

Compatibility of PTB7 and [70]PCBM as a Key Factor for the Stability of PTB7:[70]PCBM Solar Cells

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The rapid degradation of organic photovoltaic (OPV) devices compared to conventional inorganic solar cells is one of the critical issues that have to be solved in order to make OPV a competitive commercial technology. The understanding of the fundamental mechanisms that reduce the power conversion efficiency (PCE) over time is beneficial for the design of new materials with enhanced stability. This paper focuses on bulk heterojunction organic solar cells based on thieno [3,4-b] thiophene-alt-benzodithiophene (PTB7) mixed with [6,6]-phenyl-C71-butyric acid methyl ester ([70]PCBM). In spite of being promising in terms of PCE, devices based on this blend are unstable and have a short lifetime. When exposed to light in inert atmosphere, the PCE drops by 15% in less than 1 h and by 35% in 8 h; this degradation is induced by the ultraviolet (UV) part of the spectrum. This paper analyzes the effect induced by UV light on the transport of charges in PTB7:[70]PCBM. Contrary to expectations, the electron transport shows evidence of trapping, while the transport of holes appears unaffected. Furthermore, it is proven that the loss of PCE is due to a reaction between PTB7 and [70]PCBM, while the intrinsic instability of the polymer plays a marginal role.

for commercial viability.^[8] However, the stability of OPV devices remains a major concern,^[9,10] hindering the commercial success of this technology. Therefore, an increasingly large number of publications in the OPV field focuses on understanding how organic solar cells degrade and on improving their stability.^[11–24]

The knowledge of how changes in the physics of the devices are related to the degradation of the performance is currently lacking. To the best of our knowledge, for instance, the deterioration of charge transport properties of organic blends or the appearance of trapping states upon exposure to light has received little attention, although the transport of charges is a crucial factor in determining the efficiency of OPV devices.^[25–27]

Most of the record-efficiency OPVs achieved in the last few years have been realized with donor polymers based on benzo[1,2-b:4,5-b']dithiophene (BDT).^[28–33]

Among these polymers, the most studied is the donor–acceptor copolymer thieno[3,4-b]thiophene alt-benzodithiophene (PTB7), blended with [6,6]-phenyl-C71-butyric acid methyl ester ([70]PCBM). Devices made with this blend exceed PCE of 9% in optimized device structures.^[28,29] The properties of PTB7 have been extensively studied^[34–37] and many publications have focused on the optimization of PTB7:[70]PCBM solar cells.^[28,29,38–41] In spite of the relatively high PCE achievable with PTB7, several researchers have reported that PTB7:[70]PCBM solar cells are unstable when exposed to light and to the ambient.^[42–46] It has been shown that the principal mechanism of PTB7 degradation, both in neat films and in blends with [70]PCBM, is via photooxidation with the highly reactive singlet ¹O₂ species;^[42,43] the effect of photooxidation at the molecular level was described in a later publication by Razzel-Hollis et al.^[44] Furthermore, it has been shown that the presence of [70]PCBM accelerates the degradation of PTB7 due to increased production of singlet oxygen.^[43,44]

The results reported in refs.^[42–44] regard a photochemical degradation process that requires the combined exposure of the blend to both light and oxygen. It has been noted, however, that the performance of PTB7:[70]PCBM solar cells also degrades in inert atmosphere when the devices are exposed to light.^[45] The photoinduced degradation of polymer:fullerene blends in inert atmosphere has been attributed to the absorption of ultraviolet (UV) photons, that in polymers, and in particular in conjugated polymers, can induce reactions such as chain scissions,

1. Introduction

Over the past decade, third-generation solar technologies based on polymer:fullerene blend films have strongly attracted the interest of researchers. The field of organic photovoltaics (OPV) offers several advantages: the relatively low cost and ease of device fabrication,^[1] the possibility of producing flexible devices with high power density,^[2,3] and the environmental sustainability.^[4,5] Aiming at the commercialization of OPV technologies capable to compete with conventional inorganic solar cells, both the efficiency and the stability of OPV devices need to be improved. Power conversion efficiencies (PCE) above 10% have been achieved both in single layer and in tandem architecture,^[6,7] approaching the efficiency threshold

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cross-linking, and side-chain rearrangement.^[11,12] Lim et al. proved that the photoinduced degradation of PTB7:[70]PCBM solar cells in the absence of oxygen is due to UV light: inverted devices, in which the UV part of the radiation is filtered by the electron transport layer (ETL), have higher stability under illumination.^[45] For their study, they processed PTB7:[70]PCBM using 1,8-diiodooctane (DIO) as solvent additive. Although the best performance for PTB7:[70]PCBM was obtained using DIO,^[38] this additive remains in the blend after deposition of the active layer^[47,48] and has a negative impact on the stability of the devices.^[41] Thus, the degradation observed by Lim et al. may be due to the effect of DIO rather than an intrinsic instability of PTB7:[70]PCBM.

