

High efficiency and stability small molecule solar cells developed by bulk microstructure fine-tuning

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ABSTRACT

Morphological control over the bulk heterojunction (BHJ) microstructure of a high-efficiency small molecule photovoltaic system composed of a quinquethiophene based molecule (DRCN5T) as electron donor and [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₀BM) as electron acceptor is demonstrated using three different post-processing strategies, including thermal annealing (TA), solvent vapor annealing (SVA), and two-step annealing (TA-SVA) treatments. We systematically analyze the processing condition-microstructure-device property relationships, explore the corresponding morphology evolution and their effects on carrier transport and recombination dynamics in BHJs as well as understand the nature of phase-separation process resulting in light-induced degradation mechanisms. Within the investigated results, the causative relations between annealing sequence, photovoltaic parameters, morphology evolution and charge carrier dynamics are for the first time delineated. In addition, the observed trade-offs in device efficiency and stability with respect to the well-defined morphologies are highlighted. The in-depth picture of the bulk microstructure formation and its kinetic evolution as a function of the specific post-processing approaches is a valuable asset for the design of new photovoltaic materials and thin film nanoscale architectures that are more efficient and better aid future commercialization efforts.

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1. Introduction

Solution-processed organic solar cells (OSCs) have received great attention in the past two decades due to their advantages, including low cost, flexibility, lightweight, and roll-to-roll processing compatibility [1–3]. Optimization of their active layers generally requires convergence of a range of materials science and engineering expertise, including organic chemistry, emerging

nanoscale characterization methodologies, optical-electronic process optimization, and device physics [4]. The most implemented active layer architecture for OSCs, a bulk heterojunction (BHJ), consists of a mixture of a photoactive polymer or a small molecule (as electron donor) with a fullerene derivative or another small molecule (as electron acceptor) [5–7]. Several constraints must be managed to engineer BHJ layers with efficient charge generation, transport and extraction [8–12]. Firstly, nanoscale phase separation impact excitons on their way to reach critical donor/acceptor (D/A) interfaces [13,14]. Secondly, internal order within these phases affects charge carrier transport [15]. Finally, the formation of interpenetrating networks of donor and acceptor phases changes the way that photogenerated holes and electrons are collected

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at the respective electrodes [16,17]. In an ideal situation, all these structural requirements are fulfilled at the point of film formation [4]. An optimal morphology is, however, seldomly achieved during film formation due to the materials' properties and external factors [18,19]. Nevertheless, numerous strategies to improve the key metrics of BHJ OSCs by influencing the BHJ structural control during or after their solution-deposition have been explored. This includes casting solvent optimization, additives, thermal annealing (TA), solvent vapor annealing (SVA), etc [5,6,20,21]. A better understanding of the BHJ evolution employed by different processing conditions provides opportunities to establish clear structure-property relations. The latter will enable the precise control of optoelectronic properties in organic materials by targeting optimized microstructures [8,21–28].

It has been demonstrated that multiple solution processed BHJ systems benefit from post-processing strategies (e.g. TA, SVA and post-additive soaking), normally leading to morphologies, which are distinctly different from those seen in low performance devices without any annealing treatment (WO) [5,6,29]. Apart from these post-treatment techniques, the literature documents that a combined two-step annealing (TSA) treatment involving TA and SVA processes improves dramatically the bulk microstructure formation [30,31]. In addition, device performance, carrier transport, and lifetime as well as recombination mechanisms, [6,8,12,17,21,30–32] critically depend on the annealing sequences.

Apart from the overall photovoltaic performance, it was recently reported that several device degradation mechanisms correlate with the BHJ morphology [6,20,33]. A well-known intrinsic degradation mechanism is the light-induced burn-in effect, mainly determined by microstructural characteristics [33–36]. Initial investigations suggest that a higher degree of donor crystallinity significantly reduces the light-induced burn-in degradation [33,37]. Understanding the morphology dependent photo-degradation mechanisms progressed, however, more slowly than the general understanding of the decisive photo-physical processes in BHJ materials [33,38]. Controlling light-induced burn-in degradation as a function of phase morphology constitutes, therefore, a real challenge.

Note that OSCs can be divided into two categories: polymer and small molecule based devices. Part of the motivation behind using a small molecule system lies in their well-defined molecular structure, high reproducibility, easy purification, and low cost fabrication [18,39]. Previous investigations on solution processed small molecule systems showed that a number of post-processing techniques (e.g. TA and SVA) impact the bulk microstructure, and

thus may assist in overcoming geminate and non-geminate recombination losses [8,21,31,32,40]. In this contribution, we systematically investigate the influence of different post-processing conditions, including TA, TA-SVA, and SVA (detailed information on the preparation of these films can be found in the Experimental Section) on a BHJ system based on a small molecule electron donor (2,2'-((5,5'-((3,3',3'',4'-tetraoctyl-[2,2':5',2'':5'',2''':5''',2''''-quiquethiophene]-5,5''''-diyl)bis(methanylylidene))bis(3-ethyl-4-oxothiazolidine-5,2-diylidene))dimalononitrile) (DRCN5T) blended with [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₀BM) as electron acceptor (Fig. 1). Here, we explore such a well-defined molecular system and focus on three main questions. First, we investigate the explicit correlation between the photovoltaic performance and the processing conditions. Second, given the complexity of the micro/nanostructure as a function of processing, we apply optical, electro-optical and electronic spectroscopy methods to elucidate the interplay between microstructure and fundamental photo-physical processes. Finally, we discuss the correlation between microstructure formation and photo-stability under burn-in degradation. Within this systematical and in-depth analysis, we show a quantitative relation between annealing sequence, blend morphology, carrier dynamics, device efficiency and photo-stability mechanisms. As such, our work demonstrates that device efficiency and stability can be optimized in parallel.

