Flash-Lamp Processing of Charge Extraction Layers for Polymer Solar Cells

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Thermal annealing (TA) is one of the most used processing techniques for the fabrication of polymer solar cells. The method is not only used to dry solution-processed films but also for improving the electrical conductivity and the optical absorption of the materials after coating as films. Its use is questionable in combination with high throughput manufacturing techniques such as roll-to-roll large-scale production since annealing times of several minutes already put high demands on oven lengths. Furthermore, the commonly used flexible substrates are not compatible with high processing temperatures. Therefore, there is a need for more rapid treatment techniques, which do not negatively affect the plastic substrate. Herein, it is successfully demonstrated that flash lamp annealing (FLA) can be a valid alternative to TA. The FLA technique is applied at various pulse durations and thus energy doses to PEDOT:PSS and SnO₂ films used as charge extraction layers in conventional and inverted solar cells architectures. In combination with PM6:Y6 photoactive layer, the obtained device’s performances are comparable or even better than the devices treated with the classical TA on a hotplate. In terms of energy efficiency, the FLA is clearly more efficient than the TA, even at the size of prototypes.

1. Introduction

Conjugated polymer-based organic solar cells are potentially cheaper and have lower embedded energy than inorganic photovoltaic technologies because they are solution-processed and can be fabricated at low temperatures on thin plastic films. The challenge for commercialization is therefore to develop a large-scale and low-cost production. In the case of laboratory scale, printing and coating techniques such as spin-coating, doctor blading, drop casting, screen printing, inkjet printing, and pad printing are often used for small substrates. On the other hand, high-throughput manufacturing techniques such as roll-to-roll (R2R) production are based on slot-die coating, which is suited for fast, cheap, and high-throughput industrial production. Besides coating and printing, additional processing steps such as UV-curing, drying, or annealing may be required. In particular, drying and annealing processes, often done by either hot air or infrared lamps, are limited to processing temperatures of up to 120°C in the case of plastic substrates such as polyethylene terephthalate (PET). Since typical annealing times are in the range of several minutes, an oven must have a length corresponding to the feed rate of the substrate. For example, for a feed rate of only 10 m min⁻¹ and a 5 min annealing time, it would be necessary to use an oven of 50 m in length. Of course, this puts high demands on the scale of the production line, which adds considerably to its costs. Flash lamp annealing (FLA), on the other hand, is ultra-short in time (just a few milliseconds) and can induce temperatures of several hundred degrees Celsius within the targeted layer while keeping the substrate at moderate temperatures due to limited heat transport within the layer stack. In this regard, FLA is a very interesting method for annealing materials during R2R organic photovoltaic processing.

The light is generated by the xenon arc lamps using high voltage to decompose the inert gas within the lamp envelope. Then, the generated pulse energy, delivered in a short time and high-intensity pulse, is sufficient to cause sintering. In addition to the fact that the short processing time (of the order of a few milliseconds) guarantees high efficiency and productivity, the substrate does not...
need to be cooled since only the surface of the substrate or layer is heated, the rest remaining cold.\textsuperscript{[10,11]} The technique also has the advantage of consuming less energy, making it cost-effective.

Galagan et al. used inkjet silver nanoparticles as a front electrode to fabricate ITO-free organic solar cells. The current-collecting grids were subjected to photonic flash sintering, and the conductivity and resistivity of grids produced by photonic sintering at 5 s and those thermally treated in an oven at 130 °C for 6 h were found to be equivalent.\textsuperscript{[12]} Angmo et al. used photonic flash sintering on silver grids printed on PET foil as the front electrode. The resulting flexible module has an active area of 15.4 cm\textsuperscript{2} and consists of 16 solar cells connected in series. The pulse duration was set to 0.5 ms with a maximum electrical pulse energy of 830 J, and 1, 2, or 4 successive flashes were administered to the silver grids. As the number of flashes increased, they noticed an increase in short circuit current and a decrease in sheet resistance.\textsuperscript{[13]} Polino et al. extended the concept of photonic flash sintering of inkjet-printed silver nanoparticles to the back electrode (grid-based or full-surface). They used a variety of sintering parameters with varying pulse intensities and durations. They demonstrated that photonic sintering degraded device performance with grid-based or full-surface silver electrodes compared to thermal sintering. They were able to block high-energy wavelengths and prevent photodegradation of the photovoltaic material by using a polyimide (KAPTON) sheet as a UV filter. The device performance obtained with two 0.5 ms pulses of 0.891 J cm\textsuperscript{2} power was comparable to thermal sintering for both small and large area cells.\textsuperscript{[14]} For the first time, Helgesen et al. successfully implemented a complete roll-to-roll process under ambient conditions, using the photonic sintering technique for thermocleaving of the active layer (a copolymer based on dithienylthiazolo[5,4-d] thiazole (DTZ) and silolodithiophene (SDT) and the fullerene acceptors PCBM). After being exposed to high-intensity flashing, they recorded a performance of up to 0.53%, and they concluded that the flash system promotes the selective heating of a thermocleavable semiconducting layer.\textsuperscript{[15]}

