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## Device physics of polymer:fullerene bulk heterojunction solar cells

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## CHAPTER 6

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# UV-INDUCED DEGRADATION OF PTB7:[70]PCBM SOLAR CELLS

### Summary

The degradation of organic photovoltaics (OPV) compared to conventional inorganic technologies 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 will be beneficial for the design of new materials with enhanced stability. This chapter focuses on bulk heterojunction organic solar cells based on PTB7 mixed with [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 one hour and by 35% in eight hours; this degradation is induced by the ultraviolet (UV) part of the spectrum. This chapter analyses 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 PTB7 is not intrinsically unstable when exposed to UV light, and that [70]PCBM plays an active role in the UV-induced degradation of PTB7:[70]PCBM solar cells.

## 6.1 Introduction

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 above 10% have been achieved both in single layer and in tandem architecture,<sup>[1,2]</sup> approaching the efficiency threshold for commercial viability.<sup>[3]</sup> However, the stability of OPV devices remains a major concern,<sup>[4,5]</sup> 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.<sup>[6–14]</sup>

Most of the record-efficiency OPVs achieved in the last few year have been realized with donor polymers based on benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT).<sup>[15–20]</sup> Among these polymers, the most studied is the donor-acceptor copolymer thieno[3,4-*b*]thiophene-alt-benzodithiophene (PTB7), blended with [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester ([70]PCBM). Devices made with this blend exceed PCE of 9% in optimized device structures.<sup>[15,16]</sup> The properties of PTB7 have been extensively studied<sup>[21–24]</sup> and many publications have focused on the optimization of PTB7:[70]PCBM solar cells.<sup>[15,16,25–28]</sup> In spite of the good PCE achievable with PTB7, several researchers have reported that PTB7:[70]PCBM solar cells are unstable when exposed to light and to the ambient.<sup>[29–33]</sup> It has been shown that the principal mechanism of PTB7 degradation, both in neat films and in blends with [70]PCBM, is *via* photo-oxidation with the highly reactive singlet <sup>1</sup>O<sub>2</sub> species;<sup>[29,30]</sup> the effect of photo-oxidation at the molecular level was described in a later publication by Razzel-Hollis *et al.*<sup>[31]</sup> Furthermore, it has been shown that the presence of [70]PCBM accelerates the degradation of PTB7 due to increased production of singlet oxygen.<sup>[30,31]</sup>

The results reported in Ref. 29–31 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.<sup>[32]</sup> The photoinduced degradation of polymer:fullerene blends in inert atmosphere has been attributed to the absorption of ultraviolet (UV) photons, that in aromatic polymers can induce reactions such as chain scissions, cross-linking and side-chain rearrangement.<sup>[6,7]</sup> Lim *et al.* showed 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.<sup>[32]</sup> For their study, they processed PTB7:[70]PCBM using 1,8-diiodooctane (DIO) as solvent additive. Although the best performance for PTB7:[70]PCBM has been obtained using DIO,<sup>[25]</sup> it has been proven that this additive remains in the blend after deposition of the active layer<sup>[34]</sup> and has a negative impact on the stability of the devices.<sup>[28]</sup> Thus, the results obtained by Lim *et al.* may be showing the effect of DIO rather than an intrinsic instability of PTB7:[70]PCBM.

In this chapter, we investigate 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,<sup>[35,36]</sup> the knowledge of how transport properties degrade in PTB7:[70]PCBM blends is currently lacking. We analyse the effect of UV on the charge transport properties. We fabricate 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 process the blend from pristine *ortho*-dichlorobenzene (*o*DCB) solution. We measure the transport of charges in PTB7:[70]PCBM blend and how it changes upon illumination in N<sub>2</sub> atmosphere. While the transport of holes remains unaltered, exposure to UV light has an effect on the transport of electrons, which becomes less effective. This may indicate that the electron transporting material, [70]PCBM, is affected by the degradation of the blend. We compare the efficiency of devices in which either only the polymer or both polymer and fullerene have been exposed to light. To selectively expose only the polymer, we fabricate PTB7:[70]PCBM solar cells *via* sequential processing.<sup>[27,37]</sup> 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 what is obtained from the one-step deposition of the blend.<sup>[27,37,38]</sup> Sequential processing enables us to compare what happens when the polymer is exposed to light before or after the addition of [70]PCBM; we observe that the performance of the solar cell is not reduced if the exposition to UV light occurs in the absence of the fullerene derivative on the time scale of our experiment.