In this paper, we investigated the UV-induced degradation of PTB7:[70]PCBM solar cells without DIO. In spite of the importance of the charge transport in determining the efficiency of OPV devices,^[25,26] the knowledge of how transport properties degrade in PTB7:[70]PCBM blends is lacking. We analyzed the effect of UV on the charge transport properties. We fabricated conventional devices, so that the UV part of the radiation is not filtered by the ETL. To exclude any effect from the solvent additive, we processed the blend from pristine ortho-dichlorobenzene (oDCB) solution. We measured the transport of charges in the pristine materials and in their blend and how it changes upon illumination in N₂ atmosphere. While the transport of holes in pristine PTB7 is deteriorated by UV exposure, the hole transport properties of the blend remain unaltered; at the same time, exposure to UV light has an effect on the transport of electrons in the blend, which becomes less effective. This may indicate that the electron transporting material, [70]PCBM, is affected by the degradation of the blend.

We compared the efficiency of devices in which either only one or both the materials have been exposed to light. To selectively expose only the polymer, we fabricated PTB7:[70]PCBM solar cells via sequential processing.^[40,49] Briefly, sequential processing consists of a two-step deposition of the active layer, firstly the polymer and then the fullerene derivative. A correct choice of the solvents for the two steps results in the intermixing of polymer and fullerene, to give a morphology that is similar to that which is obtained from the one-step deposition of the blend.^[40,49,50] Sequential processing enables us to compare what happens when the polymer is exposed to light before or after the addition of [70]PCBM; we observed that the performance of the solar cell is not reduced if the exposure to UV light occurs in the absence of the fullerene derivative on the time scale of our experiment. Similarly, no deterioration of the PCE is observed when [70]PCBM is selectively exposed before mixing it with the polymer.

Our results prove that the UV-induced degradation of the blend is due to a photochemical reaction that involves both materials, while the intrinsic instability of PTB7 appears to have no effect on the stability of the blend. Since fullerene derivatives such as [70]PCBM and its C₆₀-equivalent PCBM are used as electron acceptor material in many state-of-the-art organic solar cells,^[8,51] understanding the effect of UV radiation on polymer:[70]PCBM blends and indicating which physical properties (e.g., the electron transport) are mostly affected by UV is crucial: it will direct the research toward the design of new donor materials, compatible with [70]PCBM, or alternatively

toward the design of new electron acceptors, in order to improve device stability.

2. Results and Discussion

In this section we present the results of our measurements of the stability of PTB7:[70]PCBM solar cells processed from oDCB solution and exposed to light in inert atmosphere, the characterization of the transport of electrons and holes in the pristine materials and in the blend, and the results obtained by selective exposure of the two materials. All the details about the fabrication and characterization of the samples are in the Experimental Section. The exposure to light for all the samples presented in this paper was carried out in inert atmosphere (a N₂ atmosphere, with less than 0.1 ppm H₂O, and less than 0.6 ppm O₂); during the exposure and the measurement, the temperature was kept constant (295 K).

2.1. Solar Cell Performance upon UV Exposure

We fabricated conventional bulk heterojunction (BHJ) solar cells with a PTB7:[70]PCBM (Figure 1) blend. To determine how much the PCE of the device diminishes due to UV exposure in inert atmosphere, we measured the current–voltage (*JV*) characteristic of one solar cell every 30 min for 8 h, keeping it continuously under the light of a solar simulator. When not measuring the *JV* curve, we kept the device in open-circuit conditions.

The normalized PCE of the device is displayed in Figure 2a: a fast reduction of the PCE is visible in the first hours of light exposure, after which the performance decreases at a slower rate. At the end of the observation period, the PCE is reduced to 65.7% of the initial value. To prove that the UV light is causing the reduction of the performance, we measured the *JV* curve of a second device keeping a long-pass filter in front of the lamp during all the observation time. The spectrum of the incident light is shown in Figure 2b; by applying the long-pass filter, all the light with wavelengths below 425 nm is blocked, while the intensity of light with wavelengths between 425 and 525 nm is reduced. When the UV part of the radiation is filtered, the reduction of the PCE of the device is much slower.

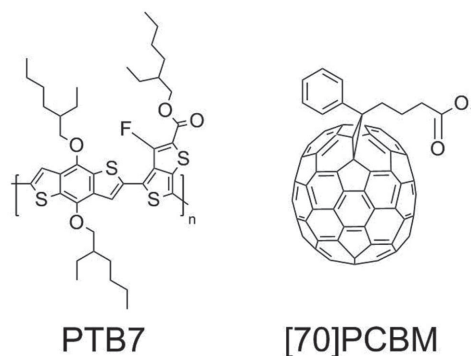


Figure 1. Chemical structures of PTB7 and [70]PCBM.

