

Performance and stability of PTB7:PC₇₁BM based polymer solar cells, with ECZ and/or PVK dopants, under the application of an external electric field

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Received: 20 October 2015 / Accepted: 17 February 2016 / Published online: 25 February 2016
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Abstract The effect on the J–V behavior of polymer solar cells (PSCs) based on the active layer PTB7:PC₇₁BM under a previous application of an external electric field (E_{ext}) is presented. The active layer is doped with 0.01–0.04 wt. ratio (with respect to PTB7) of poly(9-vinylcarbazole) (PVK) as a photoconductor, and/or 0.25–0.5 wt. ratio of 9-ethylcarbazole (ECZ) as plasticizer. The general PSC structure was Glass-ITO/PEDOT:PSS/PTB7:PC₇₁BM:*dopant*/PFN/FM where *dopant* means PVK, ECZ or a mixture of them. Field's metal (FM) is an eutectic alloy with a melting point above 62 °C, which is deposited in a vacuum free atmosphere. Electric fields of 5 or –70 V/ μm (forward and reversed polarity, respectively) are applied. For PSCs doped with PVK, under forward polarity, it is observed a remarkable variation (36 %) on J_{sc} : from 7.7 to 4.9 mA/cm², while V_{oc} remains almost constant: ~ 0.76 V; whereas with the reversed polarity, a drastic variation of 95 % is observed on V_{oc} : from 0.76 to 0.04 V; while J_{sc} value changes from 7.4 to 5.6 mA/cm² (24 %). On the other hand, PSCs doped with the combination of ECZ and PVK, an increase of 10 % in J_{sc} is reached for reversed bias ($E_{\text{ext}} = -70$ V); and without applying any field, and keep them under N₂ atmosphere, a

slower photovoltaic degradation, with respect to that one from all the other studied samples, is shown over 57 days of monitoring them: FF variation is of just 6 % and PCE decays only 21 %.

1 Introduction

The growing interest in the last decade for the study of polymer solar cells (PSCs), is due to their promising advantages such as: light weight, mechanical flexibility, slimness, transparency, adaptability of their chemical and physical properties and the possibility of implementing them through versatile and easy many manufacturing techniques including spin-coating, roll to roll, doctor blading, inkjet printing, screen printing, spray-coating, etc. The use of a variety of materials and different architectures in the fabrication of PSCs, has allowed achieving more than 10 % of power conversion efficiency (PCE) [1–3]. A high PCE value is a key factor for the possibility of commercialization of PSCs technology. Other key factor is the lifetime of these devices: under some specific experimental conditions of fabrication and operation PSCs have shown lifetimes of the order of thousands of hours [4], however, this factor, for the generality of the devices has to be further improved to accomplish the maturity of this technology. Even when also it is necessary having a deeper comprehension of the physical and chemical phenomena involved in PSCs operation, the possibility of developing new materials, with adequate band-gaps and properties, the capacity to build tandem arrangements [5] and better conversion efficiencies, makes PSCs one of the technologies with a great potential for the near future.

Regarding molecular orientation and charge transport in different layers of PSCs and their effect on the overall

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photovoltaic (PV) performance, there have been attempts to produce a certain degree of nano-structural order or orientation by applying electric fields, under different conditions, to improve charge separation, device efficiency and/or stability [6–14]. For instance, in the early report of Sentein et al. [6], it was applied a static electric field through an amorphous polymer film, while heating near the glass transition temperature (T_g) and thus, orienting polar dopant molecules, it produced current–voltage characteristics strongly asymmetric. The applied bias was among ~ -50 and -150 V/ μm . In this work, push–pull polar molecules DR1 and DBANS were used as well as PVK and PMMA. In a second early work from the same group, Sicot et al. [7] used the mentioned previous studies and interpretations shown in Ref. [6], to improve the PV performance of PSCs cell based on polythiophene films with a double layer structure in between ITO and Au electrodes. The applied biases were of -43 and -83 V/ μm having an increase of about one order of magnitude on efficiency conversion between non-oriented and oriented cells, however, at that time, this efficiency was very small: $\sim 10^{-5}$ – 10^{-6} %.

In more recent works, for instance, Li et al. [9] performed a theoretical study of the photoinduced charge transport in a BT:PC₆₁BM (BT = a low molecular weight molecule) active layer system, controlled by an external electric field. This study found that the exciton separation rate increases by one order when such field increases and that exciton dissociation is not the limiting factor in PSCs. Chaturvedi et al. [10], fabricated PSCs with the inverted structure ITO/ZnO/P3HT:PCBM/Ag, where the electron transfer layer (ETL) ZnO was deposited using a spray coating nozzle under an electric field of 0.25 V/ μm (1000 V applied in between the needle and a metallic ring separated 4 mm). This procedure was conducted in order to make the ZnO layer smoother and crystalline in the solar cell. A power conversion efficiency around 2.7 % and a good stability with only 20 % degradation in PCE after 105 days were obtained; without the use of this procedure, the PCE value was of 2.1 % and cells had a 46 % of degradation for the same period. Other similar work was carried out from the same group, with the solar cells structure ITO/PEDOT:PSS/P3HT:PCBM/Al, where PEDOT:PSS was deposited in spray applying externally 700 V (0.18 V/ μm) [11]. Smoother films morphologies and increased conductivities were reached: from 0.6 S/cm to 18 S/cm, which in turn improved the J_{sc} value 42 % (from 8.6 to 12.2 mA/cm²) and the PCE value 69 %: from 1.3 to 2.2 % (even when the FF value was rather small: from 0.29 to 0.33). In the literature there are some other cases of applied electric fields to PSCs and OLEDs simultaneously with solvent annealing process or during the active layer solvent drying. For instance, Li et al. [12], applied a constant reversed electric field of -60 V/ μm (for over 10 min) in between PSC

electrodes, the cell configuration was ITO/PEDOT:PSS/MEH-PPV:C₆₀/Al. Simultaneously, it was given a 120 °C (above T_g polymer temperature) heat treatment for 10 min. With this procedure, J_{sc} increased from 0.25 to 1.5 mA/cm² and PCE improved from 0.104 to 0.56 %, it means an enhancement of a factor of 6 and 5.4, respectively. Solanki et al. [13] applied a forward electric field of 0.14 V/ μm (600 V between ITO and an aluminum plate separated 4.3 mm from the active layer) to a PSC based on P3HT nanofibers (NF) with the architecture ITO/PEDOT:PSS/P3HT-NF:PCBM/Al. This field was applied over 30 min during the active layer drying process at room temperature. Current densities from 1.76 to 2.16 mA/cm² were reached without and with the field, respectively, and the PCE improved more than 22 %: from 1.76 to 2.16 %. Padinger et al. [14] fabricated ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al PSCs; these devices were thermally treated at 75 °C for 4 min simultaneously with 2.7 V (forward bias) applied between cell electrodes (i.e., $E_{ext} \sim 14$ V/ μm). Not treated cells had J_{sc} , V_{oc} , FF and PCE values of 2.5 mA/cm², 0.3 V, 0.4 and 0.4 %, while treated PSCs showed 8.5 mA/cm², 0.55 V, 0.6 and 3.5 % values, respectively.

