Degradation through Directional Self-Doping and Homogeneous Density of Recombination Centers Hindered by 1,8-Diiodooctane Additive in Non-Fullerene Organic Solar Cells

Osbel Almora,* Julius Wiegand, Pilar López-Varo, Gebhard J. Matt, and Christoph J. Brabec

1. Introduction

Organic solar cells (OSCs) are among the most promising emerging photovoltaic technologies due to their easy and low-cost fabrication methods and their perspective applications for building integration, indoors, and wearables.[1-6] These devices are typically structured as a sequence of layers where an active material is comprised by the selective contacts for electrons and holes.[7-9] The active layer is most typically a blend including donor and acceptor organic molecules which absorbs the photons and initiates the charge-carrier separation for selective extraction through the electrodes.[10]

Several materials and structure modifications have been studied and optimized for OSCs during the last two decades.[9] More recently, the introduction of non-fullerene acceptors (NFAs)[11-16] has made possible to perform over the 18% in power conversion efficiency (PCE).[17-19] However, in terms of long-term photostability, there is still much more room for improvement in OSCs.[20-23] Moreover, the understanding of degradation mechanisms and the possible alternatives are still poor.[24-27]

Particularly on NFAs, most of the photostability studies are in early stages.[28-33] For instance, among the most recent works, Greenbank el al.[34] correlated reversible degradation, when assessed in ISOS-O-1 outdoor conditions, with the presence of...
charge trap formation. Sudakov et al.\textsuperscript{[35]} highlighted the importance of the reactive oxygen species in P3HT:FBR blends and found that the generation of singlet oxygen by energy transfer from the FBR triplet state is responsible for the poor stability of FBR and for the accelerated photodegradation at later times of the entire blend. Deb et al.\textsuperscript{[36]} presented an intensity-modulated photocurrent spectroscopy study suggesting that defect formation and charge recombination at device contact interfaces is chiefly responsible for performance degradation. Wang et al.\textsuperscript{[37]} measured the built-in potential via transient photocurrent measurement, and found that retaining high values of this parameter mitigates degradation mechanisms. Moreover, Yang et al.\textsuperscript{[38]} have found the use of polymer additives as acceptor doping strategy to be beneficial for thermal stability. Lee et al.\textsuperscript{[39]} suggested that PC\textsubscript{71}BM as additive can lead to enhanced electron mobility and balanced charge transport. Similarly, Fan et al.\textsuperscript{[40]} reported that the photo-initiator bifunctional bis-benzophenone as a solid additive, can lead to more balanced carrier transport and more effective exciton dissociation.

In our previous works,\textsuperscript{[31,32]} the photostability of state-of-the-art OSCs have been investigated including the NFA 3,9-bis(2-methylene-[(3,1-dicyanomethylene)-6,7-difluoro-indanone])-5,5,11,11-tetrakis(4-hexylyphenyl)-dithieno[2,3-d,2',3'-d']-s-indaceno [1,2-b:5,6-b']dithiophene (ITIC-2F, also known as ITIC-F, IT-4F, ITIC-DF) and the polymer donor poly[(2,6-(4,8-bis(5-(2-ethylhexyl) thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene)-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-e']dithiophene-4,8-dione)]) (PBDB-T) with fluoroalkyl side chains, i.e., PBDB-T-2F (PM6) as in Figure 1a. These devices with IT-4F:PM6 active material composites show improved intrinsic photostability despite a characteristic loss of fill factor (FF) in the current density-voltage ($J-V$) curve under illumination. In particular, morphology changes were related to the reduction of electron mobility during aging, whereas hole mobility was less affected (using the space-charge-limited current method in single carrier devices), and also connected to the increase in traps noted from the photo-induced charge-carrier extraction by linearly increasing voltage. The degradation mechanism in this case\textsuperscript{[32]} was proposed to be a consequence of the formation of acceptor trap levels during the reorganization of polymers and diffusion-limited aggregation of NFAs under illumination. Moreover, the use of 1,8-Diiodooctane (DIO) as additive has also been reported\textsuperscript{[32,41]} to be beneficial for the device performance by making the active layer more ordered in terms of higher crystallinity.

In this work, we investigate the degradation mechanisms for IT-4F:PM6-based OSCs with and without the use of DIO additive during the fabrication process, named as DIO and No DIO samples, respectively. In particular, the focus of our analyses is on the impedance spectroscopy (IS) measurements under different illumination and bias regimes before and after degradation. Our findings suggest the variation of the energetic scheme by increase of 1) shallow trap levels acting as space-oriented self-doping concentrations and 2) homogeneously distributed recombination centers favoring leakage currents, as confirmed via drift-diffusion (DD) simulations. These behaviors are nearly inhibited when DIO additive is added as functional additive.