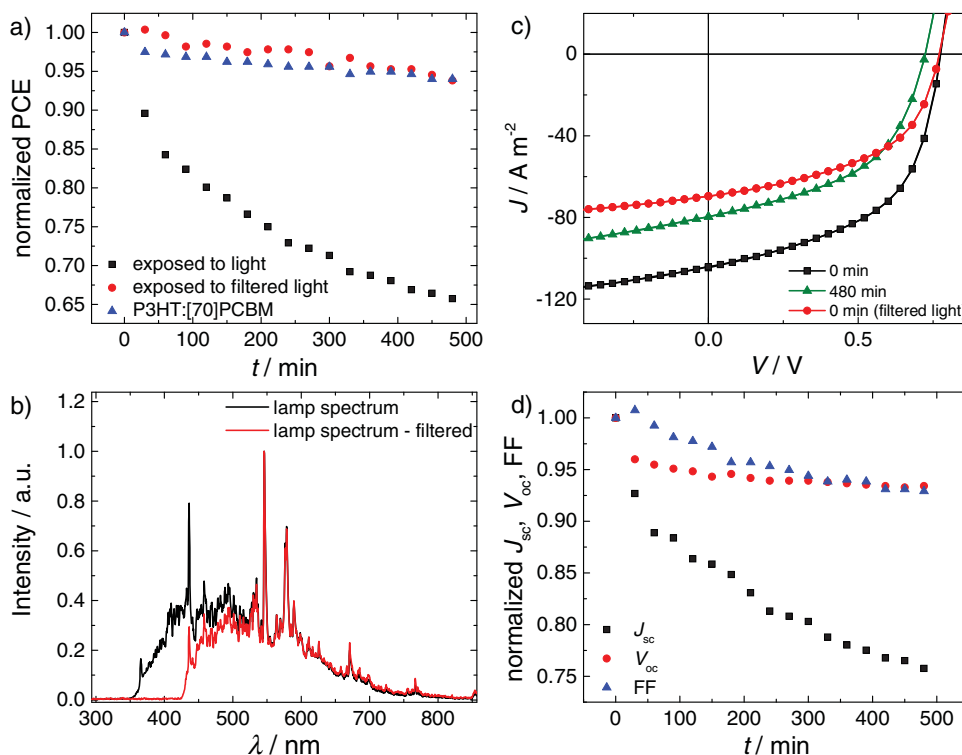


Figure 2. a) Normalized PCE versus time for a PTB7:[70]PCBM solar cell continuously exposed to light with and without using a long-pass filter to cut UV radiation and for a reference P3HT:[70]PCBM solar cell. The thickness of the active layer is 100 nm for PTB7:[70]PCBM, 220 nm for P3HT:[70]PCBM; b) spectra of the light of the solar simulator recorded with and without the long-pass filter in front of the spectrometer; c) *JV* characteristics of PTB7:[70]PCBM solar cells as spun and after 8 h of exposure to light. We note that the difference between the black and the green curve is only due to the presence of the long-pass filter; d) normalized J_{sc} , V_{oc} , and FF for the PTB7:[70]PCBM solar cell continuously exposed to light without using long-pass filter.

Furthermore, we compared the normalized PCE of PTB7:[70]PCBM solar cell under illumination with the performance of a reference device made with poly(3-hexylthiophene) (P3HT) blended with [70]PCBM. The P3HT:[70]PCBM sample shows only a slight reduction of performance during the first hours of light exposure.

The performance of PTB7:[70]PCBM solar cells decreases rapidly during the first hours of light exposure. The PCE of a PTB7:[70]PCBM solar cell is 4.32% for the fresh device, and drops to 2.84% after 8 h of exposure (Figure 2c). Performing the measurements in an oxygen-free atmosphere excludes the photooxidation reaction described by Soon et al.^[43] as a cause for the reduction of PCE. Figure 2a clearly shows that this reduction is largely due to the effect of UV radiation. Atomic force microscopy images of the topography of the film before and after exposure do not reveal any change in the morphology upon UV exposure (see the Supporting Information, Figure S1); therefore, we conclude that the degradation is due to a photochemical reaction triggered by UV radiation.

As a result of this photochemical reaction, the power generated by the cell, given by the maximum $|JV|$ product (Table 1), drops from 43.2 W m^{-2} (fresh device) to 28.4 W m^{-2} after 8 h of UV exposure.

Figure 2d reports the normalized short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF) of the cell exposed to

light without a long-pass filter; J_{sc} is the most affected parameter, dropping to $\approx 75\%$ of its initial value after 8 h. V_{oc} drops slightly at the beginning of the observation period and then remains almost constant, FF decreases slowly in time; both these parameters are at $\approx 90\%$ of their initial values after 8 h.

A trivial solution to avoid the effect of UV would be to use a long-pass filter. Although this would stabilize the blend, it would also reduce the number of incident photons, and hence the number of photogenerated charges. This would decrease the generated power to 27.1 W m^{-2} (see Figure 2c and Table 1). It is therefore important to understand the fundamental mechanism of the UV-induced loss of efficiency, in order to suppress it and at the same time exploit the short-wavelength photons.

The loss of performance is possibly related to a decrease in the internal quantum efficiency, which implies a reduction of the rate of the photogeneration of charge carriers (G). From the value of the current density at -2 V (saturation current, J_{sat}), we calculated G according to^[52]

Table 1. Solar cell parameters of the *JV* curves reported in Figure 2c.