In relation to the stated in the previous paragraph, an important parameter to control in the fabrication of PSCs of high performance is the molecular orientation on the active layer film relative to donor/acceptor heterojunctions. For instance, Ma et al. [15] applied to ITO/ZnO/P3HT:PCBM (1:1 wt. ratio)/NiO/Ag PSCs, an electric field, with external electrodes, of ~ 0.5 V/ μm . J_{sc} and PCE improved, with respect to cells without field, from 9.15 to 9.83 mA/cm² and from 3.16 to 3.51 %, respectively. Zhou et al. [16] added about 6 wt% of 5CT, a liquid crystalline compound, into the active layer of an ITO/PEDOT:PSS/P3HT:PCBM (1:1 wt. ratio)/LiF/Al based PSCs. An external field of 0.6 V/ μm was applied during the active layer drying to influence the P3HT ordering. A PCE of 3.5 % was reached in comparison to 2.4 % efficiency for the pristine P3HT-PCBM blend without field. It has been observed that there exists a direct relation between the degree of molecular orientation and J_{sc} and FF parameters [17], being these two factors susceptible to be improved if the active layer microstructures are closely packed and properly oriented [18]. Regarding PTB7 polymer, it has relatively large local internal dipoles (through its BDT and TT moieties). It has been calculated that the thienothiophene (TT) monomer component in this polymer has a transition-state dipole moment $\mu_{tr} = 8.23$ D, an excited-state dipole moment $\mu_e = 7.13$ D and a ground-state dipole moment $\mu_g = 3.76$ D, leading to one of the largest dipole change of the PTB polymer series [19]. As a comparison, the dipole moment of the P3HT polymer is in the range 1.0–1.6 D [13]. The large dipole moment value of PTB7 compound could enable its molecular orientation under an external

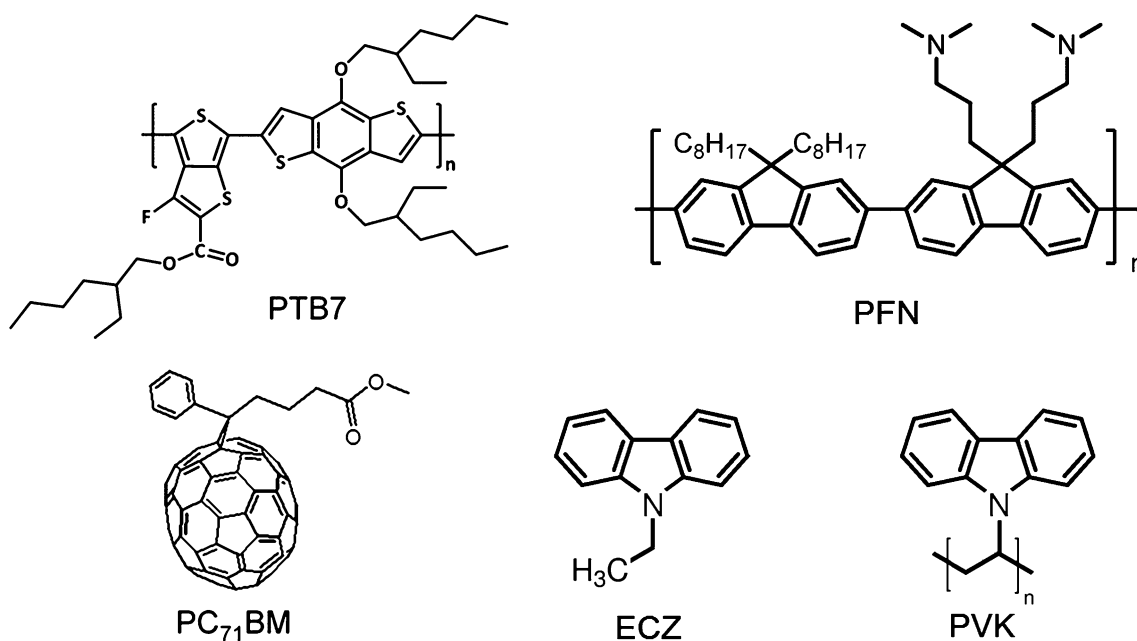


Fig. 1 Chemical structures of the organic compounds used in this work for PSC devices

application of an electric field. This possibility deserves investigation of PSCs based on the mixture PTB7:PC₇₁BM, which show one of the largest PCEs [2, 3].

In this work, for PSCs based on the active layer PTB7:PC₇₁BM under the BHJ architecture, an external electric field (E_{ext}) is applied in between the cell electrodes, simultaneously with illumination, in order to influence the materials orientation and its effect on the J–V characteristics and device stability. Interesting elastic behaviors in the PSC electrical parameters and temporal improvements in the J_{sc} values by the application of the electric field are observed. The used cathode is Field's metal (FM) due to its practical and rapid prototyping capability to deposit it on top cell by the dropping technique under normal room conditions, i.e., without vacuum evaporation [20]. It is a eutectic alloy of 32.5 % Bi, 51 % In and 16.5 % Sn, with a melting point above 62 °C. As an attempt to allow the active layer to be more influenced by the interactions between the polymer dipole moment, E_{ext} and light, small amounts of poly(9-vinylcarbazole) (PVK) and/or 9-ethylcarbazole (ECZ) were incorporated into the active film. PVK is a well known photoconductive polymer used as a hole carrier in photorefractive applications [21–23], and less often in organic solar cells [7, 24, 25], while ECZ is a plasticizer and charge carrier to increase bulk flexibility [21–23]. ECZ possess similar electronic structure than PVK, in such a way that the partial plasticization and low quantity of the dopants does not disturb strongly the molecular arrangement of the compounds. Also these additions could give consistency to the blend and the

possibility of having a better order of the PTB7 polymer. For PSCs doped simultaneously with PVK and ECZ, with a $-70 \text{ V}/\mu\text{m}$ electric field application, alternant fluctuations of V_{oc} and J_{sc} were observed, such that the latter parameter showed a 10 % increase with respect to the initial value; after 78 days, the device PCE decay was of 70 %. However, with these same dopants mixture and without any applied electric field, a slower degradation is shown for PSCs (kept under N_2 atmosphere) over 57 days of monitoring them: FF variation was of just 6 % and PCE decayed only 21 %. To the best of our knowledge, there are not previous works on the application of an external electric field to PTB7 based PSCs neither the simultaneous use of PVK and ECZ in the active layer doping process to influence polymer orientation and device stability.

2 Experimental

2.1 Materials

Polymers PTB7 (average MW 125,000 g/mol) and PFN (average MW 22,000 g/mol) [26] were purchased from 1-Material Inc. PC₇₁BM was acquired from American Dye Source; all of them were used as received. Figure 1 shows the molecular structure of the used compounds in this work. The hole transfer layer (HTL) PEDOT:PSS (Clevios P AI4083) was acquired from Heraeus-Clevios, PVK polymer (average MW 1,100,000 g/mol, $T_g = 220 \text{ }^\circ\text{C}$) and ECZ were acquired from Aldrich. Prior to use, PVK was

purified two times by recrystallization from dichloromethane and methanol, ECZ (97 % purity) was also purified twice by recrystallization from chloroform. ITO/glass substrates with 4–10 Ω /square were purchased from Delta Technologies and FM from Rotometals. Chlorobenzene was obtained from Aldrich and 1,8-diiodooctane from Alfa Aesar and used as received.

2.2 Sample preparation

Figure 2 shows the architecture of the manufactured PSCs. ITO substrates were ultrasonically cleaned in four sequential steps: liquid soap, deionized water, acetone and isopropanol and treated with oxygen plasma for 5 min. PEDOT:PSS was deposited by spin-coating to get a layer of approximately 40 nm in thickness, treated with heat at 80 °C for 15 min, and allowed to cool down. A blend of PTB7:PC₇₁BM (blend ratio 1:1.5, 14 mg/ml of PTB7) was dissolved in chlorobenzene and 9 μ l of 1,8-diiodooctane (97:3 % by volume) and stirred for 20 h at 40 °C inside of a glove box filled with N₂. This base solution for the active layers was placed into 5 vials with equal volumes to form the following 5 types of active layer PSCs: (I) non-doped PTB7:PC₇₁BM based cells; and PTB7:PC₇₁BM based cells doped with (II) PVK at 0.01 wt. ratio; (III) PVK at 0.04 wt. ratio; (IV) ECZ at 0.5 wt. ratio and, (V) simultaneously ECZ and PVK at 0.25:0.01 wt. ratio, see Table 1.

Solutions of Table 1 were bar-stirred 4 h at 40 °C inside the glove box, before active layer deposition. The prepared PEDOT:PSS substrates, were spin-casted with the active

blends to get layers (about 100 nm in thickness) and thermally treated at 80 °C for 15 min, inside the N₂ glove box. PFN polymer (ETL) was dissolved in methanol (2 mg/ml concentration) and 10 μ l of acetic acid to prepare 5 ml of a standard solution, after dilution with methanol (1:5 v/v), solutions were spin-coated at 6500 rpm over 1 min on top of the active layer (film thickness: \sim 6 nm) and thermally treated at 80 °C for 10 min. Finally, the FM alloy cathode was deposited by drop casting technique heating it at 95 °C on a hot plate, this procedure is described elsewhere [20, 27], the area of the active layers cells, 0.03 cm², were defined by shadow masks.