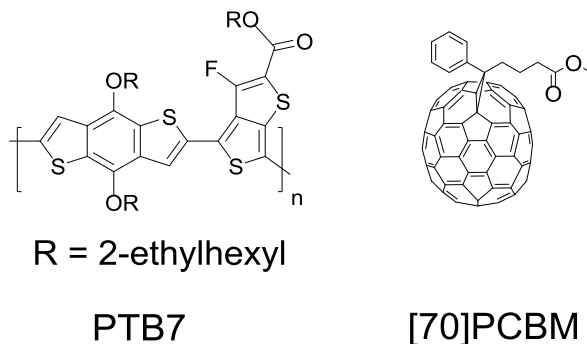
Our results prove that PTB7 is not intrinsically unstable when exposed to UV light, and that the UV-induced degradation of the blend is due to the presence of [70]PCBM. Since fullerene derivatives such as [70]PCBM and its C<sub>60</sub>-equivalent PCBM are used as electron acceptor material in many state-of-the-art organic solar cells,<sup>[3,39]</sup> understanding the effect of [70]PCBM on the stability of the devices is crucial: it will direct the research towards the design of new donor materials, compatible with [70]PCBM, or alternatively towards the design of new electron acceptors, in order to improve device stability.

## 6.2 Results and discussion

In this section we present the results of our measurements regards the stability of PTB7:[70]PCBM solar cells processed from *o*DCB solution and exposed to light in inert atmosphere, the characterization of the transport of electrons and holes in the PTB7:[70]PCBM blend, and the results obtained from the sequential processing experiment. All the details about the fabrication and characterization of the samples are in the Experimental Section. The exposition to light for all the samples presented in this paper has been carried out in inert atmosphere (a N<sub>2</sub> atmosphere, with less than 0.1 ppm H<sub>2</sub>O, and less than 0.6 ppm O<sub>2</sub>); during the exposure and the measurement, the temperature was kept constant (295 K).

### 6.2.1 Solar cells performance upon UV exposure

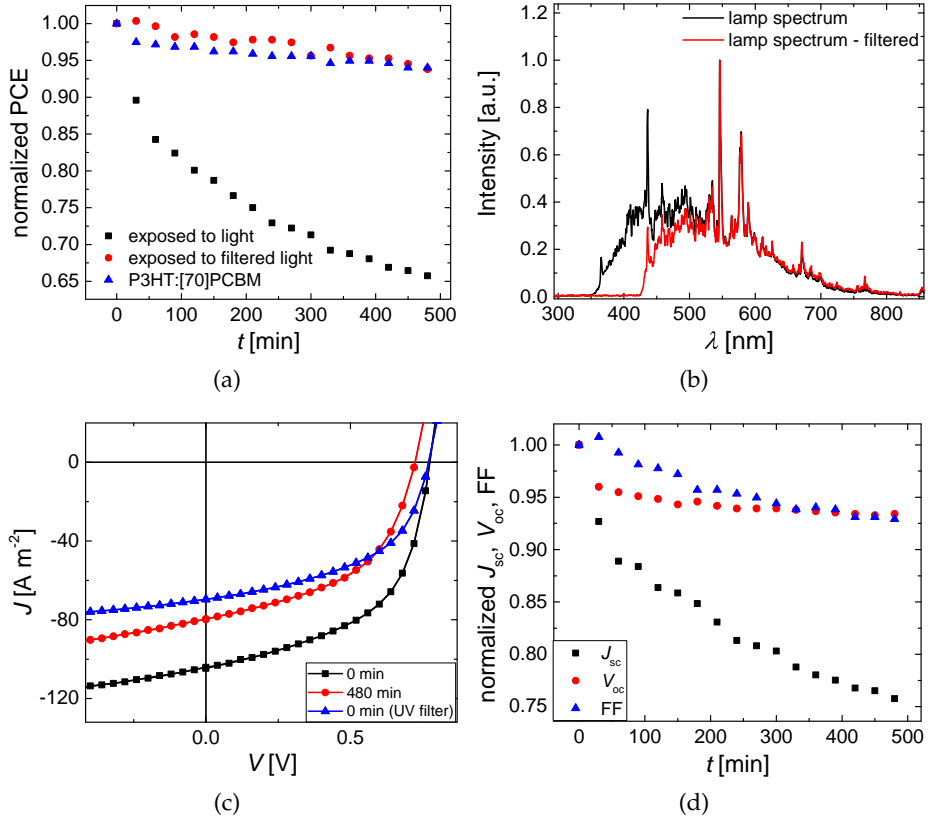
We fabricate conventional BHJ solar cells with a PTB7:[70]PCBM (Figure 6.1) blend. To determine how much the PCE of the device diminishes due to UV exposure in inert atmosphere, we measure the  $JV$  characteristic of one solar cell every 30 minutes for 8 hours, keeping it continuously under the light of a solar simulator. When not measuring the  $JV$  curve, we keep the device in open circuit conditions.