Previous studies have only looked at using FLA on electrodes or active layers. The technique should be possible in all fabrication steps for the complete production of solar modules in a roll-to-roll process. Therefore, we moved to the charge transport layers (CTLs) processing and investigated the feasibility of using a flash lamp to anneal the poly(3,4-ethylenedioxy thiophene):polystyrene sulfonate (PEDOT:PSS) hole transport layer (HTL) and tin (IV) oxide (SnO\textsubscript{2}) electron transport layer (ETL) in poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thieno-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’:4’,6’:5’,7’.c’][3,4’-dithiophene-4,8-dione]):2,2’-(2Z,2’Z)-(12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2’,3’:4’,5’]pyrrolo[3,2-g]thieno[2’,3’:4’,5’]thieno[3,2-b]indole-2,10-diyl) bis(methanylylidene))-bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (PM6:Y6) solar cells with conventional and inverted architectures, respectively. FLA was applied to both charge transport layers with varying pulse durations, and the performance of the generated solar cells was compared to those of devices processed by the traditional thermal annealing approach with a hot plate, as well as to unprocessed materials. An optoelectrical characterization of the films and produced devices, as well as a direct impact of processing parameters on the work function of the CTLs, were explored.

2. Results and Discussion

The chemical structures of the donor and acceptor materials employed in this study are shown schematically in Figure 1a.
Figure 2. Transmittance spectra with various processing conditions of a) PEDOT:PSS and b) SnO₂ on ITO glass.

Figure 3. J–V characteristics of the PM6:Y6 solar cells with various processing conditions applied on PEDOT:PSS and SnO₂. a) conventional devices, b) inverted devices. External quantum efficiency (EQE) spectra of the PM6:Y6 solar cells c) conventional devices, d) inverted devices.
The applied architectures of the fabricated devices are shown in Figure 1b.

The main focus of this paper is not only to demonstrate the variation of the above but rather on the processing of two charge transport layers, commonly applied for the hole (PEDOT:PSS) and electron (SnO2) extraction. While PEDOT:PSS seemingly interacts with light more than SnO2, the optical characteristics of PEDOT:PSS and SnO2 did not differ significantly under different processing conditions, as illustrated in Figure 2. In return, this means that the flash lamp annealing does not disintegrate these charge extraction layers, and deviations from untreated or hot plate annealed samples remain subtle.

Table 1 summarizes the characteristics of the photovoltaic parameters of the best solar cell devices, and the statistical analysis of photovoltaic parameters performed on the 12 best devices is depicted in Figure S1, Supporting Information.

With a short-circuit current density ($J_{sc}$) of 24.23 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 830 mV, and a fill factor (FF) of 66%, the device with the thermally annealed PEDOT:PSS achieved a power conversion efficiency of 13.09% for the conventional architecture. In comparison to the device with non-treated PEDOT:PSS, these values show some improvement. With a one-time flashing, the best PCE of 13.08% was obtained for a flashing time of 2 ms. This result is comparable – if not identical – to the thermally annealed PEDOT:PSS reference device. With double flashing, the processing condition of twice 2 ms yielded a $J_{sc}$ of 24.31 mA cm$^{-2}$, a $V_{oc}$ of 837 mV, a FF of 65%, and a PCE of 13.20%. When compared to the device prepared using the traditional thermal annealing, the hole extraction is marginally improved.