2.3 Characterization and testing

Manufactured cells were characterized under air atmosphere by using a Keithley 2400 source meter and a Xenon lamp calibrated to 1 sun (AM 1.5 light condition) with an Oriel reference cell. To achieve molecular orientation and study its effects on PSCs performance, an external DC electric field (E_{ext}) was applied during 30 s across the PSC electrodes [12], with a polarization of either 5 or -70 V/ μ m, and simultaneously the device was illuminated (AM 1.5 light condition). This process was performed at normal room environment. The amplitude of the external electric fields applied to the solar cells was determined based on the layers thickness in between the ITO and FM electrodes. For instance, for a typical sample (see Fig. 2), the total thickness is of approximately 146 nm corresponding to PEDOT:PSS (40 nm), PTB7:PC₇₁BM:dopants (100 nm) and PFN (6 nm). Thus, the electric fields were set to attain typical values used in the literature for having orientational birefringence in photorefractive and PSCs devices [10–16, 21–23], then, DC applied voltages of -10.2 and 0.73 V (-70 and 5 V/ μ m) for reversed and forward bias were applied, respectively (see Fig. 3). In addition, for the forward bias case, the applied voltage was kept slightly below the V_{oc} initial value of our PSCs (~ 0.75 V) in order to achieve a current density close to zero, see also Ref. [12]. J–V curves were measured at normal room conditions, after the application of the external field, firstly every 15 min for

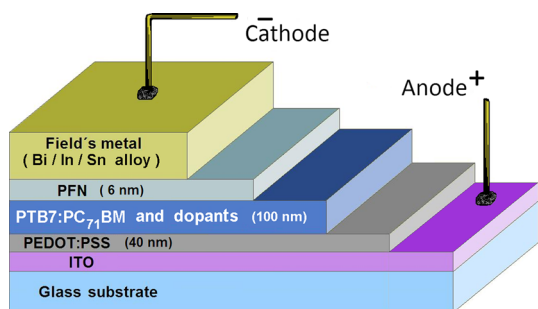


Fig. 2 Used architecture for the PSCs devices

Table 1 Weight proportions of the used materials for the PSCs active layers

Sample type	Active layer composition	wt. ratio
I	PTB7:PC ₇₁ BM	(1:1.5)
II	PTB7:PC ₇₁ BM:PVK	(1:1.5:0.01)
III	PTB7:PC ₇₁ BM:PVK	(1:1.5:0.04)
IV	PTB7:PC ₇₁ BM:ECZ	(1:1.5:0.5)
V	PTB7:PC ₇₁ BM:ECZ:PVK	(1:1.5:0.25:0.01)

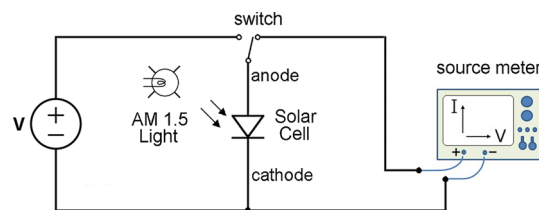


Fig. 3 Schematic of the experimental set up to apply the two electric field polarizations: $V = -10.2$ V ($E_{\text{ext}} = -70$ V/ μ m) reversed bias and $V = 0.73$ V ($E_{\text{ext}} = 5$ V/ μ m) forward bias (assuming a photodiode analogy), during 30 s

the initial 2 h, then every third day for the following 15 days, finally electrical measurements were acquired every 20 days for about 60 more days. PSCs were stored in N₂ atmosphere after each test. For the active layer, thermogravimetric analysis (TGA), for the decomposition temperature (T_d) measurements, were carried out in air and under nitrogen at a heating rate of 10 °C/min on a DuPont 951 thermogravimetric analyzer. The glass transition temperature (T_g) was evaluated by differential scanning calorimetry (DSC) measured at 10 °C/min on DuPont 910 equipment.

3 Results and discussion

Figure 4 shows the average reached J–V curves (from 6 fabricated devices of each composition) for the PSCs with different active layer composition, fabricated with our method (vacuum-free deposited cathode) and tested under normal room atmosphere. Here are observed the electrical characteristics for those PSCs (at zero E_{ext}) based on PTB7:PC₇₁BM (1:1.5 wt. ratio) (type I), PTB7:PC₇₁BM:PVK (1:1.5:0.01 and 1:1.5:0.04 wt. ratio) (type II and III), PTB7:PC₇₁BM:ECZ (1:1.5:0.5 wt. ratio) (type IV), and PTB7:PC₇₁BM:ECZ:PVK (1:1.5:0.25:0.01 wt. ratio) (type V), with a PCE of 4.5, 3.3, 2.8, 4.8 and 4.2 %, respectively. In general, the addition of slight amounts of PVK decreased the PSCs efficiency, while the small addition of ECZ slightly increases such light conversion. Simultaneous little addition of PVK and ECZ tend to produce devices with similar efficiency compared to that

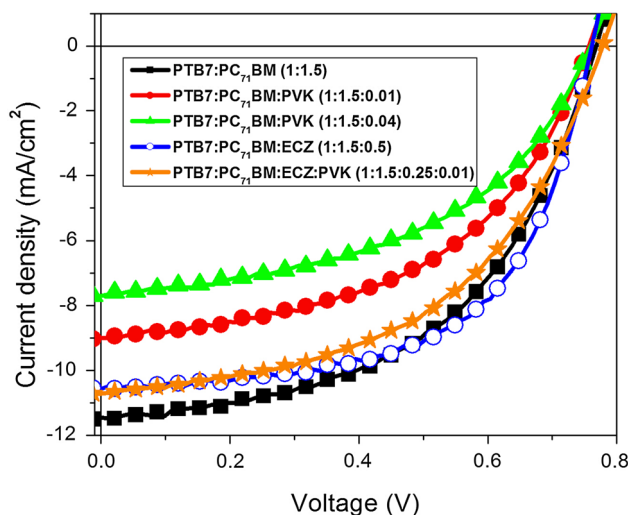


Fig. 4 Average J–V curves (from 6 fabricated devices of each composition), at E_{ext} = 0: for type I (black filled squares), II (red filled circles), III (green filled triangles), IV (blue open circles) and V (orange filled stars), see Table 1. They were manufactured under our method (no vacuum deposited cathode) and tested in a regular room atmosphere (Color figure online)

for undoped PSCs. For the case of the addition of just PVK, possible reasons of the efficiency reduction could be: large difference in charge mobility for PTB7 with respect to PVK: ~10⁵ or 10⁶ times larger for PTB7 [28, 29], large molecular weight ratio for PVK:PTB7, which is about 9 times in our case, large difference for energetic levels (PVK absorption is in the UV), etc.

Figure 5a, b shows the temporal evolution of J–V plots of a PTB7:PC₇₁BM (1:1.5 wt. ratio) (type I) based undoped PSCs without any external electric field applied on them. Graphic in Fig. 5a illustrates the typical degradation curve of a PSC, where J_{sc} values were decreasing from 11.5 to 9.3 mA/cm², while V_{oc} remained almost constant to 0.76 V and, the PCE variation was from 4.5 to 3.2 %, it means an efficiency reduction of 29 %, in a time period of 57 days (see Fig. 5b).