Sample	J_{sc} [A m ⁻²]	V_{oc} [V]	FF	J_{max} [A m ⁻²]	V_{max} [V]	PCE [%]	P [W m ⁻²]
Not exposed	104.14	0.774	0.536	71.927	0.600	4.32	43.2
Exposed to light	78.90	0.723	0.498	54.833	0.520	2.84	28.4
Exposed to filtered light	69.94	0.770	0.505	47.124	0.576	2.71	27.1

$$G = \frac{J_{\text{sat}}}{qL} \quad (1)$$

where L is the thickness of the active layer and q is the elementary charge. We assume here that -2 V is a sufficient bias to extract all the photogenerated charges. After 8 h of exposure to unfiltered light, G drops from its initial value of 8.22×10^{27} to $7.21 \times 10^{27} \text{ m}^{-3} \text{ s}^{-1}$. Therefore, we identify the reduction of G as a cause of the drop in the short-circuit current of the device. The higher voltage dependence of the JV curve of the degraded sample, resulting in a lower FF if compared to the pristine device, suggests that the drop in G is possibly due to an enhancement of the geminate recombination in the bulk of the device. We verified that the UV-vis absorption of the blend does not vary significantly upon UV exposure (see the Supporting Information, Figure S2). Thus, bleaching is not the cause of the observed degradation.

2.2. Charge Transport

To characterize the transport of holes and electrons in the pristine materials and in the blend, we fabricated single carrier devices in which the active layer is sandwiched between selective electrodes that suppress the injection of electrons (hole-only devices) or holes (electron-only devices). The current flowing through the devices was measured before and after exposing the active layer to the light of the solar simulator. Both the bottom and top contacts of hole-only and electron-only devices are opaque, and it is not possible to study the effect of UV on the current as a function of the exposure time using a single device. Thus, we fabricated more samples of each kind; before evaporating the top contact, the devices were exposed to light in inert atmosphere for different times. To minimize sample-to-sample variations, we spin cast every sample from the same solution and with the same procedure, we carefully kept the temperature at 295 K during the light exposure, and we evaporated the top contact simultaneously for devices of the same kind. We are, therefore, confident that the differences that we observed in the JV curves for different exposure times are due to the effect of UV light, and not to sample-to-sample variations. Figure 3 displays the JV characteristics of single carrier devices fabricated with pristine materials and kept in the dark or exposed to light for 1 h. The hole current flowing through PTB7 is reduced upon exposure to UV light; on the other hand, the electron transport properties of [70]PCBM are not affected by the exposure to UV radiation.

From the single carrier devices of the pristine materials and from the comparison between PTB7:[70]PCBM and P3HT:[70]PCBM solar cells in Figure 2, one can conclude that [70]PCBM is stable and that PTB7 degrades when exposed to UV. Thus, when single carrier devices of PTB7:[70]PCBM are exposed to light, a deterioration of the hole transport properties would be expected. Surprisingly, though, we obtained the opposite result with single carrier devices of PTB7:[70]PCBM: the hole current in the blend only slightly diminishes after exposure to UV, and it is almost constant already after 15 min of exposure; the electron current is more significantly reduced upon exposing the active layer to UV radiation (Figure 4).

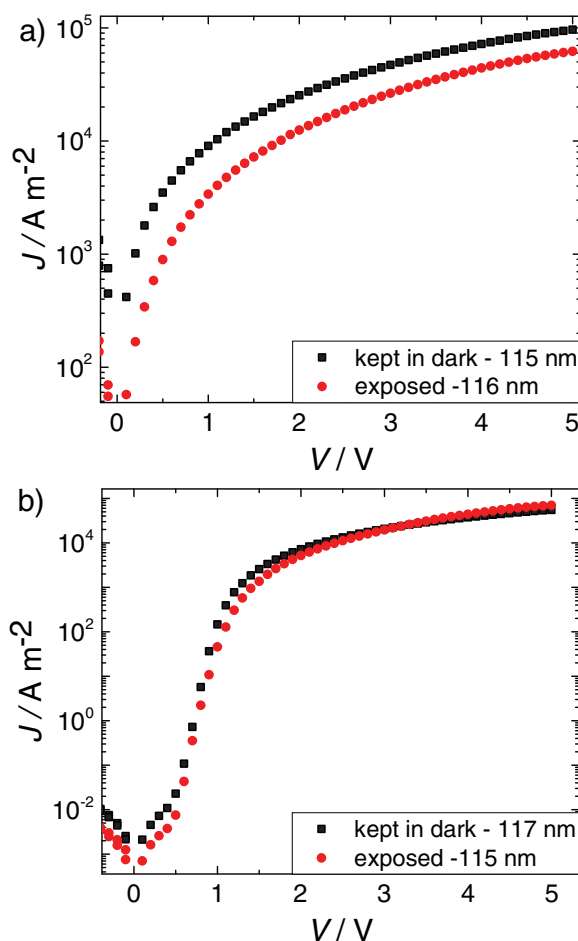


Figure 3. a) JV characteristics of hole-only devices of PTB7 and (b) electron-only devices of [70]PCBM kept in dark and exposed to light for 1 h. The thickness of the active layer of each sample is reported in the legends.

