Thermally induced degradation of PBDTTT-CT:PCBM based polymer solar cells

Shahidul Alam\textsuperscript{1,2}, Alexey Gavrik\textsuperscript{4}, Rico Meitzner\textsuperscript{1,2}, Stephanie Hoeppener\textsuperscript{2,3}, Vladimir Dyakonov\textsuperscript{4,5}, Andreas Baumann\textsuperscript{4,5}, Ulrich S Schubert\textsuperscript{1,2} and Harald Hoppe\textsuperscript{1,2}

\textsuperscript{1} Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany
\textsuperscript{2} Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldstr. 10, 07743 Jena, Germany
\textsuperscript{3} Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany
\textsuperscript{4} Experimental Physics VI, Julius Maximilian University of Würzburg, Am Hubland, 97074 Würzburg, Germany
\textsuperscript{5} Bavarian Center for Applied Energy Research (ZAE Bayern), Magdalene-Schoch-Str. 3 Würzburg, 97074, Germany

E-mail: shahidul.alam@uni-jena.de and harald.hoppe@uni-jena.de

Received 18 April 2019, revised 16 July 2019
Accepted for publication 15 August 2019
Published 9 September 2019

Abstract
Thermally induced degradation of photovoltaic performance in bulk-heterojunction (BHJ) polymer solar cells as a result of changes either in the active layer morphology or at interfaces during operation at elevated temperature is a common phenomenon. In this work, we have studied the thermal stability of a high performance polymer:fullerene BHJ PSC comprising a conjugated polymer poly\{[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b\textsubscript{0}]dithiophene-2,6-diyl]-alt-[2-(20-ethyl-hexanoyl)-thieno[3,4-b]thiophen-4,6-diyli]\} (PBDTTT-CT) and a fullerene derivative [6,6]-phenyl-C\textsubscript{70}-butyric acid methyl ester photoactive layer within a conventional device architecture of glass/ITO/PEDOT:PSS/active layer/Mg/Al. By varying the temperature exposure conditions, the degradation path has been identified as an interfacial change in the device rather than a bulk effect. Furthermore, charge carrier dynamics studied by open circuit corrected charge carrier extraction has shown that post-annealed devices suffer from charge extraction due to the development of interfacial changes as compared to the non-treated devices in both pristine and with 1,8-Diiodooctane added scenarios.

Keywords: thermal degradation, bulk-heterojunction, polymer solar cells, interlayer formation

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)
1. Introduction

Recent progress in the fabrication of high efficiency organic solar cells based on conjugated polymers [1–5] beyond former predictions is beginning to satisfy the quest for a cheaper, flexible and roll-to-roll process-able [6–9] renewable energy source. Notably, due to the capability for solution processing, tune-ability of molecular energy levels and potential for improved chemical stability, polymer solar cells (PSCs) have gained remarkable interest over the past decade. However, preferential segregation by photoactive materials at the interface with the transport layers or electrodes upon annealing has not been thoroughly studied so far. The general device performance especially in terms of the power conversion efficiency (PCE) for most of PSC is limited by sub-optimal morphologies and increased charge recombination losses. Among the mentioned treatments, a prominent approach is to add a small amount of solvent additive into the host solvent, and 1,8-Diiodooctane (DIO) is a very popular solvent additive that has been used to achieve an optimum morphology with consequently reduced charge recombination losses. Among the mentioned treatments, a prominent approach is to add a small amount of solvent additive into the host solvent, and 1,8-Diiodooctane (DIO) is a very popular solvent additive that has been used to tune the crystallinity and the domain size in polymer-fullerene blends [30, 31].

Moreover, the domains of the polymer become significantly purer when DIO is used as an additive [32], and the balanced domain sizes constituting the bulk heterojunction is part of the optimization process for improving the device performances [33–36]. Besides a high device performance, the thermal and long-term operational stability of polymer-based solar cell remains a vital expansion goal, as it constitutes an essential requirement for application and commercialization. One of the drawbacks of polymer-based solar cells is its sensitivity to photochemical degradation in combination with water or oxygen [37]. Sources for water and oxygen are either side-ingress from the edges of the device sealing, and even within the device water could be released from the hole transport layer (HTL) PEDOT:PSS, which altogether may critically contribute to the degradation of the solar cells [38]. However, reduced performance of the solar cells via morphological degradation cannot be ignored at all [39, 40].