**Figure 6.1:** Chemical structures of PTB7 and [70]PCBM.

The normalized PCE of the device is displayed in Figure 6.2a: 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 measure 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 6.2(b); by applying the long-pass filter, all the light with wavelength below 425 nm is blocked, while the intensity of light with wavelength between 425 nm 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.

Furthermore, we compare 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.



**Figure 6.2:** 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 the 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)  $J$ - $V$  characteristics of PTB7:[70]PCBM solar cells as spun and after 8 hours of exposition to light. We note that the difference between the black and the blue 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.

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 hours of exposure (Figure 6.2(c)). Performing the measurements in inert atmosphere excludes the photo-oxidation reaction described by Soon *et al.* [30] as a cause for the reduction of PCE. Figure 6.2a clearly shows that this reduction is largely due to the effect of UV radiation. Atomic force microscopy (AFM) images of the topography of the film before and after exposition do not reveal any change in the morphology upon UV exposure (data not shown); 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 6.1), drops from 43.2 W/m<sup>2</sup> (fresh device) to 28.4 W/m<sup>2</sup> after 8 hours of UV exposure.

Figure 6.2(d) reports the normalized short circuit current ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ), and fill-factor (FF) of the cell exposed to light without long-pass filter;  $J_{sc}$  is the most affected parameter, dropping to  $\sim 75\%$  of its initial value after 8 hours.  $V_{oc}$  drops slightly at the beginning of the observation period and then remains almost constant, FF decreases slowly in time; both these parameters are at  $\sim 90\%$  of their initial values after 8 hours.

**Table 6.1:** Solar cell parameters of the  $JV$  curves reported in Figure 6.2(c)

Exposure time [min]	$J_{sc}$ [A/m <sup>2</sup> ]	$V_{oc}$ [V]	FF [-]	$J_{max}$ [A/m <sup>2</sup> ]	$V_{max}$ [V]	PCE [%]	$P$ [W/m <sup>2</sup> ]
0	104.14	0.774	0.536	71.927	0.600	4.32	43.2
480	78.90	0.723	0.498	54.833	0.520	2.84	28.4
0 (UV filter)	69.64	0.770	0.505	47.124	0.576	2.71	27.1

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<sup>2</sup> (see Figure 6.2(c) and Table 6.1). 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 low-wavelength photons.

We verify that the UV-vis absorption of the blend does not vary significantly upon UV exposure (data not shown); the number of photogenerated excitons is thus the same in the fresh device and after 8 hours of exposure. 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,  $J_{\text{sat}}$ ), we calculate  $G$  according to<sup>[40]</sup>

$$G = \frac{J_{\text{sat}}}{qL} \quad (6.1)$$

where  $L$  is the thickness of the active layer. We assume here that -2 V is a sufficient bias to extract all the photogenerated charges. After 8 hours of exposure to unfiltered light,  $G$  drops from its initial value of  $8.22 \times 10^{27} \text{ m}^{-3} \text{ s}^{-1}$  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. The absorption of the blend does not change upon one hour of UV exposure (data not shown), excluding the photobleaching as a cause of the degradation.

