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Reduced Bimolecular Recombination in Blade-Coated, High-Efficiency, Small-Molecule Solar Cells

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Abstract

To realize the full promise of solution deposited photovoltaic devices requires processes compatible with high-speed manufacturing. We report the performance and morphology of blade-coated bulk heterojunction devices based on the small molecule donor p-DTS(FBTTh₂)₂ when treated with a post-deposition solvent vapor annealing (SVA) process. SVA with tetrahydrofuran improves the device performance of blade-coated films more than solvent additive processing (SA)

Author contributions

HWR performed device optimization, SE X-ray scattering analysis, SE & AB performed impedance analysis, AH TEM analysis. LR, DD, and CS participated in X-ray data acquisition. All authors contributed to manuscript preparation.

with 1,8-diiodooctane. In spin-coating, SA and SVA achieve similar device performance. Our optimized, blade coated, SVA devices achieve power conversion efficiencies over 8 % and maintain high efficiencies in films up to ≈ 250 nm thickness, providing valuable resilience to small process variations in high-speed manufacturing. Using impedance spectroscopy, we show that this advantageous behavior originates from highly suppressed bimolecular recombination in the SVA-treated films. Electron microscopy and grazing-incidence X-ray scattering experiments show that SA and SVA both produce highly crystalline donor domains, but SVA films have a radically smaller domain size compared to SA films. We attribute the different behavior to variations in initial nucleation density and relative ability of SVA and SA to control subsequent crystal growth.

Keywords

Solvent vapor annealing; X-ray diffraction; Impedance spectroscopy; Small molecule; Bulk-heterojunction

Introduction

Organic electronics based on π -conjugated polymers and small molecules are of broad and current interest, as they promise flexible, low weight and low cost devices.[1–3] Steady development of better materials in combination with sustainable manufacturing practices utilizing non-toxic, earth-abundant materials and low thermal budgets make organic photovoltaic (OPV) devices competitive with other thin film technologies based on environmental considerations.[4, 5] Peak power conversion efficiencies (PCE) of single junction devices exceed 11 % [6] and the first products have been launched in the market.[7] Currently, the most successful OPV devices are based on the bulk heterojunction structure, [8, 9] where exciton dissociation is facilitated by high internal surface area due to the self-assembled nanoscale separation of donor- and acceptor-rich phases. Of utmost importance is the understanding and control of this self-assembly, as the film morphology determines the device performance. Naively contradictory goals must be achieved in a functional bulk heterojunctions (BHJs). High local order is typically desired, to support good transport of the separated charges. However, both ripening of ordered domains must be avoided to support high surface area and extremely fine mixing must be avoided to support continuity of all regions to the contacts. High performance BHJ structures are generally non-equilibrium and extremely sensitive to processing conditions. This can lead to difficulties when scaling systems demonstrated by spin-coating to high volume manufacturing.[10]

Early successful BHJ devices were based on polymer donors and fullerene acceptors[11, 12] as the connectivity of the polymer facilitates self-limiting phase separation. However purity and polydispersity are difficult to control for polymers, so much interest has been applied to the development of small molecule based BHJs.[13] 7,7'-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(6-fluoro-5-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole), p-DTS(FBTTh₂)₂ (Figure 1), has emerged as a promising OPV material. Spun-coat BHJ devices processed with a high boiling point solvent additive (SA), 1,8-diiodooctane (DIO), result in PCE over 7 % in both conventional and inverted architectures.[14–18] However, the system has tight processing tolerances: the additive

optimizes at a precise, small loading (0.4%), and good devices are only produced in a narrow (90 to 110) nm thickness range.