Therefore, the addition of [70]PCBM to the polymer stabilizes the transport of holes, but simultaneously destabilizes the transport properties of electrons. The stabilizing action may be due to a light screening effect of the fullerene derivative or to a chemical effect (e.g., radical scavenging) as suggested in ref.^[20]. A possible cause for the observed reduction of the electron current in the blend is the formation of electron trapping states as a product of a UV-induced reaction that involves both PTB7 and [70]PCBM. The presence of electron trapping states is capable of explaining the stronger voltage dependence of the electron current if compared to the hole current^[53] and the slight clockwise hysteresis^[54] in the electron-only JV curves in Figure 4.

2.3. Trap-Assisted Recombination in PTB7:[70]PCBM Solar Cells

It is well known that trapped charges may undergo Shockley-Read-Hall (SRH) recombination^[55,56] and that such trap-assisted recombination pathway results in a stronger dependence of V_{oc} on the light intensity^[57] if compared to a trap-free solar cell.^[58] The slope of V_{oc} versus the natural logarithm of the light intensity can be expressed as a function of the

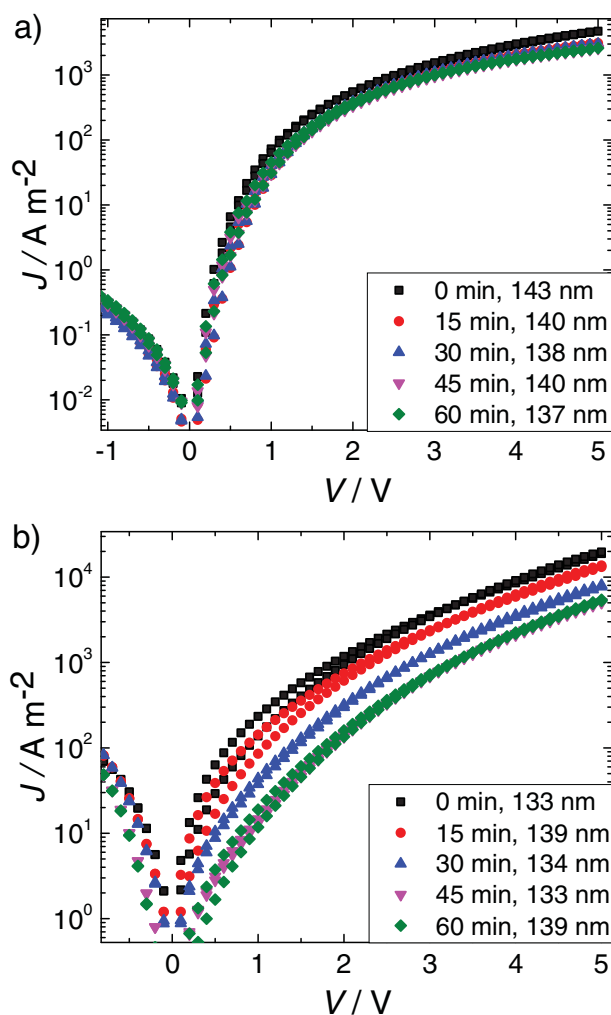


Figure 4. JV characteristics of (a) hole-only and (b) electron-only devices of PTB7:[70]PCBM exposed to light for different times. The thickness of the active layer of each sample is reported in the legends.

thermal voltage $V_T = K_B T_q$, where K_B is the Boltzmann constant and T is the temperature; if the SRH recombination is absent, the slope is equal to V_T .

To check whether the UV radiation introduces more electron traps in PTB7:[70]PCBM solar cells, we measured the dependency of V_{oc} on the light intensity for a fresh sample and after every hour of light exposure, for a period of 2 h. We changed the intensity of the incident light by using a set of neutral density filters. To block the photoinduced reaction during the intensity scan, we used the long-pass filter in combination with the neutral density filter. For this reason, the maximum light intensity at which the measurements are performed was lower than 1 Sun (1000 W m^{-2}). The outcome of this experiment is shown in Figure 5. For the fresh device, the slope is $1.33 V_T$; it increases to $1.41 V_T$ and $1.46 V_T$ after 1 and 2 h of light exposure, respectively. Repeating the experiment with the UV radiation blocked during all the time of light exposure results in an almost constant slope.

These results confirm that a small amount of electron traps is present in the blend and that the exposure to UV radiation