## 6.2.2 Charge transport

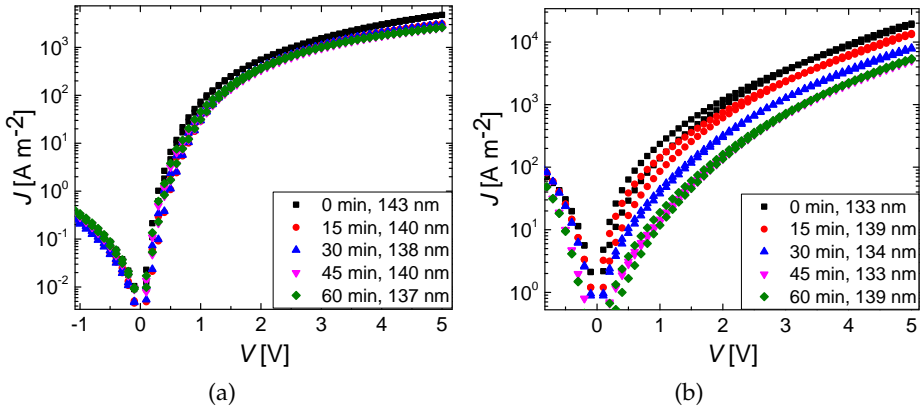
To characterize the transport of holes and electrons in the blend, we fabricate single carrier devices in which a layer of PTB7:[70]PCBM is sandwiched between selective electrodes that suppress the injection of electrons (hole-only devices) or holes (electron-only devices). The current flowing through the devices is measured before and after exposing the active layer to the light of the solar simulator. Figure 6.3 displays the  $JV$  characteristics of single carrier devices for different illumination times. The hole current only slightly diminishes for longer exposure times, and it is almost constant already after 15 minutes of exposure; the electron current is more significantly reduced upon exposing the active layer to UV radiation. Therefore, the loss of performance is related to a deterioration of the electron transport properties.

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 fabricate more samples of each kind; before evaporating the top contact, the devices are 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 keep the temperature at 295 K during the light exposures, and we evaporate the top contact simultaneously for devices of the same kind. We are therefore confident that the differences which we observe in the  $JV$  curves for different exposure times are due to the effect of UV light, and not to sample-to-sample variations.

## 6.2.3 Trap-assisted recombination in PTB7:[70]PCBM solar cells

From the comparison between PTB7:[70]PCBM and P3HT:[70]PCBM solar cells in Figure 6.2, it can be concluded that PTB7:[70]PCBM is unstable when exposed to UV. No





**Figure 6.3:**  $JV$  characteristics of hole-only (a) and electron-only (b) 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.

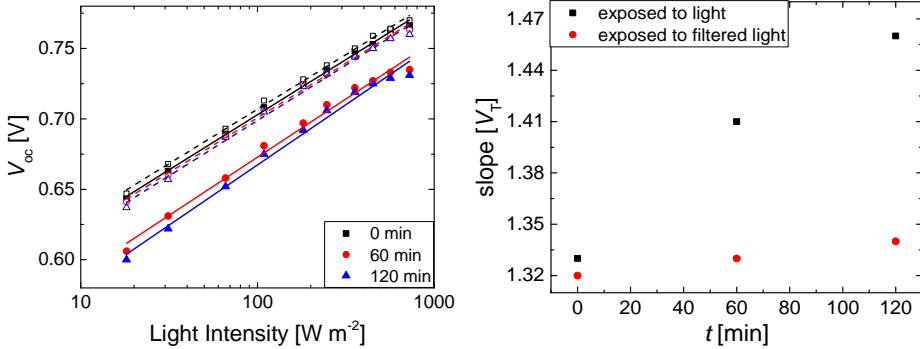
reduction of the PCE is observed for the reference P3HT:[70]PCBM cell; one may therefore consider [70]PCBM to be stable, and expect to observe a drop in the hole transport properties of the blend upon UV exposure, PTB7 being the hole transporting material. Thus, it is surprising to obtain a drop in the electron transport properties.