2. Results

2.1. Device characteristics

Fig. 1a shows the molecular structure of DRCN5T for a BHJ OSCs based on a conventional structure of ITO/PEDOT: PSS/DRCN5T: PC₇₀BM (1:0.8, wt%)/Ca/Al. The respective energy levels of the materials are shown in Fig. 1b. Achieving high PCE with DRCN5T requires appropriate processing conditions [31]. Here, we apply three different post-processing techniques, including TA, TA-SVA, and SVA treatments, to delineate the causative relations between the photovoltaic parameters and processing conditions. The impact of posttreatment is seen in Fig. 1c, with the relevant photovoltaic parameters summarized in Table 1. A DRCN5T:PC₇₀BM film spin-coated from chloroform gives a relatively modest PCE of 3.57% with an open-circuit voltage (V_{oc}) of 982 mV, a short-circuit current density (J_{sc}) of 7.53 mA cm⁻², and a fill factor (FF) of 48.24%. TA treatment applied to this film leads to a simultaneous increase in J_{sc} (12.27 mA cm⁻²) and FF (58.81%) resulting in an

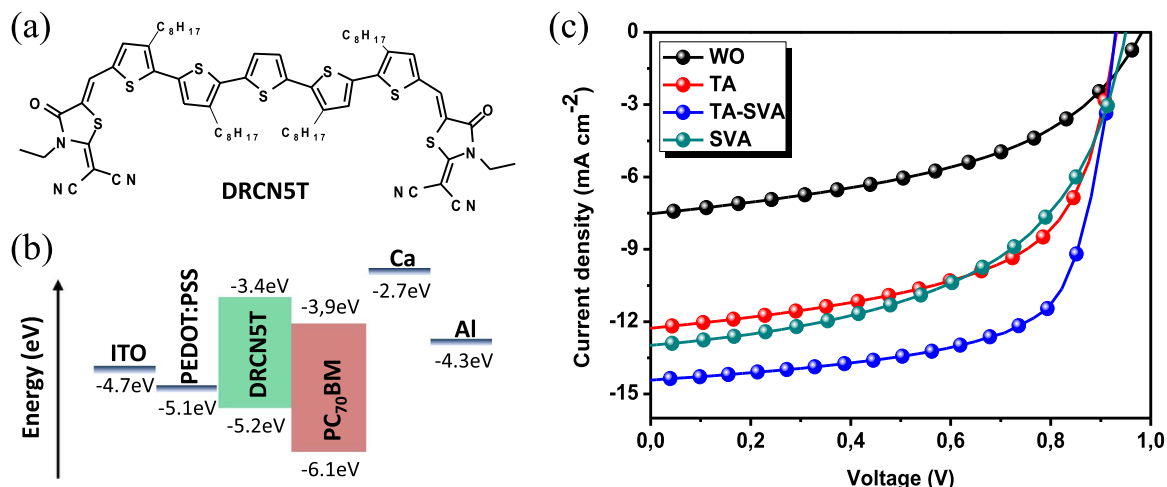


Fig. 1. (a) Chemical structure of DRCN5T. (b) The schematic figure of energy level alignments in the DRCN5T:PC₇₀BM BHJ solar cells. (c) J - V characteristics of the cells with various processing conditions evaluated under AM 1.5 G solar simulator illumination.

Table 1
Photovoltaic parameters of DRCN5T:PC₇₀BM BHJ solar cells fabricated under different processing conditions.

Processing conditions	V_{oc} [mV]	J_{sc} [mA cm ⁻²]	FF [%]	PCE _{max} [%]	PCE _{ave} ^a [%]
WO	982	7.53	48.24	3.57	3.23
TA	932	12.27	58.81	6.73	6.21
TA-SVA	930	14.45	66.78	8.97	8.33
SVA	952	12.58	55.45	6.64	6.22

^a The average PCE value is obtained from twelve devices. Cells were tested in air without encapsulation, illumination intensity was 100 mW cm⁻².

overall increase in PCE up to 6.73%. If a TA processed active layer is placed in a glass Petri dish for 60 s of SVA treatment, the efficiency is further increased to 8.97%, benefitting from a significantly improved J_{sc} (14.45 mA cm⁻²) and FF (66.78%) while retaining a high V_{oc} of 930 mV. In contrast, 6.64% PCE, which is similar with the best TA device, is achieved for the devices treated only with 60 s SVA treatment. The calculated J_{sc} obtained from the integration of EQE data (Fig. S1, Supporting Information (SI)) are close to the J_{sc} measured under one sun, which confirm the distinct J_{sc} differences for the above-mentioned devices. As compared to the EQE spectra of the non-annealed device, the relevant annealing sequences not only increase the EQE in the entire absorption range but also red-shift the EQE spectra of annealed devices with an obvious shoulder found at approximately 700 nm.

The detailed photovoltaic parameters for the devices with various processing conditions are presented in Fig. S2. Fig. S2a not only exhibits the average J_{sc} , but also shows the trend in device photocurrent measured at $-3V$ ($J_{ph}(-3V)$) with the reverse photocurrent ($J_{ph}=J_L-J_D$) being defined as the difference between the dark (J_D) and the light current density (J_L) under one sun [25]. The relative change between J_{sc} and $J_{ph}(-3V)$ is found to be the smallest for the TA-SVA devices exhibiting only negligible voltage dependent recombination in contrast to the non-annealed and other annealed devices [21,25,41]. All annealed films show a photocurrent of app. 14.5 mA cm⁻² at $-3V$, indicating comparable photogeneration rates. Different recombination rates are observed when measuring the $J-V$ curves at an illumination intensity of 0.1 sun (Fig. S2b). For all the samples the FF measured at 0.1 sun is higher than the one at 1 sun. The relative decrease in FF from 0.1 to 1 sun is smallest for the TA-SVA devices, suggesting that this approach provides the most suitable blend morphology with efficient carrier extraction and minimized carrier recombination losses [21,25].

2.2. Morphology and schematic structure

Before discussing morphological characterizations, we firstly investigate the influence of processing conditions on film properties via UV-vis absorption spectroscopy (Fig. S3). As compared to the as-cast film, all annealed films show red-shifted absorption spectra with a distinct shoulder at app. 700 nm, indicating enhanced molecular ordering [17]. The same trend holds for the EQE data (Fig. S1). We further employed atomic force microscopy (AFM), energy filtered transmission electron microscopy (EFTEM), grazing-incidence wide angle X-ray scattering (GIWAXS), and resonant soft X-ray scattering (RSoXS) to directly understand the origin of the observed changes in optical properties upon different annealing treatments, and the nature of the molecular order suggested by UV-vis spectroscopy.

