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Film morphology evolution during solvent vapor annealing of highly efficient small molecule donor/acceptor blends

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Abstract

Solution-processable small molecule photovoltaics based on the novel molecular donor, benzodithiophene terthiophene rhodanine (BTR), recently have shown maximum power conversion efficiencies above 8 % for active layer thicknesses up to 400 nm, using post process solvent vapor annealing (SVA) with tetrahydrofuran (THF). Here we report an in-situ study on the morphology evolution during SVA using the moderate solvent THF and the good solvent chloroform (CF). The combination of real-time grazing incidence X-ray diffraction (GIXD) and grazing incidence small angle X-ray scattering (GISAXS) allows us to draw a complete picture of the evolution of crystallinity and phase purity during post process annealing. We find that the relative crystallinity compared to the as-cast films is only modestly affected by SVA and solvent choice. However, both the phase purity and the characteristic domain sizes within the film vary significantly and are controlled by the solvent quality as well as exposure time. Using THF, films

with high phase purity and desirable characteristic length scales of about 30 nm can be achieved, while the use of CF rapidly leads to excessive film coarsening and less preferable domain sizes on the order of 60 nm, too large for optimized charge separation.

Keywords

In-situ; Solvent vapor annealing; Small molecule; Bulk-heterojunction

Introduction

In recent years solution processable small molecule based organic photovoltaics (OPV) have garnered significant interest, as they promise easily reproducible material characteristics relative to the high batch-to-batch variations in polymer based devices due to classical polymer synthesis.[1, 2] While early attempts lacked performance compared to their polymeric counterparts, a variety of molecular motifs with reported power conversion efficiencies (PCE) above 7 % in donor/fullerene based organic solar cell devices have now been demonstrated.[3–10] Nevertheless, a rather limited number of these materials can be employed in the thick active layer structures ($\sim$ 250 nm) necessary for reliable coating by large scale fabrication techniques such as roll-to-roll (R2R).[11–13] One promising material is benzodithiophene terthiophene rhodanine (BTR, Figure 1), that, in combination with PC₇₁BM, has a demonstrated maximum PCE of > 8 % for active layer thicknesses up to 400 nm and record efficiencies of up to 9.5 % in 310 nm thick films and an unusually high reduction in recombination rates.[5, 14] Optimized processing of this material system involved solvent vapor annealing (SVA) of the prepared bulk-heterojunctions (BHJ) using tetrahydrofuran (THF), a moderate solvent for the small molecule donor. SVA improved the crystallinity, while maintaining a 3D-interconnected network throughout the 250 nm thick film, enabling improved charge transport and extraction. This facilitated high fill factors of above 70 % for a wide range of film thickness.

Especially in the field of small molecule based organic solar cells, solvent vapor annealing is seeing increased use as a post processing technique. While the effect of SVA on the device performance of polymer based BHJs was investigated in the late 2000s – early 2010s for a few polymer systems with limited success [15–18], the device performance of a number of small molecule based BHJs has been shown to significantly benefit from SVA.[9, 10, 19–27] Like the use of processing additives (e.g. 1,8-diiodooctane, DIO) for morphology control in polymeric semiconductors, SVA has a low-thermal budget and therefore is attractive for R2R-processing on flexible substrates with low glass transition temperatures. However, similar to additives, the selection rules and mechanisms by which the chosen solvent vapor alters the film morphology are not yet well understood. A significant step towards this goal was achieved by Park, et al. [28] and Sun, et al. [20] who investigated the influence of the solvent quality of the annealing vapor on P3HT and DPP(TBFu)₂ based solar cells respectively, leading to the observation that a poor to moderate solvent quality, with respect to the donor material, leads to optimum device performance while a good solvent can lead to excessive phase separation.

Here we report the in-situ characterization of the film morphology in BTR/PC₇₁BM films during SVA, comparing the results of both a good (CF) and moderate (THF) solvent to each other and to thermal annealing. Grazing incidence X-ray diffraction (GIXD) and grazing incidence small angle X-ray scattering (GISAXS) are used to monitor the evolution of crystallinity and crystal size, as well as phase purity and characteristic domain sizes, for initially blade coated BTR/PC₇₁BM BHJs. The most significant difference in final film structure after SVA with the two solvents is the characteristic domain size.

Results & Discussion

Solar cell devices and active layers for in-situ X-ray diffraction were prepared via the blade-coating technique, which is commonly accepted as industrially relevant as it mimics roll-to-roll techniques such as slot-die and knife-over-edge coating.[29] In-situ measurements benefit from the stationary sample and moving blade geometry, easing measurement compared to spin-coating for a variety of analysis tools such as white light transmission and reflection as well as X-ray diffraction techniques. In this study, devices consisting of benzodithiophene terthiophene rhodanine: phenyl-C71-butyric-acid-methyl ester, BTR:PC₇₁BM, mass ratio 1:1 and film thickness of ≈ 200 nm were prepared inside a N₂ purged glove box by blade coating solutions of 60 mg total solids/mL of chloroform:chlorobenzene 1:1 by volume. While devices prepared directly after coating (as-cast) yielded relatively low power conversion efficiencies of around 2.5 %, device performance reached ≈ 6.5 % PCE after 30 s solvent vapor annealing with the moderate solvent THF (BTR solubility of 89 mg/mL [5] in THF, PC₇₁BM solubility < 10 mg/mL in THF). The other two post-processing methods, 15 s SVA with the excellent solvent CF (BTR solubility of 211 mg/mL[5] in CF, PC₇₁BM solubility 30 mg/mL[30] in CF) and thermal annealing at 110 °C, also lead to increased device performance compared to the as-cast case (5.4 % and 3.9 % PCE respectively), but remained below the maximum achieved PCE of the THF case, see Figure 2 and Table 1.