Solvent additives (SA) have become common-place in the optimization of the BHJ nanoscale phase separation and local order (crystallinity) of the active layer components. [19–21] Recently, a quite complete picture of the influence of additives in the prototypical p-DTS(FBTTh₂)₂ system was drawn, via combined in-situ grazing-incidence X-ray diffraction (GIXD) and grazing-incidence small angle X-ray scattering (GISAXS) for both blade coating [22] and spin coating.[23] It was found that the additive both induces increased crystallinity by plasticizing the mixed amorphous phase resulting from the rapid drying and coarsens the spatial scale of phase separation by controlling the nucleation density via solvent quality. Small molecule solar cells can exhibit excessive crystal growth, film coarsening and eventual device failure if the additive concentration or coating conditions deviate only slightly from the optimum case. An alternate approach to morphology control with potentially higher reproducibility is solvent vapor annealing (SVA). Solvent vapor annealing has been previously used to enhance the performance of OPVs for both polymeric [24–29] and small molecule donor systems [30–37]. Miao et al. [33] demonstrated > 8 % PCE based on 100 nm thick p-DTS(FBTTh₂)₂: PC₇₁BM spun-coat films via SVA with a good solvent (dichloromethane, DCM) for the small molecule donor. Sun et al. have suggested that marginal solvents are optimal for SVA [31] and recently demonstrated that for a benzodithiophene terthiophene rhodamine (BTR) based small molecule BHJ efficiencies > 9 % PCE could be achieved via SVA with a moderate solvent, tetrahydrofuran (THF).[36] Importantly, in the BTR system, high performance was maintained for thick (> 200 nm) films.

It is generally accepted that solvent deposition based manufacturing is facilitated by thickness tolerant films [38] that can be coated at >200 nm. Thick active layers additionally enable better light absorption. Detailed device modelling [39] indicates that a high fill factor in thick films requires both high mobility and reduced (relative to the Langevin limit) bimolecular recombination. Experimental characterization of systems that achieve high fill factor at > 200 nm have found significantly suppressed bimolecular recombination.[40–43] Bimolecular recombination is also critical in establishing the open circuit voltage of a device.[44]

Here we report on the results of optimization of blade-coated p-DTS(FBTTh₂)₂:PC₇₁BM BHJ films with either the solvent additive DIO or SVA with the moderate solvent THF. We find SVA significantly superior to SA processing. Detailed morphology studies suggest a comparably higher nucleation density in blade-coated, as-cast films that limits characteristic domain sizes during SVA to a much more preferable size, compared to the SA processed BHJ. Detailed electrical characterization with impedance spectroscopy indicates that the SVA optimized film exhibits significantly suppressed bimolecular recombination, relative to the Langevin limit, supporting optimal performance for films in excess of 200 nm thickness.

Results & Discussion

Devices

All results are reported for films blade-coated with a low-angle-blade-coating system described previously.[45] We recently demonstrated excellent correlation between polymer BHJ films coated with the system and films coated via slot-die on a flexible web.[46] Based on established spin-coating protocols, we utilized DIO as a solvent additive. DIO loading studies indicate that 0.3 % is optimal for the blade-coat processes. The DIO SA films are compared to additive free films treated via SVA with THF post deposition. Shown in Figure 2 are representative device characteristics for thin (100 nm) and thick (200 nm) films from various processes. We found it difficult to achieve typical spun-coat performance, (7 to 8) % PCE, via blade-coating with the solvent additive. However, the SVA treated, blade-coated films reproduce the maximum PCE achieved by Miao for spun-coat, SVA treated films, and additionally are able to maintain high PCE in significantly thicker (>200 nm) active layers than reported with spin-coating.

Film Morphology—In the following, we thoroughly investigate structural differences between thick SVA devices and devices coated from SA based solutions. The morphology of spun-coat films has been extensively studied.[22, 23, 47] It is well established that as-cast, additive free films are characterized by very low donor crystallinity and fine, nearly homogeneous phase mixing. Blade-coat, additive-free films are similarly disordered, see Fig. S2 and Ref [22]. Shown in Figure 3 are grazing incidence X-ray diffraction (GIXD) results for a SVA, blade-coated film.