Figure 1. Performance stability of ITIC-2F:PM6-based OSCs: a) Schematic device architecture and chemical structure of molecules in the active layer; b) Current-voltage curves (see Table S1, Supporting Information, for absolute parameters) and c) EQE spectra before and after degradation under white LED during 1400 h for devices with and without use of DIO, as indicated. Lines in (b) are the DD simulations corresponding to the model in Figure 2f,g, 3 and Table S2, S3, Supporting Information. The arrows indicate the degradation direction.

2. Results and Discussion

The fabrication procedure for the studied samples has been already described in our previous work,\textsuperscript{[32]} and it is also reproduced in Section S1, Supporting Information. Importantly, an annealing at 100 °C for 10 min was applied for optimizing morphology and reducing the DIO residual,\textsuperscript{[42]} which could still be present, despite it has been reported to be completely removed with 120 °C for 5 min.\textsuperscript{[43]} Note that the device architecture (ITO/ZnO/active layer/MoO\textsubscript{3}/Al) is schemed in Figure 1a, along with
the respective donor, acceptor, and additive molecules for the active layer. The $J$–$V$ curves were performed under standard 1 sun AM1.5G spectrum illumination in a Newport AAA solar simulator at room conditions. For the measurements of external quantum efficiency (EQE), an Enli Technology QE-R setup was utilized and a Zahner Zennium Pro/PP211 impedance workstation, with its LSW-2 white light-emitting diode (LED) light source, was used for the IS analyses.

For the stability test, the cells were set at open-circuit in a self-made degradation chamber with $N_2$ circulation, during 1400 h under 1 sun white LED spectrum illumination intensity at 35 °C. The only variable between samples was the presence/absence of additive DIO. Note that the used white LED spectrum prevented potential UV-induced degradation contributions from the ZnO layer and radical formation of possible residual DIO.[43]

A typical outcome from the $J$–$V$ curves before and after degradation, for DIO and No DIO samples, is shown in Figure 1b (dots). The complete time evolution of the performance parameters and $J$–$V$ curves is shown in Figure S1, Supporting Information, with starting values as Table S1, Supporting Information. When using DIO, the performance stability is significantly steadier as compared to devices without DIO. Interestingly, while the open-circuit voltage ($V_{oc}$) is similarly stable for both DIO and No DIO samples, the short-circuit current ($J_{sc}$) and the FF are up to 30% better when using DIO after 1400 h of degradation. For instance, DIO and No DIO samples would deliver 9.0 and 6.3 Wh cm$^{-2}$, respectively, after 1000 h of operation in the conditions of the stability test (see Figure S1, Supporting Information).

From the EQE spectra in Figure 1c, one can see no significant differences between fresh/aged or DIO/No DIO samples around the bandgap region ($E_g = 1.58$eV$\pm$5meV).[46] A similar trend holds for the UV–vis absorption spectra in Figure S2, Supporting Information. Interestingly, as the photon energy increases, one can identify systematic energy localized differences when comparing fresh and degraded EQE spectra (see Figure S3, Supporting Information). The understanding of this behavior lies beyond the scope of this article and would require further systematic experimental evidence and theoretical modeling. Nevertheless, one may suggest that optical interference and/or energy-dependent recombination should be the most probable explanations. Regarding interference, one may expect changes in the thickness and/or the refractive index of the layers within the device, or even some experimental inaccuracy artifacts. Yet, there is some evidence on unchanging absorption spectra (e.g., Figure S2, Supporting Information) and one can also note analogous patterns of EQE degradation among similar PBDB-T:ITIC devices, unlike PBDB-T:PC$_{70}$BM cells, characterized in our previous work (see Figure S3, Supporting Information).[29] On the other hand, the decrease in charge extraction at short-circuit for specific photon energies can also be due to, for instance, an increase in recombination trap centers with strong coulombic capture, given small scattering rates for long thermalization times.[57] Moreover, the energy dependency of recombination in OSCs is better studied via the internal quantum efficiency and should be explored in detail in future works.

The analysis of both the $J$–$V$ curves and EQE spectra for the stability test evidence that recombination at low forward bias is significantly enhanced after degradation in No DIO devices. Interestingly, this is a region typically dominated by leakage currents which can hinder the charge extraction.

