



**HAL**  
open science

# Interplay of Interfacial Layers and Blend Composition To Reduce Thermal Degradation of Polymer Solar Cells at High Temperature

Sadok Ben Dkhil, Martin Pfannmöller, Rasmus Schröder, Riva Alkarsifi,  
Meriem Gaceur, Wolfgang Köntges, Hamed Heidari, Sara Bals, Olivier  
Margeat, Jörg Ackermann, et al.

## ► To cite this version:

Sadok Ben Dkhil, Martin Pfannmöller, Rasmus Schröder, Riva Alkarsifi, Meriem Gaceur, et al.. Interplay of Interfacial Layers and Blend Composition To Reduce Thermal Degradation of Polymer Solar Cells at High Temperature. ACS Applied Materials & Interfaces, 2018, 10 (4), pp.3874 - 3884. 10.1021/acsami.7b17021 . hal-01775245

**HAL Id: hal-01775245**

**<https://amu.hal.science/hal-01775245>**

Submitted on 1 Feb 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**This item is the archived peer-reviewed author-version of:**

Interplay of interfacial layers and blend composition to reduce thermal degradation of polymer solar cells at high temperature

**Reference:**

Ben Dkhil Sadok, Pfannmöller Martin, Schroeder Rasmus R., Alkarsifi Riva, Gaceur Meriem, Koentges Wolfgang, Heidari Harried, Bals Sara, Margeat Olivier, Ackermann Jorg, ....- Interplay of interfacial layers and blend composition to reduce thermal degradation of polymer solar cells at high temperature

ACS applied materials and interfaces - ISSN 1944-8244 - 10:4(2018), p. 3874-3884

Full text (Publisher's DOI): <https://doi.org/10.1021/ACSAMI.7B17021>

To cite this reference: <https://hdl.handle.net/10067/1493090151162165141>

## Article

**Interplay of interfacial layers and blend composition to reduce thermal degradation of polymer solar cells at high temperature**

Sadok Ben Dkhil, Martin Pfannmöller, Rasmus R. Schroeder, Riva Alkarsifi, Meriem Gaceur, Wolfgang Köntges, Hamed Heidari, Sara Bals, Olivier Margeat, Jörg Ackermann, and Christine Videlot-Ackermann

*ACS Appl. Mater. Interfaces*, **Just Accepted Manuscript** • DOI: 10.1021/acsami.7b17021 • Publication Date (Web): 12 Jan 2018

Downloaded from <http://pubs.acs.org> on January 12, 2018

**Just Accepted**

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

# Interplay of interfacial layers and blend composition to reduce thermal degradation of polymer solar cells at high temperature

*Sadok Ben Dkhil,<sup>1</sup> Martin Pfannmöller,<sup>2,#</sup> Rasmus R. Schröder,<sup>3</sup> Riva Alkarsifi,<sup>1</sup> Meriem Gaceur,<sup>1</sup> Wolfgang Köntges,<sup>3</sup> Hamed Heidari,<sup>2</sup> Sara Bals,<sup>2</sup> Olivier Margeat,<sup>1</sup> Jörg Ackermann,<sup>1,\*</sup> Christine Vidélot-Ackermann.<sup>1,\*</sup>*

<sup>1</sup> Aix Marseille Univ., UMR CNRS 7325, CINaM, Marseille, France.

<sup>2</sup> University of Antwerp, Electron Microscopy for Materials Research (EMAT), Groenenborgerlaan 171, 2020 Antwerp, Belgium.

<sup>3</sup> Centre for Advanced Materials, Heidelberg University, 69120 Heidelberg, Germany.

\* Corresponding authors: [ackermann@cinam.univ-mrs.fr](mailto:ackermann@cinam.univ-mrs.fr); [videlot@cinam.univ-mrs.fr](mailto:videlot@cinam.univ-mrs.fr)

# Present address: Centre for Advanced Materials, Heidelberg University, 69120 Heidelberg, Germany

**Abstract**

The thermal stability of printed polymer solar cells at elevated temperatures needs to be improved to achieve high-throughput fabrication including annealing steps as well as long-term stability. During device processing, thermal annealing impact both the organic photoactive layer and the two interfacial layers making detailed studies of degradation mechanism delicate. A recently identified thermally stable PTB7:PC<sub>70</sub>BM blend as photoactive layer in combination with PEDOT:PSS as hole extraction layer is used here to focus on the impact of electron extraction layer (EEL) on the thermal stability of solar cells. Solar cells processed with densely packed ZnO nanoparticle layers show still 92% of the initial efficiency after constant annealing during one day at 140°C, while partially covering ZnO layers as well as an evaporated calcium layer lead to performance losses up to 30%. This demonstrates that the nature and morphology of EELs highly influence the thermal stability of the device. We extend our study to thermally unstable PTB7:PC<sub>60</sub>BM blends to highlight the impact of ZnO on the device degradation during annealing. Importantly, only 12% loss in photocurrent density is observed after annealing at 140°C during one day when using closely packed ZnO. This is in stark contrast to literature and addressed here to the use of a stable double-sided confinement during thermal annealing. The underlying mechanism of the inhibition of photocurrent losses is revealed by electron microscopic imaging and spatially resolved spectroscopy. We found that the double-sided confinement suppresses extensive fullerene diffusion during annealing step, but with still an increase in size and distance of the enriched donor and acceptor domains inside the photoactive layer by an average factor of five. The later result in combination with comparably small photocurrent density losses indicates the existence of efficient transport of minority charge carriers inside donor and acceptor enriched phases in PTB7:PC<sub>60</sub>BM blends.

1  
2  
3 **Keywords:** Polymer solar cells, interfacial layer, ZnO nanoparticles, nanoscale morphology,  
4 thermal stability.  
5  
6  
7

## 8 9 **1. Introduction**

10  
11  
12 In the competitive field of renewable energy sources, polymer solar cells (PSCs) are  
13 nowadays promising candidates for niche markets. Thanks to extensive research in novel  
14 organic semiconductors and device structures, PSCs have reached power conversion  
15 efficiencies (PCEs) over 13% at lab scale level and 7% at module level.<sup>1-8</sup> However,  
16 efficiency and stability of PSCs using high-throughput roll-to-roll (R2R) processing are still  
17 low hindering limiting their introduction into the market. PSCs are multi-layer devices that  
18 require successive annealing steps up to 140°C during processing of each layer.<sup>9</sup> Therefore,  
19 thermal stability of each material used in PSC processing remains one of the most challenging  
20 factors, especially as a temperature increase occurs not only during processing but also  
21 inevitably during operation under illumination. Thermal stability is also a key challenge for  
22 other solution processed photovoltaic technologies such as efficiency perovskite solar cells  
23 involving constant efforts to enhance the device stability and durability.<sup>10-13</sup> Since PSCs are  
24 formed of stacked layers, performance losses can be related to degradation of electronic  
25 properties in each layer constituting the device, i.e. electrodes, interfacial layers (ILs) and  
26 photoactive layer.<sup>9,14-17</sup> The photoactive layer of high efficiency organic devices consists of a  
27 bulk heterojunction (BHJ) that is a bicontinuous interpenetrating network of nano-sized  
28 donor- and acceptor-enriched phases. By the fact that the BHJ is generally a meta-stable state,  
29 thermal stress will introduce phase separation leading to micrometer-sized domains of  
30 acceptor molecules inside the polymer blend and thus a loss in photocurrent. In the case of  
31 fullerene acceptors, their diffusion through the polymer donor phase leads to the formation of  
32 large fullerene crystals via Ostwald ripening, which is considered to be the main factor for  
33 thermal instability.<sup>9,14,15,18</sup>  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 Over the last decade thermal stability of PSCs related to the photoactive layer has been studied  
4 intensively and was improved by a large palette of approaches.<sup>19-38</sup> However, the impact of  
5 the interfacial buffer layers—which are highly relevant for the performance of the solar  
6 cells—on the thermal stability of the solar cells has only been considered marginally.<sup>39,40</sup> For  
7 example, it is known that metal ions can diffuse into the organic layer creating substantial  
8 leakage current.<sup>41,42</sup> Furthermore, chemical reactions at the metal/organic interface can alter  
9 the contact properties, forming interfacial dipole barriers and defect states that pin the Fermi  
10 level.<sup>43,44</sup> It is important to mention that investigation of the thermal degradation of PSCs  
11 related to the ILs is very delicate because thermal annealing can also degrade the BHJ  
12 simultaneously. Due to this strong interplay between photoactive layer and ILs, the stability of  
13 the photoactive layer is typically studied by thermal annealing of the polymer blend followed  
14 by successive deposition of the IL and the electrode to complete the device. By consequence,  
15 the photoactive layer is therefore often annealed in the condition of single-sided confinement.  
16 Recently, we have demonstrated that high efficiency solar cells with unprecedented thermal  
17 stability at 140°C over several days can be obtained when using a double-sided or sandwich-  
18 like confinement during thermal annealing, defined as a post-annealing in the following.<sup>38,45</sup>  
19 We used a regular device structure composed of solution processed ILs with hole extraction  
20 layers (HELs) based on poly(3,4-ethylenedioxythiophene) polystyrene sulfonate polymer  
21 (PEDOT:PSS) and electron extraction layers (EELs) made of ZnO nanoparticles; the devices  
22 were completed by evaporated Al cathodes.<sup>38</sup> The photoactive layer consisted of a low band  
23 gap polymer poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-  
24 fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) blended with [6,6]-  
25 Phenyl-C71-butyric acid methyl ester (PC<sub>70</sub>BM). We could show that fullerene diffusion was  
26 suppressed in PTB7:PC<sub>70</sub>BM blends while annealing at 140°C. The thermal stability of the  
27 blend was attributed to highly stable mixed phases, forming PTB7:PC<sub>70</sub>BM aggregates and  
28 inhibiting fullerene diffusion between polymer- and fullerene-enriched phases. It is important  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 to highlight that those results also suggest that the used ILs, namely PEDOT:PSS and ZnO,  
4  
5 were thermally stable.