In agreement with earlier reports on spun-coat BHJs, a highly edge-on texture with up to 3 orders of the (001)-diffraction are observable suggesting high local order. Similar improvement in order is found for the DIO processed films (Fig. S2). Compared to DIO SA films, the SVA films exhibit a slightly increased contribution from randomly oriented crystals indicating increased bulk nucleation (Fig. S2 and S3). All films show signs of polymorphism, evidenced by splitting of the high order diffraction features, with variations in the relative fraction of each polymorph that are uncorrelated with both the total degree of crystallinity and corresponding solar cell device performance. Additionally, in all cases a pronounced angle-of-incidence dependence of the relative diffraction intensity of the p-DTS(FBTTh₂)₂ (001)-series compared to the amorphous PC₇₁BM halo is seen, see Fig. S6, suggesting the presence of a thin, p-DTS(FBTTh₂)₂ rich, surface segregation layer. Complementary surface sensitive NEXAFS spectra indicate this is a highly phase pure layer, see Fig. S6 for further details.

The relative degree of crystallinity (rDOC) was obtained from the integration of the (001)-pole figures. Following earlier reported procedures, the data was corrected to account for geometric limitations of the grazing incidence geometry that lead to a missing “wedge” in momentum space and to account for air-scatter.[48, 49] The obtained rDOC values for each of the three conditions are also shown in Figure 3. We find a higher degree of crystallinity for the SVA film relative to the DIO SA film.

The real-space morphology of the films was studied by atomic force microscopy (AFM) height images and low-angle annular dark field (LAADF) scanning transmission electron microscopy (STEM) images, Figure 4. The main difference between the different processing conditions lies in the displayed characteristic length scales. The as-cast film shows little domain contrast suggesting a well intermixed donor and fullerene. Consistent with earlier studies on both spun- and blade-coated thin films, the DIO processed films reveal large rice grain or fiber-like features at the film surface.[11, 47, 50] In contrast to this the SVA film shows a radically finer morphology.

To better quantify the morphology, GISAXS data was used to determine the characteristic

length scales and the integrated scattering intensity ($ISI = \int_{q_{\min}}^{q_{\max}} I(q) \cdot q^2 dq$), an approximate to Porod's invariant and measure for phase purity.[51–53] Figure 5 shows examples of GISAXS results, both $I(q)$ and Lorentz-weighted plots (Iq^2), for 250 nm thick BHJs cast without DIO prior and after solvent annealing as well as the SA DIO case. Table 1 summarizes the obtained characteristic length scales from fits of the GISAXS data (see

Figure 5a) to a Teubner-Strey [54] correlation function, $\gamma(r) \propto \frac{\sin(2\pi r/d)}{2\pi r/d} \exp(-r/\xi)$, with a constant offset to account for incoherent background and a power-law term to account for low- q surface roughness. We report both the long period (d) and the correlation length (ξ). In the SA DIO case, compared to the as-cast non-DIO containing BHJ, the ISI is increased, in agreement with recent studies aiming to understand the effect of DIO on phase purity and solar cell performance in thin p-DTS(FBTTh₂)₂: PC₇₁BM films.[22, 55, 56] The increase in purity has an associated significant increase in the long period d and slight increase in correlation length ξ , indicating a coarsening of the morphology and possibly a slight reduction in polydispersity. As in an earlier study [22], we interpret the observable long period as the fiber-width or fiber-to-fiber distance. The long fiber-axis is on the order of several hundred nm, see AFM and TEM images above, and could not be observed due to the low- q experimental limit of $\approx 2\pi/(150 \text{ nm})$. Both the as-cast and DIO SA scattering functions are in excellent agreement with RSoXS results for spun-coat films.[57] See the SI for a detailed discussion. Solvent vapor annealing of the BHJ cast from a non-additive containing solution leads to the highest observable ISI of the three cases, while avoiding the significant coarsening observed for the SA case. The $\approx 46 \text{ nm}$ length scale of the SVA films is expected to be favourable for charge separation, consistent with the higher short circuit current density J_{sc} of the SVA films.