For high performance, the optimal morphology (i.e. blend distribution and scale of phase separation) of the bulk-heterojunction (BJH) is not necessarily thermodynamically stable, as especially the fullerene based molecules incline to diffuse and re-crystallize, which is especially pronounced upon temperature increase [41]. At accelerated thermal stressing, these degradation mechanisms are the main responsible for the morphological destruction leading to reduced network percolation, interlayer formation, and reduced charge transport properties resulting in an overall decrease in solar cell performance. Doumon et al. have reported it that the role of DIO in the degradation process that there is a possibility to significantly altered the nanostraucuture morphology of the active layer under the influence of the illumination [30].

In this study we report the thermally induced degradation of high-performance polymer:fullerene BHJ solar cells comprising a conjugated polymer poly{[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)]-benzo[1,2-b:4,5-b]dithiophene-2,6-diyl]-alt-[2-(20-ethyl-hexanoyl)-thieno[3,4-b′]-thiophen-4,6-diyl]}(PBDTTT-CT) and a fullerene derivative [6,6]-phenyl-C71-butyric acid methyl ester (PCBM) photoactive layer with a conventional device architecture of glass/ITO/ PEDOT:PSS/active layer/Mg/Al. By applying different device annealing scenarios, the degradation path has been recognized as an interfacial transformation in the device. Moreover, charge carrier dynamics by open circuit corrected charge carrier extraction (OTRACE) [42] has shown that post-annealed devices suffer from insufficient charge extraction compared to the as-prepared devices for both processing scenarios without and with the DIO additive.

In order to investigate the thermal degradation, the solar cells were prepared and treated under three different annealing conditions (i) as-cast (no thermal treatment) (ii) pre-annealed (thermally annealed before cathode deposition) (iii) post-annealed (after cathode deposition). For the latter, the overall PCE is reduced by 50%, in contrast to another material system, especially P3HT:PCBM BHJ, which requires thermal annealing to achieve their ultimate performance. In order to determine the thermally induced degradation of the solar cells under continuous illumination, solar cells were tested under two different conditions. Current–voltage (I–V) measurements were recorded automatically on the devices every half an hour in temperature controlled aging chambers in accordance with the ISOS-protocols [43]. OTRACE measurements could further confirm that the elevated temperature applied to the device limits the charge carrier extraction.

2. Experimental

2.1. Materials

As a donor material Poly{[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)]-benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl]-alt-[2-(20-ethyl-hexanoyl)-thieno[3,4-b′]thiophen-4,6-diyl]} (PBDTTT-CT) has been used and purchased from Solarmer Material Inc. And, the acceptor material Phenyl-C_{70}-butyric acid methyl ester (PCBM) was purchased from Solenne BV. Poly[3,4-ethylenedioxythiophene)-poly(styrene sulfonate (PEDOT:PSS) (Clevios PH) was employed as holes transporting layers (HTL) and purchased from Heraeus. As a solvent additive DIO was used and bought from Sigma Aldrich. As a donor material Poly{[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)]-benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl]-alt-[2-(20-ethyl-hexanoyl)-thieno[3,4-b′]thiophen-4,6-diyl]} (PBDTTT-CT) has been used and purchased from Solarmer Material Inc. And, the acceptor material Phenyl-C_{70}-butyric acid methyl ester (PCBM) was purchased from Solenne BV. Poly[3,4-ethylenedioxythiophene)-poly(styrene sulfonate (PEDOT:PSS) (Clevios PH) was employed as holes transporting layers (HTL) and purchased from Heraeus. As a solvent additive DIO was used and bought from Sigma Aldrich. All materials were used as received, and figure 1(a) depicts the chemical structure of the PBDTTT-CT, PCBM, and DIO.