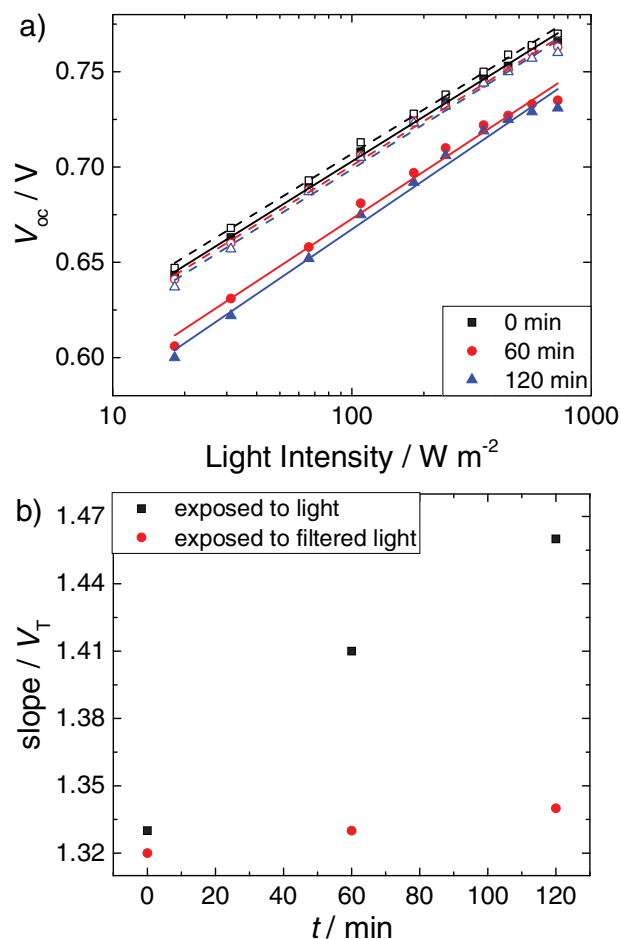


Figure 5. a) V_{oc} versus incident light intensity for PTB7:[70]PCBM solar cells, measured for the fresh device and after exposing the cell to light for 1 and 2 h. We analyzed two samples, one exposed to unfiltered light (full symbols), the other exposed to filtered light (empty symbols); b) slope of V_{oc} versus the natural logarithm of light intensity for the two devices.

increases the number of trap states, resulting in a stronger SRH recombination.

2.4. Selective UV Exposure of PTB7 and [70]PCBM

The stabilizing effect of [70]PCBM on the hole transport properties of the blend suggests that, although the polymer is slightly unstable when exposed to UV, the main cause for the initial fast loss of PCE of PTB7:[70]PCBM solar cells under illumination in inert atmosphere is a photochemical reaction that involves both the donor and acceptor materials. To prove that the intrinsic instability of PTB7 is playing a minor role in the degradation of the solar cells, we fabricated devices via sequential processing (Figure 6a). A list of proper solvents for the sequential processing of PTB7:[70]PCBM is given in ref.^[40] We chose chlorobenzene (CB) as a solvent for PTB7 and a mixture of 2-chlorophenol (2-CP) and 1-butanol (50:50 vol. ratio) as a solvent for [70]PCBM.

Depositing PTB7:[70]PCBM in two steps enables us to expose the active layer to light in different moments; therefore, we can

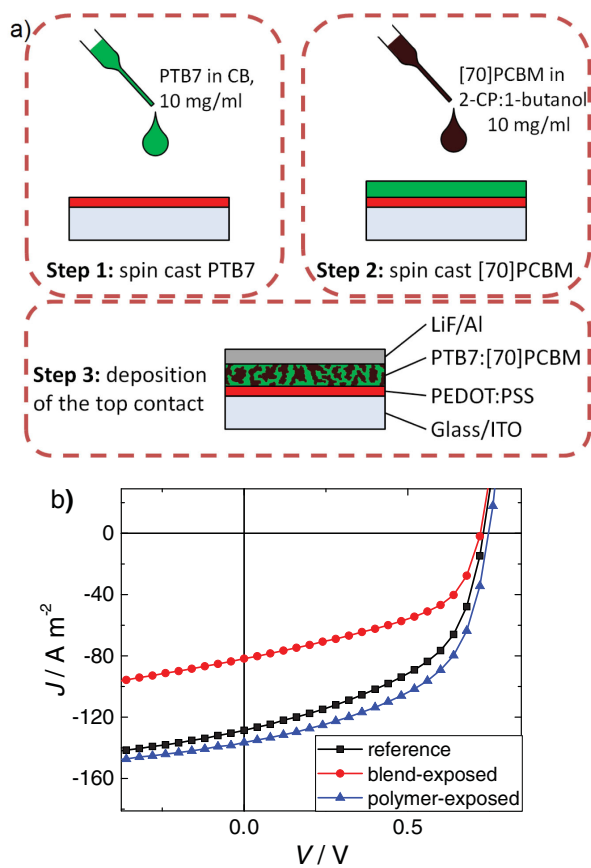


Figure 6. a) Schematic outline of the sequential processing of PTB7:[70]PCBM solar cells. b) *JV* characteristics of the samples fabricated via sequential processing. The reference sample is kept in the dark until the moment of the measurement. The blend- and polymer-exposed samples are exposed to light for 1 h before Step 3 and before Step 2, respectively.

measure the performance of devices in which the polymer is exposed to light either in the presence or in the absence of [70]PCBM. Comparing the results with a pristine reference device, we can establish whether the presence of [70]PCBM during light exposure is a necessary condition for the loss of efficiency.

We fabricated three different samples via sequential processing. One, which serves as a reference, was kept in the dark until the moment of the measurement. A second sample (which we call “blend-exposed”) was exposed to light for 1 h before evaporating the top contact. Finally, a third sample (“polymer-exposed”) was exposed to light for 1 h before the deposition of [70]PCBM.

The *JV* characteristics of the three samples under illumination are shown in Figure 6b. The PCE of the blend-exposed sample is 61% of the PCE of the reference sample. Interestingly, the sample exposed to light before the deposition of [70]PCBM does not show any reduction of PCE with respect to the reference sample. This proves that the degradation of the solar cell is not due to the instability of the polymer and that the fullerene derivative is actively involved in the photochemical reaction occurring in PTB7:[70]PCBM upon UV exposure.