We started our morphology analysis by investigating the microstructure through AFM and EFTEM measurements. AFM shows rather flat and uniform surfaces for the un-annealed and annealed films with small root-mean-square (RMS) surface roughness (Fig.

S4). More insight into the bulk microstructure came from EFTEM investigations. Fig. 2 exhibits elemental maps based on EFTEM imaging of sulfur (S) using the S L edge. This allows distinguishing between the small molecule (sulfur rich) and the fullerene (carbon rich) domains. As only DRCN5T comprises sulfur, the sulfur signal is used to visualize the donor domains. Due to the difference of the carbon content of the electron acceptor (C-PC₇₀BM: 83.7%) relative to the electron donor (C-DRCN5T: 40.9%) the carbon signal can be used to visualize PC₇₀BM rich domains (see right column in Fig. S5). The non-annealed films exhibit almost no discernible structure, suggesting a strongly inter-mixed DRCN5T:PC₇₀BM microstructure without any significant crystallization or phase separation. In contrast, in the case of TA films the formation of separated PC₇₀BM domains (diameters of 30–40 nm) with a bi-continuous interpenetrating network becomes clearly discernible (Fig. 2b and Fig. S5d). EFTEM images of the TA-SVA films show significantly better developed bi-continuous interpenetrating networks with well-expressed fibrillary structures. These propagate throughout the film with a characteristic width of 40–60 nm and lengths of about 100 nm. These domains are assigned to crystalline DRCN5T [31]. In addition, the SVA film possesses similar morphological characteristics as the TA-SVA film, but with slightly larger DRCN5T crystalline fibrils (Fig. 2d and Fig. S5h). In short, both TA and SVA provide sufficient energy to the molecules to diffuse within the blends and find a thermodynamically more stable environment. While TA leads to an equilibrium between the two solids, SVA sets up the means for a three phase equilibrium, where the solvent phase can bind a significant amount of the better soluble molecule. Due to the lower temperature (ca. 25 °C) adopted in the SVA and the presence of the solvent phase, it is not surprising to find different equilibrium microstructures [10,42,43].

Advanced X-ray techniques, including two-dimensional (2D) GIWAXS and RSoXS, were employed to probe the detailed molecular microstructure. The 2D GIWAXS patterns of pristine and BHJ thin films are depicted in Fig. S6. The well expressed scattering features of the pristine DRCN5T films confirm its intrinsically high crystallinity (Fig. S7 for 1D GIWAXS profiles). All of the annealed films display well defined scattering rings in addition to scattering spots. In contrast, the non-annealed films feature only scattering rings. From this we imply that mixing DRCN5T with PC₇₀BM disturbs the molecular ordering of DRCN5T, which can be only recovered by annealing. The crystallization behavior under various annealing conditions is further discussed by probing the well-defined in-plane (010) peak originating from DRCN5T π - π stacking as shown in Fig. S8. From the 1D GIWAXS profiles, as depicted in Fig. S8, the blend with SVA treatment shows relatively weak peaks at $q \approx 1.3 \text{ \AA}^{-1}$ from PC₇₀BM aggregation and $q \approx 1.7 \text{ \AA}^{-1}$ from DRCN5T π - π stacking, suggesting that the blend is slightly less ordered as compared to the blends with TA and TA-SVA treatments. In addition, the dependence of the (010) π - π stacking coherence length under different annealing conditions is plotted in Fig. S9. It is apparent that SVA induces lower molecular ordering than TA and TA-SVA. Again, this suggests distinctly different thermodynamic driving forces for these two post-treatment technologies.

RSOXS is a complementary tool to GIWAXS to probe mesoscale domains, including domain spacing, relative domain purity with high spatial resolution and chemical sensitivity. Fig. 3 illustrates the Lorentz corrected circular RSoXS profiles of several blends. The scattering energy is chosen as 284.2 eV to enhance the material contrast between electron donor-rich domains and electron acceptor-rich domains [21,25,44]. From the scattering profiles of the TA blend in Fig. 3a we observe only slight variations to the non-annealed film, and, in turn, similar mesoscale phase separation. Interestingly, the annealing processes including SVA (i.e., TA-SVA and SVA) shift the dominant scattering peak towards low- q , implying that larger domains are formed after SVA. The relative