Electrical Characterization—To understand the superior device performance of the 250 nm thick solvent vapor annealed BHJs in more detail and elucidate the relationship between the morphology and charge carrier lifetime and mobility, we conducted impedance measurements on the solvent vapor annealed BHJ and the BHJ processed from the solution containing 0.3% DIO. Figure 6 shows selected Nyquist-plots of the obtained complex impedance, Z , for the SVA BHJ and the DIO SA BHJ under illumination equivalent to 1 sun and under dark conditions. Unlike for thin films where the reported reactance, $Im(Z)$, vs. resistance, $Re(Z)$, consists of one arc (attributed to charge carrier generation and

recombination) and a small high frequency “foot” (attributed to charge transport), the DIO SA BHJ exhibits a pronounced double arc behaviour when forward biased.

In the following, we will analyse the impedance data of the SVA treated device in detail using an equivalent circuit model consisting of two RC elements representing the generation of charges within the device (chemical capacitance C_μ and recombination resistance combining to a recombination lifetime τ_μ) and charge transport (transit time $\tau_t = R_t C_p$). [58, 59] The impedance spectroscopy extracted equivalent parallel capacitance C_p and phase angle as function of frequency and bias, after accounting for a series resistance of the ITO, are shown in the supporting information.

It is important to stress that, while describing the well behaved SVA device, this simple model is insufficient to describe the experimental data of the DIO processed device. This is understandable after inspection of the $J(V)$ -characteristics of these devices (Figure 2). In the DIO device under 1 sun illumination, a weak S-shape character can be observed near open circuit voltage, indicating a blocking layer possibly due to a Schottky-barrier. This is further supported by the dark $J(V)$ -characteristics delayed “turn-on” in the DIO treated device ($\approx 0.55\text{V}$) when compared to the SVA device ($\approx 0.35\text{V}$). Additionally, in the case of the DIO SA BHJ, at low frequencies (high resistance) a negative capacitance (NC) region, positive reactance, is observable (see SI and discussion). A similar NC was recently reported for OLEDs, and has been well studied for inorganic tunnel diodes and quantum wells where it is often attributed to charge trapping and slow transit time of injected carriers as well as bias dependent conductivity. [60–64] Commonly a third RC-element would be incorporated to describe the effect of the Schottky-barrier; however, the available impedance data is insufficient to constrain a three RC-element equivalent circuit due to strong correlations between the fit time constants. Attempts to model the impedance data of the DIO SA device with a simple two RC-element circuit yield unphysical bias dependencies of the time constants, see SI. Thus, in the following, we will discuss only the SVA annealed device.

Shown in Figure 7 are the extracted time constants for the solvent vapor annealed BHJ under 1-sun illumination. As impedance spectroscopy is an indirect method to determine device parameters such as charge carrier density and recombination rate, the results might be model dependent and fit uncertainties of the equivalent sub-circuit elements do not necessarily represent realistic estimates. However, characteristic time constants can be derived directly from the data and are prone to less uncertainty in interpretation. Miao et al. have determined the charge carrier lifetime via transient photovoltage measurements under open circuit conditions in thin solvent vapour annealed p-DTS(FBTTh₂)₂: PC₇₁BM to $1.6 \cdot 10^{-6}\text{ s}$ prior and $2.2 \cdot 10^{-6}\text{ s}$ after SVA. Our estimated charge carrier lifetimes $\tau_\mu = (2.7 \pm 0.3) \cdot 10^{-6}\text{ s}$ at open circuit agree well with their findings. The bias dependent lifetimes are comparable to those of poly(3-hexylthiophene-2,5-diyl) based BHJs, P3HT:PC₆₁BM, and are on the order of 10^{-6} s and 10^{-4} s in the forward biased and reverse biased device, respectively.

