsulated inverted OPVs under comparison. In all cases, normalized V_{oc} is between 96–98% after 1000 h of exposure. On the other hand, normalized J_{sc} is varying significantly between the compared inverted OPVs (Fig. 3(b)). Zonyl-based devices exhibit 70% normalized J_{sc} after 1000 h of exposure and much steeper drop compared with the other two inverted OPVs. In addition, the other Dynol- and mixture-based inverted OPVs exhibit similar drop trend and normalized J_{sc} values of about 85% after 1000 h of exposure. As for normalized Fill Factor (Fig. 3(c)) we observe normalized values between 96–93% for all the inverted OPVs under comparison with similar drop trends. Finally, normalized PCE vs time of exposure graph (Fig. 3(d)) indicates much faster degradation of Zonyl-based devices compared with the other two inverted OPVs. Zonyl-based inverted OPVs reach T_{80} (time to reach 80% of the initial value) a little before 290 h of exposure in contrast with Dynol- and mixture-based inverted OPVs which are steady above 90% of their initial efficiency for more than 400 h and then reach T_{80} after ~ 650 h of exposure under harsh humidity conditions. In all cases, the most vulnerable photovoltaic parameter under humidity conditions is J_{sc} rather than FF and V_{oc} and is the major reason for the PCE drop.