Table 1. Summarized photovoltaic parameters of the conventional and inverted polymer solar cell based on the average of 12 PM6:Y6 devices.

| Architecture | Processing condition | $J_{sc}$ [mA cm$^{-2}$] | $V_{oc}$ [mV] | FF [%] | PCE best [%] | PCE average [%] | $R_s$ [Ω] | $R_p$ [Ω] |
|--------------|---------------------|------------------------|--------------|--------|--------------|-----------------|----------|----------|
| Conventional | Pristine            | 24.02                  | 801          | 61     | 11.88        | 11.57           | 7        | 1862     |
|              | Annealing           | 24.23                  | 830          | 66     | 13.09        | 12.79           | 7        | 2141     |
|              | 0.5 ms              | 24.11                  | 822          | 64     | 12.81        | 12.65           | 7        | 2031     |
|              | 1 ms                | 24.08                  | 824          | 63     | 12.67        | 12.48           | 7        | 2131     |
|              | 1.5 ms              | 24.20                  | 826          | 64     | 12.87        | 12.71           | 7        | 2286     |
|              | 2 ms                | 24.29                  | 832          | 65     | 13.08        | 12.83           | 6        | 2242     |
|              | 2 ms + 0.5 ms       | 24.15                  | 829          | 63     | 12.69        | 12.49           | 7        | 2215     |
|              | 2 ms + 1 ms         | 24.33                  | 827          | 63     | 12.77        | 12.51           | 7        | 2060     |
|              | 2 ms + 1.5 ms       | 24.29                  | 825          | 63     | 12.89        | 12.60           | 7        | 2241     |
|              | 2 ms + 2 ms         | 24.31                  | 837          | 65     | 13.20        | 12.94           | 6        | 2249     |
| Inverted     | Pristine            | 22.94                  | 797          | 56     | 10.82        | 10.38           | 12       | 1122     |
|              | Annealing           | 23.40                  | 832          | 59     | 11.30        | 11.06           | 10       | 1383     |
|              | 0.5 ms              | 23.49                  | 830          | 58     | 11.02        | 10.88           | 13       | 1238     |
|              | 1 ms                | 23.72                  | 828          | 58     | 11.27        | 11.04           | 12       | 1392     |
|              | 1.5 ms              | 23.76                  | 829          | 58     | 11.13        | 10.95           | 13       | 1390     |
|              | 2 ms                | 23.89                  | 835          | 60     | 11.96        | 11.64           | 9        | 1526     |
|              | 2 ms + 0.5 ms       | 23.62                  | 831          | 59     | 11.42        | 11.26           | 11       | 1322     |
|              | 2 ms + 1 ms         | 23.90                  | 830          | 59     | 11.45        | 11.22           | 10       | 1424     |
|              | 2 ms + 1.5 ms       | 23.94                  | 832          | 59     | 11.72        | 11.37           | 10       | 1530     |
|              | 2 ms + 2 ms         | 23.72                  | 839          | 61     | 12.08        | 11.71           | 9        | 1448     |

The exciton dissociation and the charge collection behavior were studied in both conventional and inverted devices and Figure S2, Supporting Information displayed the plots of the photocurrent density ($J_{ph}$) versus the effective voltage ($V_{eff}$ = $V_{oc}$–$V_{fs}$). At high $V_{eff}$, $J_{sat}$ corresponding to the...
saturated $J_{ph}$ is obtained and the $J_{ph}/J_{sat}$ value can correspond to the exciton dissociation probability ($P_{diss}$) or the charge collection probability ($P_{coll}$) when the measurement is done under short-circuit and maximal power point conditions respectively.[16,17] The higher $P_{diss}$ and $P_{coll}$ values indicate that more efficient exciton dissociation and charges collection can occur in the devices with PEDOT:PSS and SnO$_2$ flashed at 2 ms + 2 ms and confirmed the results previously observed from the J–V characteristics.

The work function was measured on the films after thermal annealing and flashing to better understand the results of the device performances, and the results are displayed in Figure 4a. The work function of the PEDOT:PSS is increased by both traditional thermal annealing and flash annealing. However, as compared to thermal annealing, the increase is reduced during flashing, and the work functions of the films flashed at 2 ms and 2 ms + 2 ms are similar to the work function of the thermally annealed film (Figure 4b). This result explains the highest charge selectivity and the performance as measured by the J–V measurement for the conventional architecture devices. In the case of SnO$_2$, flashing lowers the work function marginally. This may contribute to lowering the energy barrier between SnO$_2$ and the acceptor Y6 at the interface (Figure 4c).