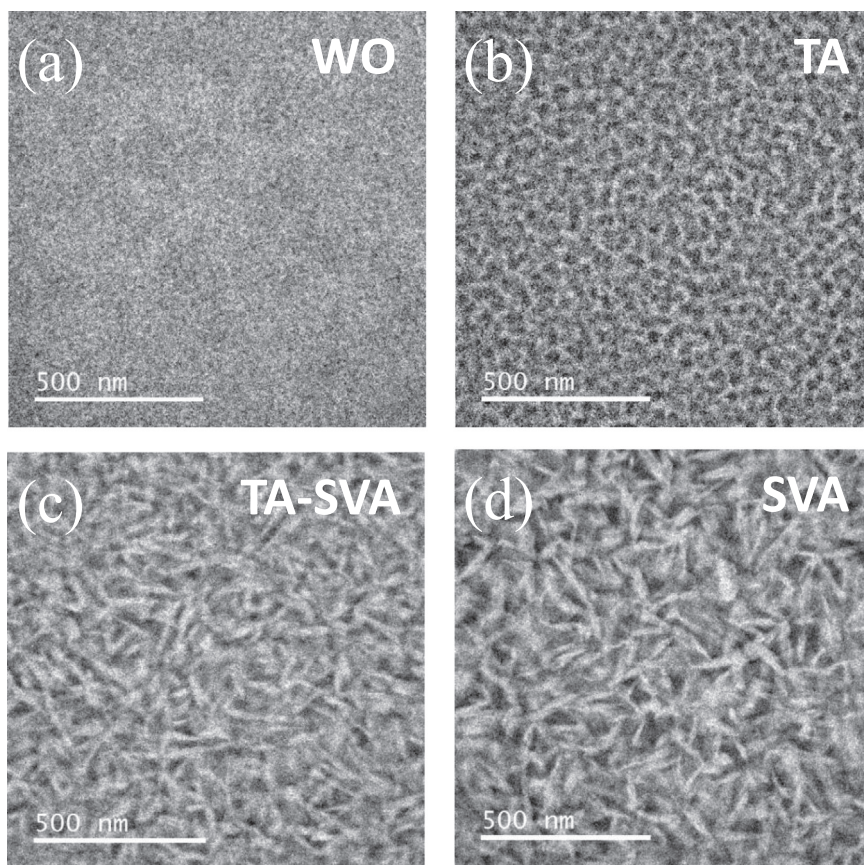


Fig. 2. (a–d) Elemental maps of sulfur based on energy filtered TEM (EFTEM) imaging of the blends based on (a) WO, (b) TA, (c) TA-SVA and (d) SVA treatments. White regions are sulfur-rich (indicating donor molecules), while black regions correspond to carbon-rich regions (compare Fig. S5 in SI, primarily from PC₇₀BM). The scale bar represents 500 nm in all EFTEM images.

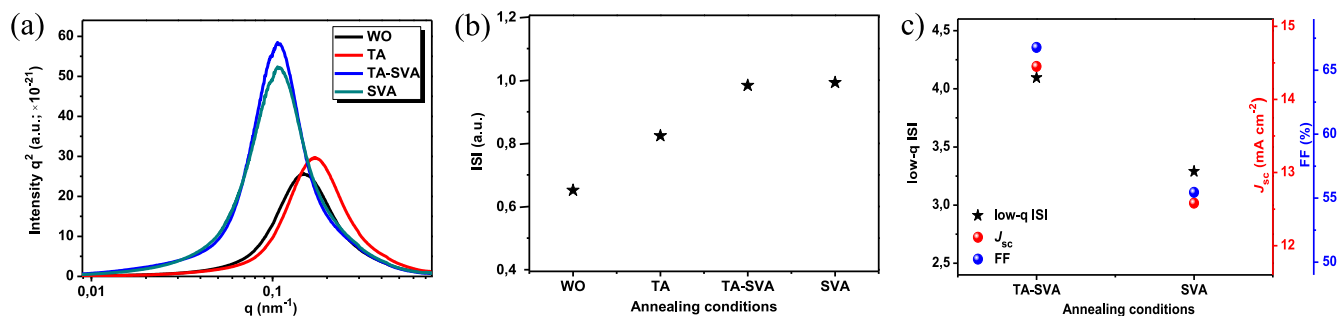


Fig. 3. (a) Lorentz-corrected and thickness normalized circular RSoXS profiles of DRCN5T:PC₇₀BM films with different processing conditions. All data were taken under 284.2 eV, which maximizes inter-domain scattering and eliminates fluorescence background. (b) Total integrated scattering intensity (ISI) of the related blends. (c) The J_{sc} and FF are over-plotted with low-q ISI as a function of different annealing conditions. Note: low-q ISI represents the integrated scattering intensity of the low-q fit peak. The fitting procedures are depicted in Supporting Information.

domain purity, which has been found to impact recombination processes, [8,45] is proportional to the square root of the total integrated scattering intensity (ISI, as illustrated in Fig. S10). The total ISI of different blends are plotted in Fig. 3b, [8,45–47] highlighting that all annealing processes contribute towards higher domain purity and better phase separation as compared to that of non-annealed films. Note that TA alone enhances domain purity to lesser extent in contrast to SVA based treatments inducing a stronger low q peak [21]. Furthermore, the RSoXS profiles are also quantitatively compared with images in real space. The power spectral density (PSD) of AFM phase images, rather than height images match well with 284.2 eV RSoXS results (see Fig. S11), indicating that these phase images reflect the material contrast between donor-rich domains and acceptor-rich domains within the bulk of the blends [47,48].

From the device performance as shown in Table 1, TA and SVA resulted in similar FF and current densities. However, the total ISI of TA and SVA blends are revealed different from each other. Hence, multi-peak fitting (MPF) is implemented to all RSoXS profiles to extract information regarding domain spacing and domain purity at multi-length scales. The MPF results are shown in Fig. S12. Scattering profiles of non-annealed and TA films can be fit by two peaks (denoted as middle- q and high- q), while the films with TA-SVA and SVA treatments require a three peak fit (denoted as low- q , middle- q and high- q in Fig. S13). Two interesting observations are made: On the one hand, SVA treatment leads to the formation of a low- q peak. On the other hand, the various annealing processes do not impact the position of each fitting peak (i.e. domain spacing). ISI of the low- q peaks under different annealing processes is plotted, together with J_{sc} and FF in Fig. 3c. J_{sc}