6  
7 Here, we study more in details the degradation mechanisms in PSCs under thermal stress  
8  
9 related to cathode buffer material and morphology in combination with PTB7:fullerene blends.  
10  
11 Amongst the large choice of EEL materials including organic and inorganic materials,<sup>39,40,46</sup>  
12  
13 we selected ZnO and calcium (Ca) as both materials were used in former stability studies of  
14  
15 regular device structures using PTB7 donor polymers.<sup>32,38</sup> Furthermore both materials allow  
16  
17 EEL processing with varying layer thicknesses and thus morphologies without alternating  
18  
19 device performance strongly. By using first PTB7:PC<sub>70</sub>BM blend as thermally stable active  
20  
21 layer we demonstrate that only densely packed ZnO layers generate high thermal stability,  
22  
23 while partially covered or porous ZnO layers leads to strong degradation. In contrast that Ca  
24  
25 based EELs lead to strong performance losses up to 40% after a constant post-annealing at  
26  
27 140°C independently of layer morphology. These results show the importance of both  
28  
29 material selection and layer morphology for EELs to gain thermal stability. Furthermore the  
30  
31 thermally stable ILs were used to perform a detailed investigation of the thermal degradation  
32  
33 of solar cells using a known thermally unstable polymer blend, namely PTB7 mixed with the  
34  
35 smaller fullerene derivative PC<sub>60</sub>BM,<sup>30,32</sup> during annealing in a double-sided confinement. We  
36  
37 show that the photocurrent density in PTB7:PC<sub>60</sub>BM solar cells using the double-sided  
38  
39 confinement is only reduced by 12%. This leads to an overall efficiency of 3.2% after a  
40  
41 constant post-annealing at 140°C over 1 day, which is in stark contrast to literature where  
42  
43 much stronger degradation is observed when using a single-sided confinement.<sup>30,32</sup> The  
44  
45 underlying mechanism of the improved thermal stability is addressed to reduced fullerene  
46  
47 diffusion on the blend surface using the double-sided confinement, which inhibits the  
48  
49 formation of large fullerene crystals on the blend surface. Importantly analytical electron  
50  
51 microscopy (electron spectroscopic imaging, ESI) is used for the first time to visualize  
52  
53 morphological changes in the PTB7:PC<sub>60</sub>BM blend under thermal annealing. We could show  
54  
55  
56  
57  
58  
59  
60



1  
2  
3 that although photocurrent density only drops by 12% there is an increase in size and distance  
4  
5 of the enriched donor and acceptor domains by an average factor of 5. The observed  
6  
7 photocurrent losses due to the morphological changes are discussed in the context of exciton  
8  
9 diffusion and ambipolar transport inside the mixed and the donor-enriched phases, but also in  
10  
11 the acceptor-enriched phase.  
12  
13  
14

## 15 16 **2. Experimental Section**

17  
18 **Materials.** ZnO nanocrystals and ZnO-based solutions were prepared as published  
19  
20 elsewhere.<sup>47,48</sup> Cluster free ZnO nanocrystal solutions in isopropanol at 7.5 mg/mL were  
21  
22 prepared by mixing 0.2 vol.% of ethanolamine (EA). PTB7 was purchased from 1-Materials,  
23  
24 PC<sub>60</sub>BM and PC<sub>70</sub>BM with a purity of 99 % were purchased from Solemn and Nano-C,  
25  
26 respectively. The solvent additive 1,8-diiodoctane (DIO) was purchased from Sigma-Aldrich.  
27

28  
29 **Solar cell fabrication and characterization.** Solar cells using PTB7 as donor in regular  
30  
31 device structure were processed as detailed in former work.<sup>38</sup> ITO substrates (purchased from  
32  
33 Lumtec, 15 Ohm.sq<sup>-1</sup>) were thoroughly cleaned by sonication in acetone and ethanol followed  
34  
35 by rinsing with water and sonication in isopropanol. A final ultraviolet-ozone treatment was  
36  
37 applied for 15 min. A thin layer of poly(3,4-PEDOT:PSS) (CLEVIOS<sup>TM</sup> AI 4083) was spin-  
38  
39 coated on the cleaned ITO pre-coated glass substrate at the speed of 4000 rpm for 60 s  
40  
41 followed by an annealing step on a hot-plate at 140°C for 15 min leading to a layer thickness  
42  
43 of 40 nm. The substrates were then transferred to a nitrogen-filled glove box. PTB7  
44  
45 (concentration of 10 mg.mL<sup>-1</sup>) was mixed with PC<sub>70</sub>BM or PC<sub>60</sub>BM (ratio of 1:1.5) in solvent  
46  
47 mixture of chlorobenzene and 1,8-diiodoctane (DIO) at 97:3% volume ratio. The  
48  
49 PTB7:PC<sub>70</sub>BM and PTB7:PC<sub>60</sub>BM blends with a nominal thickness of 90 nm were prepared  
50  
51 by spin-coating the corresponding solution at 1800 rpm for 2 min. After dried in vacuum  
52  
53 overnight, different interfacial layers (ILs) were processed on top of the photoactive layer. ILs  
54  
55 based on ZnO nanoparticles were processed by spin-coating ZnO inks, with a concentration of  
56  
57  
58  
59  
60

1  
2  
3 7.5 mg/mL and 0.2 vol.% of ethanolamine, on top of the active layers at 1500 rpm for 60 s  
4 followed by annealing for 5 min at 80°C; all processes were done inside the glovebox. ILs of  
5 calcium (Ca) were processed by thermally evaporation at  $1 \times 10^{-7}$  Torr to a thickness of either  
6  
7 10 nm or 30 nm. Aluminum (Al) metal electrodes were thermally evaporated (MBRAUN  
8 evaporator) at  $2 \times 10^{-6}$  Torr to a thickness of 100 nm using a shadow mask that define the  
9 device area of the solar cells to  $0.27 \text{ cm}^2$ .  
10  
11

12  
13  
14  
15  
16 The current density–voltage (J-V) characteristics of the solar cells were measured inside the  
17 glove box using a Keithley 238 Source Measure Unit and a Newport class AAA 1.5 Global  
18 solar simulator (Oriel Sol3ATM model n° 94043A) with an irradiation intensity of 100  
19  $\text{mW}/\text{cm}^2$ . The light intensity was determined with a Si reference cell (Newport Company,  
20 Oriel n°94043A) calibrated by National Renewable Energy Laboratory (NREL). Spectral  
21 mismatch factors (M) were calculated according to a standard procedure and a typical M  
22 value of 1.02 was obtained for the PTB7:PC<sub>70</sub>BM devices.<sup>47</sup> The value was used to correct the  
23 measured  $J_{\text{sc}}$  values of the solar cells to  $J_{\text{sc}}$  values corresponding to AM1.5G conditions.  
24  
25

26  
27  
28  
29  
30  
31  
32  
33 Shadow masks were used to well-define the illuminated area to  $0.27 \times 1.0 \text{ cm}^2$ . We present  
34 performance of the best devices, while average PCEs were obtained with standard deviation  
35 analysis calculated using 9 devices.  
36  
37

38  
39  
40  
41  
42  
43  
44  
45  
46 External quantum efficiency (EQE) measurements were performed in air using a homemade  
47 setup consisting of a Keithley 238 Source Measure Unit and Newport monochromator. Light  
48 intensity was measured with a calibrated Si-diode from Newport Company.

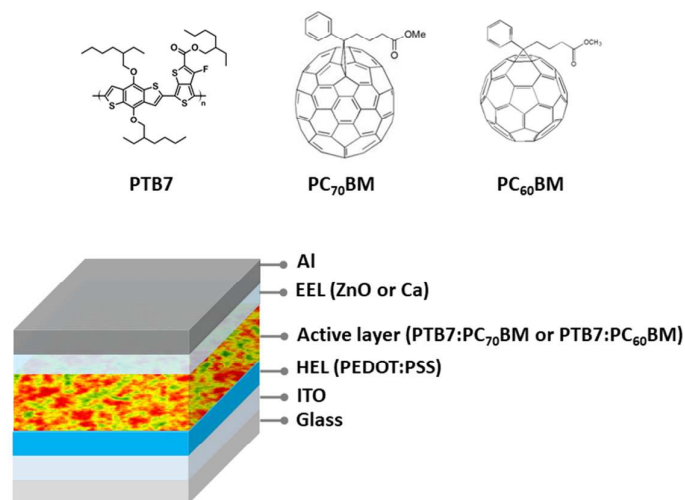
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
***Thermal stress application.*** The thermal stress treatments were applied to stack layers in a  
double- or single-sided confinement. The thermal annealing at 140°C was either applied  
directly on the complete PTB7:PC<sub>60</sub>BM solar cell (defined as the post-annealing) or before  
the ZnO and Al depositions (defined as the pre-annealing) on a hot plate at 140°C inside the  
glovebox during a controlled time.

1  
2  
3 **Morphological analysis.** The surface morphology of the ZnO layers was studied by atomic  
4 force microscopy (AFM) using a Nanoscope III in tapping mode. Light microscope analyses  
5 were performed with a confocal laser scanning microscope (LSM710 Zeiss) on layers  
6 deposited on glass substrate with identical deposition parameters as used in solar cells and  
7 exposed to the annealing temperature (140°C) in air. In order to visualize the nanoscale  
8 morphology of PTB7:PC<sub>60</sub>BM blends under double side confinement inside the device, we  
9 processed first a layer stack composed of ITO/PEDOT:PSS/PTB7:PC<sub>60</sub>BM/ZnO under  
10 identical conditions. After annealing of the whole stack we applied ESI analyses to the  
11 samples to visualize the blend morphology via measuring through the ZnO layer. The  
12 photoactive layers with and without ZnO were floated on top of deionized water by dissolving  
13 the PEDOT:PSS layer. Pieces of the floating layer were collected with a grid covered with  
14 holey carbon film (QUANTIFOIL®). For non-annealed sample of PTB7:PC<sub>60</sub>BM that are not  
15 covered with ZnO, ESI measurements were performed in transmission electron microscopy  
16 mode with a Libra 200 MC microscope (Carl Zeiss Microscopy, Germany) at 60 kV  
17 acceleration voltage using series of energy-filtered images as previously shown.<sup>49</sup> ESI  
18 measurements and dark-field images for all other layers were recorded in a Titan 60-300  
19 microscope (Thermo Fisher Scientific, USA). Since some samples were covered with the  
20 additional ZnO layer, a larger inelastic mean-free path was achieved by raising the electron  
21 energy to 120 keV. Single-scattering distributions were computed by Fourier-log  
22 deconvolution allowing unambiguous fitting of the bulk plasmon peak energies. These  
23 energies were spatially mapped out in 2D images to represent morphological maps. Layers  
24 covered with ZnO were still below a total of 100 nm in thickness, thus layers were thin  
25 enough to assume to a first approximation a linear contribution of the different materials to  
26 the energy-loss spectra. To determine the ZnO contribution to the spectra, reference spectra of  
27 pure materials were measured. The STEM-ESI data sets were then fitted to the three pure  
28 spectra as reference data (PTB7, PC<sub>60</sub>BM, and ZnO) by a multiple linear least-squares

algorithm. The contribution of ZnO was subtracted from the measured mixed signal pixel by pixel, i.e. spectrum by spectrum, so that the subsequently determined plasmon peak energy represents the signals from the organic active layer only. All data processing of ESI spectra was performed using HyperSpy (<http://hyperspy.org>).