Figure 5 displays the electroluminescence spectra measured on solar cell devices with various PEDOT:PSS or SnO$_2$ processing conditions. All devices show a peak at about 930 nm, corresponding to CT-state energy of 1.32 eV. For each device architecture, the devices with PEDOT:PSS or SnO$_2$ flashed once or twice for 2 ms exhibit a better charge injection. This result is in line with the earlier results showing enhanced performance due to better charge extraction and selectivity at the interface between the active layer and the corresponding charge transport layer.

The light intensity dependence of current-voltage characteristics (LID-IV) of the treated CTLs-based devices was investigated to better understand the recombination mechanism. The measured $J_{sc}$ and $V_{oc}$ were respectively plotted against the intensity of the light (I). The light source was a monochromatic LED light with a wavelength of 520 nm. The power-law relationship between $J_{sc}$ and the light intensity can be expressed as[18]:

$$J_{sc} \propto I^\alpha$$

Where $\alpha$ is the slope of linear fitting in the log-log-plot.

![](Figure 4. a) Measured work functions after the various processing conditions. Energy level diagrams of the polymers solar cells, b) conventional structure, c) inverted structure.

![](Figure 5. Electroluminescence spectra of solar cell devices with various processing conditions a) conventional structure, b) inverted structure.)
When the value of $\alpha$ is close to unity, the photocurrent is not limited by the bimolecular recombination or is not space-charge limited.\cite{16} The treatment of both CTLs after spin-coating the films enhanced the value of $\alpha$ and contributed to the suppression of bimolecular recombination in the devices, as shown in Figure 6a,b. For both solar cell architectures, the devices with thermal annealing, 2 ms flashing, and 2 ms + 2 ms flashing have reduced bimolecular recombination compared to the other devices.

On the other hand, the $V_{oc}$ is proportional to the logarithm of light intensity and the linear fit of the plot gives the slope $S$ which is given in units of $kT/q$. Where $k$ is the Boltzmann constant, $T$ is the Kelvin temperature, and $q$ is the elementary charge. Bimolecular recombination dominates in the devices when the slope is equal to $kT/q$.\cite{19} The slope is bigger than $kT/q$ in all of our devices as illustrated in Figure 6c,d. It means that trap-assisted recombination is involved in the devices as well. The trap-assisted recombination can be lowered by thermal annealing or flashing. By flashing twice at 2 ms + 2 ms and once at 2 ms, the charge carriers recombine less. These results support the fact that the devices processed under these conditions outperformed non-treated or thermally annealed devices.

To confirm the effectiveness of the flash annealing on the CTLs, some solar cells were also fabricated with a fullerene-derivate photoactive material system. The conventional architecture devices were fabricated of ITO/PEDOT:PSS/PCDTBT:PC$_{70}$BM(methanol overcast)/Al, while the inverted architecture was built of ITO/SnO$_2$/PCDTBT:PC$_{70}$BM/MoO$_3$/Al. Table 2 summarizes the photovoltaic parameters of the best solar cell devices. With this system, only a single flash for 0.5 ms is necessary to achieve the best device performance for the solar cells with the conventional architecture. For inverted architecture, the device with a double flashing of the SnO$_2$ performed better than the ones with thermal annealing or single flashing, with the best performance coming from the double flashing with 2 ms + 2 ms. This result is comparable to that
of the PM6:Y6 active material. While SnO₂ requires more energy for flashing than PEDOT:PSS, still a single flash of only 0.5 ms was sufficient to reach the same performance level as by thermal annealing.

Since the device performance obtained by flash lamp annealing is comparable and in some cases even better than that by thermal annealing for both charge transport layers, a comparison of the energy requirements for both processing methods became interesting. Table 3 shows the estimated energy investment in the case of PEDOT:PSS, based on details of the calculations provided in the supporting information in Section 3. The energy consumed normalized to the treatment area in case of thermal annealing with a hot plate was a stunning 31.82 MJ m⁻². Only 1.1% of this processing energy (0.36 MJ m⁻²) is required to achieve comparable device performance by flashing of PEDOT:PSS for 2 ms. This energy value is also 22 times lower than the energy needed in the industrial oven for thermal annealing of the same material. While the absolute numbers may vary to a certain extent, it is very encouraging to note that flash lamp annealing can lower the energy requirements for annealing of a single transport layer down to less than 5% of a typical industrial oven and even down to 1% of the energy typically applied through hot-plate annealing.