In agreement with Sun, et al.[5] the short circuit current density (J_{sc}) and fill factor (FF) increase upon annealing, while a slight decrease in open circuit voltage (V_{oc}) from 980 mV to below 900 mV can be observed. The drop in V_{oc} is often observed and is commonly attributed to changes in the film's energetic landscape, mainly changes of the highest occupied molecular orbital (HOMO) level of the donor component upon improved order. [31, 32] For many crystalline polymers, e.g. P3HT and PffBT4T-2OD, the increase in order upon post treatment can be readily observed via transmission measurements. Therefore, we have conducted absorbance measurements on BTR active layers for the four above reported cases. In all cases a weak vibronic shoulder in the wavelength region between 600 nm and 650 nm can be seen. After annealing, a small shift of the absorbance spectra to longer wavelengths, corresponding to lower energies, can be observed. Overall the different annealing schemes seem to lead to very similar absorbance changes.

We used atomic force microscopy (AFM) and low-angle annular dark-field STEM (LAADF-STEM) to characterize the films and gain an initial insight into the morphology differences between the films. In the as-cast BHJs we observe a relatively smooth surface, with rice grain shaped features arranged in a liquid crystalline manner, see Figure 3a. Upon thermal

annealing this morphology slightly coarsens while the characteristic flow field remains intact (Figure 3b). In the case of the SVA with CF on the other hand, the morphology drastically changes and the surface roughness increases (Figure 3c). The surface morphology closely resembles that reported for semi-crystalline polymer blends like P3HT/PC₆₁BM.[33–35] In the case of SVA with THF (that leads to optimum device performance), the morphology is somewhere in between the thermal annealing and SVA with CF cases. The liquid crystalline aspect of the film appearance is decreased, yet still observable. The film roughness increases only slightly when compared to the as-cast case.

The LAADF-STEM images reveal that underneath the coarse film surface, a bulk morphology with domain sizes on the order of 30 nm can be observed (see Fig. S2). Please note that these features are smaller than those observed in the film topography, which suggests the presence of an additional surface segregation layer or surface skin. However, similar to the AFM images the STEM images indicate the same trends upon annealing. While the as-cast film shows a finely structured morphology with low contrast suggesting relatively impure domains, annealing increases both the characteristic length scales and contrast, implying an increase in phase purity. Again, the coarsest and most contrast rich morphology is observed after SVA with CF.

The relative crystallinity of the samples shown in Figure 3 was determined via GIXD. Shown in Figure 4 are GIXD detector images, line profiles near $q_{xy} \approx 0$, (01-1) pole-figures and a plot of the relative crystallinity (see SI for details - please note that the first order peak cannot be unambiguously indexed in the studied films. Assuming an “edge on” orientation with the low free energy alky side-chains presented at the air and substrate interface results in either the (010) or (01-1) planes parallel to the surface. Based on estimates of the diffraction strength, the (01-1) is most likely and that assignment is used throughout.)

All films show pronounced donor crystallinity, with two orders of the (01-1)-diffraction plane visible, while the PC₇₁BM remains in an amorphous state indicated by the halo at $1.3 \text{ \AA}^{-1}$. Unlike spin cast films, we do not see the rearrangement of crystallites from edge-on to face-on orientation upon annealing[5], instead all films show a large isotropic fraction of crystallites in the bulk and only a second small edge-on fraction, possibly located at the film interfaces. Upon solvent vapor annealing of the as-cast film, the relative degree of crystallinity (*RDC*), obtained from the (01-1) pole-figure, increases to similar values for both CF and THF treatments. However, the thermal annealing shows no change in the *RDC*. Earlier reports have shown that thermal annealing in spin-cast devices leads to an overgrowth of crystallites and excessive domain coarsening eventually leading to device failure.[5] This clearly is not the case for our blade coated films, which we attribute to different nucleation densities and solidification times in slow solvent evaporation in blade coated films vs. rapidly quenched spin-cast films.

The vertical line profiles show only slight differences between the samples. The SVA annealed cases show an interlayer spacing of about $(1.85 \pm 0.03) \text{ nm}$, the as-cast and thermal annealed films show a slightly increased interlayer spacing of $(1.88 \pm 0.03) \text{ nm}$. In agreement with Sun, et al., SVA leads to a decreased interlayer spacing that is in good agreement with the corresponding lamellar spacing of 1.83 nm observed for spin-coated

films.[5] Note the single crystal diffraction of the (001), (010) and (01-1) correspond to real space distances of 1.92 nm, 1.78 nm and 1.77 nm respectively. The observed shift and intermediate q -spacing suggests a redistribution between different coexisting crystal orientations.