Figure 5c, d shows the temporal evolution of J–V curves for PSCs based on PTB7:PC₇₁BM:PVK (1:1.5:0.01 wt. ratio) (type II) as active layer, where after ~7.9 days was applied a 5 V/μm (forward bias) electric field and later on, at day 8.2, a field of –70 V/μm (reversed bias). It was made with the finality to see if the same set of PSC was susceptible to respond under different behavior for the two field polarities. It was confirmed as seen in plots 5c, d. For this type II of solar cells, from the graphics it is observed how from day 0 to day 8.1, V_{oc} is 0.75 volts with some fluctuations on J_{sc} from 9.3 to 7.3 mA/cm². Only after the second DC electric field of –70 V/μm (applied to the same cell), at day ~8.2, the J–V plots started to have drastic variations in the V_{oc} values: from 0.75 to <0.1 V; this behavior is better observed in Fig. 5d. J_{sc} presented a kind of oscillated fluctuations, where, at day 22 the peak value was 9.3 mA/cm² (initial value: 9.0 mA/cm²).

Figure 6a shows the J–V temporal evolution plot of PTB7:PC₇₁BM:PVK (1:1.5:0.04) (type III) based PSCs doped with PVK and –70 V/μm electric field application (at day 2). This graphic illustrates a drastic fall in the fill factor (FF), from 0.43 to 0.23, where V_{oc} values, once again, were decreasing from 0.76 to 0.04 V, while J_{sc} had a smaller variation from 7.4 to 5.6 mA/cm², the PCE fluctuation was from 2.4 to 0.06 %, it means a decrease of more than 97 % in a time period of 78 days, see Fig. 6b.

Figure 6c shows a J–V temporal evolution curve for a different set of PSCs based on PTB7:PC₇₁BM:PVK (1:1.5:0.04 wt. ratio) as active layer (type III), where it was applied a 5 V/μm (forward bias) electric field (at day 7.7). In this graphic is observed a totally different effect in relation to the one shown in Fig. 6a (where the applied field was –70 V/μm). Here V_{oc} is ~0.76 volts having a more drastic variation in J_{sc} values: from 7.7 to 4.9 mA/cm²; this behavior is better observed in Fig. 6d, where J_{sc} presented a kind of oscillated fluctuations. Also, a variation in the FF from 0.48 to 0.39 was observed and the PCE

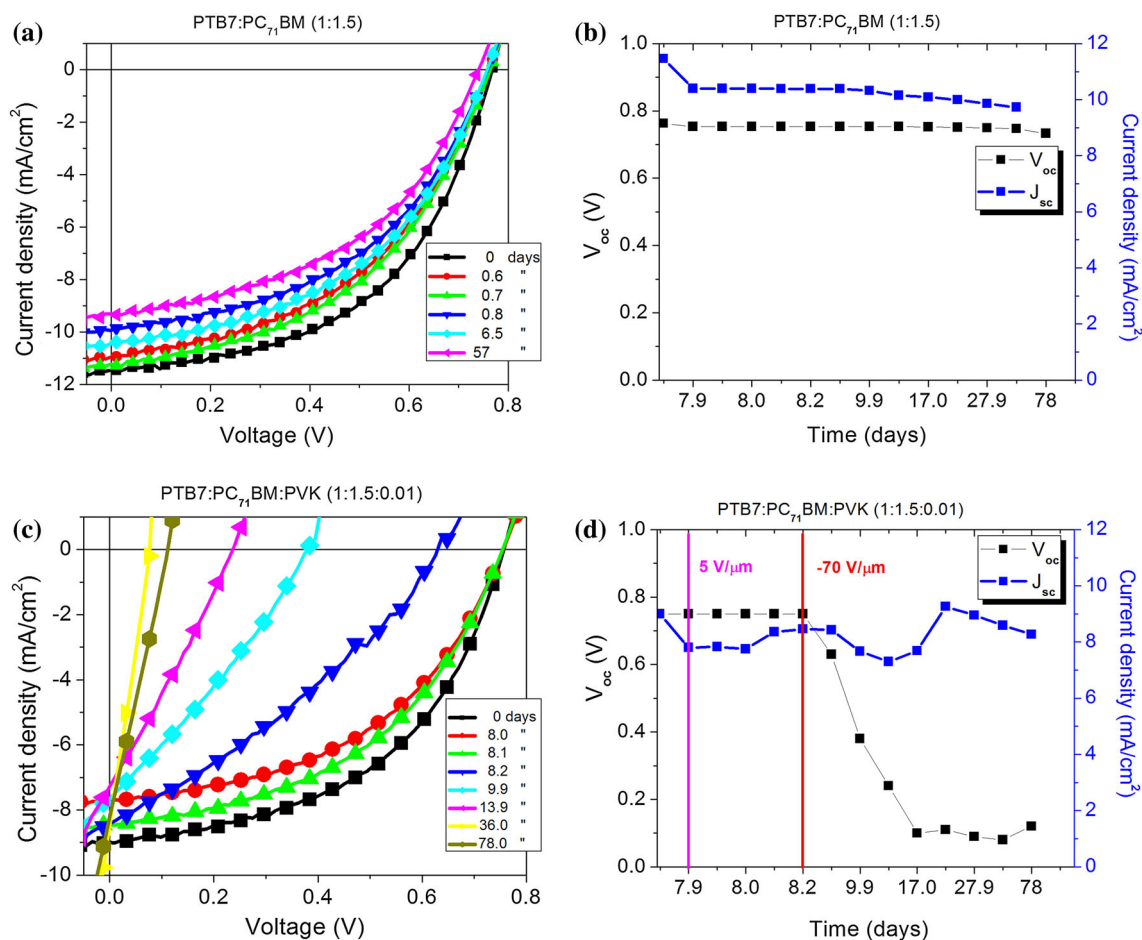


Fig. 5 Temporal evolution of **a** J–V curves and, **b** V_{oc} and J_{sc} values for a PTB7:PC₇₁BM (1:1.5 wt. ratio) based PSC (type I) without any applied E_{ext} . **c**, **d** Temporal evolution of the J–V plot and, V_{oc} and J_{sc}

values for a PTB7:PC₇₁BM:PVK (1:1.5:0.01 wt. ratio) based cell (type II), where at day ~ 7.9 was applied an $E_{ext} = 5 \text{ V}/\mu\text{m}$ (during 30 s) and at day ~ 8.2 : $E_{ext} = -70 \text{ V}/\mu\text{m}$ (30 s) (to the same PSC)

reduction was from 2.8 to 1.7 %, it means a decrease of 39 %.

Regarding type IV cells, similar PV performance was observed as that one in Fig. 6a. However, because of some manufacturing difficulties, complete data are not presented; nevertheless, partial information is seen in Table 2.

Figure 7 shows the performance of two different sets of PSCs based on PTB7:PC₇₁BM:ECZ:PVK (1:1.5:0.25:0.01 wt. ratio) (type V); in one case without applying any electric field (Figs. 7a, b) and in the other one applying $-70 \text{ V}/\mu\text{m}$ (Fig. 7c, d). In the first case, it was observed a regular degradation curve where J_{sc} was falling softly with some fluctuations from 10.9 to 9.4 mA/cm² (after 57 days) and V_{oc} remained almost constant to 0.77 V; PCE variation was of just 21 %. In the second case (see Fig. 7c, d), after the application of the field $-70 \text{ V}/\mu\text{m}$ (during 30 s), alternant fluctuations in J_{sc} and V_{oc} values were observed, range 11.0–7.4 mA/cm² (sometimes with larger values than the initial one) and 0.76–0.48 V, respectively (over 78 days). Here the fill factor change

was from 0.50 to 0.28 and the PCE had a variation from 3.9 to 1.1 % (70 %).

Tables 2 and 3 summarize the main parameters and variations found in the current fabricated PSCs. Here, it is observed that, from all the studied cases, type V PSCs based on the mix of PVK:ECZ, without any applied electric field, were the devices that showed less lifetime decay under the mentioned experimental conditions. Further, as it can be seen from Fig. 7d under the application of the reversed external field ($-70 \text{ V}/\mu\text{m}$) for these same type V cells, an increase of a maximum 10 % on J_{sc} was reached in the test time interval 10–28 (see also footnote in Table 2).