A possible cause for the observed reduction of the electron current for longer exposition times is the formation of electron trapping states as a product of the UV-induced reaction. The presence of electron trapping states is capable to explain the stronger voltage dependence of the electron current if compared to the hole current<sup>[41]</sup> and the slight clockwise hysteresis<sup>[42]</sup> in the electron-only  $JV$  curve (Figure 6.3).

It is well known that trapped charges may undergo Shockley-Read-Hall (SRH) recombination<sup>[43,44]</sup> and that such trap-assisted recombination pathway results in a stronger dependence of  $V_{oc}$  on the light intensity<sup>[45]</sup> if compared to a trap-free solar cell.<sup>[46]</sup> The slope of  $V_{oc}$  versus the natural logarithm of the light intensity can be expressed as a function of the thermal voltage  $V_T = \frac{k_B T}{q}$ , where  $k_B$  is the Boltzmann constant,  $T$  is the temperature and  $q$  is the elementary charge; 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 measure 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 hours. We change the intensity of the incident light by using a set of neutral density filter. To block the photoinduced reaction during the intensity scan, the long-pass filter is used in combination with the neutral density filter. For this reason, the maximum light intensity at which the measurements are performed is lower than 1 sun ( $1000 \text{ W/m}^2$ ). The outcome of this experiment is

shown in Figure 6.4. For the fresh device, the slope is  $1.33 V_T$ ; it increases to  $1.41 V_T$  and  $1.46 V_T$  after one and two hours 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.



**Figure 6.4:** a)  $V_{oc}$  vs incident light intensity for PTB7:[70]PCBM solar cells, measured for the fresh device and after exposing the cell to light for one hour and two hours. We analysed 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.

These results confirm the hypothesis that a small amount of electron traps is present in the blend and that the exposition to UV radiation increases the number of trap states, resulting in a stronger SRH recombination.

### 6.2.4 The role of [70]PCBM

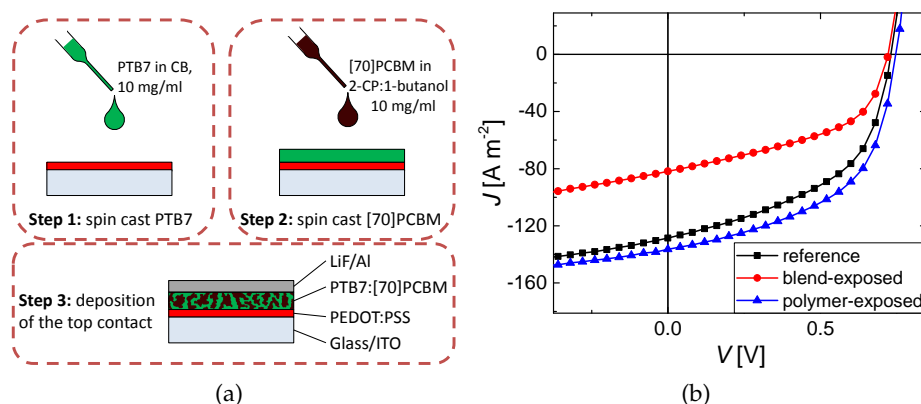
To check whether the presence of [70]PCBM is a key factor for the UV-induced photochemical reaction in PTB7:[70]PCBM, we fabricate solar cells *via* sequential processing (Figure 6.5a). A list of proper solvents for the sequential processing of PTB7:[70]PCBM is given in Ref. 27. We choose chlorobenzene (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 step enables us to expose the active layer to light in different moments; therefore, we can 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 fabricate three different samples. One, which serves as a reference, is kept in the dark until the moment of the measurement. A second sample (which we call "blend-exposed") is exposed to light for one hour before evaporating the top contact. Finally, a

third sample (“polymer-exposed”) is exposed to light for one hour before deposition of [70]PCBM.