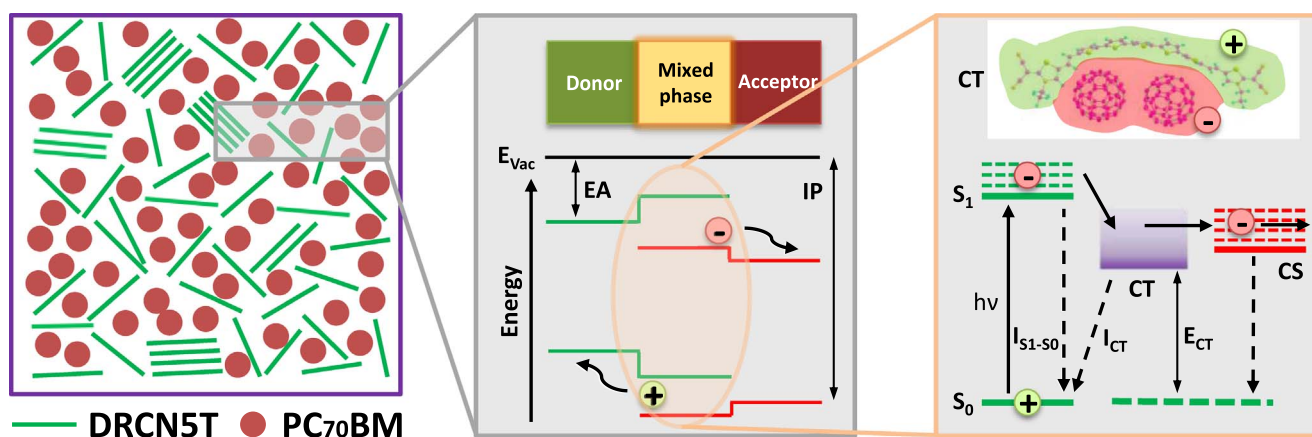


Fig. 4. Schematic representation of the small molecule-fullerene BHJ morphology illustrating potential shifts in the local energetic landscape due to presence of pure donor and acceptor as well as mixed phases, following the reported models [8,12]. The left diagram shows the morphological characteristic of DRCN5T:PC₇₀BM film. The middle (energy band diagram) and right (the related charge separation dynamics by electron and hole transfer) panels show bimolecular recombination in mixed region due to charges trapped in such aggregates if they are insufficiently connected. Block arrows in the middle and right panels indicate the direction of the external applied electric field. E_{vac} : energy reference level (vacuum); EA: electron affinity; IP: ionization potential; CS: charge separation.

and FF correlate fairly well with the low- q ISIs. It is important to note that from Fig. S11 the low- q peak correspond to a domain spacing of ca. 60 nm, which is smaller than film thickness. A relatively higher domain purity of the low- q peak is expected to promote charge transport as well as to suppress recombination [8,45]. In summary, several different annealing conditions evoke well-ordered microstructures, as observed by AFM, EFTEM, GI-WAXS and RSoXS. As expected, better performance is seen for films with larger and more pure domains as well as higher crystallinity. However, we also note that the good performance of the TA films is not directly evidenced by the methods so far.

2.3. Optical, electro-optical and electronic characterization

The choice of processing conditions enables changing the D/A interfacial area and fine tuning the molecular ordering. This, in turn, is likely to cause changes in the fundamental photo-physical processes as depicted in Fig. 4 [8,21]. Next, we investigated the photo-excited states and charge carrier dynamics in these blends by photoluminescence (PL), electroluminescence (EL), time-resolved photoinduced absorption spectroscopy (PiA) and space charge limited current (SCLC) measurements.

In particular, we recorded PL spectra under 488 nm photo-excitation (Fig. S14) to understanding the impact of the processing conditions on the exciton dissociation [49,50]. A strong quenching of the PL intensity is observed in the non-annealed film when compared with films of pristine DRCN5T. This comes as a result of the dominantly amorphous intermixing BHJ. Upon annealing, the PL intensity is partially recovered proportionally to the increase in phase purity and domain size (Fig. S14b). The recovery of PL is strongest for the TA-SVA films, which is in excellent agreement with the device findings. We recently reported the Figure of Merit (FoM) concept to probe the molecular quality of the D/A interface [49]. The quality of the D/A interfacial area can not be assessed by the microstructure investigation methods, but is essential for changes in exciton dissociation, carrier generation and recombination mechanisms (see Fig. 4) [8,21]. Thus, we applied the FoM concept to gather insights into the relation between the above-mentioned microstructures and their effects on exciton dissociation and carrier dynamics in DRCN5T:PC₇₀BM.

In order to determine the FoM, the spectra from Fig. S14b are deconvoluted for their DRCN5T singlet emission and their charge transfer emission (CTE) (Fig. S14c and S14d, respectively). These deconvoluted spectra allow us to calculate a FoM, which is

determined by dividing the relative intensity of CT emission (I_{CT}) by the relative intensity of singlet emission (I_{S1-S0}) [49]. It was previously demonstrated that an enhanced FOM_{PL} relates to a better solar cell performance. The FoM concept was proved to be most beneficial for developing suitable optimization recipes, including ink formulation, additives or post-processing treatments [49]. For all of our films, we find excellent proportionalities between FOM_{PL} and J_{sc} (Fig. 5). Such correlations are even more remarkable as PL measurements are contactless and, therefore, do not consider electrical contacts, carrier extraction limitations, or resistance losses. From these results, we conclude that the origin of the enhanced performance of TA-SVA cells does not originate from the microscopic film features but rather from the quality of the molecular interfaces between the electron donor and the electron acceptor. In line with this concept is the expectation that the performance of the single composites differs in their generation/recombination rate rather than in their extraction efficiency. A series of EL measurements with devices containing pristine DRCN5T films and its blends (Fig. S15a and S15b, respectively) confirms the insight gained from PL. In particular, the FOM_{EL} values are in excellent agreement with the J_{sc} trend (Fig. 5). In short, the FoM ratio I_{CT}/I_{S1-S0} from PL as well as EL corroborate that the enhanced performance of the TA-SVA is based on an improved

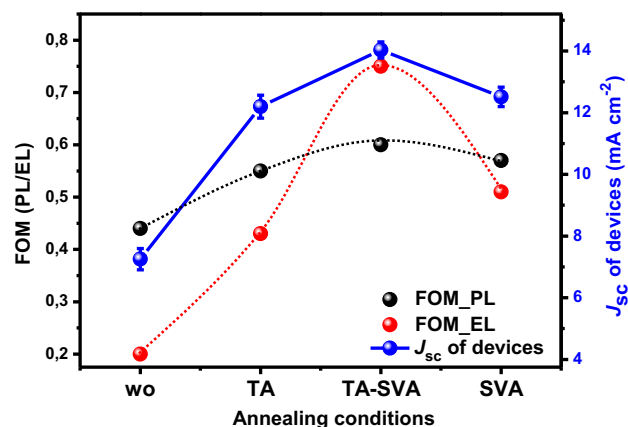


Fig. 5. (a) The FOM_{PL}, FOM_{EL} and J_{sc} trends based on films without annealing treatment (WO), with TA, TA-SVA and SVA treatments. PL, EL and J - V characteristics of the films were measured from the same active layer. The lines are guides to the eye; the symbols are the measurement points.

generation/recombination behavior originating from improved molecular ordering.