Few reports regarding the use of PVK in PSCs are found in the literature [7, 24, 25, 30, 31]. For instance, Lin et al. [30] studied an inverted PSC based on P3HT:ICBA:PVK as active layer (1:1:0.1 wt. ratio). In this cited work a mix of DCB and CB solvents was used to improve the solubility of the active layer solution and control its dried time. PVK was added to reduce the horizontal phase separation caused

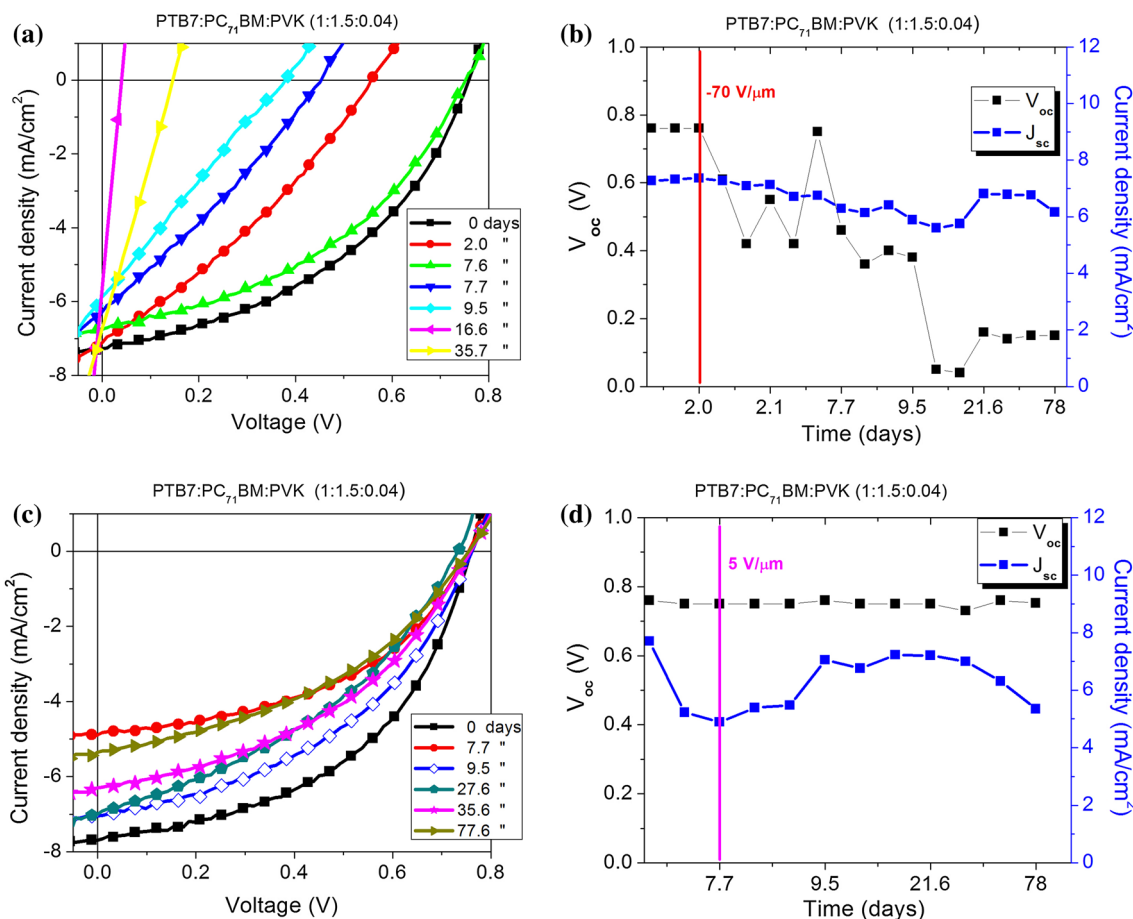


Fig. 6 a, b Temporal evolution of the J–V curves and, V_{oc} and J_{sc} values for PTB7:PC₇₁BM:PVK (1:1.5:0.04 wt. ratio) based PSCs (type III), with $E_{ext} = -70$ V/ μ m (at day 2 during 30 s). c, d Temporal evolution of the J–V plots and, V_{oc} and J_{sc} values for a

different set of PTB7:PC₇₁BM:PVK (1:1.5:0.04 wt. ratio) based cells (type III), where it was applied an $E_{ext} = 5$ V/ μ m (at day 7.7 during 30 s)

Table 2 PV parameters and evolution of the studied PSCs

Sample type	E_{ext} (V/ μ m)	V_{oc} max. (V)	V_{oc} min. (V)	J_{sc} initial (mA/cm ²)	J_{sc} max. (mA/cm ²)	J_{sc} min. (mA/cm ²)	FF max.	FF min.	PCE initial (%)
I	0	0.76	0.74	11.5	11.5	9.3	0.52	0.45	4.5
II	5 (-70) ^a	0.75	0.08	9.0	9.3	7.3	0.49	0.23	3.3
III	-70	0.76	0.04	7.3	7.4	5.6	0.43	0.23	2.4
III	5	0.76	0.73	7.7	7.7	4.9	0.48	0.39	2.8
IV	-70	0.75	0.06	10.7	10.7	9.4	0.59	0.25	4.8
V	0	0.77	0.75	10.7	10.9	9.4	0.50	0.47	4.2
V	-70	0.76	0.48	10.1	11.0 ^b	7.4	0.50	0.28	3.9

For the active blend composition (sample type), see Table 1

^a Firstly, it was applied 5 V/ μ m at day 7.9 and later on, -70 V/ μ m at day 8.2 (same sample)

^b J_{sc} improved 10 % around day 18

by the different boiling point of the used solvents. With this PVK addition, it was observed through AFM, that the active layer phase was a bulk without breaks between regions, which was the opposite for samples without PVK.

It was reported an enhancement on V_{oc} from 0.66 to 0.82 V and on PCE from 2.6 to 3.81 % in comparison to the same cells without PVK. Dridi et al. [31], reported the use of PVK (concentration: 5 mg/ml) to control the interfacial