Both the charge carrier density n and recombination rate under illumination can be estimated from the chemical capacitance and recombination resistance, shown in **Error! Reference source not found.** The chemical capacitance is the increase in charge carrier density with a change in quasi Fermi level. By integrating the chemical capacitance across the device,

Basham, et al. found the following approximation of the charge carrier density with applied bias voltage V : [58]

$$n = \frac{1}{L} \int C_{\mu} dE_f + n_0 = \frac{1}{qL} \int C_{\mu} \alpha dV + n_0, \quad (1)$$

where α is a proportionality constant relating the voltage to the shift of the quasi Fermi level for each carrier type that, for a symmetric density of states, yields 1/2. We choose to treat α as fitting parameter and will determine it later via a fit of the $J(V)$ -curve. Note Eq. (1) is based on the assumptions that the contacts are ohmic and that the applied bias is able to shift the Fermi levels directly in the investigated bias range. Some deviations are thus expected for non-ideal Schottky-barriers, or fixed charge.

The charge carrier concentration n_0 under short circuit conditions can be estimated from the short circuit current density J_{sc} , active layer thickness L , electrical charge q and transit time

τ_t as $n_0 \approx \frac{1}{qL} J_{sc} \tau_t + R \tau_t = \frac{1}{qL} J_{sc} \tau_t \cdot \left(1 - \frac{\tau_t}{\tau_{\mu}}\right)^{-1}$. [58] We use the derived charge carrier density to obtain the charge carrier recombination rate R , independent of further assumptions such as the np dependence for Langevin or bimolecular recombination, via:

$$R \approx \frac{n}{\tau_{\mu}(n)}. \quad (2)$$

For well-behaved cells, with high fill factors and shunt resistances, it was found that the charge carrier generation rate within the device is nearly field independent and as such the $J(V)$ -curve can be estimated using the easily measureable short circuit current density J_{sc} and the recombination rate [58]

$$J(V) \approx -J_{sc} + qLR(V). \quad (3)$$

This allows for an estimate of the recombination rate at open circuit conditions with directly measurable quantities such as the short circuit current density and film thickness

$R(V_{oc}) \approx \frac{J_{sc}}{qL}$ and thus also for the estimation of the charge carrier density $n(V_{oc}) \approx \frac{J_{sc}}{qL} \tau_{\mu}$. Furthermore, we can model the $J(V)$ -curve and refine the unknown value of proportionality constant α used in Eq. 1. Shown in the Supplemental (Fig. S15) are the experimental and modelled $J(V)$ -curve. The best agreement between both curves was found for $\alpha = 0.16$ that is used to generate the charge carrier density shown in Fig. 7 and subsequent quantities. The excellent agreement between the device $J(V)$ and Eq. (3) with R from Eq. (2) gives us high confidence in the accuracy of the EIS analysis.

The results of the obtained mobile charge carrier density and recombination rate are shown in Figure 7b. At biases around and above the open circuit voltage V_{oc} the observed charge

carrier densities imply unhindered charge carrier injection. Below V_{oc} the charge carrier density changes about two orders of magnitude between +1 V and short circuit conditions, at the same time the charge carrier recombination rate changes from $10^{22} \text{ cm}^{-3}\text{s}^{-1}$ to $10^{19} \text{ cm}^{-3}\text{s}^{-1}$ in the +1 V and 0 V biased device, respectively.

In the following we analyse the charge carrier recombination rates under operating conditions and compare them to the Langevin case. For ease of comparison with other systems, we introduce a bimolecular recombination reduction factor

$\frac{\beta_L}{\beta} = \frac{R_L}{R} \approx \frac{q}{\varepsilon_0 \varepsilon_r} \frac{\mu n^2}{R} \approx \frac{q}{\varepsilon_0 \varepsilon_r} \cdot \mu \tau_\mu \cdot n$, where β_L is the Langevin-type bimolecular recombination coefficient, β the experimentally observed recombination coefficient, ε_0 the vacuum dielectric permittivity and ε_r the static dielectric constant (on the order of 3.5 for most organic systems).[65] In the equation above we have approximated the product of the charge carrier densities np , which determines the bimolecular recombination rate, by n^2 , as impedance allows only access to the faster charge carriers.