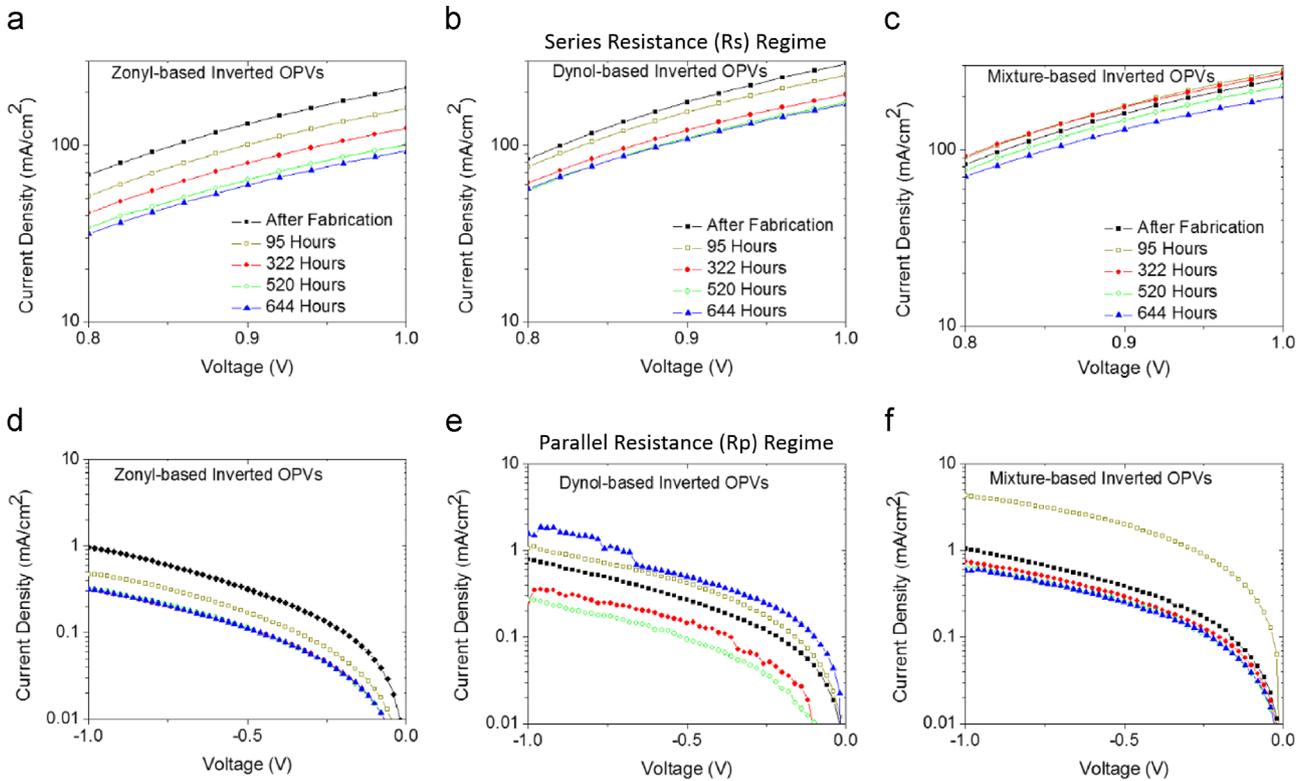


Fig. 4. Extracted J/V parameters of the inverted OPVs after fabrication (black filled squares), after 95 h (yellow open squares), 322 h (red filled circles), 520 h (green open circles) and 644 h (blue filled triangles) of exposure under Dark – RH=85% – $T=30\text{ }^{\circ}\text{C}$. The top and bottom row illustrates the series and parallel resistance regime respectively for (a) and (d) Zonyl-based, (b) and (e) Dynol-based and (c) and (f) Mixture-based inverted OPVs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The above findings are in accordance with other literature results indicating similar normalized V_{oc} , J_{sc} , FF and PCE drop trends over time of exposure under harsh humidity conditions in inverted OPVs using PEDOT:PSS hole selective contacts [11]. Despite the same device structure for all of the three series of inverted OPVs under study (ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag) the different wetting agent treatment of PEDOT:PSS layer, results in significantly different accelerated lifetime performance between the three inverted OPVs under study.

Attempting to identify the origin of the faster Zonyl-based degradation compared with the other two inverted OPVs a series of measurements have been performed. Fig. 4 demonstrates the R_s (top row) and R_p (bottom row) regimes of the J/V characteristics of three representative inverted OPVs after various hours under accelerated humidity conditions (Dark – RH=85% – $T=30\text{ }^{\circ}\text{C}$).

In all cases R_s is increasing over time of exposure under harsh humidity conditions (Fig. 4(a), (b) and (c)). Though, the R_s increase is much larger in Zonyl-based compared with Dynol-based and mixture based inverted OPVs. Mixture-based exhibit the lowest increase in R_s after time of exposure under harsh humidity conditions, compared with the two other inverted OPVs under study.

On the other hand, we observe different R_p behavior between the three compared series of inverted OPVs. Zonyl-based inverted OPVs exhibit a constant increase of R_p over time of exposure under humidity and stabilizes from 322 h and after. In contrast, Dynol-based inverted OPVs does not seem to follow a trend in R_p region exhibiting random values under harsh humidity conditions. Finally, mixture-based inverted OPVs seem to have an initial increase of R_p and then drop slightly after 322 h of exposure.

Based on the above observations, the larger increase of R_s occurring over time of exposure under harsh humidity conditions within Zonyl-based compared to the other two inverted OPVs could be attributed in two general mechanisms: either in faster

disorientation of the optoelectronic properties of the bulk PEDOT:PSS treated with Zonyl wetting agent compare with PEDOT:PSS treated with dynol or Zonyl/Dynol or an interaction with the active layer that is occurring only or faster in devices using Zonyl treated PEDOT:PSS.

In order to identify which of the two mechanisms of degradation of PEDOT:PSS is dominant under harsh humidity conditions, electrical conductivity and atomic force microscopy (AFM) studies have been performed over time of exposure under accelerated humidity conditions (RH=85% – $T=30\text{ }^{\circ}\text{C}$ – Dark), on the three compared PEDOT:PSS PH layers (Fig. 5).

Bulk electrical conductivity measurements over time of exposure under accelerated humidity lifetime conditions do not indicate a disorientation of any of the three differently treated any PEDOT:PSS layers under study. All of PEDOT:PSS layers under investigation present a slight drop of their bulk electrical conductivity over the first 20 h of exposure and then exhibit stable values of $\sim 10^{-2}\text{ S/cm}$ in all cases. In addition, atomic force microscopy studies on the differently treated thin films of PEDOT:PSS PH do not reveal any surface topography change after 200 h of exposure under accelerated humidity lifetime conditions. Based on the above observations, we suggest that the lower accelerated humidity lifetime of Zonyl-Based inverted OPVs, compared to the other two, it doesn't seem to be originated from faster bulk PEDOT:PSS optoelectronic properties degradation, since electrical conductivity and morphology of the layers doesn't deviate significantly from the as fabricated status.