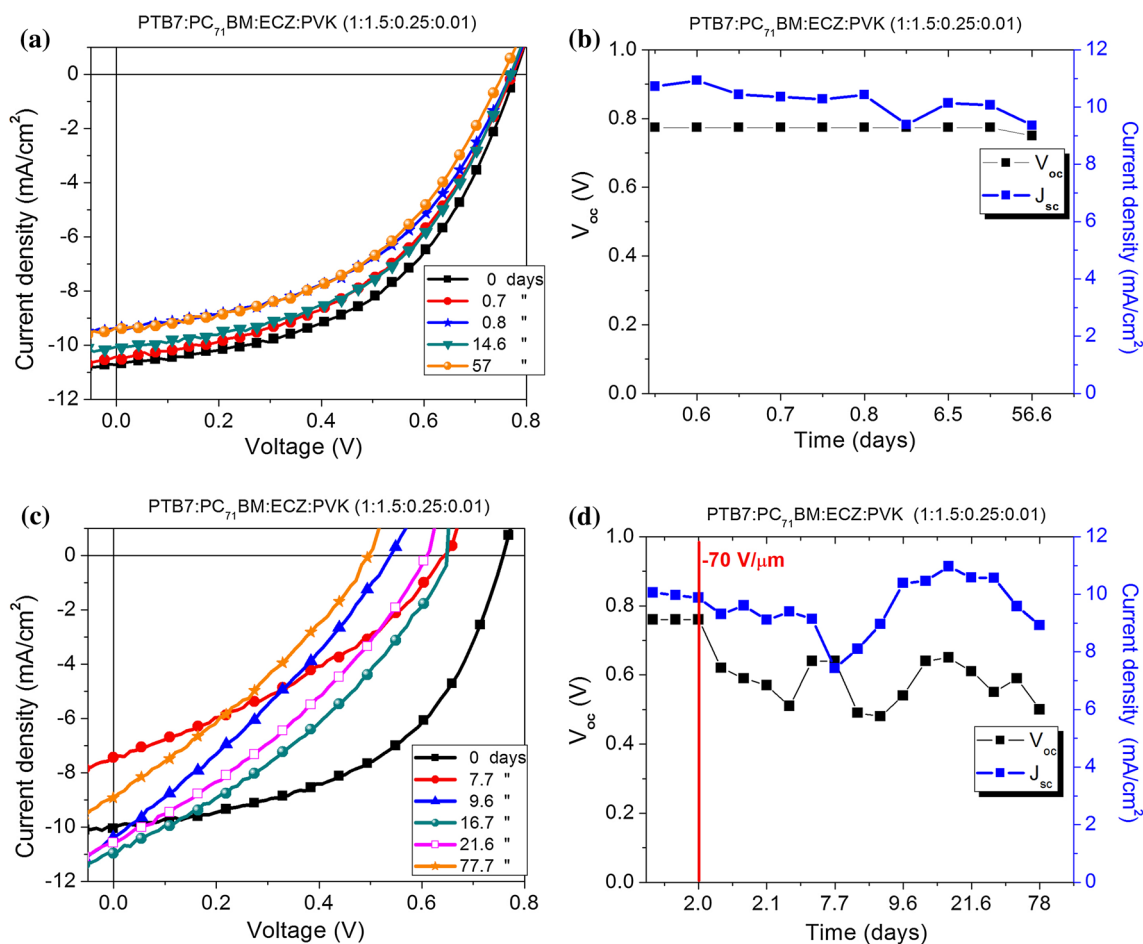


Fig. 7 **a, b** Temporal evolution of the J–V curves and, V_{oc} and J_{sc} values for PSCs based on PTB7:PC₇₁BM:ECZ:PVK (1:1.5:0.25:0.01 wt. ratio) as active layer (type V), without any E_{ext} . **c, d** Temporal evolution of the

J–V plots and, V_{oc} and J_{sc} values for a different set of PTB7:PC₇₁BM:ECZ:PVK (1:1.5:0.25:0.01 wt. ratio) based cells (type V), under the application of $E_{ext} = -70$ V/ μ m

Table 3 Variation of the main PV parameters of the different studied cells (For sample type, see Table 1)

Sample type	E_{ext} (V/ μ m)	Test time (days)	V_{oc} % variation	J_{sc} % variation	FF % variation	PCE % variation	T_g (°C)	T_d (onset, °C)
I	0	57	3	19	13	29	59	320
II	5 (–70) ^a	78	89	21	53	94	59	320
III	–70	78	95	24	47	97	67	340
III	5	78	4	36	19	39	67	340
IV	–70	8	92	12	58	97	–	120
V	0	57	3	14	6	21	66	120
V	–70	78	37	33	44	70	66	120

Here are also shown the glass transition (T_g) and decomposition (T_d) temperatures values for the active films

^a Firstly, it was applied 5 V/ μ m at day 7.9 and later on, –70 V/ μ m at day 8.2 (same sample)

areas of the donor and acceptor species in an ITO/nanocrystalline-TiO₂:PVK/Al PSC structure. Even when the PV performance of these solar cells was much reduced, they obtained improvements in J_{sc} from

3.57×10^{-5} to 1.43×10^{-4} mA/cm², in V_{oc} from 0.37 to 0.64 V and in the PCE from 5.7×10^{-6} to 2.7×10^{-5} %. Kim et al. [24] studied the influence of PVK on PSCs with a bilayer heterojunction architecture based in a metallo-

porphyrin and Alq3. One system was ITO/PVK:ZnTNPP (20:1 wt%)/Alq3/Al and the other one without PVK. The first device exhibited $V_{oc} = 0.61$ V, $J_{sc} = 0.68$ mA/cm², FF = 0.31 and PCE = 0.033 %, while the second one, without PVK, presented $V_{oc} = 0.63$ V, $J_{sc} = 0.15$ mA/cm², FF = 0.30 and PCE = 0.007 %. Tian-Hui et al. [25], fabricated ITO/PVK:porphyrin:Alq3/Al heterojunction based PSCs, two type of porphyrins were used: TPP and CuTCIPP at different weight proportions. Results showed that TPP is better than CuTCIPP in enhancing the performance of the PVK:Alq3 solar cells. With the weight ratio (1:1.5:1) of PVK:TPP:Alq3 the best cell performance was reached: V_{oc} of 0.87 V, J_{sc} of 0.018 mA/cm², FF of 0.23 and PCE of 0.004 %. As shown in Fig. 4, in our case, with the small addition of just PVK, PCE was reduced (see also Table 2, samples type II and III), however, with the simultaneous doping of ECZ and PVK, PCE was similar to the efficiency of those without any dopant (see Table 2, sample type V at $E_{ext} = 0$), nevertheless, these kind of cells presented the less reduced PCE after 57 days of testing (see Table 3, sample type V at $E_{ext} = 0$).

ECZ was added as a plasticizer to decrease the glass transition temperature (T_g) as an attempt to increase the bulk flexibility of the polymer active blend PTB7:PC₇₁BM (without and with PVK) [21–23], increasing the mechanical tolerance of the composite and enabling poling at room temperature; however, according to the literature [21–23], to reach properly these facts, a much larger amount of PVK and ECZ than that one used in this work, are needed. Nevertheless, when adding greater quantities of PVK or ECZ, the PV performance of our PSC drastically decayed, mainly with the use of PVK, for this latter case, possible reasons were mentioned at the first paragraph of this Results and Discussion section, thus, we reduced the amount of both compounds until having an acceptable performance with respect to samples based only on PTB7:PC₇₁BM. PVK and ECZ did not have any problem to be incorporated to the PTB7 active blend due to the low used amounts. The estimated T_g values from DSC experiments, are observed in Table 3. As can be seen, this tiny addition of PVK and/or ECZ did not have an appreciable reduction on T_g . Another fact to use ECZ together with PVK is the similarity of their electronic structures and the possibility to accommodate their common carbazole units face to face in the bulk. This issue, according to [32], enables short intermolecular distances and delocalized charges with highly ordered arrays. On the other hand, to the best of our knowledge, there are not previous reported data adding ECZ to the active layers of PSCs.

As mentioned in the introduction section, there are some previous studies where external electric fields [7–16] are applied to modify PSCs performance; however, very few reports are found where the external field is directly applied

to the device electrodes similarly to the described in this current work. For instance, Li et al. [12] applied the electric field in a cell (for over 10 min, reversed electric field of -60 V/ μ m) with an ITO/PEDOT:PSS/MEH-PPV:C₆₀/Al structure, in between the ITO and Al electrodes, i.e., across all layers of the PSC. Under this situation, even when the PV performance of these mentioned cells was rather small, J_{sc} increased six times from 0.25 to 1.5 mA/cm² and the PCE improved by a factor of 5.4: from 0.104 to 0.56 %. Padinger et al. [14] report PSCs based on P3HT:PCBM thermally treated at 75 °C for 4 min simultaneously with 2.7 V (forward bias) applied between cell electrodes (i.e., $E_{ext} = \sim 14$ V/ μ m). Treated PSCs showed 8.5 mA/cm², 0.55 V, 0.6 and 3.5 % values and not treated devices had J_{sc} , V_{oc} , FF and PCE values of 2.5 mA/cm², 0.3 V, 0.4 and 0.4 % parameters. Kong et al. [33] connected the electrodes of an ITO/PEDOT:PSS/P3HT:PC₇₀BM/TiO_x/Al PSC to an external bias circuit and performed a frequency-modulated Kelvin probe force microscopy (FM-KPFM) study to observe its external-biased potential distributions. It was found that the effect of the electric field in the active layer was nearly field-free, their PSCs had a PCE of 3.9 % and a FF of 0.66. Karak et al. [34] on ITO/PEDOT:PSS/p-DTS(FBTTh₂)₂:PC₇₁BM (3:2 wt. ratio)/Ca/Al PSCs structure, used C₆₀-N, a fullerene derivative, as a dipole additive in the active layer. Devices were treated with 0.5–2 h of electric field poling (~ 32 V/ μ m) in between their electrodes and others biases. The PCE increased from 7.2 to 8 % (10 %), the authors mention a more efficient extraction of the photogenerated charge carriers under the mentioned mechanism.