In recently proposed theoretical frameworks [39, 40, 66] supported by experimental data, active layers capable of high PCEs when coated thick are characterized by a large charge carrier mobility and strong non-Langevin recombination. [40, 43, 65, 67, 68] In addition to the recombination rate, we estimate the charge carrier mobility using a transit-time analysis based on the RC time constant τ_t ($V=0$). Assuming an internal field approximated by the open circuit potential, we derive an upper limit of the charge carrier mobility under short

circuit conditions of $\mu = \frac{L^2}{V_{oc} \tau_t}$ which is about $(3.4 \pm 1.0) \cdot 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the SVA device, in good agreement with mobilities reported for thin devices near V_{oc} ($5 \cdot 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) by Arredondo et al.[69] and slightly higher than extracted by Proctor et al. ($1 \cdot 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) for DIO SA spun-coat films.[68] Shown in Figure 8 are the estimated Langevin suppression factor (β_L/β) and recombination order as function of the applied device bias. We assume a constant, bias independent charge carrier mobility in order to estimate the recombination factor for operationally relevant bias and charge carrier concentrations. The recombination order was estimated from the mobile charge carrier

density and recombination rate via: Order of Recombination $\approx \frac{\partial \log(R)}{\partial \log(n)}$. [58] The Langevin suppression factor reaches values of ≈ 60 near the maximum power point and V_{oc} , while the device exhibits a recombination order near 2 indicating bimolecular but strongly non-Langevin recombination. At short circuit conditions in the nearly depleted device the order of recombination is near unity. The mobile charge carrier density within the device at J_{sc} is only on the order of 10^{15} cm^{-3} , corresponding to an average charge carrier distance of several tens of nm, suggesting trap dominated recombination, not bimolecular recombination consistent with the low order.

From this analysis we suggest that the superior performance of the SVA device is mainly based on the high charge carrier mobility and drastically suppressed, relative to Langevin, bimolecular recombination. The suppression factor for the SVA case is between that of the

reduction factor of the recently reported BTR system [70] and the $\frac{\beta_L}{\beta} \approx 50$ reported by Stolterfoht [67] for 230 nm thick PTB7:PC₇₁BM.

It is interesting to reflect on the origin of the low bimolecular recombination rate. For the semi-crystalline polymer P3HT, that exhibits a $\frac{\beta_L}{\beta} > 100$, the low bimolecular recombination rate has been attributed to phase separation and energy gradients in the mixed amorphous phase.[66, 71–76] The observation of reduced bimolecular recombination in the SVA system that is characterized by a (relative to DIO SA and spun-coat) short length scale of phase separation indicates that phase separation is not key, consistent with recent theoretical arguments.[77] Similarly, the observation that the device optimizes with the highest relative phase purity indicates that mixed amorphous phases are not critical. This suggests that the origin of the reduced bimolecular recombination rate maybe in a rapid CT state escape rate, as discussed by Murthy, et al.[42]

Summary

We have characterized the morphology of thick small molecule based solar cells blade-coat from DIO containing solutions and those of solvent vapor annealed BHJs cast from non-additive containing solutions. We show SVA treated devices exhibit the highest crystallinity and phase purity while maintaining small characteristic morphology length scales. The device performance of the as-cast, SA DIO and SVA devices follow the previously observed trends that PCE and phase purity are directly correlated. [55–57, 78] Impedance spectroscopy data reveal further details of the process-performance relationship. The SVA solar cell exhibits high charge carrier mobilities and a relatively high suppression of bimolecular recombination relative to the Langevin limit. The results suggest that differences in coating conditions (rapid drying during spin-coating vs slower drying following blade-coating) can give rise to critical differences (nucleation density) in films requiring care in subsequent optimization. In this case it is found that the optimized blade-coat films actually exceed the typical spun-coat films in process tolerance (film thickness variation) with no compromise in power conversion efficiency.

Methods

The small molecule donor p-DTS(FBTTh₂)₂ was purchased from one-material¹ and PC₇₁BM from Nano-C. Solutions were prepared in chlorobenzene (Sigma Aldrich) at 80 mg/mL total dissolved solids at a mass ratio of 3: 2 small molecule donor: fullerene and dissolved at 90 °C for 2 h. Solutions were stored inside mininert vials at 70 °C until dispensed.