The  $JV$  characteristics of the three samples under illumination are shown in Figure 6.5b. The PCE of the blend-exposed sample is 61% of the PCE of the reference sample. Interestingly, the sample exposed to light before deposition of [70]PCBM does not show any reduction of PCE with respect to the reference sample. The PCE of the polymer-exposed sample is actually slightly higher than the PCE of the reference sample. The lack of a reduction of the solar cell performance when the polymer is exposed to UV in the absence of [70]PCBM is a clear proof that this fullerene derivative is actively involved in the photochemical reaction occurring in PTB7:[70]PCBM upon UV exposure.

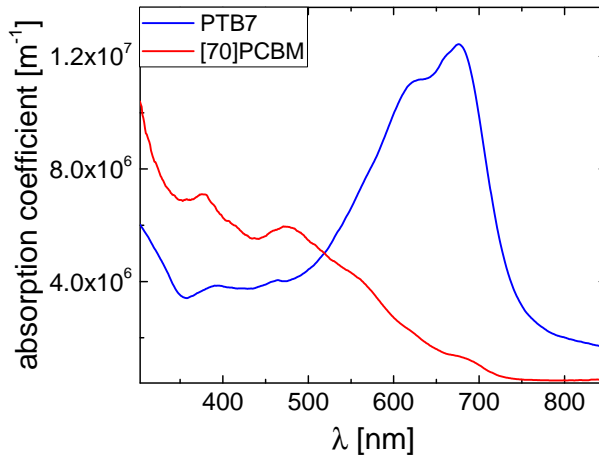


**Figure 6.5:** a) Schematic outline of the sequential processing of PTB7:[70]PCBM solar cells. b)  $JV$  characteristics of the samples fabricated *via* sequential processing. The reference sample is kept in dark until the moment of the measurement. The blend- and polymer-exposed samples are exposed to light for one hour before Step 3 and before Step 2, respectively.

Moreover, the sequential processing experiments 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 and the electrical contacts. The exposure to light for the devices fabricated *via* sequential processing occurs before evaporation of the LiF/Al top contact; reactions at the interface between the active layer and LiF are thus not responsible for the lower PCE of the blend-exposed sample when compared to the reference. If instead the degradation is caused by photoinduced reaction at the PEDOT:PSS/PTB7:[70]PCBM interface, the PCE of the polymer-exposed sample would also be lower than that of the reference sample.

One may argue that the [70]PCBM triggers the UV-induced degradation of the polymer by absorbing the UV part of the radiation and subsequently transferring energy to PTB7. To verify this, we measure the absorption spectra of PTB7 and [70]PCBM (Fig-

ure 6.6): although [70]PCBM absorbs more than PTB7 in the spectral region 350 - 450 nm, the difference between the absorption coefficients of the two materials in the UV region is no more than a factor of 2. Thus, the polymer is also absorbing a significant fraction of the UV light and the fact that the fullerene derivative has the only role of absorbing UV radiation can be ruled out.



**Figure 6.6:** Absorption coefficient of PTB7 and [70]PCBM. In the spectral region 350 - 450 nm, [70]PCBM absorbs more light than PTB7.

It is known that [70]PCBM accelerates the degradation of PTB7 in the presence of oxygen,<sup>[30,31]</sup> The results reported here are a clear proof that [70]PCBM is also responsible for 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 beyond the scope of this work.

## 6.3 Conclusion

We presented a study of the UV-induced degradation of PTB7:[70]PCBM solar cells in 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. From the point of view of the device physics, the drop in PCE upon UV exposure is related to the reduction of the photogeneration rate of charges and by the deterioration of the electron transport properties of the blend. Additionally, our results indicate that the strength of the trap-assisted recombination increases when the blend is exposed to UV light.

The results provided in this chapter highlight that [70]PCBM plays a key role in the UV-induced degradation of PTB7:[70]PCBM solar cells. PTB7 is not intrinsically unstable when exposed to UV radiation: 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.