2.2. Device preparation

The fabrication of solar cells started with cleaning the glass/ITO substrates in an ultrasonic bath successively using acetone and isopropanol for 15 min each. PEDOT:PSS was spin-cast
from aqueous solution on top of ITO at 3000 rpm as a HTL. The substrates were then annealed on a hot plate for 15 min at 180 °C in order to remove the residual water content from the films. Afterward, the samples were transferred to a nitrogen-filled glovebox and cooled down to room temperature. The photo-active layers were prepared from PBDTTT-CT:PCBM mixtures in m-xylene with polymer:fullerene blending ratio of 1:1.5 [44]. For the additive containing solutions, four vol.-% DIO was added to the host solution just before the film casting. Pristine solutions were stirred overnight at 45 °C in a N₂ glovebox and then spin-cast on top of the HTL at 1200 rpm for 45 s. Solar cells were finished with the thermal evaporation of 50 nm of magnesium (Mg), and 100 nm of aluminum (Al) deposited sequentially through a shadow mask as an electron collecting electrode resulting in 0.42 cm² active area of the solar cells. All samples were encapsulated under glass using epoxy-based UV-curing glue inside the glove box prior to characterization. Pre- (before metallization) and post- (after metallization) production thermally treated samples were annealed for 10 min at 140 °C on a hot plate inside the glove-box. The schematic of the solar cell structure is presented in figure 1(b).

2.3. Measurement and characterizations

Current–voltage (I–V) measurements of the solar cell devices were performed under a class A AM1.5 solar simulator and were recorded with a Keithley 2400 source-meter-unit (SMU). The intensity of the light source was calibrated by a photo bolometer to confirm AM1.5 condition and the intensity of 100 mW cm⁻². Dark I–V measurements were also recorded with the same measurement setup, in order to recognize the effect of thermal annealing on series resistance, shunt resistance and ideality factor [45].

External quantum efficiency (EQE) was recorded under monochromatic light with an additional halogen bias light, providing an excitation intensity of about one sun. A Si detector was used to calibrate the system; the wavelength was controlled with a monochromator.

Reflection (R) and transmission (T) spectra were recorded with two Avantes AvaSpec-ULS3648-USB2-UA-25 fiber spectrometers over the wavelength range from 300 nm to 1100 nm, and absorption (A) was calculated from the same.

Contactless and non-destructive thin film steady-state photoluminescence (PL) spectra were recorded with an Avantes AvaSpec-ULS-2048 fiber spectrometer over a
wavelength range from 500 nm to 1100 nm and normalized to the absorption value at the laser excitation wavelength of 405 nm. For the investigation of the aging effects, also complete solar cells were investigated concerning their PL; in this case, the measurements were done through the semitransparent glass/ITO/PEDOT:PSS contact.

To gain further insight into the morphology and the effect of DIO in the blends, atomic force microscope (AFM) measurements were performed in tapping mode on an NTegra Aura (NT-MDT) using tapping mode cantilevers from Mikromasch (NSC35) and the images were analyzed by the Gwyddion software.

Electroluminescence (EL) spectra were recorded with an AvaSpec ULS-2048 fiber spectrometer in a home built setup. A Keithley 2601 Source Meter Unit was used for the excitation of the samples with a 50 mA injection current under forward bias.

In order to determine the effect of aging under elevated temperature and illumination, the solar cells underwent aging within two different stability measurement setups in accordance with the ISOS-L1 and ISOS-L2 conditions. While in one chamber the temperature was adjusted to 45 °C, the second one was set to 65 °C. All samples were measured for 70h without interruption. The temperatures were controlled at 45 °C and 65 °C, respectively. In both cases, the illumination light source was a solar simulator with the light intensity of 1000 W m$^{-2}$ with a spectrum close to the AM1.5G-spectrum. In both setups, the $I-V$ characteristics of the cells were computer-controlled measured every 30 min with a Keithley 2400 SMU and a Keithley 7700 multiplexer module.

To determine the charge carrier mobility and the density of the photo-generated charge carriers in the solar cells, OTRACE measurements were applied to the solar cells under operating conditions. Further details of the OTRACE measurement technique can be found elsewhere [42].

3. Results and discussion

The optical and morphological properties of PBDTTT-CT:PCBM system was investigated in order to determine the effect of DIO in the blends. Figure 2(a) shows the absorption spectra of the pristine blend film and the film prepared with 4% DIO added in the blend.

Figure 3. Topography AFM images (5 µm × 5 µm) for the PBDTTT-CT:PCBM films (a) as-cast: wo/DIO, (b) annealed: wo/DIO, (c) as-cast: w/DIO and (d) annealed: w/DIO.
The absorption \( (A = 100 - R - T) \) was calculated from the reflection \( (R) \) and transmission \( (T) \) spectra \( (R \text{ and } T \text{ data are shown in figure S1 (a) ((stacks.iop.org/JPhysD/52/475501/ mmedia))}) \). The transmission spectra in both cases show similar behavior in the whole measured spectral range. However, the transmission of the DIO added film is around 10% higher compared to pristine film.