¹Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Solar cell devices

Patterned glass/ITO substrates (Thin Film Devices) were cleaned subsequently by chloroform, acetone and isopropanol before a 15 min UV-Ozone treatment. A PEDOT:PSS (Clevois® P VP Al 4083) layer was spin-coated at $2\pi \times 4000 \text{ rad}^{-1}$ (4000 RPM) for 60 s and dried at 140 °C for 15 min. Still hot devices were then transferred into a glovebox for active layer deposition. Films of 100 nm to 250 nm film thickness were prepared via blade-coating, depositing $\approx 20 \mu\text{L}$ of solution from a 70 °C syringe under a glass blade which was translated at a height of 200 μm over the PEDOT:PSS treated glass/ITO substrates, held at 40 °C. The film thickness of the active layer was adjusted via variation of the blade velocity. For additive-processed devices, DIO was added to the solution shortly before blading. To ensure complete removal of DIO, these films were dried at 80 °C for 5 min in inert atmosphere once the main solvent evaporated.

Films for solvent vapor annealing together with 1 mL of THF were then transferred to a glass petri dish (3 cm diameter) and covered with a glass lid. The samples were exposed to the solvent vapor for 120 s. All films were dried in the glovebox in the dark before thermal deposition of Ca (20 nm) and Al (80 nm) contacts yielding devices with an area of 0.04 cm^2 . Current density-voltage curves were measured under simulated AM1.5G 100 mW/cm^2 illumination using an Keithley 2600 source measure unit in an Ar atmosphere. The OPV device performance was referenced to a KG5 filtered silicon photodiode calibrated by the National Renewable Energy Laboratory.

Impedance measurements were carried out in the frequency range between 20 Hz and 2 MHz using an Agilent E4980A LCR meter. A small, 25 mV, AC signal was superimposed with a DC bias (−1V to 2V) across the active layer. During the measurement the device was illuminated by a white light LED at an equivalent intensity of “1 sun”. Impedance spectra were fitted to a equivalent circuit model consisting of 2 RC-elements and a single resistance R_s , all connected in series. R_s is attributed to the resistive losses of ITO and PEDOT:PSS. C_μ is related to the chemical capacitance and attributed to charge carrier generation.

X-ray Scattering

X-ray scattering measurements were performed at the Advanced Light Source beam line 7.3.3, with a beam energy of 10 keV, following the previously described methodology.^[22] Briefly, samples were bladed in air at a sample to detector distance of 262 mm for GIXD and 3831 mm for GISAXS. Calibration was performed with a silver behenate standard. GIXD and GISAXS data reduction was performed with the Nika software package.^[79]

Transmission electron microscopy

Films were analyzed using a variety of transmission electron microscopy (TEM) methods. Low-angle annular dark field (LAADF) images were collected in scanning (STEM) mode using a 4 mrad convergence angle and a 22 mrad collection angle. TEM images were collected using an imaging energy filter. All images were carried out using a primary beam energy of 300 keV. Zero-loss filtered images were collected by centering the energy selection slit (10 eV wide) around the zero-loss peak of the energy loss dispersion. Plasmon ratio images were produced by dividing an image collected with the energy-selection slit (5

eV wide) centered on the low-energy shoulder of the plasmon loss peak with one collected with the slit centered on the high-energy shoulder as described in our previous publication. [80]

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Chemical structure of p-DTS(FBTTh₂)₂ (top) and PC₇₁BM (bottom)

Figure 2.

Current vs Voltage ($J(V)$) characteristics, under illumination of 1 sun (top left) and under dark conditions (top right) of 100 nm and 250 nm thick p-DTS(FBTTh₂)₂: PC₇₁BM solar cells. The $J(V)$ -curves correspond to a BHJ without DIO, the solvent vapor annealed BHJ w/o DIO and the BHJ processed from a 0.3 % DIO containing solution dried at 80 °C for 5 min. The film thickness dependent PCE for SVA annealed films and BHJs cast from the additive containing solution are shown on the bottom. Lines are guides for the eye. Each point, and each $J(V)$ -characteristic is the average of at least 3 devices. Error bars correspond to the maximum and minimum obtained PCE for the respective condition.