## References

- [1] Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jian, H. Lin, H. Ade, H. Yan, *Nat. Commun.* **2014**, *5*, 5293.
- [2] J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li, Y. Yang, *Nat. Comm.* **2013**, *4*, 1446.
- [3] C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. Jia, S. P. Williams, *Adv. Mater.* **2010**, *22*, 3839.
- [4] M. Jørgensen, K. Norrman, F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 686.
- [5] M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, F. C. Krebs, *Adv. Mater.* **2012**, *24*, 580.
- [6] A. Rivaton, J.-L. Gardette, *Angew. Macromol. Chem.* **1998**, *261/262*, 173.
- [7] A. Rivaton, S. Chambon, M. Manceau, J.-L. Gardette, N. Lemaître, S. Guillerez, *Polym. Degrad. Stabil.* **2010**, *95*, 278.
- [8] M. O. Reese, A. M. Nardes, B. L. Rupert, R. E. Larsen, D. C. Olson, M. T. Lloyd, S. S. Shaheen, D. S. Ginley, G. Rumbles, N. Kopidakis, *Adv. Funct. Mater.* **2010**, *20*, 3476.
- [9] J. Bhattacharya, R. W. Mayer, M. Samiee, V. L. Dalal, *Appl. Phys. Lett.* **2012**, *100*, 193501.
- [10] A. Tournebize, P.-O. Bussière, P. Wong-Wah-Chung, S. Thérias, A. Rivaton, J.-L. Gardette, S. Beaupré, M. Leclerc, *Adv. Energy Mater.* **2013**, *3*, 478.
- [11] A. Garg, S. K. Gupta, J. J. Jasieniak, T. B. Sing, S. E. Watkins, *Prog. Photovolt. Res. Appl.* **2014**, *23*, 989.
- [12] J. Adams, G. D. Spyropoulos, M. Salvador, N. Li, S. Strohm, L. Lucera, S. Langner, F. Machui, H. Zhang, T. Ameri, M. M. Voigt, F. C. Krebs, C. J. Brabec, *Energy Environ. Sci.* **2015**, *8*, 169.
- [13] A. Savva, E. Georgiou, G. Papazoglou, A. Z. Chrusou, K. Kapnisis, S. A. Choulis, *Sol. Energy Mater. Sol. Cells* **2015**, *132*, 507.
- [14] L. A. Frolova, N. P. Piven, D. K. Susarova, A. V. Akkuratov, S. D. Babenko, P. A. Troshin, *Chem. Commun.* **2015**, *51*, 2242.
- [15] Z. He, C. Zhong, S. Su, M. Xu, H. Wu, Y. Cao, *Nat. Photonics.* **2012**, *6*, 591.
- [16] L. Lu, L. Yu, *Adv. Mater.* **2014**, *26*, 4413.
- [17] S. H. Liao, H. J. Jhuo, Y. S. Cheng, S. A. Chen, *Adv. Mater.* **2013**, *25*, 4766.