### 3. Results and Discussion

The device and the molecular structures of the donor and acceptor materials are shown in **Figure 1**. PEDOT:PSS was applied as the HEL material at constant thickness, while ZnO and Ca were used as EEL materials, with different layer thickness and morphology to study their impact on the device stability. Devices with bare aluminium (Al) cathode and bare indium tin oxide (ITO) anode were studied as references.



**Figure 1.** Molecular structures of PTB7, PC<sub>70</sub>BM, and PC<sub>60</sub>BM together with the schematic multi-layer device structure of solar cells.

#### 3.1 Interfacial layer related thermal degradation of polymer solar cells

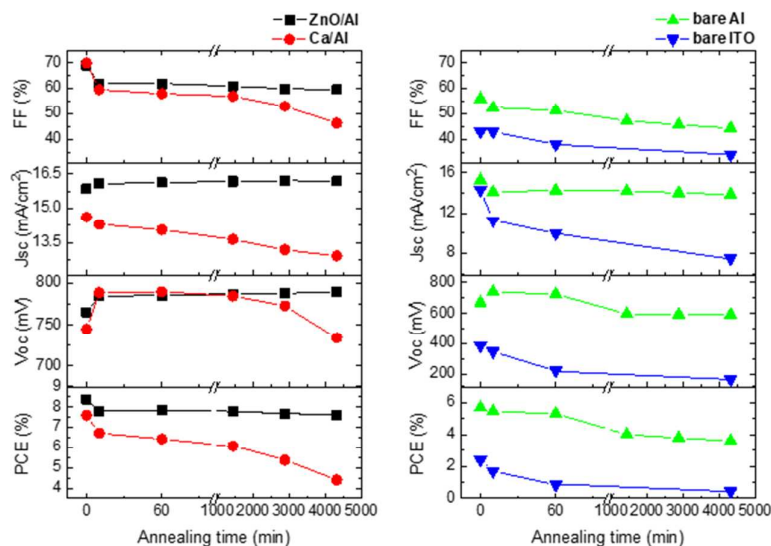
To study the role of EELs in detail, we first compare the performances of PTB7:PC<sub>70</sub>BM solar cells using either ZnO/Al or Ca/Al contacts with devices using bare Al contacts. The

entire devices were exposed to a post-annealing treatment of 140°C of various times. This means that the PTB7:PC<sub>70</sub>BM blend layers are annealed in a double-sided confinement. **Table 1** and **Figure 2** present the time evolution of photovoltaic parameters (fill factor FF, short-circuit density J<sub>sc</sub>, open-circuit current V<sub>oc</sub>, and, power conversion efficiency PCE) for the different devices under a constant thermal stress at 140°C up to 3 days. The corresponding J-V curves are shown in **Figure S1**.

**Table 1.** Photovoltaic parameters (PCE, V<sub>oc</sub>, J<sub>sc</sub> and FF; additionally an average PCE of 9 devices with standard deviation is provided) of PTB7:PC<sub>70</sub>BM solar cells exposed continuously to a post-annealing thermal stress at 140°C up to 3 days processed with the following device structures:

- ITO/PEDOT:PSS/PTB7:PC<sub>70</sub>BM/**ZnO/Al** with ZnO as interfacial layer
- ITO/PEDOT:PSS/PTB7:PC<sub>70</sub>BM/**Ca/Al** with Ca as interfacial layer
- ITO/PEDOT:PSS/PTB7:PC<sub>70</sub>BM/**Al** with bare Al contact
- **ITO/PTB7:PC<sub>70</sub>BM/ZnO/Al** with bare ITO contact

	PCE (%)	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	Average PCE (± std. dev.)
ZnO/Al					
As-prepared	8.38	765	15.86	69	8.22 ± 0.11
140°C 10 min	7.8	785	16.08	62	7.52 ± 0.19
140°C 1 hour	7.84	786	16.13	62	7.49 ± 0.23
140°C 1 day	7.79	787	16.18	61	7.58 ± 0.19
140°C 2 days	7.67	788	16.22	60	7.4 ± 0.25
140°C 3 days	7.62	789	16.19	60	7.26 ± 0.22
Ca/Al					
As-prepared	7.60	745	14.62	70	7.49 ± 0.11
140°C 10 min	6.72	789	14.30	60	6.43 ± 0.21
140°C 1 hour	6.49	790	14.06	58	6.24 ± 0.16
140°C 1 day	6.07	785	13.64	57	5.51 ± 0.40
140°C 2 days	5.38	773	13.18	53	4.85 ± 0.49
140°C 3 days	4.40	734	12.92	46	3.64 ± 0.50
bare Al					
As-prepared	5.70	671	15.28	56	5.45 ± 0.20
140°C 10 min	5.46	740	14.10	52	5.27 ± 0.14
140°C 1 hour	5.32	726	14.28	51	5.03 ± 0.27
140°C 1 day	4.01	598	14.20	47	3.46 ± 0.38
140°C 2 days	3.81	595	14.02	46	3.33 ± 0.34
140°C 3 days	3.65	593	13.86	44	2.96 ± 0.58
bare ITO					
As-prepared	2.38	387	14.31	43	2.15 ± 0.21
140°C 10 min	1.69	349	11.29	43	1.36 ± 0.25
140°C 1 hour	0.84	223	9.97	38	0.5 ± 0.26
140°C 3 days	0.42	168	7.51	34	0.22 ± 0.13



**Figure 2.** Time evolution of photovoltaic parameters of PTB7:PC<sub>70</sub>BM solar cells exposed continuously to a post-annealing thermal stress at 140°C up to 3 days processed with the following device structures: ITO/PEDOT:PSS/PTB7:PC<sub>70</sub>BM/ZnO/Al with a ZnO interfacial layer (black squares), ITO/PEDOT:PSS/PTB7:PC<sub>70</sub>BM/Ca/Al with a Ca interfacial layer (red circles), ITO/PEDOT:PSS/PTB7:PC<sub>70</sub>BM/Al with a bare Al contact (green up triangles) and ITO/PTB7:PC<sub>70</sub>BM/ZnO/Al with a bare ITO contact (blue down triangles).

While devices using ZnO/Al contacts are stable over the whole period of observation, solar cells using Ca buffer layers show a continuous degradation of FF,  $J_{sc}$  and thus PCE under a thermal stress at 140°C. Only the  $V_{oc}$  shows a spontaneous increase under the post-annealing at 140°C in both cases. The later can be addressed to the diffusion of fullerene to the blend surface during the first minutes of annealing induced by the DIO evaporation. The accumulation of fullerene at the blend surface improves then the charge carrier extraction at the cathode and thus  $V_{oc}$ .<sup>38</sup> Similar increase in  $V_{oc}$  is observed for solar cells using a bare Al contact. The losses of PCE when using Ca are primarily ascribed to strong losses in  $J_{sc}$  and FF. This can be attribute to thermally activated Ca ion diffusion and/or chemical reaction of Ca with the polymer blend. Both processes lead to strongly increased recombination.<sup>9</sup> In case of

1  
2  
3 the bare Al contact, only the FF constantly decreases, which can be addressed to chemical  
4  
5 reaction of Al with the polymer surface inducing an increasing amount of recombination  
6  
7 centres.<sup>9</sup> Importantly, we show that ZnO is a highly stable EEL material as almost unaltered J-  
8  
9 V curves (see **Figure S1**) and photovoltaic parameters (see **Table 1** and **Figure 2**) are  
10  
11 observed under post-annealing treatment at 140°C during 3 days. This proves that the  
12  
13 electronic properties of ZnO EELs as well as the ZnO/polymer blend interfaces are stable  
14  
15 under thermal stress at 140°C. Furthermore, ZnO efficiently protects the polymer blend  
16  
17 against thermally induced damages from the Al electrode. For an in-depth investigation of the  
18  
19 role of the ZnO EELs, we processed ZnO layers with different morphologies, i.e. closely  
20  
21 packed ZnO layers or with nanoscopic holes as shown in **Figure S2**. This could be obtained  
22  
23 by processing ZnO EELs using solution of lower ZnO nanoparticle concentration, while  
24  
25 keeping identical solvent and deposit conditions. **Figure S2** and **Table S1** depict the time  
26  
27 evolution of photovoltaic parameters during a post-annealing treatment at 140°C as a function  
28  
29 of the ZnO-based layer morphology. Importantly, we find similar degradation for ZnO EELs  
30  
31 containing holes as observed for bare Al contacts (see **Figure 2** and **Table 1**). This clearly  
32  
33 indicates that not only the ZnO material itself but also a densely packed layer morphology are  
34  
35 crucial to obtain high thermal stability in PSCs (92% of the initial efficiency for a densely  
36  
37 packed ZnO EELs after one day vs. 30% for a partially covering ZnO EELs). In the case of a  
38  
39 non-annealed solar cell based on a densely packed ZnO EEL, losses of PCE are higher with  
40  
41 84% of the initial efficiency after one day (**Figure S3** and **Table S2**). This drastic initial loss  
42  
43 can be addressed to the presence of DIO in the blend.<sup>38</sup> It should be mentioned that we also  
44  
45 varied the thickness of the Ca layers from 10 to 30 nm to ensure that the Ca EEL is complete  
46  
47 without any pinholes. In all cases, we observed strong degradation under a post-annealing  
48  
49 treatment at 140°C demonstrating that not layer porosity is at the origin of the degradation of  
50  
51 Ca EELs based solar cells, but the material Ca itself.  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 As next step, we studied the role of the PEDOT:PSS as HEL in the thermal stability of the  
4 studied solar cells. To evaluate the effect of the HEL, we process devices using densely  
5 packed ZnO based EELs together with a bare ITO anode. As it can be seen in **Table 1**, the  
6 lack of PEDOT:PSS generates solar cells with much lower initial efficiencies of 2.38% as can  
7 be expected from literature since PEDOT:PSS improves hole extraction at the anode.<sup>50</sup> But  
8 more importantly, thermal stress at 140°C leads to a very fast degradation of all photovoltaic  
9 parameters with a loss of more than 60% of the initial PCE only after 1 hour. These results  
10 indicate that ITO is by far the most reactive interface of the solar cell and more importantly,  
11 PEDOT:PSS is a very efficient material to protect the polymer blend against thermally  
12 induced damages from the transparent ITO anode.