With the goal to provide more meaningful information than just the lifetime, Roesch et al. established a model to calculate the lifetime energy yield (LEY) of solar cells by integrating where applicable a fitted biexponential function to the efficiency decay of photovoltaic devices, while assuming a constant illumination power of 100 mW cm⁻² or 1000 W m⁻² over the whole device operation. As one of the best results at that time, a LEY of 900 kWh m⁻² was obtained (see supporting information [21,22]. The fitting result is depicted in Figure 7.

This lifetime energy yield is then to be compared to the embedded energy, invested for the production of the photovoltaic device.

Table 2. Summarized photovoltaic parameters of the conventional and inverted polymer solar cell based on the average of 12 PCDTBT:PC₇₀BM devices.

| Architecture | Processing condition | Jsc [mA cm⁻²] | Voc [mV] | FF [%] | PCE best [%] | PCE average [%] | Rₚ [Ω] | Rₛ [Ω] |
|--------------|----------------------|---------------|----------|--------|--------------|----------------|--------|--------|
| Conventional | Pristine             | 9.61          | 846      | 42     | 2.98         | 2.57           | 27     | 700    |
|              | Thermal 0.5 ms       | 10.88         | 900      | 55     | 6.05         | 5.88           | 9      | 1729   |
|              | 1 ms                 | 10.98         | 904      | 57     | 6.39         | 6.04           | 9      | 1735   |
|              | 1.5 ms               | 10.73         | 894      | 53     | 5.57         | 5.01           | 7      | 1235   |
|              | 2 ms                 | 10.61         | 889      | 52     | 5.38         | 4.91           | 8      | 1171   |
|              | 2 ms + 0.5 ms        | 10.53         | 911      | 51     | 5.26         | 4.86           | 8      | 1315   |
|              | 2 ms + 1 ms          | 10.41         | 871      | 49     | 4.57         | 4.14           | 8      | 1216   |
|              | 2 ms + 1.5 ms        | 10.37         | 930      | 51     | 4.87         | 4.51           | 8      | 1395   |
|              | 2 ms + 2 ms          | 10.7          | 874      | 49     | 4.58         | 4.36           | 9      | 1095   |
| Inverted    | Pristine             | 10.04         | 876      | 47     | 4.14         | 3.91           | 31     | 1063   |
|              | Thermal 0.5 ms       | 10.30         | 895      | 50     | 4.62         | 4.48           | 23     | 1104   |
|              | 1 ms                 | 10.29         | 889      | 53     | 4.68         | 4.55           | 15     | 1237   |
|              | 1.5 ms               | 10.04         | 875      | 51     | 4.51         | 4.33           | 14     | 1198   |
|              | 2 ms                 | 9.92          | 891      | 53     | 4.65         | 4.38           | 15     | 1253   |
|              | 2 ms + 0.5 ms        | 10.09         | 899      | 51     | 4.63         | 4.59           | 18     | 1170   |
|              | 2 ms + 1 ms          | 10.29         | 876      | 53     | 4.84         | 4.75           | 11     | 998    |
|              | 2 ms + 1.5 ms        | 10.20         | 880      | 51     | 4.74         | 4.62           | 15     | 1026   |
|              | 2 ms + 2 ms          | 10.36         | 882      | 54     | 5.02         | 4.73           | 16     | 1063   |

Table 3. Estimation for the energy investment of different processing methods of PEDOT:PSS.
device. Doing so for that exemplary device, the energy consumed by flash sintering of one charge extraction layer truly is marginal, constituting only about a tenth of a promille of the LEY. On the other hand, the lab-scale technology of using hot plates for thermal annealing of a single layer requires already about 1% of the energy return during the lifetime.

3. Conclusion

In summary, we investigated the feasibility of employing flash lamp annealing to treat charge transport layers (PEDOT:PSS and SnO2) for PM6:Y6 solar cell devices, both in conventional and inverted architecture. Devices fabricated with various flash durations were compared to those fabricated with the traditional thermal annealing approach and untreated layers. For both charge transport layers, the device performance by flash lamp annealing was better for a single flash of 2 ms and also better for two flashes of 2 ms than the corresponding device processed via thermal annealing. For similarly processed PCDTBT:PC70BM solar cells devices, a single flash of only 0.5 ms was sufficient, to reach and overcome the performance of devices processed by classical thermal annealing. The estimated energy required for both approaches revealed that flashing requires only a minor fraction of the energy typically provided by hot plates or industrial ovens. In terms of photovoltaic performance, time requirements, and last but not least, energy investments, flash lamp annealing of charge transport layers outperforms thermal annealing and is a promising alternative for lowering polymer solar cell production costs as well as energy payback times.