- [18] L. Ye, S. Zhang, W. Zhao, H. Yao, J. Hou, *Chem. Mater.* **2014**, *26*, 3603.
- [19] J. You, C.-C. Chen, L. Dou, S. Murase, H.-S. Duan, S. A. Hawks, T. Xu, H. J. Son, L. Yu, G. Li, Y. Yang, *Adv. Mater.* **2012**, *24*, 5267.
- [20] S. Guo, J. Ning, V. Körstgens, Y. Yao, E. M. Herzig, S. V. Roth, P. Müller-Buschbaum, *Adv. Energy Mater.* **2015**, *5*, 1401315.
- [21] S. Foster, F. Deledalle, A. Mitani, T. Kimura, K.-B. Kim, T. Okachi, T. Kirchartz, J. Oguma, K. Miyake, J. R. Durrant, S. Doi, J. Nelson, *Adv. Energy Mater.* **2014**, *4*, 1400311.
- [22] B. Ebenhoch, S. A. J. Thomson, K. Genevičius, G. Juška, I. D. W. Samuel, *Organic Electron.* **2015**, *22*, 62.
- [23] J. Kniepert, I. Lange, J. Heidbrink, J. Kurpiers, T. J. K. Brenner, L. J. A. Koster, D. Neher, *J. Phys. Chem. C* **2015**, *119*, 8310.
- [24] C. H. To, A. Ng, Q. Dong, A. B. Djurišić, J. A. Zapien, W. K. Chan, C. Surya, *ACS Appl. Mater. Interfaces* **2015**, *7*, 13198.
- [25] Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, *Adv. Mater.* **2010**, *22*, E135.
- [26] C. Gu, Y. Chen, Z. Zhang, S. Xue, S. Sun, C. Zhong, H. Zhang, Y. Lv, F. Li, F. Huang, Y. Ma, *Adv. Energy Mater.* **2014**, *4*, 1301771.
- [27] J. C. Aguirre, S. A. Hawks, A. S. Ferreira, P. Yee, S. Subramaniam, S. A. Jenekhe, S. H. Tolbert, B. J. Schwartz, *Adv. Energy Mater.* **2015**, *5*, 1402020.
- [28] W. Kim, J. K. Kim, E. Kim, T. K. Ahn, D. H. Wang, J. H. Park, *J. Phys. Chem. C* **2015**, *119*, 5954.
- [29] S. Alem, S. Wakim, J. Lu, G. Robertson, J. Ding, Y. Tao, *ACS Appl. Mater. Interfaces* **2012**, *4*, 2993.
- [30] Y. W. Soon, H. Cho, J. Low, H. Bronstein, I. McCulloch, J. R. Durrant, *Chem. Commun.* **2013**, *49*, 1291.
- [31] J. Razzel-Hollis, J. Wade, W. C. Tsoi, Y. Soon, J. R. Durrant, J.-S. Kim, *J. Mater. Chem. A* **2014**, *2*, 20189.
- [32] F. J. Lim, A. Krishnamoorthy, G. W. Ho, *ACS Appl. Mater. Interfaces* **2015**, *7*, 12119.
- [33] T.M. Abdel-Fattah, E. M. Younes, G. Namkoong, E. M. El-Maghraby, A. H. Elsayed, A. H. Abo Elazm, *Synth. Metals* **2015**, *209*, 348.
- [34] L. Ye, Y. Jing, X. Guo, H. Sun, S. Zhang, M. Zhang, L. Huo, J. Hou, *J. Phys. Chem. C* **2013**, *117*, 14920.

- 
- [35] V. D. Mihailetschi, H. Xie, B. de Boer, L. J. A. Koster, P. W. M. Blom, *Adv. Funct. Mater.* **2006**, *16*, 699.
- [36] A. Guerrero, N. F. Montcada, J. Ajuria, I. Extebarria, R. Pacios, G. Garcia-Belmonte, E. Palomares, *J. Mater. Chem. A* **2013**, *1*, 12345.
- [37] J. J. van Franeker, S. Kouijzer, X. Lou, M. Turbiez, M. M. Wienk, R. A. J. Janssen, *Adv. Energy Mater.* **2015**, *5*, 1500464.
- [38] V. S. Gevaerts, L. J. A. Koster, M. M. Wienk, R. A. J. Janssen, *ACS Appl. Mater. Interfaces* **2011**, *3*, 3252.
- [39] T. Liu, A. Troisi, *Adv. Mater.* **2013**, *25*, 1038.
- [40] A. M. Goodman, A. Rose, *J. Appl. Phys.* **1971**, *42*, 2823.
- [41] P. W. M. Blom, M. J. M. de Jong, J. J. M. Vleggaar, *Appl. Phys. Lett.* **1996**, *68*, 3308.
- [42] L.-L. Chua, J. Zaumseil, J.-F. Chang, E. C. W. Ou, P. K. K. Ho, H. Sirringhaus, R. H. Friend, *Nature* **2005**, *434*, 194.
- [43] W. Shockley, W. T. Read, *Phys. Rev. B* **1952**, *87*, 835.
- [44] R. N. Hall, *Phys. Rev. B* **1952**, *87*, 387.
- [45] M. M. Mandoc, F. B. Kooistra, J. C. Hummelen, B. de Boer, P. W. M. Blom, *Appl. Phys. Lett.* **2007**, *91*, 263505.
- [46] L. J. A. Koster, V. D. Mihailetschi, R. Ramaker, P. W. M. Blom, *Appl. Phys. Lett.* **2005**, *86*, 123509.