The recombination mechanisms for DIO/No DIO samples before and after the stability test were characterized via IS, as shown in Figure 2 and Section S3, Supporting Information. The cells were kept at quasi-steady-state open-circuit regime while the steady-state illumination intensity was varied with a white LED light source.[50–52] In these experiments, the photo-generated charges due to illumination are forced to recombine with a characteristic lifetime by the action of the external forward bias (which equals $V_{oc}$). Thus, a flat-band splitting of the quasi-Fermi levels proportional to the $V_{oc}$ is provided and the transport regimes are tested by sweeping the $V_{oc}$. Furthermore, while changing the illumination and the corresponding forward bias in this quasi-open-circuit mode, the direct current (DC) operation is minimized, which reduces noise and inductive artifacts to the IS spectra.[52,53]

The IS spectra in Nyquist plot representation under 1 sun equivalent white LED is shown in Figure 2a, showing larger resistances for DIO than for No DIO samples. In the quasi-open-circuit situation of this experiment, the larger the recombination resistance, the larger the lifetime and the better the device performance.[53] However, no significant difference is observed on the way they change after degradation, in agreement with the observations from $J$–$V$ curves (see Figure 1b and Figure S1, Supporting Information), where the main performance decay is due to $J_{sc}$ and FF losses. This suggests focusing on the low forward bias region, and thus a wide range of $V_{oc}$ values/illuminations were explored, as in the spectra of Figure S4, Supporting Information. There, the experimental data is presented as dots along with the fittings to the equivalent circuit (EC) model in Figure 2b. The EC includes series resistance $R_s$, contact charge extraction resistance $R_e$, bulk recombination resistance $R_b$, geometrical capacitance $C_g$, and chemical capacitance $C_p$. All the fitting parameters, as well as the resulting characteristic times, are shown in Figure S5, Supporting Information. There one can observe how the values for $R_s$ and $C_g$ are far lower than $R_b$ and $C_p$, respectively, being the latter characteristically exponential.[54]

The series resistance in Figure 2c increases after degradation for the DIO sample, as expected from a typical reduction in the cell performance. In contrast, $R_s$ is more significantly reduced in the No DIO case after the stability test. The reduction in ohmic losses can be related with lowering of contact barriers at the interfaces or enhancement of the conductivity in some bulk regions.[35]

The bulk recombination resistance in Figure 2d follows two exponentially decaying regimes depending on the $V_{oc}$ value/illumination. At higher forward bias, again, there is no significant difference between DIO/No DIO samples. In contrast, the use of DIO seems to inhibit the change in recombination resistance at lower forward biases, while in the absence of DIO the $R_b$ values diminish significantly. This may indicate an increase in the leakage currents for No DIO samples, which may experiment changes in defect concentrations.

The Mott–Schottky (MS) analysis was also considered in our study. In the MS formalism, the dark capacitance $C$ at a constant appropriate frequency is measured via IS. Then the
donors/acceptors self-doping defect concentration $N$ and the built-in voltage $V_{bi}$ can be found in the one-side-abrupt $p$-$n$ junction approximation matching the depletion layer capacitance$^{[55–57]}$:

$$C_{dl} = \frac{\varepsilon\varepsilon_0}{w} = \sqrt{\frac{q\varepsilon_0 N}{2(V_{bi} - V)}}$$  \hspace{1cm} (1)$$

where $q$ is the elementary charge, $\varepsilon_0$ the vacuum permittivity, $\varepsilon$ the dielectric constant, and $w$ the width of the space charge region. Note that the use of MS analysis is not straightforward in OSCs due to the most often found $p$-$i$-$n$ doping profile in these devices$^{[58–60]}$. Nevertheless, several studies have been reporting on the evolution of MS plots with optimization$^{[61,62]}$ or degradation$^{[63–65]}$ of OSCs.

In Figure 2e, the fresh/aged DIO cases and the No DIO cell before degradation show the typical MS plot of a $n$-$i$-$p$ junction where the width of the intrinsic region $w_i$ (thickness of the semiconductor composite) is practically that of the complete depletion region $w$. One can easily see that when $w \approx w_i$, in Equation (1) no significant change in $C_{dl}$ can be recorded for reverse and, depending on the nature of the space charge regime, also for low forward bias below $V_{bi}$. The corresponding charge density profile is shown in Figure 2f, where $w_i$ corresponds to the thickness of the active layer and $w$ is larger only by the small regions within the electron and/or hole-transport layers, ETL, and HTL respectively.