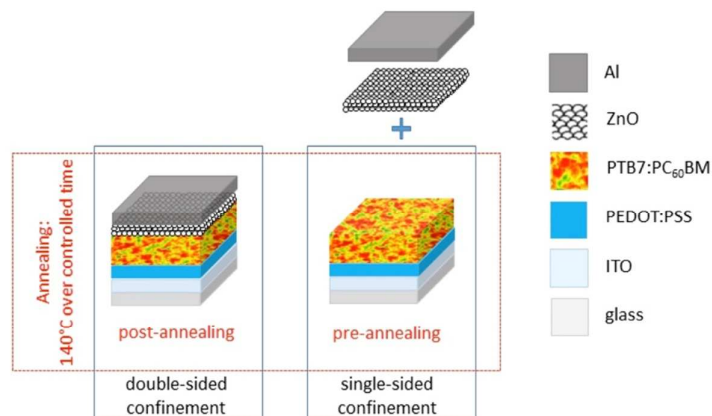
13  
14 PEDOT:PSS and densely packed ZnO nanoparticle based ILs could be identified as highly  
15 stable materials protecting polymer solar cells against thermal damage during annealing in a  
16 double-sided confinement. However, there is a common feature, a small degradation in  
17 performance and more precisely in FF that occurs in all devices during the first few minutes.  
18 Indeed, as it can be seen in **Figures 2** and **S2**, in all device configurations identical losses in  
19 FF occur within the first 10 min of the post-annealing treatment at 140°C, while further but  
20 slower decrease in FF follows depending on the IL material used. There is only one exception,  
21 which are solar cells processed without PEDOT:PSS that show constant values of FF during  
22 the first 10 min. It seems therefore likely that the initial fast degradation in FF is related to the  
23 interface between PEDOT:PSS and the polymer blend. Further studies are however needed to  
24 study the origin of the drop in FF in more detail. It leads to a non-negligible average loss of  
25 10% in this parameter and will be addressed in future work.

### 3.2. Blend composition related thermal degradation in polymer solar cells

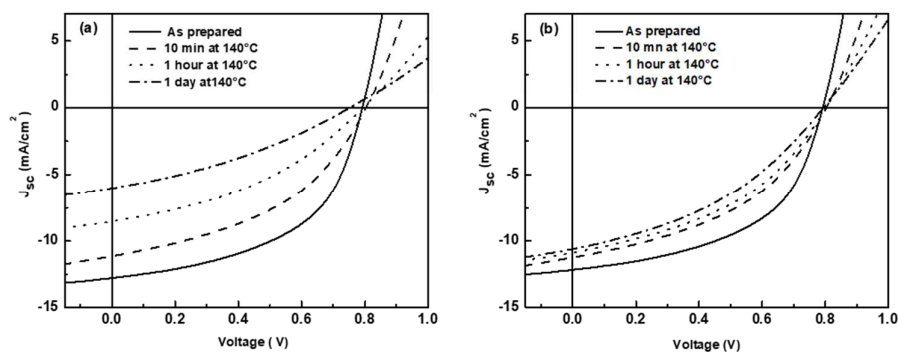
26 From literature it is known that PTB7:PC<sub>60</sub>BM blends rapidly form large fullerene crystals  
27 under thermal stress at 140-150°C,<sup>30,32</sup> while PTB7:PC<sub>70</sub>BM blends, as shown previously, are



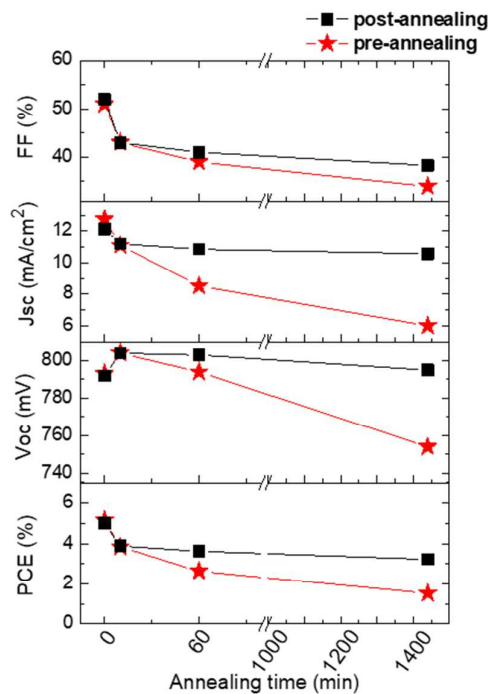
1  
2  
3 stable at such temperatures.<sup>38</sup> The difference in thermal stability related to the size of the  
4 fullerene crystals was attributed to local minima in the mixing enthalpy of the blend, forming  
5 only stable phases in the case of PTB7:PC<sub>70</sub>BM.<sup>38</sup> The low thermal stability related to the use  
6 of PC<sub>60</sub>BM was first verified by comparing light microscope images of as-cast PTB7:PC<sub>60</sub>BM  
7 blends with of those exposed to thermal annealing at 140°C during 1 day. As it can be seen in,  
8 **Figure S4** the annealed blends clearly show the formation of larger structures, most likely  
9 fullerene crystals. Wantz *and coll.* have recently demonstrated that the performances of  
10 PTB7:PC<sub>60</sub>BM solar cells degrade rapidly from 5% to 0.9% after heating for 16 h at 150°C.<sup>32</sup>  
11 The strong loss in performance was associated to the thermal instability of the polymer blend.  
12 It is important to mention that the authors first annealed the polymer blend at 150°C before  
13 completing the device with a successive deposition of Ca and Al. In such a study, only one  
14 side of the polymer blend is in contact with an IL during annealing (here the supporting  
15 substrate layer) thus leading to a single-sided confinement. The application of thermal  
16 annealing to this device stack can be defined as a thermal pre-annealing process. In the  
17 present study, we choose to complete first the PTB7:PC<sub>60</sub>BM based solar cells by spin-  
18 coating a densely packed ZnO layer on top of the blend, depositing the Al contact by thermal  
19 evaporation and subsequently do the annealing step, here called post-annealing process.  
20 Furthermore, we compare the obtained performances to those of solar cells using identical  
21 final device structures but exposed to a pre-annealing step at 140°C during 24 h. **Figure 3**  
22 provides a schematic representation of both thermal annealing processes, i.e. post-annealing  
23 and pre-annealing, together with the corresponding confinement, i.e. double- and single-sided  
24 confinements. **Figures 4** and **5** compare the evolution of J-V curves and the photovoltaic  
25 parameters of the PTB7:PC<sub>60</sub>BM solar cells between pre- and a post-annealing treatments as a  
26 function of the applied annealing time. **Table S3** summarizes the photovoltaic parameter  
27 values.



**Figure 3.** Schematic representation of thermal stress treatments applied to stack layers in double- and single-sided confinements. The thermal annealing at 140°C was either applied directly on the complete PTB7:PC<sub>60</sub>BM solar cell (post-annealing) or before the ZnO and Al depositions (pre-annealing).



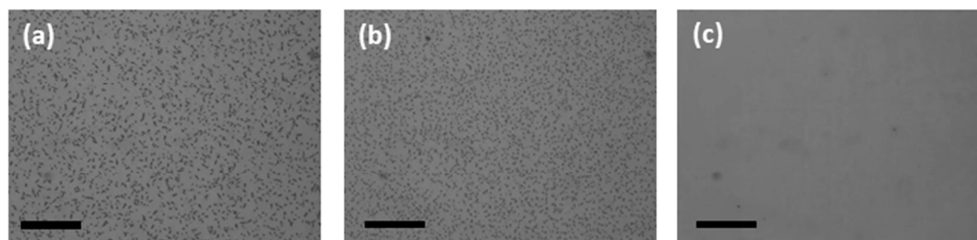
**Figure 4.** Time evolution of J-V curves of PTB7:PC<sub>60</sub>BM solar cells as function of (a) pre-annealing (single-sided confinement) and (b) post-annealing (double-sided confinement) thermal stress. The device structure is ITO/PEDOT:PSS/PTB7:PC<sub>60</sub>BM/ZnO/Al.



**Figure 5.** Time evolution of photovoltaic parameters (FF,  $J_{sc}$ ,  $V_{oc}$  and PCE) of PTB7:PC<sub>60</sub>BM solar cells as function of post-annealing (double-sided confinement) and pre-annealing (single-sided confinement) thermal stress.