On the other hand, the application of an external electric field in manufactured PSCs, could make that polymer chains (with an intrinsic dipole moment) inside the photoactive layer, change their original orientation along the direction induced by the field [12, 13, 35]. As mentioned, the incorporation of a plasticizer at different concentrations could help to optimize this orientational kinetics [36], also, it could enhance the charge mobility leading to an improvement in the current density values as it was observed in the cells with PVK and ECZ (see Fig. 7d). The enhancement in J_{sc} is not just due to the simple increasing of the morphological order, but the combination of this structural order and the percolation pathways [12].

Variations on J_{sc} and V_{oc} values could arise from the stress and relaxation of the partial and temporal polar orientational alignment induced by E_{ext} . A possible explanation for the V_{oc} drop with the reversed bias (-70 V/ μ m) could be that the PVK polymer structure is partially reordered increasing the amount of PVK:PC₇₁BM interfaces and modifying the V_{oc} value. Also, the improvement of three-dimensional order in the polymers with the field application could induce a lower oxidation potential [12],

which also reduces the V_{oc} . On the other hand, the polymer ordering given by the forward bias ($5 \text{ V}/\mu\text{m}$) helps to sustain the PTB7:PC₇₁BM interfaces with almost not affectations in the V_{oc} value (see Tables 2 and 3).

Regarding sample stability, the studied cells containing both ECZ and PVK (type V) exhibited a certain degree of stability, with not applied electric field ($E_{ext} = 0$) (Fig. 7b), see also Tables 2 and 3: after 57 days, variation for V_{oc} was 3 %, 14 % for J_{sc} , 6 % for FF and 21 % for PCE. This stability on PV performance was better than that for the manufactured cells with not dopands or just ECZ or PVK. For example, type I cells (Fig. 5b), showed a total percentage variation for V_{oc} , J_{sc} , FF and PCE of 3, 19, 13 and 29 %, respectively, while type III devices (Fig. 6a, b), with just PVK and type IV cells with only ECZ, both under $E_{ext} = -70 \text{ V}/\mu\text{m}$, showed a total V_{oc} percentage variation of 95 % and 92 %, respectively, their total PCE variation was 97 % in both cases. On the other hand for type V cells (Fig. 7d), with the two dopants and under same E_{ext} value, V_{oc} showed a variation of 37 %, J_{sc} of 33 %, FF of 44 % and PCE of 70 %. Ribierre et al. [36] mention that the concentration of ECZ plasticizer (ranging from 0 to 0.4 wt. ratio) used with PVK and polystyrene, might offer the possibility to reduce phase segregation and improve sample stability. On the other hand, it is clear the overall negative influence of the reversed polarity for type V samples containing same dopants at the same concentration. However, as previously mentioned, it can be seen from Fig. 7d) and footnote in Table 2, an increase of a maximum 10 % on J_{sc} was reached in the test time interval 10–28 days.

Another feature that is important to mention is regarding the orientation type given to the PTB7 polymer structure. According to Liang et al. [37], under the BHJ approach, PTB7 polymer chain stack on the substrate in the face-on conformation that favors charge transport. So, if it is the best orientation (face-on stacking) to give to the PTB7 polymer in the bulk for charge transport and best PCE in PSCs, this situation is not happening in our case, because the applied electric field is in the vertical orientation (perpendicular to the solid films and electrodes of these PSCs devices, see Figs. 2 and 3) and it would place most of the PTB7 dipoles in an orientation restricting the charge transport. It could explain the initial decay in J_{sc} observed in some of our measurements and possibly the fall on the fill factor value. Then, it is reasonable to speculate that if E_{ext} is applied along the plane direction of the films, it could give advantages to the final electrical characteristics of the manufactured PSCs. However, this feature presents some no practical technical details, like the large horizontal voltage that needs to be applied of around six orders of magnitude greater than the one used for the vertical alignment experiment. It is due to the PV cell size in the horizontal orientation is on the order of millimeters while

the multilayer stacking (for vertical orientation) is on the nanometer scale.

4 Conclusions

The effect on the J–V curves of PTB7:PC₇₁BM:dopants active layer based cells under the application of an external electric field and AM 1.5 light condition, with a forward and reversed polarity was presented. Active layer dopants were poly(9-vinylcarbazole) (PVK) as a photoconductor or/and 9-ethylcarbazole (ECZ) as plasticizer. As general tendency, in our PSCs samples under forward polarity ($E_{ext} = 5 \text{ V}/\mu\text{m}$), drastic variations on the J_{sc} were observed while V_{oc} was kept almost constant. Under the reversed polarity, notorious V_{oc} variations were mainly presented while J_{sc} remains with less notorious changes. However, for PSCs based on PTB7:PC₇₁BM:ECZ:PVK, an increase of 10 % in J_{sc} was reached for the reversed bias ($E_{ext} = -70 \text{ V}$). These observed phenomena could be related to the dipole change in the thienothiophene (TT) monomer of the PTB7 compound, where the applied field produces some temporal dipolar material orientations in the PSC active layer. Also, under N₂ atmosphere, cells containing these two dopants at $E_{ext} = 0$, showed better stability trends: a slower degradation was observed during 57 days of monitoring the devices with just 6 % of FF decrease and 21 % of PCE fall, which were the lowest PV parameters changes for all series of the studied samples.

Acknowledgments This work was supported by CONACYT-SENER (México) Project 153094 and CeMIE-Sol 207450/27 (México) call 2013-02, Fondo Sectorial CONACYT-SENER-SUSTENTABILIDAD ENERGETICA. Also, from Fondo CONACYT-SEP CB-151842 and DGAPA-UNAM (PAPIIT IN 105314-3). AAF thanks CONACYT for the granted scholarship and to Universidad Autónoma de Aguascalientes (UAA) for its support. Authors also thank Martín Olmos for his technical assistance.

References

1. S.H. Liao, H.J. Jhuo, P.N. Yeh, Y.S. Cheng, Y.L. Li, Y.H. Lee, S. Sharma, S.A. Chen, Single junction inverted polymer solar cell reaching power conversion efficiency 10.31 % by employing dual-doped zinc oxide nano-film as cathode interlayer. *Sci. Rep.* **4**, 6813-1–6813-7 (2014)
2. J. Yu, Y. Zheng, J. Huang, Towards high performance organic photovoltaic cells: a review of recent development in organic photovoltaics. *Polymers* **6**, 2473–2509 (2014)
3. J. Yan, B.R. Saunders, Third-generation solar cells: a review and comparison of polymer:fullerene, hybrid polymer and perovskite solar cells. *RSC Adv.* **4**, 43286–43314 (2014)
4. M. Jørgensen, K. Norrman, S.A. Gevorgyan, T. Tromholt, B. Andreasen, F.C. Krebs, Stability of polymer solar cells. *Adv. Mater.* **24**, 580–612 (2012)
5. S. Sista, Z. Hong, L.M. Chen, Y. Yang, Tandem polymer photovoltaic cells-current status, challenges and future outlook. *Energy Environ. Sci.* **4**, 1606–1620 (2011)