On the other hand, reflection spectra show slightly different behavior; it can be noticeably seen in the absorption spectrum that by adding a small amount of DIO the signal becomes slightly different. Furthermore, a shoulder appears at 715 nm indicating the improved order in the polymer phase with DIO. In order to further investigate possible changes related to the materials conformation, PL measurements of the PBDTTT-CT:PCBM films were conducted.

PL spectra of the PBDTTT-CT:PCBM films prepared without and with DIO are shown figure 2(b). The PL intensity notably decreased in the presence of DIO which is possibly due to the strong PL quenching of the polymer emission by fullerene as a result of a better-interpenetrated network formed by adding DIO. To gain further insight into possible morphological changes, we conducted AFM on the same films that were used for optical characterizations. Figure 3 shows the surface topography images of the blend films without and with DIO. Surface morphologies in the two blends show noticeably different structures. It is noted that domains appear coarsened in the blend by adding DIO. However, there are no noticeable changes in the pristine blend after thermal annealing on the film. On the other hand, in the DIO added case, upon thermal annealing degree of phase separation and domain sizes tend to increase further.

The light and dark current density–voltage \( (J-V) \) characteristics of the solar cells upon different annealing conditions for the devices, prepared without and with DIO are shown in figure 4. Clear trends of decreasing photocurrents as well as decreasing fill factor upon the annealing of the devices are observed. However, there are only minor changes in the open circuit voltage \( (V_{oc}) \). Fill factor (FF) losses in organic solar cells may depend on several factors, like the formation of unfavorable buffer layers (stratification), decreased domain size, \( \pi–\pi \) stacking direction, and domain purity [45].

The overall efficiency follows the drop in the FF and photocurrent \( (J_{SC}) \) and decreases the PCE to about 50% in the...
case of post-annealing, in both pristine and DIO added cases. A substantial reduction in the parallel resistance ($R_p$) indicates a reduced selectivity for charge extraction/injection or naturally higher recombination due to the dark saturation current in agreement with the dark $J$–$V$ characteristics. In the case of annealing, the DIO processed devices exhibited an overall more significant drop in photocurrent, than those prepared without DIO. The photovoltaic parameters corrected by the EQE data shown in figure 5(a) and the photovoltaic parameters are listed table 1. The PCE is corrected by the absolute short-circuit current obtained by EQE measurements with bias illumination. The short circuit current density ($J_{sc}$) of the solar cells was calculated using the spectral response of the solar cell using the following equation:

$$J_{sc} = q \int \phi(\lambda) \cdot EQE(\lambda) \, d\lambda$$

where $q$ is the electron charge, and $\phi$ is the photon flux of a standard AM1.5G solar spectrum.

Differences in $J_{sc}$ as well as PCE from $I$–$V$ and EQE measurements, can generally be due to a spectral mismatch of the solar simulator spectrum, erroneous light intensity or wrongly assumed cell areas.

Figure S2 in the supplementary material visualizes the photovoltaic parameters as a function of the pre and post-annealed solar cells compared to as-cast samples as reference. In both cases, the trend indicates that upon annealing the devices have reduced PCE. The significant reduction in $V_{oc}$ indicates that the charge extraction becomes less directed.

To further investigate the reason for the decrease in performance of annealed PBDTTT-CT:PCBM solar cells, optical and electrical characteristics were investigated. In order to observe the optical changes of the solar cells treated upon different annealing conditions, reflection and PL measurements were performed on the solar cells. Later on, the relative absorption figure 5(b) was calculated from the reflection spectra shown in figure S1(b). Pre and post-production thermal annealing does not significantly modify the corresponding absorption spectrum of solar cells above the band gap. Absorption curves of the as-cast and annealed samples are almost identical and do not exhibit any energetic shifts neither in the blue nor the red region. However, pristine samples show higher absorption compared to the samples prepared with DIO.

To further inspect possible changes related to the material’s conformation of the PBDTTT-CT:PCBM solar cells processed under these different conditions, PL measurements were conducted and normalized to the absorption at excitation wavelength shown in figure 6(a). The PL peak is quenched in the solar cells prepared with DIO, but not as strong as for the pristine films (figure 2). However, there was again only little impact on the PL signal strength upon different annealing conditions.