4. Experimental Section

Materials: Prestructured ITO glass of size of 1 inch by 1 inch was purchased von Xinyan Corp. (Shuzhu, China). PEDOT:PSS (Clevios P VP Al4083) was purchased from Heraeus and employed as a hole transporting layer (HTL). Tin (IV) oxide, 15 wt.% in aqueous colloidal dispersion (purchased from Alfa Aesar) and poly[(9,9-bis(3′-((N,N-dimethyl-N-ethylammonium)-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] dibromide (PFN-Br) (purchased from Luminescence Technology Corp.) were employed as electron transporting layers (ETLs). The donor materials PBDB-T-2F or PM6 and the poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2,1,3-benzothiadiazole)] (PCDPTB) were purchased from Brilliant Matters and 1-Material respectively. The nonfullerene acceptor (NFA) molecule BTP-4F or Y6 was purchased from Brilliant Matters and the fullerene acceptor Phenyl-C60-butyric acid methyl ester (PC61BM) was originally purchased from Solenne BV.

Device Preparation: The conventional solar cells were fabricated using an ITO/PEDOT:PSS/PM6:Y6/PFN-Br/Ag layer stack architecture. The patterned indium tin oxide (ITO) substrates (with a sheet resistance of 10 Ω sq⁻¹) were first cleaned by ultrasonication in toluene and isopropanol successively. They were then dried with a nitrogen-blowing gun before and treated with argon-plasma for 10 minutes to remove the organic contaminants. The PEDOT:PSS film was processed under ambient conditions by spin-coating on the cleaned ITO-glass substrates at 3000 rpm for 35 s after filtering of the PEDOT:PSS solution through a 0.45 µm PES filter. For the reference devices, pristine (without treatment) and annealed (at 178 °C for 15 min in the air) PEDOT:PSS films were used. Alternatively, PEDOT:PSS films were annealed by flashing using the SINTERON 2000 pulsed light sintering system from Xenon Corporation. The system consists of a 19" electronics rack with a power supply, a controller, a pulse forming network, and a lamp housing model LH-910 with a 107 mm diameter spiral xenon flash lamp. The pulse energy ranges from 450 to 2000 Joules over a sintering area of 3”×3”. A blower is provided to cool the lamp. Different pulse durations were used, and the varying parameters are given in Table 4. Thereafter, all the films were immediately placed into a nitrogen-filled glovebox, and the active layer deposition took place. The PM6:Y6 blend (ratio 1:1.2) was dissolved in chloroform solution (7.27 mg mL⁻¹ of PM6 and 8.73 mg mL⁻¹ of Y6 with 0.5 vol.% of 1-Chloronaphtalene as additive) and spin-coated at 2000 rpm for 1 min. The photoactive layers were further treated with thermal annealing at 110°C for 10 minutes. The PCDTBT:PC70BM mixture with a blend ratio of 1:2 (i.e., 5 mg of PCDTBT and 10 mg of PC70BM) was dissolved in a mixture of chlorobenzene and chloroform (1:1) and stored inside the glove-box at 50°C on a hotplate by a continuously stirring at 750 rpm for two weeks. The solution was coated at 1200 rpm and the resulting photoactive layer was annealed for 10 min at 80 °C. PFN-Br, dissolved overnight in methanol solution (0.5 mg mL⁻¹) by continuous stirring, was spin-coated on the active layer at 3000 rpm for 40 s. Finally, 150 nm of silver (Ag) were evaporated as a top electrode.

Table 4. Overview of the varying processing conditions of the PEDOT:PSS and SnO2.

| Charge transport layer | Processing condition | Treatment 1 | Treatment 2 | Electrical energy per pulse (J) |
|------------------------|---------------------|-------------|-------------|-------------------------------|
| PEDOT:PSS & SnO2       | 1                   | As cast     | None        | None                          |
|                        | 2                   | Thermal     | None        | None                          |
|                        | 3                   | Flash 0.5 ms| None        | 830                           |
|                        | 4                   | Flash 1.0 ms| None        | 1490                          |
|                        | 5                   | Flash 1.5 ms| None        | 1762                          |
|                        | 6                   | Flash 2.0 ms| None        | 2070                          |
|                        | 7                   | Flash 2.0 ms| Flash 0.5 ms| 2070 + 830                   |
|                        | 8                   | Flash 2.0 ms| Flash 1.0 ms| 2070 + 1490                  |
|                        | 9                   | Flash 2.0 ms| Flash 1.5 ms| 2070 + 1762                  |
|                        | 10                  | Flash 2.0 ms| Flash 2.0 ms| 2070 + 2070                   |