It is more likely Zonyl-based inverted OPVs to degrade faster compared with the two other inverted OPVs due to an interaction with the P3HT:PCBM layer. A potential explanation of this interesting observation is the poorest adhesion of Zonyl-treated compared with Dynol and mixture Zonyl/Dynol treated PEDOT:PSS PH, on P3HT:PCBM layer. Fig. 6 demonstrates the surface energy

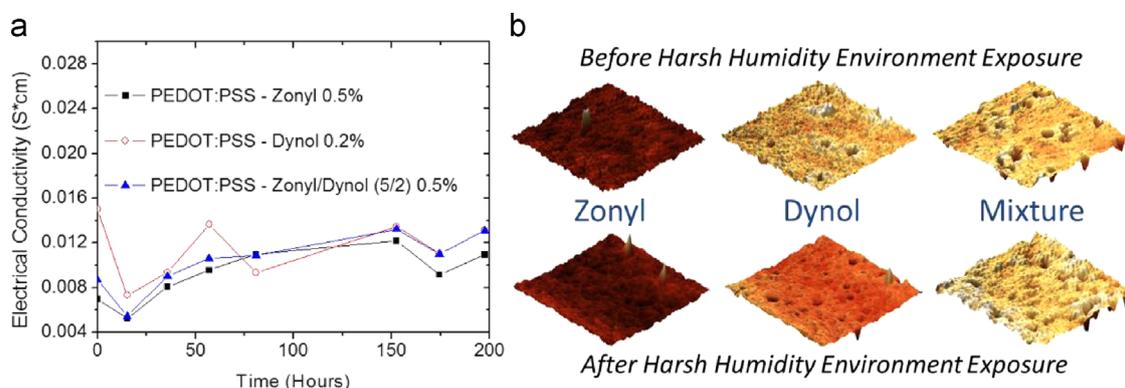


Fig. 5. (a) Electrical conductivity of PEDOT:PSS PH treated with Zonyl 0.5% (black filled squares) with dynol 0.2% (red open circles) mixture of Zonyl/Dynol (5/2) 0.5% (blue filled triangles) after several hours of exposure in accelerated humidity lifetime conditions, RH=85% - $T=30^{\circ}\text{C}$ - Dark. (b) AFM measurements of PEDOT:PSS layers treated with Zonyl or Dynol or their mixture before (top row) and after 200hours of exposure in accelerated humidity lifetime conditions, RH=85% - $T=30^{\circ}\text{C}$ - Dark (bottom row). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

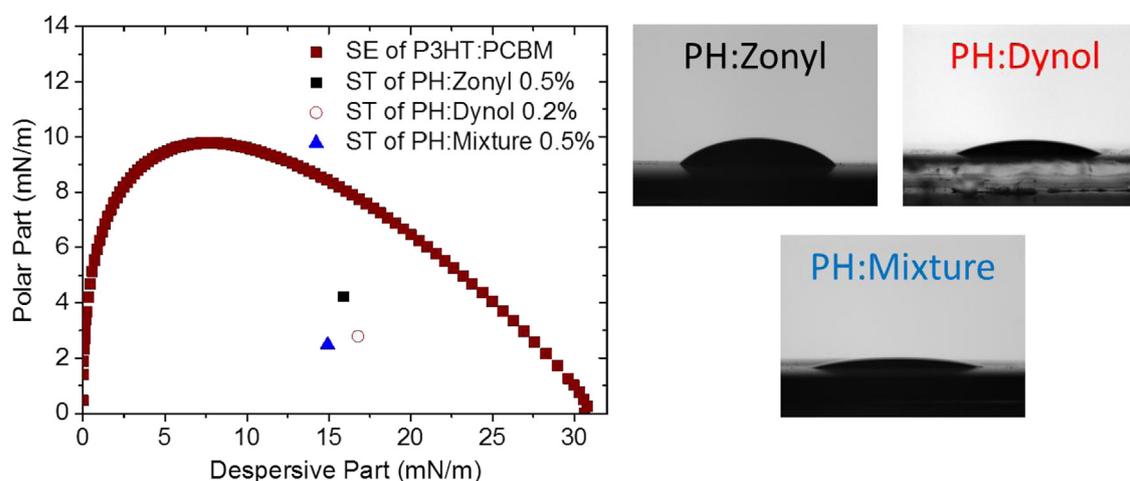


Fig. 6. The right image depicts surface energy and tension calculations of P3HT:PCBM layer (wine filled squares), PEDOT:PSS PH/Zonyl 0.5% (black filled square), PEDOT:PSS/Dynol 0.2% and PEDOT:PSS/Zonyl:Dynol-5:2 0.5 wt%, solutions. The left images depict the contact angle images of the three differently treated PEDOT:PSS solutions on top of P3HT:PCBM layer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and tension calculations of the P3HT:PCBM layer as well as the three, differently treated PEDOT:PSS PH solutions.