Time-resolved PIA spectroscopy is particularly suited to monitor excited state features and carrier kinetics in thin films. In particular, transient spectra with time delays in the ns to μ s regime give insights into the geminate or non-geminate charge recombination dynamics of carriers in organic solar cells [51]. To facilitate the spectral assignment in the PIA spectra (Fig. S16b–f), we performed a preliminary spectroelectrochemical (SEC) characterization. To this end, differential absorption spectra were recorded at a potential, where the one electron oxidation of DRCN5T sets in [31]. Upon electrochemical oxidation of DRCN5T, bleaching of the ground state absorption band at 410 and 605 nm accompanied by a new absorption band at 475 and 725 nm extending up to 1200 nm are observed. These features are assigned to the absorption features of the DRCN5T hole polarons (DRCN5T^{•+}) (Fig. S16a). Laser photoexcitation of DRCN5T and of the different blends at 610 nm gives rise to photoinduced absorption at 488 nm, which is correlated with a higher DRCN5T singlet-singlet transitions, and features between 900 and 1400 nm, which are ascribed to the DRCN5T^{•+} polarons. DRCN5T photobleaching is recorded at 425 nm as well as at 710 nm due to $S_1 \rightarrow S_2$ (Fig. S16b–f). The non-annealed films and the DRCN5T in dichloromethane show an additional photobleaching at 660 nm. Due to the molecular order, this peak is much weaker in the annealed films. The carrier recombination dynamics are probed at 1000 nm and best described by a bi-exponential fit with τ_1 and τ_2 (Fig. S17). We may ascribe the shorter recombination time τ_1 in the ns regime to geminate recombination and the longer time τ_2 in the ns- μ s regime to non-geminate carrier recombination. As geminate recombination is not dominant in these high performance devices, we focus the discussion on τ_2 , which showed an enhancement from 11 to 60 ns after TA-SVA treatment (Fig. 6a and Table 2). Time-resolved PIA strongly underpins the findings from FoM studies and, highlights the fact that the enhanced device performance relates mainly to slower recombination as a consequence of the improved molecular ordering.

Finally, we determined the hole and electron only mobilities from SCLC measurements for representative thin film devices. The charge carrier mobilities are measured by analyzing the J - V characteristics of single carrier devices in dark conditions (Fig. 6b and Table 2). The fitting results determined by the Mott-Gurney law [21] illustrate that the hole and electron mobilities rise sharply for all annealing treatments. The average hole and electron mobilities of non-annealed films are 5.26×10^{-6} and

Table 2

Geminate and non-geminate recombination lifetimes (τ_1 and τ_2 , respectively) in ns and their fitting factor A as well as summary of the fitting data for hole-only devices and electron-only devices based on different processing conditions.

Processing conditions	τ_1 (ns)/ A1	τ_2 (ns)/ A2	Ave. mobility ^a (μ_h , $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Ave. mobility ^b (μ_e , $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
WO	1.1/ 0.60	11/ 0.40	5.26×10^{-6}	1.20×10^{-5}
TA	7.4/ 0.64	51/ 0.36	5.37×10^{-3}	3.11×10^{-4}
TA-SVA	7.7/ 0.61	60/ 0.39	8.59×10^{-3}	3.92×10^{-4}
SVA	5.7/ 0.67	48/ 0.33	5.26×10^{-3}	1.47×10^{-4}

^a An average value based on six hole only devices with various processing conditions, the structure of hole only device is ITO/PEDOT/Semiconductor layer/MoO₃/Ag.

^b An average value based on six electron only devices with various processing conditions, the structure of electron only device is ITO/ZnO/Semiconductor layer/Ca/Ag.

$1.20 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. The TA-SVA film showed the best hole and electron mobilities of 8.59×10^{-3} and $3.92 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. All the other annealed films show comparable results. Note that TA and TA-SVA films exhibit slightly higher hole and electron mobility as compared to the other two annealed films. Although these differences in mobility will not likely impact the solar cell performance, we note that this trend is consistent with the enhanced ordering of the electron donor and acceptor phases as discussed above. The results of the FoM analysis coupled with the charge carrier dynamic analysis finally complement the results of the morphology characterizations and give detailed insight into subtle mechanisms being responsible for device improvement as a function of processing conditions.

2.4. Device stability

We finally explored the short-time and long-time light-induced stability of the differently annealed films. Fig. S18 shows the relative change and statistics of the recorded photovoltaic parameters of these five solar cell stacks. Among the annealed systems, SVA film shows the poorest stability with a light-induced PCE degradation of 17% (down to 83%) after 110 h, mainly resulting from V_{oc} and FF losses. Mainly FF losses lead to ca. 11% degradation

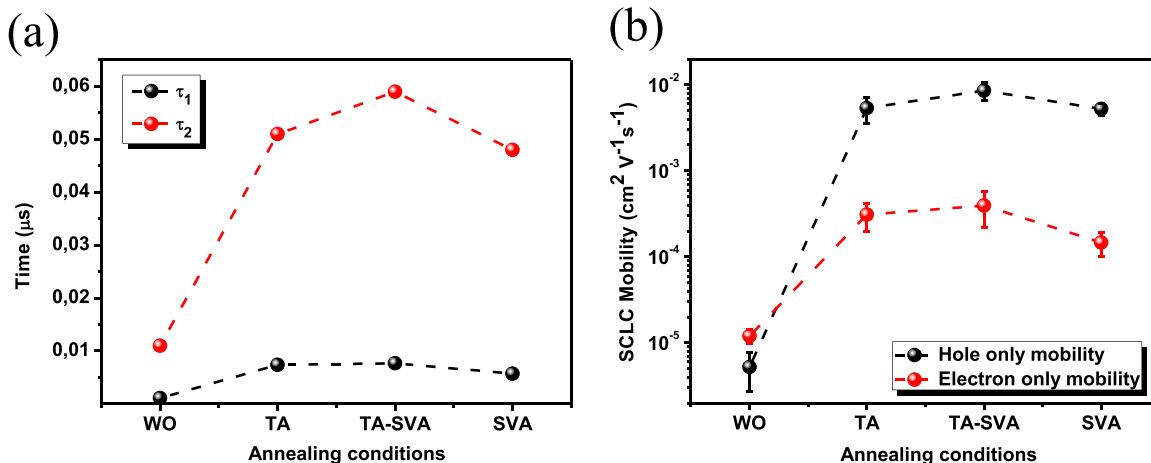


Fig. 6. (a) Geminate τ_1 and non-geminate τ_2 recombination lifetimes determined by time-resolved PIA measurements. (b) Hole and electron only mobilities measured in single carrier diodes obtained from these films. For the SCLC measurements, the values were made on six devices of each type, and the error bars represent plus or minus 1 standard deviation from the mean.