Figure 7. Efficiency decay curve of a record PCDTBT:PC70BM based polymer solar cell. The solar cell was held at near AM 1.5 illumination conditions at about 45 °C. Red boxes depict the device performance determined within the aging setup, while blue crosses depict performance obtained from measurements under the solar simulator. The green curve shows the biexponential fit to the aging data, from which a lifetime of 30 000 h and a LEY of 900 kWh m⁻² could be calculated. [30]
by physical vapor deposition at less than 10\textsuperscript{-6} mbar through a shadow mask, resulting in a photovoltaic device with an active area of 0.42 cm\textsuperscript{2}.

The inverted solar cells were fabricated using an ITO/SnO\textsubscript{2}/PM6:Y6/MoO\textsubscript{3}/Ag layer stack architecture. A SnO\textsubscript{2} solution diluted to 10 wt.% in distilled water from the starting solution was spin-coated on top of the cleaned and Ar-plasma treated ITO-glass substrates at 3000 rpm for 30 s. The films were then either left untreated or annealed at 150 °C for 30 min in the air or annealed by flash lamp annealing. The samples were then immediately transferred to a nitrogen-filled glovebox where the active layer deposition took place. Then, the substrates were placed in an evaporation chamber and 10 nm SnO\textsubscript{2} films coated onto ITO. \cite{21} The absorptance was calculated from these two spectra. The work function was determined on the same films in the air by using a single-point Kelvin probe system from Anfatec Instruments AG. A highly oriented pyrolytic graphite (HOPG) with a known work function of 4.46 ± 0.04 eV was used for the calibration of the Kelvin probe system. The current density-voltage (J–V) characteristics of the solar cell devices were performed under a class A AM1.5 solar simulator (intensity 100 mW cm\textsuperscript{-2}) and in dark conditions. All the measurements were recorded with a Keithley 2400 source measurement unit. \cite{23} The external quantum efficiency (EQE) of the solar cell was recorded using a Bentham PVE 300 photovoltaic system by illuminating the cell with a monochromatic light beam, swept in the wavelength range of 300–1100 nm. Ge and Si detectors were used to calibrate the EQE system. Electroluminescence spectroscopy (ELS) was recorded on solar cell devices by applying a constant current of 50 mA from a Keithley 2400 SMU. This corresponds to an injected current density of about 120 mA cm\textsuperscript{-2}.

The emitted light was transmitted via fiber optics to Si (Avantes AvaSpec NIR256-1) and cooled InGaAs (Avantes AvaSpec ULS-2048) and measured with an integration time of 5 s. Light intensity-dependent current-voltage (LID-IV) measurements were carried out by measuring the J–V characteristics of solar cells upon variation of the light intensity from a monochromatic high-power LED (wavelength: 520 nm) by using different neutral optical filters. \cite{23}

Device Characterization: Transmittance and reflectance spectra were recorded with two Avantes AvaSpec-ULS3648-USB2-UA-25 fiber spectrometers with an integration time of 13 milliseconds on PEDOT:PSS and SnO\textsubscript{2} films coated onto ITO. \cite{21} The absorbance was calculated from these two spectra. The work function was determined on the same films in the air by using a single-point Kelvin probe system from Anfatec Instruments AG. A highly oriented pyrolytic graphite (HOPG) with a known work function of 4.46 ± 0.04 eV was used for the calibration of the Kelvin probe system. The current density-voltage (J–V) characteristics of the solar cell devices were performed under a class A AM1.5 solar simulator (intensity 100 mW cm\textsuperscript{-2}) and in dark conditions. All the measurements were recorded with a Keithley 2400 source measurement unit. \cite{23} The external quantum efficiency (EQE) of the solar cell was recorded using a Bentham PVE 300 photovoltaic system by illuminating the cell with a monochromatic light beam, swept in the wavelength range of 300–1100 nm. Ge and Si detectors were used to calibrate the EQE system. Electroluminescence spectroscopy (ELS) was recorded on solar cell devices by applying a constant current of 50 mA from a Keithley 2400 SMU. This corresponds to an injected current density of about 120 mA cm\textsuperscript{-2}.