The PCE of the polymer-exposed sample is slightly higher than the PCE of the reference sample. This is somewhat

surprising, given the fact that the hole transport properties of pristine PTB7 are deteriorated upon UV exposure. We measured the mobility of holes in the pristine polymer (fresh and degraded) and in the blend by fitting the *JV* curves of the single carrier devices (see the Supporting Information, Figure S3). The hole mobility in the pristine polymer is $1.5 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. Upon UV exposure, the mobility drops to $4.0 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is similar to the hole mobility in the blend ($2.2 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$). For this reason, the performance of the polymer-exposed sample is not worse than the performance of the reference sample.

It is not possible to fabricate samples depositing first [70]PCBM and then PTB7, because the deposition of the polymer would wash away the fullerene derivative from the substrate. To selectively expose only the fullerene derivative, we prepared a solution of [70]PCBM in oDCB and exposed it to the light of a UV lamp for 1 h. Then, we added PTB7 to the solution and we fabricated a solar cell (“fullerene-exposed” sample). We also exposed to UV for 1 h a solution containing both the materials, and with this fabricated a sample (again, we call this sample “blend-exposed”, although it is not the same sample shown in Figure 6b). The *JV* curves of the two samples are displayed in Figure 7, together with the *JV* curve of the reference sample, fabricated from a solution of PTB7:[70]PCBM kept in the dark. Again, the PCE of the sample fabricated with the blend in which only one material has been exposed to light is very similar to the PCE of the reference sample, while the sample fabricated after exposing simultaneously the two materials to UV light clearly performs worse. Together with the electron-only devices of pristine [70]PCBM, the selective exposure of [70]PCBM before adding PTB7 confirms that the observed deterioration of electron transport properties of PTB7:[70]PCBM is not merely due to degradation of the fullerene derivative.

The lack of reduction of the solar cell performance when the donor (acceptor) is exposed to UV in the absence of the acceptor (donor) is a clear proof that the fast loss of PCE induced by UV light is mainly caused by a reaction to which both PTB7 and [70]PCBM take part. Moreover, the experiments presented above rule out the possibility that the degradation of the PTB7:[70]PCBM solar cell exposed to UV light is due to light-induced reaction at the interface between the active layer

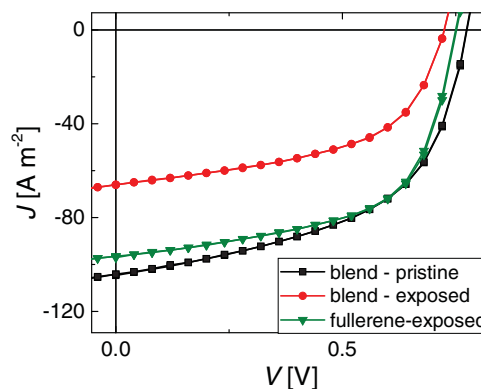


Figure 7. *JV* characteristics of the samples fabricated from a solution kept in the dark (reference), from a solution of PTB7:[70]PCBM exposed for 1 h to UV light (solution-exposed), and from a solution prepared by adding PTB7 only after exposing [70]PCBM to UV for 1 h (fullerene-exposed).

and the electrical contacts. Finally, the occurrence of degradation when the two materials are exposed to UV light when they are in solution excludes the possibility that the reduction of PCE is caused by changes in the film morphology.

It is known that [70]PCBM accelerates the degradation of PTB7 in the presence of oxygen. The results reported here are a clear proof that [70]PCBM is also involved in the UV-induced degradation of PTB7:[70]PCBM solar cells in inert atmosphere. The exact mechanism of the photochemical reaction that causes the loss in PCE upon UV exposure is not known. We analyzed PTB7 and PTB7:[70]PCBM by ^{13}C -, ^1H -, and ^{19}F -NMR before and after exposure to UV light (see the Supporting Information, Figure S4) and did not observe any peak-shifts or significant changes. This result implies that, whatever the photochemical products that are causing the decrease in PCE are, they are not forming in sufficient quantities to reach the detection limit of ^{19}F - and ^{13}C -NMR. In contrast to the ^{19}F - and ^{13}C -NMR, ^1H -NMR exhibited some minor changes; after irradiation, the integration of the aromatic protons decreased both in pure PTB7 and PTB7:[70]PCBM. For pure PTB7, the protons from 3.5 to 5.0 ppm, which belong to two $-\text{CH}_2-$ groups attached to the oxygen of the BDT unit and the $-\text{CH}_2-$ group adjacent to the carbonyl group on the fluorinated thienothiophene (FTT) unit, also decreased slightly after irradiation. The shape of peaks also differs slightly after irradiation. For the PTB7:[70]PCBM mixture, the proton signals from 3.5 to 5.0 ppm, which include three $-\text{CH}_2-$ groups from PTB7 and one end methyl from [70]PCBM (three peaks from three isomers), increased slightly after irradiation. The shape of these peaks, however, showed almost no change after irradiation. We stress that these changes are so slight as to be considered insignificant and may simply reflect different aggregation states, but they are visible in the spectra nonetheless. From these results we can only conclude that the exact mechanisms of the photochemical reactions are not resolvable by NMR and that there is no identifiable change between the initial and irradiated samples.