To gain deeper insight into the interfacial characteristics, EL spectra were recorded from the solar cells under a forward current of 50 mA. The EL spectra are depicted in figure 6(b). In the case of DIO, a substantial reduction of the EL signal is observed, which could be explained by a reduction in radiative recombination upon adding DIO, might due to changes in molecular orientation at donor-acceptor interfaces. In the case of processing without DIO the EL spectra peak at about 900 nm. Interestingly, the PL-spectra in figure 2 does also exhibit a shoulder at about 900 nm, indicating here the emission
from the CT-state, which got quenched for processing with DIO. The EL intensity of the solar cells strongly reduced upon pre- and further upon post-annealing and slightly red-shifted compared to pristine case. The redshift of the EL spectra indicates a higher order in the polymer or fullerene phases. As the EL intensity becomes sharply reduced, it could also mean that more disordered phases shift to non-radiative recombination.

In order to probe the average domain size as well as the charge percolation in the unaged reference devices and the devices aged 70 h under ISOS-L1 and ISOS-L2 conditions, PL and EL spectroscopy on the solar cell devices were performed, are shown figure 7. It can be noted from PL that upon annealing the blend is slightly more intermixed in case of processing without DIO; while with DIO the intermixing is already initially finer with further refinement under post-annealing. Also, the EL signal for devices processed without DIO is getting reduced by each annealing step, indicating finer intermixing and/or reduced injection efficiency. On the other hand, the EL-signal is more than a magnitude lower for the DIO processed devices, with further reduction observed for annealing steps.

For solar cells aged under ISOS-L1 condition, the PL of post-annealed solar cells processing with and without DIO approached each other, while in general devices processed without DIO exhibited a slightly larger signal and thus a slightly larger scale of phase separation. Interestingly, the EL of devices processed without DIO and those processed with increased upon aging towards the ones without any thermal treatment, indicating that aging has a reversing effect with respect to impacts on EL. However, still, the devices processed from DIO exhibited an order of magnitude lower EL signal. In the case of solar cells aged under ISOS-L2 condition showed a very similar effect than for ISOS-L1 aging and the PL the devices processed without DIO bunched at slightly higher PL signals than those processed with DIO.

The EL bunched for both groups, while those processed from DIO overall increased the EL-signal, getting closer to the ones without DIO. Thus, differences concerning current injection and charge recombination were minimized for thermal treatments. In order to better understand, whether similar effects are acting under accelerated aging with the illumination of one sun and elevated temperatures as for in situ thermally induced degradation of PBDTTT-CT:PCBM based solar cells, $I-V$ measurements under illumination on as-cast, pre- and post-annealed samples were continuously recorded in two different aging setups.

In one ISOS-L1 compatible setup, the temperature was controlled at 45 °C and in the other ISOS-L2 at 65 °C. The samples were measured for 70h, and $I-V$ measurements were recorded every half an hour, shown in figure 8. From these aging experiments, in which only the burn-in phase was investigated, it was found that both, the fill factor and the short circuit photocurrent exhibited the main losses. Interestingly, devices processed with DIO and that underwent pre-annealing exhibited the smallest relative loss. However, while in the case of 45 °C there was virtual no loss occurring, at 65 °C a substantial loss of about 20% in total performance occurred. Thus the pre-annealing step, related to a reorganization of phases or

![Figure 7](https://example.com/figure7.png)

**Figure 7.** PL and EL spectroscopy of devices aged for 70h under ISOS-L1 and ISOS-L2 that experienced different annealing conditions.
mixing ratios within certain domains, seemed to anticipate or hinder those changes typically occurring in as-cast devices.

Figure 8 shows the normalized photovoltaic parameters for the solar cells measured under continuous illumination for 70h. Absolute solar cell parameters from two separate temperature controlled environments are shown in the supplementary material. It can be observed from the solar cell parameters from both cases, that there are very minor changes..
However, significant changes are observed on the FF and $J_{sc}$. Furthermore, faster decays in photovoltaic parameters are observed on the as-cast devices.

Series resistances have tended to increase over time in both ISOS-L1 and ISOS-L2 cases. However, the series resistance of devices aged under ISOS-L2 conditions exhibits a higher slope than those aged under ISOS-L1 (see SI). Both the series and parallel resistances have a good agreement with the EL spectra of the solar cells shown in figure 7.