Figure 3.

Corrected GIXD detector image of a p-DTS(FBTTh₂)₂: PC₇₁BM BHJ blade-coated from a non-additive containing solution after SVA with THF (left). Peaks were indexed following the nomenclature of Love et al.[47], please note that in the region dominated by the PCBM halo several low intensity mixed index peaks of p-DTS(FBTTh₂)₂ might be present but could not be resolved. Extracted relative degree of crystallinity (rDOC), which is proportional to the integrated pole figure, and GISAXS integrated scattering intensity (ISI) for 250 nm thick films as a function of processing. Each point represents the average of 4 different films, error bars correspond to the standard deviation. Lines are guides to the eye. Data was normalized by the acquisition time and probed volume.

Figure 4.

Atomic force microscopy height images (a–c) and LAADF-STEM images (d–f) of p-DTS(FBTTh₂)₂: PC₇₁BM blade-coat films as a function of processing. Shown are the non-additive, as-cast film (a, d), the BHJ containing 0.3 % DIO (b, e) and the additive free film after SVA with THF (c, f). The scale bar corresponds to 2 μm and 500 nm in case of the AFM images and STEM images, respectively.

Figure 5.

a) GISAXS results for representative bladed-coated p-DTS(FBTTh₂)₂: PC₇₁BM BHJs. Thick solid lines correspond to Teubner-Strey fits of the data. b) Lorentz-weighted representation of data in a.

Figure 6.

Selected Nyquist-plots of the bias dependent impedance data obtained on a BHJ after SVA (a,c) and a BHJ cast from a solution containing 0.3% DIO(b,d). Shown data was obtained under (1 sun) illumination (a,b) as well as under dark (c,d) conditions, in the frequency range 20 Hz to 2 MHz.

Figure 7.

The two RC time constants extracted from a fit to the experimental data of the BHJ after SVA (a). Also shown are the mobile charge carrier density and recombination rate (b). Indicated via vertical broken line is the open circuit voltage of the device under 1 sun illumination. Rectangles in b) correspond to estimates of the charge carrier recombination at open circuit conditions (light blue fill) and charge carrier density at short circuit and open voltage conditions (empty rectangles), for a derivation please see the manuscript.

Figure 8.

Estimated Langevin suppression factor (β_L/β) and recombination order as function of the applied bias under 1 sun illumination. Assumed was a constant, bias independent charge carrier mobility $\mu=3.4 \cdot 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Open rectangles correspond to estimates of the Langevin suppression factor at short circuit based on the J_{sc} derived estimates.

Table 1

Characteristic length scales within BHJ films as a function of processing.

	BHJ without DIO, s-cast	BHJ with 0.3 % DIO, SA	BHJ without DIO, after SVA
d [nm]	44	136	46
ξ [nm]	8.8	11	8.2
ISI [a.u.] ^c	0.43 ± 0.25^b	0.7 ± 0.2	1.0

^aParameters obtained from the fit of the data shown in Fig. 5, the parameter uncertainty < 10%.^bError bars correspond to the standard deviation between 4 samples.^cThe total scattering intensity was calculated by integrating the experimental data from $0.01 \text{ \AA}^{-1}$ to $0.1 \text{ \AA}^{-1}$.

Table 2

Electrical characteristics of the solvent vapour annealed BHJ. Given values correspond to open circuit conditions (short circuit conditions).

	V_{oc} [V]	J_{sc} [mA/cm ²]	τ_p [s]	τ_d [s]	μ [cm ² V ⁻¹ s ⁻¹]	n [cm ⁻³]	β_i/β
SVA	0.74	16.92	2.7E-6 (2.2E-5)	2.5E-7 (2.5E-7)	(3.4 ± 1.1) E-3	3.5E16 (1E15)	40.60