Based on Fig. 6 observations, Dynol and mixture of Zonyl/Dynol are better wetting agents compared with Zonyl due to higher reduction of surface tension of PEDOT:PSS in smaller quantities. In addition the contact angle of PEDOT:PSS PH:Zonyl is higher compared to the other two PEDOT:PSS solutions under comparison. Based on the work of adhesion and the Young–Dupre equations, lowest surface tension of a solution leads to increased adhesion on top of a surface with given surface energy [37]. In addition, a decreased contact angle of PEDOT:PSS solution was found to lead in increased chemical interaction on the hydrophobic P3HT:PCBM film during processing, suggesting increased chemical interaction between the two organic layers and thus increased adhesion [38]. In general, P3HT:PCBM–PEDOT:PSS interface has been identified as the weakest interface in inverted OPVs. Adhesive failure was observed between the P3HT:PCBM active layer and PEDOT:PSS hole selective contact as verified by Larsen-Olsen et al. [39] In addition, Dupont et al. found that the synergetic effect of stress and environmental species like moisture, greatly accelerates the delamination of the weak P3HT:PCBM–PEDOT:PSS interface [40].

Thus, we suggest that the poorest accelerated humidity lifetime performance of Zonyl-based inverted OPVs (Fig. 3) seems to originates from the poorest adhesion of Zonyl-treated compared with Dynol and mixture Zonyl/Dynol treated PEDOT:PSS PH on P3HT:

PCBM layer. This is in accordance with other literature results, which indicate the poor adhesion at the interfaces would lead to faster degradation of corresponding inverted OPVs due to faster oxygen and water molecules penetration to the weak interface [13,41].

4. Summary and conclusions

In summary, the effect of the different optoelectronic properties of PEDOT:PSS formulations, Al4083, PH and PH500 in inverted structured OPVs is reported. After investigating the properties of PEDOT:PSS formulations relevant to inverted OPV device function, such as electrical conductivity, work function and PSS content, inverted OPVs using those three different PEDOT:PSS formulations as hole selective contacts, have been compared and analyzed using illuminated-dark J/V observations as well as equivalent circuit model analysis and V_{bi} calculations. Based on our observations we proposed PEDOT:PSS PH as the most suitable PEDOT:PSS derivative for high performance hole selective contact in inverted OPVs. In addition, by correlating the experimentally observed PV properties with device physics studies, we proposed that electrical conductivity of 10^{-2} S/cm and PSS content of $\sim 1:2.5$ (PEDOT to PSS) are suitable values of the PEDOT:PSS buffer layers for high performing hole selective contacts in inverted OPVs.

Furthermore, the proposed PEDOT:PSS PH derivative is treated with 3 different wetting agents, Zonyl, Dynol and their optimum

mixture and their accelerated humidity lifetime performance is investigated. Importantly, is observed that PEDOT:PSS PH Zonyl-based inverted OPVs exhibits almost half T80 (time to reach 80% of the initial performance) compared with PH:Dynol-based and PH: Mixture-based inverted OPVs under accelerated humidity lifetime conditions. We argue that the limited humidity lifetime performance of inverted OPVs using Zonyl-treated PEDOT:PSS cannot be attributed to bulk PEDOT:PSS optoelectronic properties losses. Based on the wetting analysis studies reported, we suggest, that the poorest accelerated humidity lifetime performance of Zonyl-based inverted OPVs originates from the poorest adhesion properties of Zonyl-treated PEDOT:PSS PH compared with Dynol and mixture Zonyl/Dynol treated PEDOT:PSS PH.

In conclusion, we proposed PEDOT:PH treated with Zonyl:Dynol as the most suitable choice of hole selective contact for high performance (PCE, reliability and accelerated humidity-lifetime performance) solution processed inverted OPVs. Those findings indicating the importance of PEDOT:PSS/Additives interfacial interactions during processing. Such interactions play a critical role on the properties and device performance of solution processed PVs and should be taking into account on the PV materials design/selection procedures.

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