As expected for both applied annealing processes, we observe a degradation of the performance of the solar cells based on PTB7:PC<sub>60</sub>BM blends as a function of thermal ageing. However significant differences can be observed according to the thermal annealing process. For the post-annealing step (double-sided confinement), the first hour induces a loss of 28% in the PCE, whereas during further thermal stress at 140°C up to 24 h the performance remains almost constant. More importantly, the photocurrent losses after 24 h in the double-sided confinement are only 12%. This is in stark contrast to the results reported in the literature.<sup>32</sup> In this sense, we also examined the time evolution versus thermal stress of solar cells produced with a pre-annealing step (single-sided confinement). As it can be seen in **Figures 4a and 5**, we observe indeed the well-known strong degradation in these devices

1  
2  
3 after thermal stress. After a pre-annealing at 140°C over 24 h, the PTB7:PC<sub>60</sub>BM based solar  
4  
5 cell shows a performance loss of 70%. These results clearly show that there is a pronounced  
6  
7 difference in thermally induced degradation as a function of the selected annealing treatment.  
8  
9 Moreover, our post-annealing process strongly improves the thermal stability of the solar cells,  
10  
11 although the uncovered polymer blend itself rapidly forms fullerene crystals under these  
12  
13 conditions (**Figure S4**). As shown in **Figure S5** and **Table S3**, extension of the thermal stress  
14  
15 to 3 days only leads to a final loss of 15.5% in photocurrent density highlighting that after an  
16  
17 initial 12% drop in photocurrent within the first hour, the photocurrent remains almost stable.  
18  
19 Our observation suggests that the nanoscale morphology of unstable PTB7:PC<sub>60</sub>BM blends is  
20  
21 stabilized after the first hour of annealing in a double-sided confinement while no further  
22  
23 changes is induced upon prolonged thermal stress treatment.  
24  
25  
26 To understand this stabilization phenomenon, we focus on the role of layer confinement  
27  
28 during thermal annealing of the polymer blend. Indeed in the post-annealing step, the  
29  
30 PTB7:PC<sub>60</sub>BM blend is in a double-sided confinement, i.e. sandwiched between PEDOT:PSS  
31  
32 and ZnO ILs. Therefore we compared the morphology of bare polymer-fullerene blends  
33  
34 processed on PEDOT:PSS (single-sided confinement) to an identical blend layer but covered  
35  
36 with a densely packed ZnO layer (double-sided confinement). The latter case allows  
37  
38 simulating the situation inside the device stack upon annealing. **Figure 6** shows light  
39  
40 microscopic images of PTB7:PC<sub>60</sub>BM blend layers deposited onto ITO covered with  
41  
42 PEDOT:PSS as single- or double-sided confined active layers after a thermal stress at 140°C  
43  
44 for 1 day.  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



**Figure 6.** Light microscope images of PTB7:PC<sub>60</sub>BM blend layers deposited onto ITO covered with PEDOT:PSS and exposed to a thermal stress at 140°C for 1 day in single- (a) and double-sided (b, c) confinement. The thermal annealing at 140°C for 1 day was applied on the bare PTB7:PC<sub>60</sub>BM layer (a), on the blend layer before the ZnO deposition in (b) or on the ZnO covered PTB7:PC<sub>60</sub>BM layer in (c). Scale bare corresponds to 100  $\mu\text{m}$ .

In the case of a single-sided PTB7:PC<sub>60</sub>BM blend layer (**Figure 6a**), black spots can be seen which can be assigned to the well-known fullerene crystals.<sup>38</sup> Hence, this sample can be classified as a thermally unstable polymer-fullerene blend. Almost identical images with expected fullerene crystals are obtained from PTB7:PC<sub>60</sub>BM blends processed with the pre-annealing step (**Figure 6b**). In contrast, PTB7:PC<sub>60</sub>BM blend layers covered with ZnO during the thermal annealing do not show fullerene crystals after 24 h at 140°C (**Figure 6c**). Similar results have been observed for PTB7:PC<sub>60</sub>BM blends deposited directly on bare ITO without PEDOT:PSS as HEL (**Figure S6**) indicating that the stabilization effect is independent of the bottom confinement and only related to the top confinement. These analyses reveal that the presence of a ZnO layer during thermal annealing and successive thermal stress suppresses the formation of PC<sub>60</sub>BM crystals. A double-sided spatial confinement reduces the mobility of PC<sub>60</sub>BM molecules and thus its crystallization kinetics in the BHJ layer.<sup>45</sup> The stabilization effect of ZnO is in accordance with the small losses in photocurrent density of only 11% during the post-annealing of the entire solar cells. However, whilst the optical analysis shows the lack of crystal formation, it is possible that there are still morphological changes at the

1  
2  
3 nanoscale occurring during the annealing of PTB7:PC<sub>60</sub>BM blends in the double-sided  
4  
5 confinement.  
6  
7

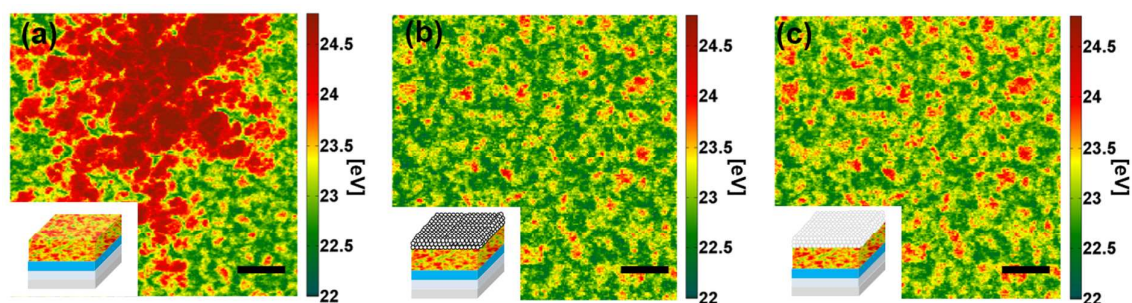
### 9 **3.3 Correlating blend morphology to photocurrent density losses**

10  
11 To investigate potential modification of the nanoscale morphology of the PTB7:PC<sub>60</sub>BM  
12  
13 blend in the two-sided confinement, we applied AFM analysis and electron spectroscopic  
14  
15 imaging in transmission electron microscopes either in scanning mode (STEM) or in imaging  
16  
17 mode (TEM) (see Experimental Section for details). ESI as imaging technique is based on the  
18  
19 recording of spatially resolved spectra of optical excitations that allow to distinguish between  
20  
21 donor-enriched and acceptor-enriched phases of the polymer blends.<sup>49,50</sup> Furthermore, mixed  
22  
23 phases can be identified.<sup>51</sup> Analyses were conducted on PTB7:PC<sub>60</sub>BM blends deposited onto  
24  
25 PEDOT:PSS which were annealed for 1 day at 140°C either as bare PTB7:PC<sub>60</sub>BM blends or  
26  
27 PTB7:PC<sub>60</sub>BM blends covered with a densely packed ZnO layer. Performing ESI on bare  
28  
29 blend layers allows to directly record signals from the organic materials. By fitting the bulk  
30  
31 plasmon peak for each spectrum to a Lorentzian, varying peak energies from the different  
32  
33 material phases can be visualized and represented as plasmon peak maps.<sup>49</sup> The resulting map  
34  
35 for the bare blend (i.e. single-sided confinement) after thermal annealing at 140°C during 1  
36  
37 day is depicted in **Figure 7a**. As expected the thermally stressed layer shows a very large  
38  
39 fullerene aggregate with a size of well over one micrometer. This confirms that in **Figure 6a**  
40  
41 and **Figure 6b** the dark spots are fullerene aggregates. More large aggregates as in **Figure 7a**  
42  
43 are shown in **Figures S7** and **S8** in dark-field STEM images. **Figure S7** also provides as  
44  
45 comparison a dark-field STEM image from a blend layer covered by ZnO. Here, no large  
46  
47 fullerene crystals are observed. Together with the light microscopy image in **Figure 6c**, this  
48  
49 proves that the ZnO capping layer prevents aggregate formation.  
50  
51

52  
53  
54 Except for the large PC<sub>60</sub>BM aggregate, changes in the nanoscale morphology is of high  
55  
56 importance. The as-cast PTB7:PC<sub>60</sub>BM blend depicted in **Figure S9** shows an optimized BHJ  
57  
58

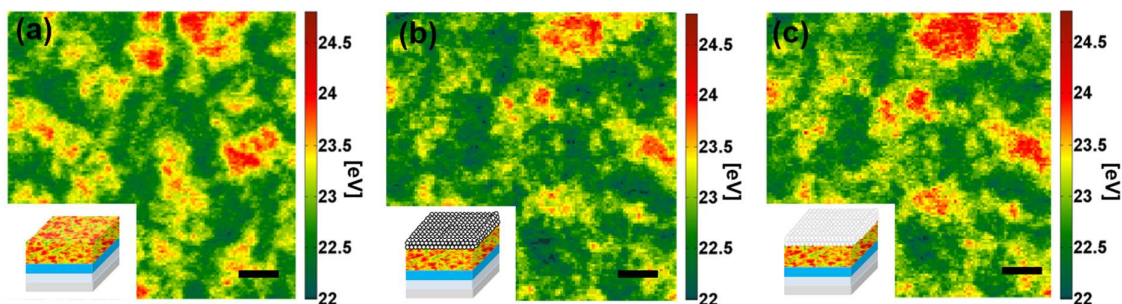
1  
2  
3 of donor and acceptor enriched phases separated by tens of nanometers, while a large amount  
4  
5 of mixed phase is present. From **Figure 7a** it can be deduced that the size of the material-  
6  
7 enriched domains and their distance to each other increase upon thermal stress, whilst the  
8  
9 amount of mixed phases is strongly reduced. In **Figure 7b** the plasmon peak map of the  
10  
11 annealed layer with ZnO capping is presented still revealing the morphology of the organic  
12  
13 blend. However, the ZnO layer contributes to the recorded spectra from the ESI-TEM data so  
14  
15 that a detailed comparison to the non-capped layer would not be possible. To quantify ZnO  
16  
17 contributions in the spectroscopic data, the low-energy-loss spectrum of pure ZnO was taken  
18  
19 from a previous 3D analysis of a tandem cell,<sup>49</sup> and used together with spectra from pure  
20  
21 PTB7 and PC<sub>60</sub>BM for a least-squares fitting of the experimental spectra. Since in total the  
22  
23 films were thinner than the inelastic mean-free-path of the high-energy electrons, the fraction  
24  
25 of the ZnO signal could be determined and subtracted from the spectra to reconstruct the  
26  
27 PTB7:PC<sub>60</sub>BM signals. Subsequently, the energies of the plasmon peak positions were again  
28  
29 determined as before for the bare layer by fitting the spectra to a Lorentzian model. Typically,  
30  
31 this correction leads to slightly elevated plasmon peak energies in the map. To the best of our  
32  
33 knowledge this is the first time that such morphological analyses at the nanoscale are  
34  
35 performed across a ZnO capping layer. More details on the analysis are given in the  
36  
37 Experimental Section and in the supporting information (**Figure S10** and **Figure S11**). The  
38  
39 resulting plasmon peak map from the blend with ZnO capping, reconstructed to represent only  
40  
41 PTB7:PC<sub>60</sub>BM signals, is shown in **Figure 7c**. Interestingly, except for the lack of large  
42  
43 PC<sub>60</sub>BM clusters, the general nanoscale morphology of this blend features similar sizes and  
44  
45 distances between donor and acceptor enriched domains as the comparable blend annealed  
46  
47 without ZnO capping layer. This is confirmed by providing plasmon peaks maps in **Figure 8**  
48  
49 from different regions on the samples and in higher magnification. For the uncovered layer  
50  
51 (**Figure 8a**) a region further away from a fullerene cluster was selected to ensure that the  
52  
53 domain compositions were not altered locally due to aggregation of fullerene molecules.  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 These results imply that during thermal annealing of PTB7:PC<sub>60</sub>BM blends the ZnO capping  
4 layer particularly inhibits only the formation of large, micrometre-sized fullerene crystals at  
5 layer particularly inhibits only the formation of large, micrometre-sized fullerene crystals at  
6 the surface of the blend layer, whereas morphological changes inside the blend related to an  
7 enlargement of the domain size and distances between enriched-donor and enriched-acceptor  
8 domains occur in both cases. In particular the average distance between donor and acceptor  
9 enriched domains increases from 10 to 50 nm (manual centre-to-centre distance  
10 measurements from enriched domains) together with a reduced amount of the mixed phase  
11 (yellow phases in the STEM-SI images) during the thermal annealing (see **Figure S9** to  
12 compare).