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.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
charge transport layers (CTLs), flash lamp annealing (FLA), organic photovoltaics (OPV), polymer solar cells (PSC)

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[1] S. Günes, H. Neugebauer, N. S. Sariciftci, Chem. Rev. 2007, 107, 1324.
[2] K. M. Coakley, M. D. McGehee, Chem. Mater. 2004, 16, 4533.
[3] H. Spanggaard, F. C. Krebs, Sol. Energy Mater. Sol. Cells 2004, 83, 125.
[4] C. J. Brabec, N. S. Sariciftci, C. J. Hummelen, Adv. Funct. Mater. 2001, 11, 15.
[5] H. Hoppe, N. S. Sariciftci, Mater. Res. 2004, 19, 1924.
[6] M. Jørgensen, K. Norrman, F. C. Krebs, Sol. Energy Mater. Sol. Cells 2008, 92, 686.
[7] F. C. Krebs, M. Jørgensen, K. Norrman, O. Hagemann, J. Alstrup, T. D. Nielsen, J. Fyenbo, K. Larsen, J. A. Kristensen, Sol. Energy Mater. Sol. Cells 2009, 93, 422.
[8] F. C. Krebs, Sol. Energy Mater. Sol. Cells 2009, 93, 1636.
[9] Y. Galagan, I. G. De Vries, A. P. Langen, R. Andriessen, W. J. H. Verhees, S. C. Veenstra, J. M. Kroon, Chem. Eng. Process. 2011, 50, 454.
[10] W. Skorupa, T. Schumann, L. Rebohle, Surf. Coat. Technol. 2017, 314, 169.
[11] L. Rebohle, S. Prucnal, W. A. Skorupa, Semicond. Sci. Technol. 2016, 31, 103001.
[12] Y. Galagan, E. W. C. Coenen, R. Abbé, T. J. Van Lammeren, S. Sabik, M. Barink, E. R. Meinders, R. Andriessen, P. W. M. Blom, Org. Electron. 2013, 14, 38.
[13] D. Angmo, T. T. Larsen-Olsen, M. Jørgensen, R. R. Søndergaard, F. C. Krebs, Adv. Energy Mater. 2013, 3, 172.
[14] G. Polino, S. Shanmugam, C. J. P. Bex, R. Abbé, F. Brunetti, A. Di Carlo, R. Andriessen, Y. Galagan, ACS Appl. Mater. Interfaces 2016, 8, 2325.
[15] M. Helgesen, J. E. Carlé, B. Andreasen, M. Hösel, K. Norrman, R. Søndergaard, F. C. Krebs, Polym. Chem. 2012, 3, 2649.
[16] S. Guang, J. Yu, H. Wang, X. Liu, S. Qu, R. Zhu, W. Tang, J. Energy Chem. 2021, 56, 496.
[17] S. Zhang, X. Ma, C. Xu, W. Xu, S. Y. Jeong, H. Y. Woo, Z. Zhou, X. Zhang, F. Zhang, Macromol. Rapid Commun. 2022, 43, 2200345.
[18] L. J. A. Koster, V. D. Mihailetchi, H. Xie, P. W. M. Blom, Appl. Phys. Lett. 2005, 87, 203502.
[19] L. J. A. Koster, V. D. Mihailetchi, R. Ramaker, P. W. M. Blom, Appl. Phys. Lett. 2005, 86, 123509.
[20] N. Espinosa, R. García-Valverde, A. Urbina, F. C. Krebs, Sol. Energy Mater. Sol. Cells 2011, 95, 1293.
[21] R. Roesch, K.-R. Eberhardt, S. Engmann, G. Gobsch, H. Hoppe, Sol. Energy Mater. Sol. Cells 2013, 117, 59.
[22] R. Roesch, T. Faber, E. van Hauff, T. M. Brown, M. Lira-Cantu, H. Hoppe, Adv. Energy Mater. 2015, 5, 1501407.
[23] A. Sokeng Djournessi, S. Alam, J. P. Madalaimuthu, A. Anand, J. Slowik, T. Pflug, R. Meitzner, R. Roesch, E. Gnecco, A. Horn, U. S. Schubert, H. Hoppe, Energy Technol. 2021, 9, 2100474.