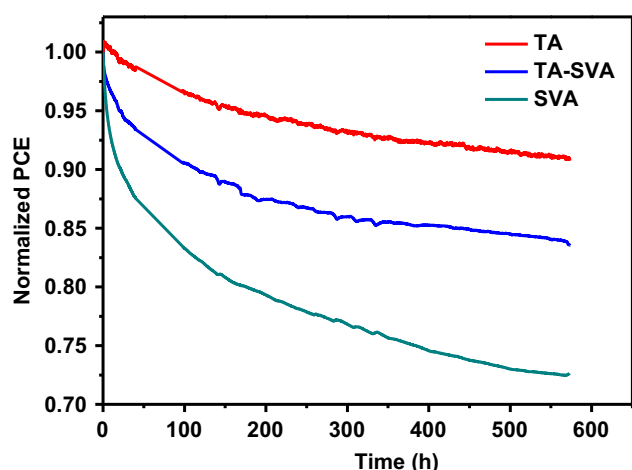


Fig. 7. Variation of normalized average PCE losses over illumination time for the encapsulated devices based on TA, TA-SVA and SVA treatments.

for the TA system and 14% for the TA-SVA system. The TA and TA-SVA systems are more stable under illumination within 110 h as compared to the SVA system. At this point we suggest to correlate the higher light stability to the enhanced donor crystallinity. Note that the enhanced stability of the non-annealed film is an artefact due to a light induced thermal post treatment effect (Fig. S19). The TA, TA-SVA, and SVA devices with PCEs over 6% are further tested under the same conditions for longer times. TA-SVA and SVA devices show a PCE degradation down to 84% and 73% within 580 h, respectively, while TA device showed the lowest PCE loss down to ca. 91% during the same period (Fig. 7). In details, V_{oc} losses are rather negligible for TA and TA-SVA films (between 2–3%, Fig. S20), but significant for SVA system with V_{oc} losses of ca. 8%. Overall, the TA devices are most stable under illumination within 580 h. Nevertheless, all the systems give rise to a continuous J_{sc} loss during illumination. Notably, the degradation behavior depends strongly on the post-processing treatment while all other factors are the same. Further studies are required to understand whether this can be assigned to a delayed burn-in effect caused by microstructural ordering or whether this is a true signature of light induced degradation.

3. Conclusion

Solar cells with DRCN5T:PC₇₀BM blends are post-annealed by various conditions and tested in terms of their photovoltaic efficiencies and stabilities. Under the appropriate annealing conditions, the DRCN5T:PC₇₀BM system can achieve high efficiencies of up to 9% due to the ability to precisely fine-tune the nanoscale morphology. As-cast films show almost no phase separation, but a rather well-mixed blend of donors and acceptors. This results in enhanced recombination and significantly limited charge carrier transport, leading to both a low J_{sc} and low FF, and thus a relatively low PCE of 3.57%. TA-SVA treatment leads a drastic increase in performance with a PCE of 8.97%. While the other annealed devices exhibit quite comparable PCEs of 6.73% for TA treatment and 6.64% for SVA treatment, respectively. The different photovoltaic parameters implied that the composite undergoes a plurality of microstructure modifications during the various annealing conditions, which were documented by absorption spectroscopy, AFM, EFTEM, GIWAXS and RSoXS measurements. In addition, optical, electro-optical and electronic characterization was performed to shed light on the carrier dynamics, which finally could explain the difference between the TA-SVA and the differently annealed devices. Most interestingly, the FoM analysis, as derived from

spectrally resolved PL and EL measurements fully predicted the distinct device properties as a function of annealing.

We summarize this extensive study by highlighting the following facts: (i) the delineation of the interrelationships between well-defined BHJ microstructures and their photovoltaic properties is consistent over a wide range of distances. (ii) optical and especially electro-optical properties do probe the complete microstructure in its whole complexity over all size regimes. However, both methods are required to correlate lateral features with temporal processes. This very extensive investigation yielded two further, major insights: (iii) the light-induced stability in BHJ devices is directly correlated to the microstructure. This was already suggested in our previous reports on burn-in studies and could be uniquely proven in this manuscript. Finally, (iv) the FoM is a surprisingly unique tool to assess the quality of a BHJ microstructure over all time and length domains. Since the FoM is a contactless method, it is exceptionally qualified to quantitatively evaluate processing strategies in real time.

4. Experimental section

4.1. Materials

DRCN5T was provided by Prof. Yongsheng Chen and PC₇₀BM was purchased from Nano-C (Westwood, MA, USA). The chloroform solvent used in device fabrication process was purchased from Alfa Aesar.