23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35 **Figure 7.** Plasmon peak maps of uncovered (single-sided confinement; a) and ZnO covered  
36 (double-sided confinement; b, c) PTB7:PC<sub>60</sub>BM blends after thermal annealing at 140°C  
37 during 1 day showing the nanoscale materials phases (PC<sub>60</sub>BM rich domains in red with high  
38 plasmon peak energy and PTB7 rich domains in green with low energy). As seen in (a), large  
39 PC<sub>60</sub>BM aggregates appear only for thermally stressed single-sided confined layers. For (c)  
40 the spectral contribution of the ZnO capping layer was removed from the data so that plasmon  
41 peak energies can be compared to the map in (a). Scale bars represent 200 nm.





**Figure 8.** Higher magnification plasmon peak maps of uncovered (single-sided confinement; a) and ZnO covered (double-sided confinement; b, c) PTB7:PC<sub>60</sub>BM blends after thermal annealing at 140°C during 1 day showing the nanoscale materials phases. For (c) the spectral contribution of the ZnO capping layer was removed from the data so that plasmon peak energies can be compared to the map in (a). The structure of layers at smaller length scales (in comparison to **Figure 7**) is independent of confinement. Scale bars represent 50 nm.

In the following we correlate the changes in the photovoltaic parameters observed during the thermal annealing by using either single-sided or double-sided confinement with the ongoing changes in the blend morphology. Taking into account that in both cases an enlargement of the domain size and spacing occur during thermal annealing at 140°C, we would expect that photocurrent density is strongly reduced also in the case of double-sided confinement, i.e. ZnO capped blend layers, due to the excitonic nature of the material. However, the photocurrent density is only reduced by 12% with a maximal  $J_{SC}$  of 12.15 mA/cm<sup>2</sup> for the as-cast solar cell and 10.59 mA/cm<sup>2</sup> after a post-annealing at 140°C for 1 day (see **Table S3**). Thus the increase in domain size during thermal annealing appears to be in stark contrast to the small drop in photocurrent. This result suggests that in the thermally altered blends there is still be efficient exciton dissociation followed by charge carrier collection. To understand this phenomenon, the evolution of FF during annealing provides important indications. It can be seen in **Table S3** that while  $J_{SC}$  is almost not affected, FF is strongly reduced from 52% to 38.3% after 1 day of post-annealing. The latter points to strongly elevated charge carrier

1  
2  
3 recombination inside the thermally modified blend, which can be correlated to the  
4  
5 enlargement of domain spacing. Taking these results into account we suggest that the high  $J_{SC}$   
6  
7 in post-annealed (double-sided confined) solar cells can be explained by sufficiently high  
8  
9 electron transport via hopping inside the donor enriched domains allowing the extraction of  
10  
11 these electrons towards the fullerene enriched domains under short circuit conditions and  
12  
13 thus maximal internal field. C.H.Y. Ho *et al.* have shown very recently that fullerene  
14  
15 percolation occurs already at low PTB7:fullerene ratio of 1:0.1 leading to reduction in  
16  
17 fullerene trap density and increase in electron mobility by several orders of magnitude.<sup>53</sup>  
18  
19 To evaluate the presence of fullerene inside the donor enriched phase, the spatially resolved  
20  
21 plasmon peak energies of **Figure 7** and **Figure 8** can be compared to pure materials reference  
22  
23 spectra. **Figure S11** shows the recorded spectrum of pure PTB7 indicating that a plasmon  
24  
25 peak energy of ca. 21.7 eV for the pure donor and contrasts with the peak energies shown e.g.  
26  
27 in **Figure 7** and **Figure 8** are in general higher inside the PTB7 enriched phase. This implies a  
28  
29 non-negligible fullerene concentration inside the donor enriched phase and thus the possibility  
30  
31 to enable fullerene percolation inside the PTB7:PC<sub>60</sub>BM blend. In order to study more in  
32  
33 detail the photocurrent generation inside the polymer blend before and after annealing,  
34  
35 external quantum efficiency measurements were used. As it can be seen in **Figure S12**, an  
36  
37 almost constant loss in photocurrent generation over the whole absorption spectrum  
38  
39 accompanies the morphological changes during annealing. Taking into account that the  
40  
41 PC<sub>60</sub>BM contributes to the photocurrent generation through light absorption in the range of  
42  
43 340 to 500 nm and PTB7 dominates absorption from 450 to 780 nm, it can thus be considered  
44  
45 that the thermal annealing and thus the on-going morphological changes impact only weakly  
46  
47 the photocurrent generation inside the donor and acceptor phases. Therefore, the high  
48  
49 photocurrent observed under  $J_{SC}$  conditions indicates that hole and electron transports occur  
50  
51 not only in the mixed phase but that minority charge carrier transport continues also inside the  
52  
53 enriched phases, i.e. holes inside the acceptor enriched phase and electrons inside the donor  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 enriched phase. This allows transporting these minority charge carriers towards to their  
4  
5 corresponding enriched domains followed by charge extraction towards the electrode under  
6  
7 the high internal field.  
8  
9

## 10 11 **5. Conclusion**

12  
13 Understanding and reducing thermal degradation of polymer solar cells is highly essential for  
14  
15 the introduction of this technology into application. In this work, we first identify the thermal  
16  
17 stability of polymer solar cells as a function of cathode buffer layer used. Here, densely  
18  
19 packed ZnO nanoparticle layers are found to be particularly suitable to gain high temperature  
20  
21 stability at thermal stress at 140°C. In the second part, application of thermally stable ILs, i.e.  
22  
23 densely packed ZnO EELs in combination with PEDOT:PSS as HELs, was used to study in  
24  
25 how far ZnO EELs that are simultaneous a capping layer for surface of the blend can affect  
26  
27 the degradation of a solar cell under thermal stress using a thermally unstable polymer blend.  
28  
29 We demonstrate that the improved thermal stability in double-sided confinement could be  
30  
31 addressed to the beneficial effect of a double-sided confinement during the thermal annealing  
32  
33 process compared to annealing of an uncovered single-sided blend. The ZnO capping EELs  
34  
35 particularly inhibit the formation of micrometre-sized fullerene crystals at the surface of the  
36  
37 blend layer and leads to a stabilization of the nanoscale morphology of a thermally unstable  
38  
39 blend such as PTB7:PC<sub>60</sub>BM by increasing only the domain spacing by a factor of 5. The  
40  
41 comparably small photocurrent density losses in the stabilized blend points towards the  
42  
43 existence of efficient ambipolar transport inside donor and acceptor enriched phases in  
44  
45 PTB7:PC<sub>60</sub>BM blends. Our results thus open new insights in thermal stabilization of solar  
46  
47 cells using ILs and designing novel polymer blends with improved tolerance against thermally  
48  
49 induced nanoscale changes in morphology.  
50  
51  
52  
53  
54  
55  
56

## 57 **Acknowledgements**

1  
2  
3 We acknowledge financial support by the French *Fond Unique Interministériel* (FUI) under  
4 the project “SFUMATO” (Grant number: F1110019V/201308815) as well as by the European  
5 Commission under the Project “SUNFLOWER” (FP7-ICT-2011-7-contract number: 287594).  
6  
7  
8 MP and RRS acknowledge support by the HeiKA (Heidelberg Karlsruhe Research  
9 Partnership) FunTech-3D materials science program.  
10  
11  
12

13  
14  
15  
16 **Supporting Information.** Additional time evolution of J-V curves and photovoltaic  
17 parameters of PTB7:PC<sub>70</sub>BM and PTB7:PC<sub>60</sub>BM solar cells. Light microscope images of as-  
18 cast and thermally stressed PTB7:PC<sub>60</sub>BM blends. Light microscope images of  
19  
20  
21  
22 PTB7:PC<sub>60</sub>BM blend layers. Dark-field STEM images of PTB7:PC<sub>60</sub>BM blend layers.  
23  
24  
25 Plasmon peak maps of as-cast and ZnO covered PTB7:PC<sub>60</sub>BM blends. Contribution of ZnO  
26  
27 to dark-field TEM and energy-loss signals. Electron energy-loss spectrum of pure PTB7 layer.  
28  
29  
30 EQE spectra of PTB7:PC<sub>60</sub>BM solar cell.  
31  
32  
33

#### 34 35 AUTHOR INFORMATION

##### 36 37 **Corresponding Authors**

38  
39 \* *E-mail address*: videlot@cinam.univ-mrs.fr (C. Videlot-Ackermann) and  
40  
41 ackermann@cinam.univ-mrs.fr (J. Ackermann)  
42  
43  
44  
45

##### 46 47 **Author Contributions**

48  
49 The manuscript was written through contributions of all authors. All authors have given  
50  
51 approval to the final version of the manuscript.  
52  
53  
54  
55