Differently, the No DIO aged sample shows in Figure 2e a clear linear trend in $C^{-2}$ which report a defect density of $N = 4.68 \times 10^{16}$ cm$^{-3}$ and $V_{bi} = 650$ mV, resulting in $w = 78$ nm. This suggests that some intrinsic reactivity during the degradation process creates shallow doping defect energy levels in the absorber layer with preferential orientation toward the electrodes and/or it may indicate a diffusion of doping defects from the interfaces. Interestingly, Deledalle et al.$^{[66]}$ has pointed out how the low doping density of the active layer favors charge extraction in OSC (e.g., DIO and No DIO fresh samples), while increasing doping diminishes the charge collection as the depletion zone shrinks. For instance, in the No DIO aged sample of Figure 2e at least a 22% of the $\approx 100$ nm of active layer should not be efficiently contributing to the charge collection. This is also in the DD simulated energy diagram of Figure 3c, where the almost flat band sections within the blend reduce the collection efficiency, approaching the effective depletion layer width to the experimental value.

The arrangement of the doping defects for the No DIO aged sample could be in several profiles to form $p$-$n$ junction charge density profile, and thus produce the characteristic MS plot of Figure 2e. Nevertheless, what is most certain is the shrinking or effective disappearing of the intrinsic region in the blend. One of the possible charge density profiles that could justify the behavior of the No DIO sample with $w >> w_i$ is qualitatively shown in Figure 2g. This resulted the best fitting scenario, as suggested by the DD simulations discussed later (see Figure 1b and 3).

The use of DIO as additive seems to inhibit self-doping processes during the stability test, confirmed with the MS analysis in dark. This conductivity has been earlier suggested to be most likely of acceptor nature$^{[13]}$ and it would be in agreement with the reduced ohmic losses, as observed in the $R_s$ values (Figure 2c). Moreover, it could explain the increase in leakage currents, evidenced in the $R_s$ trends from the IS characterization.
at different illumination intensities (Figure 2d). A possible degradation mechanism is shown in Figure 3a, in agreement with our previous work suggesting strong morphology and mobility changes.[32] Phase separation and/or mixing/demixing processed in the blend evolve in a way that the initially intrinsic homogeneous distribution of donor–acceptor molecules is modified forming donor (acceptor) richer regions toward the electron (hole) selective contact. In addition, the increase in defect density triggers the nonradiative recombination.

The modification of the charge density profile in the No DIO samples before and after aging has also been approached in this work via DD modeling. A noncommercial home-made MATLAB code was developed in our previous works,[67,68] and adapted to the studied devices by considering the surface recombination currents as described by Kirchartz and Nelson[69] with optimal contact selectivity at each electrode. The used simulation parameters are listed in Table S2, S3, Supporting Information; the simulated J–V curves are shown with solid lines in Figure 1b and the simulated energy diagrams corresponding to the short-circuit condition are shown in Figure 3b,c. Initially, the active layer of the fresh device is an homogenous donor:acceptor blend with an intrinsic conductivity (Figure 3b). In this case, the lowest unoccupied molecular orbital of the acceptor material (LUMO, conduction band level) and the highest occupied molecular orbital of the donor material (HOMO, valence band level) follow the linear electrostatic potential distribution.

The aging mechanism was simulated assuming a reorientation of the donor and acceptor composition, forming a donor/acceptor heterojunction (Figure 2g and 3c) within the active layer. This results in significant band-bending for the LUMO and HOMO levels toward the ZnO layer. In addition, a homogenous distribution of traps was included in the active layer bulk, with a 20% reduction of mobilities, which leads to an increment in the bulk recombination and a reduction in the carrier collection due to band bending. Interestingly, similar simulated currents can be obtained by assuming an ohmic hole selective contact and a 50% reduction in the electron mobility after degradation, among other slight changes in the simulation parameters. However, this solution can misread the performance of the device due to the arguably unrealistically large charge densities at the interfaces.

3. Conclusion

In summary, our study indicates a major importance of the charge density profile of the active layer bulk in the degradation
mechanisms of non-fullerene-based OSCs with the structure ITO/ZnO/IT-4F:PM6/MoO3/Al. The use of DIO as additive during the fabrication process improves the performance and stability of the devices, by preventing unbenevolence morphological changes. The latter occurs because DIO hinders the formation of space-oriented shallow trap levels in the bandgap (self-doping), which modify the intrinsic character of the absorber blend. Without DIO, the fresh p-n sample evolves into an aged p-n type cell, lowering the charge collection efficiency. The DIO also hinders the formation of homogeneous deep trap levels in the bandgap, which increases the nonradiative recombination. Without DIO additive, the trap-mediated recombination increases, which affects both the short-circuit current and the open-circuit voltage. These mechanisms may be a more common feature to be approached in other state-of-the-art photovoltaics.

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

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Conflict of Interest
The authors declare no conflict of interest.

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Research data are not shared.

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