4.2. Device fabrication and characterization

The solar cell and single carrier devices were fabricated on ITO coated glass substrates, and subsequently processed and characterized in ambient atmosphere. Pre-structured ITO coated glass substrates (as obtained from Osram) were subsequently cleaned in acetone and isopropyl alcohol for 10 min each. After drying, the substrates were bladed with 40 nm PEDOT: PSS (Heraeus, Clevis P VP.Al 4083). For electron only devices, 40–50 nm ZnO layer was doctor-bladed on top of ITO coated glass prior to the active layer. The DRCN5T bulk films (app. 120 nm) were spin-coated in ambient air from the solutions of DRCN5T: PC₇₀BM (1:0.8, wt%) in chloroform. Subsequently, the active layers were further processed with various processing conditions. For the TA treatment, the DRCN5T: PC₇₀BM blend film as cast was heated on a hotplate at 120 °C for 10 min in glovebox. For the SVA procedure, the samples were loaded in the middle of Petri dish containing 120 μ L chloroform for 60 s. The detailed SVA procedure can be found in Ref. [21]. Note that the annealed blend films should cool to room temperature for the relevant TSA treatments. And the annealed samples were removed to the glovebox for evaporating cathodes. For solar cell and electron only devices 15 nm Calcium (Ca) and 100 nm Aluminum (Al) were thermally evaporated at a base pressure below 10^{-6} mbar through shadow masks to form an active area of 10.4 mm². Hole only devices had 10 nm MoO₃ and 100 nm silver (Ag) evaporated through shadow masks. The current-voltage characteristics of the solar cells were measured under AM 1.5 G irradiation of an OrielSol1A Solar simulator (100 mW cm⁻²). The light source was calibrated by using a silicon reference cell. The EQE were measured by an Enli Technology (Taiwan) EQE measurement system.

4.3. Thin-film characterizations

The morphology was firstly investigated by AFM (Veeco Model D3100, tapping mode). The active layers for the EFTEM investigations were prepared as plan view specimens. Therefore active

layers with a thickness of 50 nm were deposited on glass using spin-coating under ambient conditions. To float off the active layer, the sample was put into a vessel with distilled water, where PEDOT:PSS dissolved, and the active layer was transferred to a Cu TEM supporting grid. The TEM investigations were performed using an FEI Titan Themis³ 300 TEM with a high brightness field emission gun (X-FEG) operated at 200 kV equipped with a high resolution Gatan Imaging Filter (GIF Quantum) used for EFTEM. Elemental maps were calculated using the three-window-technique. GIWAXS and RSoXS measurements were performed at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. GIWAXS, RSoXS, and relevant NEXAFS reference spectroscopy measurements were performed at beamline 7.3.3. [52] beamline 11.0.1.2. [53] and beamline 5.3.2.2, [54] respectively. In GIWAXS measurement, X-ray beam with 10 KeV was incident at a grazing angle of 0.13°, which maximized the scattering intensity from the bulk of the samples. In RSoXS measurement, samples are investigated under high vacuum (1×10^{-7} Torr) in order to reduce the absorption of soft X-rays in air.

4.4. Optical and electronic measurements

The optical investigations of these thin films were carried out by UV–VIS–NIR spectrometer (Lambda 950, from Perkin). The thicknesses of the thin films were measured by a profilometer (Tencor Alpha Step). PL data were collected using a Perkin-Elmer LS55 Fluorescence Spectrometer. Unless otherwise stated, the PL excitation wavelength was set to 488 nm. The PL emission of the films was dispersed by a 600 lines/mm grating monochromator (HRS-2) and detected by a Germanium (Ge) detector (ADC 403 L) through lock-in technique. The fluorescence spectrum was corrected for the optical density of the sample at the excitation wavelength, and for the detection sensitivity of the Ge detector. The EL measurements were performed by using a chopper and applying a forward bias supplied by an external current/voltage source through the devices which have an active area of 10.4 mm². The emitted light then collected by a monochromator and detected by liquid-nitrogen cooled Ge detector. The spectrum was recorded by a standard lock-in technique. The system was wavelength calibrated. SEC experiments were performed with a home-built cell and a three-electrode setup. A drop-casted DRCN5T on ITO slide was the working electrode. The counter electrode was a platinum wire, and a silver wire as quasi reference electrode was utilized. Potentials were applied and monitored with a MetrohmPGstat 101. The results are finally shown as differential spectra, that is, the difference between a spectrum with and without an applied potential. The spectra were recorded with a UV/vis/NIR spectrometer Cary 5000 (VARIAN). Nanosecond photoinduced absorption spectroscopy measurements were performed upon laser photolysis using a commercial EOS setup (Ultrafast Systems LLC to measure transient absorption dynamics in the ns–μs time regimes. An optical parametric oscillator (OPO, Rainbow VIR, Opotek/Quantel, (5 mJ/pulse) pumped by the third harmonic (355 nm) of a Nd/YAG laser (Brilliant, Quantel) was utilized for the output. The optical detection was based on a pulsed (pulser MSP 05, Müller Elektronik-Optik) xenon lamp (XBO 450, Osram), a monochromator (Spectra Pro 2300i, Acton Research), a R928 photomultiplier tube (Hamamatsu Photonics), or a fast InGaAs photodiode (Nano 5, Coherent) with 300 MHz amplification, and a 1 GHz digital oscilloscope (WavePro7100, LeCroy). Single carrier devices were fabricated and the dark current-voltage characteristics measured and analyzed in the space charge limited regime by a previously reported method [21].

4.5. Light-induced degradation testing [35]

we performed light-induced degradation experiments with one sun equivalent illumination intensity for ca. 110 or 600 h on the investigated systems based on various processing conditions. The solar cells were fabricated in a glovebox and aged under high vacuum, excluding the well-known effects of oxygen degradation from our experiments. It is important to operate all devices at temperatures below their glass transition temperature (T_g) to avoid thermally induced morphological changes. We minimized the thermal degradation by using white light LED's. To exclude any other influence of the experimental conditions on the results, all the systems were aged in the same test side by side. The investigated solar cells were built in a standard device architecture with PEDOT:PSS and Ca/Al contacts. Note that the trends of two separated tests for these systems are consistent.

Author contributions

J. M. and C. J. B. conceived the idea and designed the experiments. J. M. fabricated the solar cells and characterized the film and device properties using UV–vis absorption spectra, AFM, PL, EL and SCLC. X. C. J. measured and analyzed GIWAXS and RSoXS data. V. S. measured and analyzed PiA data. B. K. and X. W. designed and performed materials synthesis. T. H. performed stability measurement. S. F. carried out the EFTEM analysis. J. M., X. C. J. and V. S. prepared the manuscript. All authors discussed the results and commented on the manuscript. E. S., D. M. G., Y. S. C., H. A. and C. J. B. supervised the project and revised the manuscript. C. J. B. also provided excellent suggestions and comments to improve this manuscript.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2016.08.047>.

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