##### 56 57 **References**

- 1  
2  
3 (1) You J.; Dou L.; Yoshimura K.; Kato T.; Ohya K.; Moriarty T.; Emery K.; Chen C.-C.;  
4 Gao J.; Li G.; Yang Y. A Polymer Tandem Solar Cell with 10.6% Power Conversion  
5 Efficiency. *Nat. Commun.* **2013**, 4, 1446.  
6  
7
- 8  
9 (2) Li W.; Hendriks K.H.; Roelofs W.S.C.; Kim Y.; Wienk M.M.; Janssen R.A.J.  
10 Efficient Small Bandgap Polymer Solar Cells with High Fill Factors for 300 nm Thick Films.  
11 *Adv. Mater.* **2013**, 25, 3182-3186.  
12  
13
- 14 (3) Li Y. Molecular Design of Photovoltaic Materials for Polymer Solar Cells: Toward  
15 Suitable Electronic Energy Levels and Broad Absorption. *Acc. Chem. Res.* **2012**, 45, 723-733.  
16  
17
- 18 (4) Li N.; Brabec C.J. Air-processed polymer tandem solar cells with power conversion  
19 efficiency exceeding 10%. *Energy Environ. Sci.* **2015**, 8, 2902-2909.  
20  
21
- 22 (5) Ben Dkhil S.; Pfannmöller M.; Bals S.; Koganezawa T.; Yoshimoto N.; Hannani D.;  
23 Gaceur M.; Videlot-Ackermann C.; Margeat O.; Ackermann J. Square-Centimeter-Sized  
24 High-Efficiency Polymer Solar Cells: How the Processing Atmosphere and Film Quality  
25 Influence Performance at Large Scale. *Adv. Energy Mater.* **2016**, 6, 1600290.  
26  
27
- 28 (6) Zuo L.; Zhang S.; Li H.; Chen H. Toward Highly Efficient Large-Area ITO-Free  
29 Organic Solar Cells with a Conductance-Gradient Transparent Electrode. *Adv. Mater.* **2015**,  
30 27, 6983-6989.  
31  
32
- 33 (7) Hong S.; Kang H.; Kim G.; Lee S.; Kim S.; Lee J.-H.; Lee J.; Yi M.; Kim J.; Back H.;  
34 Kim J.-R.; Lee K. A Series Connection Architecture for Large-Area Organic Photovoltaic  
35 Modules with a 7.5% Module Efficiency. *Nat. Commun.* **2016**, 7, 10279.  
36  
37
- 38 (8) Zhao W.; Li S.; Yao H.; Zhang S.; Zhang Y.; Yang B.; Hou J. Molecular Optimization  
39 Enables over 13% Efficiency in Organic Solar Cells. *J. Am. Chem. Soc.* 2017, 139, 7148-7151.  
40  
41
- 42 (9) Jørgensen M.; Norrman K.; Gevorgyan S.-A.; Tromholt T.; Andreasen B.; Krebs F.C.  
43 Stability of Polymer Solar Cells. *Adv. Mater.* **2012**, 24, 580-612.  
44  
45
- 46 (10) Habisreutinger S.N.; McMeekin D.P.; Snaith H.J.; Nicholas R.J. Research Update:  
47 Strategies for improving the stability of perovskite solar cells. *APL Materials* **2016**, 4, 091503.  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 (11) Zhao X.; Kim H.-S.; Seo J.-Y.; Park N.-G. Effect of Selective Contacts on the  
4 Thermal Stability of Perovskite Solar Cells. *ACS Appl. Mater. Interfaces* **2017**, *9*, 7148-7153.  
5  
6  
7 (12) Asghar M.I.; Zhang J.; Wang H.; Lund P.D. Device Stability of Perovskite Solar Cells  
8 – A Review. *Renewable and Sustainable Energy Reviews* **2017**, *77*, 131-146.  
9  
10  
11 (13) Niu G.; Li W.; Li J.; Liang X.; Wang L. Enhancement of Thermal Stability for  
12 Perovskite Solar Cells Through Cesium Doping. *RSC Adv.* **2017**, *7*, 17473-17479.  
13  
14  
15 (14) Grossiord N.; Kroon J.M.; Andriessen R.; Blom P.W.M. Degradation Mechanisms in  
16 Organic Photovoltaic Devices. *Org. Electron.* **2012**, *13*, 432-456.  
17  
18  
19 (15) Cheng P.; Zhan X., Stability of organic solar cells: challenges and strategies. *Chem*  
20 *Soc Rev.* **2016**, *45*, 2544-2582.  
21  
22  
23 (16) Gevorgyan S.A.; Madsen M.V.; Roth B.; Corazza M.; Hösel M.; Søndergaard R.R.;  
24 Jørgensen M.; Krebs F.C. Lifetime of Organic Photovoltaics: Status and Predictions. *Adv.*  
25 *Energy Mater.* **2016**, *6*, 1501208.  
26  
27  
28 (17) Roesch R.; Faber T.; von Hauff E.; Brown T.M.; Lira-Cantu M.; Hoppe H. Procedures  
29 and Practices for Evaluating Thin-Film Solar Cell Stability. *Adv. Energy Mater.* **2015**, *5*,  
30 1501407.  
31  
32  
33 (18) Yang X.; Loos J.; Veenstra S.C.; Verhees W.H.J.; Wienk M.M.; Kroon J.M.; Michels  
34 M.A.J.; Janssen R.A.J. Nanoscale Morphology of High-Performance Polymer Solar Cells.  
35 *Nano Lett.* **2005**, *5*, 579-583.  
36  
37  
38 (19) Bertho S.; Janssen G.; Cleij T.J.; Conings B.; Moons W.; Gadisa A.; D’Haen J.;  
39 Goovaerts E.; Lutsen L.; Manca J.; Vanderzande D. Effect of Temperature on the  
40 Morphology and Photovoltaic Stability of Bulk heterojunction polymer:fullerene Solar Cells.  
41 *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 753-760.  
42  
43  
44 (20) Sivula K.; Ball Z.T.; Watanabe N.; Fréchet J.M.J. Amphiphilic Diblock Copolymer  
45 Compatibilizers and Their Effect on the Morphology and Performance of  
46 Polythiophene:Fullerene Solar Cells. *Adv. Mater.* **2006**, *18*, 206-210.  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 (21) Renaud C.; Mognier S.J.; Pavlopoulou E.; Brochon C.; Fleury G.; Deribew D.;  
4 Portale G.; Cloutet E.; Chambon S.; Vignau L.; Hadziioannou G. Block Copolymer as a  
5 Nanostructuring Agent for High-Efficiency and Annealing-Free Bulk Heterojunction Organic  
6 Solar Cells. *Adv Mater.* **2012**, 24, 2196-2201.  
7  
8  
9  
10  
11 (22) Mulherin R.C.; Jung S.; Huettner S.; Johnson K.; Kohn P.; Sommer M.; Allard S.;  
12 Scherf U.; Grennham N.C. Ternary Photovoltaic Blends Incorporating an All-Conjugated  
13 Donor–Acceptor Diblock Copolymer. *Nano Lett.* **2011**, 11, 4846-4851.  
14  
15  
16  
17  
18 (23) Zhang Y.; Yip H.; Acton O.; Hau S.K.; Huang F.; Jen A.K.Y. A Simple and Effective  
19 Way of Achieving Highly Efficient and Thermally Stable Bulk-Heterojunction Polymer Solar  
20 Cells Using Amorphous Fullerene Derivatives as Electron Acceptor. *Chem. Mater.* **2009**, 21,  
21 2598-2600.  
22  
23  
24  
25  
26 (24) Meng X.; Zhang W.; Tan Z.; Li Y.; Ma Y.; Wang T.; Jiang L.; Shu C.; Wang C.  
27 Highly Efficient and Thermally Stable Polymer Solar Cells with Dihydronaphthyl-Based  
28 [70]Fullerene Bisadduct Derivative as the Acceptor. *Adv. Funct. Mater.* **2012**, 22, 2187-2193.  
29  
30  
31  
32  
33 (25) Lin Y.; Lim J.A.; Wie Q.; Mannsfeld S.C.B.; Briseno A.L.; Watkins J.J. Cooperative  
34 Assembly of Hydrogen-Bonded Diblock Copolythiophene/Fullerene Blends for Photovoltaic  
35 Devices with Well-Defined Morphologies and Enhanced Stability. *Chem. Mater.* **2012**, 24,  
36 622-632.  
37  
38  
39  
40  
41 (26) Liao M.-H.; Tsai C.-E.; Lai Y.-Y.; Cao F.-Y.; Wu J.-S.; Wan C.-L.; Hsu C.-S.; Liao I.;  
42 Cheng Y.-J. Morphological Stabilization by Supramolecular Perfluorophenyl-C<sub>60</sub> Interactions  
43 Leading to Efficient and Thermally Stable Organic Photovoltaics. *Adv. Funct. Mater.* **2014**,  
44 24, 1418-1429.  
45  
46  
47  
48  
49  
50 (27) Bertho S.; Campo B.; Piersimoni F.; Spoltore D.; D'Haen J.; Lutsen L.; Maes W.;  
51 Vanderzande D.; Manca J. Improved Thermal Stability of Bulk Heterojunctions Based on  
52 Side-Chain Ffunctionalized Poly(3-alkylthiophene) Copolymers and PCBM. *Sol. Energy*  
53 *Mater. Sol. Cells* **2013**, 110, 69-76.  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 (28) Gevorgyan S.A.; Krebs F.C. Bulk Heterojunctions Based on Native Polythiophene.  
4  
5 *Chem. Mater.* **2008**, 20, 4386-4390.  
6
- 7 (29) Li Z.; Wong H.C.; Huang Z.; Zhong H.; Tan C.H.; Tsoi W.C.; Kim J. S.; Durrant J.  
8  
9 R.; Cabral J.T. Performance Enhancement of Fullerene-Based Solar Cells by Light Processing.  
10  
11 *Nat. Commun.* **2013**, 4, 2227.  
12
- 13 (30) Wong H.C.; Li Z.; Tan C.H.; Zhong H.; Huang Z.; Bronstein H.; McCulloch I.; Cabral  
14  
15 J.T.; Durrant J.R. Morphological Stability and Performance of Polymer–Fullerene Solar Cells  
16  
17 under Thermal Stress: The Impact of Photoinduced PC<sub>60</sub>BM Oligomerization. *ACS Nano*  
18  
19 **2014**, 2, 1297-1308.  
20
- 21 (31) Wantz G.; Derue L.; Dautel O.; Rivaton A.; Hudhomme P.; Dagron-Lartigue C.  
22  
23 Stabilizing Polymer-Based Bulk Heterojunction Solar Cells via Crosslinking. *Polym. Int.*  
24  
25 **2014**, 63, 1346-1361.  
26
- 27 (32) Derue L.; Dautel O.; Tournebize A.; Drees M.; Pan H.; Berthumeyrie S.; Pavageau B.;  
28  
29 Cloutet E.; Chambon S.; Hirsch L.; Rivaton A.; Hudhomme P.; Facchetti A.; Wantz G.  
30  
31 Thermal Stabilisation of Polymer–Fullerene Bulk Heterojunction Morphology for Efficient  
32  
33 Photovoltaic Solar Cells. *Adv. Mater.* **2014**, 26, 5831-5838.  
34  
35
- 36 (33) Lindqvist C.; Bergqvist J.; Bäcke O.; Gustafsson S.; Wang E.; Olsson E.; Inganäs O.;  
37  
38 Andersson M.R.; Müller C. Fullerene Mixtures Enhance the Thermal Stability of a Non-  
39  
40 Crystalline Polymer Solar Cell Blend. *Appl. Phys. Lett.* **2014**, 104, 153301.  
41  
42
- 43 (34) Lindqvist C.; Sanz-Velasco A.; Wang E.; Bäcke O.; Gustafsson S.; Olsson E.;  
44  
45 Andersson M.R.; Müller C. Nucleation-Limited Fullerene Crystallisation in a Polymer–  
46  
47 Fullerene Bulk-Heterojunction Blend. *J. Mater. Chem. A* **2013**, 1, 7174-7180.  
48  
49
- 50 (35) Diaz de Zerio Mendaza A.; Bergqvist J.; Bäcke O.; Lindqvist C.; Kroon R.; Gao F.;  
51  
52 Andersson M.R.; Olsson E.; Inganäs O.; Müller C. Neat C<sub>60</sub>:C<sub>70</sub> Buckminsterfullerene  
53  
54 Mixtures Enhance Polymer Solar Cell Performance. *J. Mater. Chem. A* **2014**, 2, 14354-14359.  
55  
56  
57  
58  
59  
60