Losses in fill factor and/or photocurrent could be due to a number of factors. Most dominantly changes in the mobility-lifetime product could be responsible for such losses. Thus, in order to learn more about the charge carrier dynamics, OTRACE transients on as cast, pre-annealed and post-annealed devices were measured, is shown in figure 9. An apparent shift of the extraction maximum is visible in the transient of the thermally treated solar cells. However, the samples prepared with DIO showed only small dependencies upon annealing though.

Consequently, the corresponding charge carrier mobilities determined from the transients show a reduction for post-annealed samples which may indicate an extraction barrier due to the electrode interfaces [44]. We hypothesize that in case of such thermally treated solar cells an interlayer of either PCBM near PEDOT:PSS or PBDTTT-CT near the metal back electrode is formed being more pronounced for the devices without DIO which then leads to an extraction barrier leading to reduced charge carrier mobility values. The additive DIO might preserve the film morphology of the active layer in a more intermixed state; thus upon annealing, fewer chances are given for the built-up of interfacial segregation of a pristine phase.

Having pointed out the changes in charge carrier mobility for annealed samples, we performed OTRACE measurements also on for 70h aged samples, right after the burn-in. Charge carrier mobilities were only determined for the samples prepared with DIO depicted in figure 10 (we note here that for devices without DIO the aged samples suffered from a high leakage current which made it impossible to measure OTRACE). In all cases, the charge carrier mobilities were reduced under both aging conditions. In the case of pre-annealed samples (figure 10(b)), charge carrier mobilities drop by one order of magnitude in both aging cases. However, compared to the non-treated devices aged at 65 °C, the devices are less harmed in terms of the charge carrier extraction. Means, the effect is most severe for the case of
non-treated devices at 65 °C ISOS-L2 aging (blue data point in figures 10(a) and (b)). That indicates the ability to extract charge carriers is comparatively higher for pre-annealed samples. The apparent reduction of the charge carrier mobility for the as-cast aged devices can be explained by an increased capacitance of the devices detected in the OTRACE transient. This again may be explained by an extraction barrier caused by charge accumulation at the interface to interfacial segregation of a pristine phase which leads to an inefficient charge extraction. In the case of the post-annealed devices, it is visible that the solar cell has already degraded a lot. This can be explained by the interlayer formation of preferential segregation of a PBDTTT-CT phase between the active layer and magnesium interface since the effect did not occur when the pre-annealing condition was applied (without magnesium).

4. Conclusion

In summary, the impact of thermally as well as photonically induced degradation of PBDTTT-CT:PCBM-based organic solar cells are presented for processing the active layer without and with Diiodooctane (DIO). Thermal treatments before and after electrode deposition show a substantial reduction on the overall device performance as compared to the untreated devices. By application of additional aging steps in ISOS-L1 (@45 °C) and ISOS-L2 (@65 °C) conformal conditions, bearing the identical light spectrum in both setups, an equilibrating effect for the differently treated devices was found: devices processed without or with DIO yielded in their groups upon aging same photocurrents and also the same EL intensities. However, aging in all cases promoted rising series resistances, which was more expressed for devices exposed to elevated temperatures under ISOS-L2 that did not undergo annealing of any kind before. Furthermore, pre- and post-annealed devices processed with DIO exhibited the strongest perseverance against further performance loss of all solar cells, indicating the morphology to be relatively locked in such cases. Especially, pre-annealing presumably drove DIO out from the film, and as a result, the morphological stability of the device was improved. Thus it may be concluded that the burn-in during 70h of aging was dominated by thermally induced effects affecting blend and interfacial morphology.

Based on the OTRACE characterization, it was revealed that the as-cast or untreated devices suffered most severely upon aging. Thus is may be concluded that while aging seems nullifying differences in the bulk morphology and thus the photocurrent generation within each of the two groups of active layer processing (without or with DIO, see supplementary material for absolute values), it also seems to cause charge extraction barriers at least at one extracting contact.

Acknowledgments

S A and H H are grateful for financial support via DFG in the frame of ‘PhotoGenOrder’. A B works at the ZAE Bayern, which is financed by the Bavarian Ministry of Economic Affairs and Media, Energy, and Technology. V D acknowledges financial support from the Bavarian State Ministry of Education and Culture, Science and Arts within the Collaborative Research Network ‘Solar Technologies go Hybrid’.

ORCID iDs

Shahidul Alam https://orcid.org/0000-0001-8491-2805

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