6. C. Sentein, C. Fiorini, A. Lorin, J.-M. Nunzi, Molecular rectification in oriented polymer structures. *Adv. Mater.* **9**, 809–811 (1997)
7. L. Sicot, C. Fiorini, A. Lorin, P. Raimond, C. Sentein, J.-M. Nunzi, Improvement of the photovoltaic properties of polythiophene-based cells. *Sol. Energy Mater. Sol. Cells* **63**, 49–60 (2000)
8. S. Athanasopoulos, N.C. Greenham, R.H. Friend, Field-enhanced recombination at low temperatures in an organic photovoltaic blend. *Phys. Rev. B* **92**, 125301-1–125301-7 (2015)
9. Y. Li, Y. Feng, M. Sun, Photoinduced charge transport in a BHJ solar cell controlled by an external electric field. *Sci. Rep.* **5**, 13970-1–13970-11 (2015)
10. N. Chaturvedi, S.K. Swami, A. Kumar, V. Dutta, Role of ZnO nanostructured layer spray deposited under an electric field in stability of inverted organic solar cells. *Sol. Energy Mater. Sol. Cells* **126**, 74–82 (2014)
11. N. Chaturvedi, F. Alam, S.K. Swami, V. Dutta, Effect of electric field on the spray deposited poly (3,4-ethylenedioxythiophene): poly(styrenesulfonate) layer and its use in organic solar cell. *J. Appl. Phys.* **114**, 184501-1–184501-6 (2013)
12. Y. Li, Y. Hou, Y. Wang, Z. Feng, B. Feng, L. Qin, F. Teng, Thermal treatment under reverse bias: effective tool for polymer/fullerene bulk heterojunction solar cells. *Synth. Met.* **158**, 190–193 (2008)
13. A. Solanki, B. Wu, T. Salim, E.K.L. Yeow, Y.M. Lam, T.C. Sum, Performance improvements in polymer nanofiber/fullerene solar cells with external electric field treatment. *J. Phys. Chem. C* **118**, 11285–11291 (2014)
14. F. Padinger, R.S. Rittberger, N.S. Sariciftci, Effects of postproduction treatment on plastic solar cells. *Adv. Funct. Mater.* **13**, 85–88 (2003)
15. S.Y. Ma, Y.M. Shen, P.C. Yang, C.S. Chen, C.F. Lin, Morphological modification induced by external electric field during solution process of organic solar cells. *Org. Electron.* **13**, 297–301 (2012)
16. W. Zhou, J. Shi, L. Lv, L. Chen, Y. Chen, A mechanistic investigation of morphology evolution in P3HT-PCBM films induced by liquid crystalline molecules under external electric field. *Phys. Chem. Chem. Phys.* **17**, 387–397 (2015)
17. J.R. Tumbleston, B.A. Collins, L. Yang, A.C. Stuart, E. Gann, W. Ma, W. You, H. Ade, The influence of molecular orientation on organic bulk heterojunction solar cells. *Nat. Photon.* **8**, 385–391 (2014)
18. X. Guo, N. Zhou, S.J. Lou, J. Smith, D.B. Tice, J.W. Hennek, R.P. Ortiz, J.T.L. Navarrete, S. Li, J. Strzalka, L.X. Chen, R.P.H. Chang, A. Facchetti, T.J. Marks, Polymer solar cells with enhanced fill factors. *Nat. Photon.* **7**, 825–833 (2013)
19. B. Carsten, J.M. Szarko, H.J. Son, W. Wang, L. Lu, F. He, B.S. Rolczynski, S.J. Lou, L.X. Chen, L. Yu, Examining the effect of the dipole moment on charge separation in donor-acceptor polymers for organic photovoltaic applications. *J. Am. Chem. Soc.* **133**, 20468–20475 (2011)
20. E. Pérez-Gutiérrez, J.L. Maldonado, J. Nolasco, G. Ramos-Ortíz, M. Rodríguez, U. Mendoza-De la Torre, M.A. Meneses-Nava, O. Barbosa-García, H. García-Ortega, N. Farfán, G. Granados, R. Santillan, E. Juaristi, Titanium oxide:fullerene composite films as electron collector layer in organic solar cells and the use of an easy-deposition cathode. *Opt. Mater.* **36**, 1336–1341 (2014)
21. O. Ostroverkhova, W.E. Moerner, Organic photorefractives: mechanisms, materials, and applications. *Chem. Rev.* **104**, 3267–3314 (2004)
22. J.L. Maldonado, Y. Ponce-de-León, G. Ramos-Ortíz, M. Rodríguez, M.A. Meneses-Nava, O. Barbosa-García, R. Santillán, N. Farfán, High diffraction efficiency at low electric field in photorefractive polymers doped with arylimine chromophores. *J. Phys. D Appl. Phys.* **42**, 075102-1–075102-6 (2009)
23. V.M. Herrera-Ambriz, J.L. Maldonado, M. Rodríguez, R. Castro-Beltrán, G. Ramos-Ortíz, N.E. Magaña-Vergara, M.A. Meneses-Nava, O. Barbosa-García, R. Santillan, N. Farfán, F.X. Dang, P.G. Lacroix, I. Ledoux-Rak, Highly efficient photorefractive organic polymers based on benzonitrile Schiff bases nonlinear chromophores. *J. Phys. Chem. C* **115**, 23955–23963 (2011)
24. H.S. Kim, C.H. Kim, C.S. Ha, J.K. Lee, Organic solar cell devices based on PVK/porphyrin system. *Synth. Met.* **117**, 289–291 (2001)
25. Z. Tian-Hui, Z. Su-Ling, P. Ling-Yu, X. Zheng, J. Si-Ting, L. Xiao-Dong, K. Chao, X. Xu-Rong, Solar cells based on the poly(n-vinylcarbazole):porphyrin:tris(8-hydroxyquinolinato) aluminium blend system. *Chin. Phys. B* **20**, 038401-1–038401-7 (2011)
26. D. An, J. Zou, H. Wu, J. Peng, W. Yang, Y. Cao, White emission polymer light-emitting devices with efficient electron injection from alcohol/water-soluble polymer/Al bilayer cathode. *Org. Electron.* **10**, 299–304 (2009)
27. D. Romero-Borja, J.L. Maldonado, O. Barbosa-García, M. Rodríguez, E. Pérez-Gutiérrez, R. Fuentes-Ramírez, G. de la Rosa, Polymer solar cells based on P3HT:PC₇₁BM doped at different concentrations of isocyanate-treated graphene. *Synth. Met.* **200**, 91–98 (2015)
28. B. Ebenhoch, S.A.J. Thomson, K. Genevičius, G. Juška, I.D.W. Samuel, Charge carrier mobility of the organic photovoltaic materials PTB7 PC₇₁BM and its influence on device performance. *Org. Electron.* **22**, 62–68 (2015)
29. P. D'Angelo, M. Barra, A. Cassinese, M.G. Maglione, P. Vacca, C. Minarini, A. Rubino, Electrical transport properties characterization of PVK (poly n-vinyl carbazole) for electroluminescent devices applications. *Solid-State Electron.* **51**, 123–129 (2007)
30. S.H. Lin, S. Lang, J.Y. Sun, C.F. Lin, Morphologic improvement of the P3HT:indene-C₆₀ bis-adduct (ICBA) blend film with mixed solvent in inverted polymer solar cells, in 38th IEEE Photovoltaic Specialists Conference (PVSC), IEEE, Austin, TX (2012), pp. 2761–2763
31. C. Dridi, V. Barlier, H. Chaabane, J. Davenas, H.B. Ouada, Investigation of exciton photodissociation, charge transport and photovoltaic response of poly(n-vinyl carbazole):TiO₂ nanocomposites for solar cell applications. *Nanotechnology* **19**, 375201-1–375201-11 (2008)
32. L. Qian, D. Bera, P.H. Holloway, White light emission from single layer poly (n-vinylcarbazole) polymeric light-emitting devices by mixing singlet and triplet excimer emissions. *J. Chem. Phys.* **127**, 244707-1–244707-6 (2007)
33. J. Kong, J. Lee, Y. Jeong, M. Kim, S.O. Kang, K. Lee, Biased internal potential distributions in a bulk-heterojunction organic solar cell incorporated with TiO_x interlayer. *Appl. Phys. Lett.* **100**, 213305-1–213305-3 (2012)
34. S. Karak, Z.A. Page, J.S. Tinkham, P.M. Lahti, T. Enrick, V.V. Duzhko, Raising efficiency of organic solar cells with electrochromic additives. *Appl. Phys. Lett.* **106**, 103303-1–103303-5 (2015)
35. P.S. Chung, P.H. Holloway, Photoluminescence of solution processed poly n-vinyl carbazole films. *J. Appl. Polym. Sci.* **114**, 1–9 (2009)
36. J.C. Ribierre, L. Mager, F. Gillot, A. Fort, Influence of the average molecular weight and the concentration of plasticizer on the orientational dynamics of chromophores in guest-host polymers. *J. Appl. Phys.* **100**, 043103-1–043103-9 (2006)
37. Y. Liang, Z. Xu, J. Xia, S.T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, For the bright future-bulk heterojunction polymer solar cells with power conversion efficiency of 7.4 %. *Adv. Mater.* **22**, E135–E138 (2010)