3. Conclusion

We presented a study of the UV-induced degradation of PTB7:[70]PCBM solar cells in an inert atmosphere. The loss of PCE of the devices exposed to simulated solar light is largely due to the UV component of the radiation, which mostly affects the short-circuit current. We showed that the transport of charges in PTB7:[70]PCBM is affected in a nontrivial way by the UV radiation: although the hole transport in pristine PTB7 deteriorates during UV exposure, the hole transport of the blend is stable; on the other hand, the electron transport in the blend is reduced by exposure to UV even though electron-only devices fabricated with pristine [70]PCBM do not degrade. The drop in PCE upon UV exposure is related to the deterioration of the electron transport properties of the blend and to an increase of the strength of the trap-assisted recombination. Additionally, our results indicate that a reduction of the photogeneration rate of charges contributes to the UV-induced degradation of PTB7:[70]PCBM solar cells. Since the number of absorbed photons is not changing upon UV exposure during the observation time, the reduction of the photogeneration rate of charges is not due to bleaching.

The results provided highlight that UV-induced degradation of PTB7:[70]PCBM solar cells is due to a photochemical reaction which requires the presence of both PTB7 and [70]PCBM. The intrinsic instability of PTB7 when exposed to UV is not enough to explain the fast loss of PCE observed in the solar cell: exposing the polymer to light before adding [70]PCBM to it does not affect the PCE of the device, which is very similar to the PCE of a fresh device. Only if [70]PCBM is present, does the UV radiation trigger a photochemical reaction that results in a lower performance of the device. Thus, the fullerene derivative plays an active role in the photoinduced reaction that causes the reduction of PCE; although we do not investigate further the exact mechanism of this reaction, our results suggest that the compatibility with [70]PCBM under UV radiation should be one of the main goals to achieve in the design of future donor materials.

4. Experimental Section

Solution Preparation: PTB7 and [70]PCBM were purchased from Solarmer and Solenne B. V., respectively, and were used as received. For the 1-step deposition of the blend, PTB7 and [70]PCBM had been dissolved in 1:1.5 w/w ratio in oDCB. The concentration of PTB7 in the solution was 16 mg mL^{-1} . For the sequential processing experiment, PTB7 had been dissolved in CB, [70]PCBM had been dissolved in a mixture of 2-CP and 1-butanol (50:50 vol. ratio). The concentration of both these solutions was 10 mg mL^{-1} . All the solutions had been stirred at 60°C for one night before use. The solution P3HT:[70]PCBM for the reference sample had been prepared by dissolving the two materials in 1:1.5 w/w ratio in chloroform. The concentration of P3HT in the solution was 14 mg mL^{-1} .

Device Fabrication: Solar cells were fabricated on glass substrates with a prepatterned indium tin oxide (ITO) layer. After thoroughly cleaning the substrates with detergent solution, ultrasonication in acetone and isopropyl alcohol, and subsequent UV-ozone treatment, a 60 nm thick film of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS;VP AI4083, H.C. Stark) was spin cast on them. For the conventional BHJ solar cells, the active layer was deposited by spin casting. For sequentially processed solar cells, PTB7 was spin cast from CB solution. [70]PCBM was spin cast on top of the dried PTB7 layer. All the layers were spin cast at 800 rpm in nitrogen atmosphere. The devices were finished by thermal evaporation of LiF (1 nm) and Al (100 nm), overlapping with the ITO pattern to define an active area of 4 mm^2 . Before evaporating the top contact, the P3HT:[70]PCBM device had been annealed for 10 min at 130°C . Single carrier devices were produced on glass substrates, with structure Al(20 nm)/PTB7:[70]PCBM/LiF(1 nm)/Al(100 nm) and Al(20 nm)/[70]PCBM/LiF(1 nm)/Al(100 nm) for electron-only devices and Cr(1 nm)/Au(20 nm)/PEDOT:SS/PTB7:[70]PCBM/Pd(15 nm)/Au(80 nm) for hole-only devices. The contacts were thermally evaporated, the blend was deposited with the same procedure used for the conventional BHJ solar cells.

Device Characterization and Ageing: Steady-state measurements of the *JV* characteristics of the devices were performed using a computer-controlled Keithley source meter in N_2 atmosphere. The measurements under illumination and the ageing of the samples were done using a Steuernagel SolarConstant 1200 metal halide lamp calibrated to 1 Sun intensity and corrected for spectral mismatch with the AM1.5G spectrum using a Si reference cell. A series of neutral density filters were used to measure the light-intensity dependence of the *JV* characteristics.

Optical Characterization: The absorbance spectra were recorded in a wavelength range from 300 to 850 nm at room temperature using a Shimadzu UV-3600 UV-vis-NIR spectrometer. The samples have been prepared by spin casting the materials from oDCB solution on a quartz substrate.

Emission Spectra of the Lamp: The emission spectrum of the solar simulator was measured with an Ocean Optic USB2000 spectrometer.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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