- 1  
2  
3 (36) Lindqvist C.; Bergqvist J.; Feng C.-C.; Gustafsson S.; Bäcké O.; Treat N.D.; Bounioux  
4 C.; Henriksson P.; Kroon R.; Wang E.; Sanz-Velasco A.; Kristiansen P.M.; Stingelin N.;  
5 Olsson E.; Inganäs O.; Andersson M.R.; Müller C. Fullerene Nucleating Agents: A Route  
6 Towards Thermally Stable Photovoltaic Blends. *Adv. Energy. Mater.* **2014**, 4, 1301437.  
7  
8  
9  
10  
11 (37) Richards J.J.; Rice A.H.; Nelson R.D.; Kim F.S.; Jenekhe S.A.; Luscombe C.K.;  
12 Pozzo D.C. Modification of PCBM Crystallization via Incorporation of C<sub>60</sub> in  
13 Polymer/Fullerene Solar Cells. *Adv. Funct. Mater.* **2013**; 23, 514-521.  
14  
15  
16  
17 (38) Ben Dkhil S.; Pfanmöller M.; Saba M.I.; Gaceur M.; Heidari H.; Videlot-Ackermann  
18 C.; Margeat O.; Guerrero A.; Bisquet J.; Garcia-Belmonte G.; Mattoni A.; Bals S.;  
19 Ackermann J. Toward High-Temperature Stability of PTB7-Based Bulk Heterojunction Solar  
20 Cells: Impact of Fullerene Size and Solvent Additive. *Adv Energy Mater.* **2017**, 7, 1601486.  
21  
22  
23  
24 (39) Hains A.W.; Liu J.; Martinson A. B. F.; Irwin M. D.; Marks T. J. Anode Interfacial  
25 Tuning via Electron-Blocking/Hole-Transport Layers and Indium Tin Oxide Surface  
26 Treatment in Bulk-Heterojunction Organic Photovoltaic Cells. *Adv. Funct. Mater.* **2010**, 20,  
27 595-606.  
28  
29  
30  
31  
32  
33  
34  
35 (40) Son H.J.; Kim S.H.; Kim D.H. Critical Impact of Hole Transporting Layers and Back  
36 Electrode on the Stability of Flexible Organic photovoltaic Module. *Adv. Energy Mater.* **2016**,  
37 7, 1601289.  
38  
39  
40  
41  
42 (41) Lee S. T.; Gao Z. Q.; Hung L. S. Metal Diffusion from Electrodes in Organic Light-  
43 Emitting Diodes. *Appl. Phys. Lett.* **1999**, 75, 1404.  
44  
45  
46 (42) Suemori K.; Yokoyama M.; Hiramoto M. Electrical Shorting of Organic Photovoltaic  
47 Films Resulting from Metal Migration. *J. Appl. Phys.* **2006**, 99, 036109.  
48  
49  
50  
51 (43) Uhrich C.; Schueppel R.; Petrich A.; Pfeiffer M.; Leo K.; Brier E.; Kilickiran P.;  
52 Baeuerle P. Organic Thin-Film Photovoltaic Cells Based on Oligothiophenes with Reduced  
53 Bandgap. *Adv. Funct. Mater.* **2007**, 17, 2991-2999.  
54  
55  
56  
57  
58  
59  
60

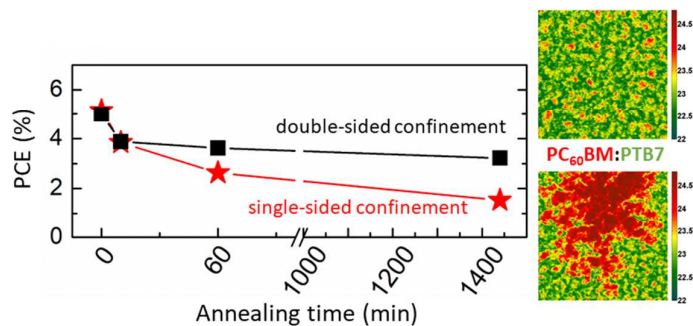
- 1  
2  
3 (44) Kumar A.; Sista S.; Yang Y. Dipole Induced Anomalous S-Shape  $I$ - $V$  Curves in  
4 Polymer Solar Cells. *J. Appl. Phys.* **2009**, 105, 094512.  
5  
6  
7 (45) Yang X.; Alexeev A.; Michels M.A.J.; Loos J. Effect of Spatial Confinement on the  
8 Morphology Evolution of Thin Poly( $p$ -phenylenevinylene)/Methanofullerene Composite  
9 Films. *Macromolecules* **2005**, 38, 4289-4295.  
10  
11  
12  
13 (46) Wang T.; Chen C.; Guo K.; Chen G.; Xu T.; Wei B. Improved Performances of  
14 Polymer Solar Cells by Using Inorganic, Organic, and Doped Cathode Buffer Layers. *Chin.*  
15  
16  
17  
18  
19  
20 (47) Ben Dkhil S.; Duché D.; Gaceur M.; Thakur A.K.; Bencheikh Aboura F.; Escoubas L.;  
21 Simon J.-J.; Guerrero A.; Bisquert J.; Garcia-Belmonte G.; Bao Q.; Fahlman M.; Vidélot-  
22 Ackermann C.; Margeat O.; Ackermann J. Interplay of Optical, Morphological and Electronic  
23 Effects of ZnO Optical Spacers in Highly Efficient Polymer Solar Cells. *Adv. Energy Mater.*  
24  
25  
26  
27  
28  
29  
30  
31 (48) Mattioli G.; Ben Dkhil S.; Saba M.I.; Mallocci G.; Melis C.; Alippi P.; Filippone F.;  
32 Giannozzi P.; Thakur A.K.; Gaceur M.; Margeat O.; Diallo A.K.; Vidélot-Ackermann C.;  
33 Ackermann J.; Bonapasta A.A.; Mattoni A. Interfacial Engineering of P3HT/ZnO Hybrid  
34 Solar Cells Using Phthalocyanines: A Joint Theoretical and Experimental Investigation. *Adv.*  
35  
36  
37  
38  
39  
40  
41  
42 (49) Pfannmöller M.; Heidari H.; Nanson L.; Lozman O. R.; Chrapa M.; Offermans T.;  
43 Nisato G.; Bals S. Quantitative Tomography of Organic Photovoltaic Blends at the Nanoscale.  
44  
45  
46  
47  
48  
49  
50  
51 (50) Guerrero A.; Pfannmöller M.; Kovalenko A.; Ripolles T.S.; Heidari H.; Bals S.;  
52 Kaufmann L.-D.; Bisquert J.; Garcia-Belmonte G. Nanoscale Mapping by Electron Energy-  
53 Loss Spectroscopy Reveals Evolution of Organic Solar Cell Contact Selectivity. *Org.*  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 (51) Pfannmöller M.; Flügge H.; Benner G.; Wacker I.; Sommer C.; Hanselmann M.;  
4 Schmale S.; Schmidt H.; Hamprecht F.A.; Rabe T.; Kowalsky W.; Schröder R.R. Visualizing  
5 a Homogeneous Blend in Bulk Heterojunction Polymer Solar Cells by Analytical Electron  
6 Microscopy. *Nano. Lett.* **2011**, 11, 3099-3107.

7  
8  
9  
10  
11 (52) Lai T.-H.; Tsang S.-W.; Manders J.R.; Chen S.; So F. Properties of interlayer for  
12 organic photovoltaics. *Mater. Today* **2013**, 16, 424-432.

13  
14  
15 (53) Ho C. H. Y.; Cheung S-H.; Li H.W.; Chiu K. L.; Cheng Y.; Yin H.; Chan M.H.; So F.;  
16 Tsang S.W.; So S.K. Using Ultralow Dosages of Electron Acceptor to Reveal the Early Stage  
17 Donor–Acceptor Electronic Interactions in Bulk Heterojunction Blends. *Adv. Energy Mater.*  
18  
19  
20  
21  
22 **2017**, 7, 1602360.

## Graphical abstract



## Highlights

- Study of thermal degradation in polymer solar cells based on PTB7 and fullerene derivatives
- Stable EELs and double-sided confinement within the device for high thermal stability
- Study of the nanoscale morphology of the blends in the two-sided confinement
- Suppression of extensive fullerene diffusion by the double-sided confinement