Next we explore the origins of the improved crystallinity and the observed lattice constant shift. In-situ measurements like the collection of absorbance, GIXD and grazing incidence small angle X-ray scattering (GISAXS) data during solidification have proven to give valuable insight on the dynamics of film formation, leading to a deeper understanding on how processing additives like ODT or DIO alter the morphology of polymer and small molecule BHJs.[36–42] In the following, we show that in-situ measurements during SVA are similarly valuable for understanding the mechanisms behind the above observed morphology changes. In order to correlate in-situ diffraction data with separately acquired in-situ scattering data and solvent uptake during SVA, we recorded white light interferometry (WLI) data at the same film spot where the X-ray data was taken. The film thickness over time, as determined from a fit of the reflection data for each time period, can be directly converted to the solvent concentration in the film.

Figure 5 shows the evolution of the GIXD profiles near $q_{xy} \approx 0$ during both the thermal as well as the solvent vapor annealing process. Also shown are the extracted lattice spacing and evolution of the relative crystallinity as obtained from the integration of the pole figures over all polar angles. In the solvent annealed films a distinct "swelling" of the lattice (shift to lower q -values) is observed in the presence of the solvent. At the same time a small decrease in the (01-1) peak width, see Figure 5e, can be observed. Interestingly, the lattice shift precedes the onset of significant change in film thickness as determined from simultaneously acquired WLI data and also appears prior to significant changes in relative crystallinity. A similar, but much less pronounced, shift is observed during thermal annealing. In case of the SVA with THF, simultaneous with the lattice expansion a nominally monotonic crystallinity *increase* can be observed. In contrast, for the SVA with CF case, and to a much lesser extent for the thermal annealing, the initial phase of the annealing step is characterized by a *decrease* of crystallinity that, in combination with the narrowing of the (01-1) peak, suggests the dissolution of small imperfect crystallites back into the mixed amorphous matrix.

To elaborate the effect of solvent annealing on the macroscopic morphology, we also recorded GISAXS enabling us to evaluate the evolution of characteristic domain sizes and phase purity in the films during annealing. Following procedures reported elsewhere, we evaluate the total internal reflection enhanced q_{xy} data near the sample horizon ($q_z \approx 0$).[41–44] Shown in Figure 6 are the q^2 -weighted, background-corrected, in-situ GISAXS results (Kratky-Plots) under comparable conditions to the above shown GIXD results. Please refer to the supporting information for a detailed description of the applied corrections. In all cases we observe an increase in scattering intensity and thus phase purity upon annealing, accompanied by an increase of the observable characteristic length scales suggesting domain coarsening. In the thermal annealing as well as SVA with THF cases, the domain growth is only a few nanometers from 28 nm in the as-cast film to 34 nm (TA) and 30 nm (SVA with THF). On the other hand, in the SVA with CF case the phase morphology significantly coarsens and domain sizes of 57 nm are observed. Interestingly, at the time frame of the

above reported crystallinity decrease (at about 20 s), a decrease in scattering intensity can be observed.

Further insight into the morphology evolution and correlation between GIXD and GISAXS data can be gained by evaluation of the time evolution of the total scattering intensity (*TSI*). [41, 42] The evolution of the *TSI* reflects both material purity of the donor/acceptor phases and the presence of the solvent vapor. For an isotropic material the *TSI* can be estimated from an integration of the data over the whole momentum range q , $TSI \propto \int I q^2 dq$. The obtained *TSI* is correlated to the number of phases and domain composition

$TSI \propto \sum_{i,j} \Delta \rho_{ij}^2 \varphi_i \varphi_j$, where ρ_{ij} is the difference in the scattering length density (*SLD*) between the phases with volume fraction φ_i and φ_j . [41] In the case of a two phase system the above approximation is exact. When analyzing the GISAXS, two significant approximations are made. First, the entire q range is not available, so the q integral is over a restricted (selected length scale) range. Second, only q_{xy} can be cleanly extracted, q_z is confounded by reflectivity effects. Thus we will adopt the notion *ISI* to denote the experimentally derived

$$ISI \equiv \int_{q_{min}}^{q_{max}} I_{xy} q^2 dq$$
. In the limit that the available q range captures the length scales relevant to phase separation, and that the vertical behavior is similar to in-plane, *ISI* will be proportional to *TSI*. Quantitative comparison of the GISAXS to LAADF-STEM (see SI) indicate that the *ISI* covers the relevant length scales for in-plane phase separation.

Figure 7 shows the evolution of the *ISI* in comparison to the evolution of crystallinity (GIXD: integrated pole figure).

In the case of thermal annealing the evolution of the *ISI* is decoupled from the evolution of crystallinity; the decrease in *RDC* at early times correlates to a slight *increase* in *ISI*, while the *RDC* is static during the significant growth of *ISI* at later times. Thus the development of a reliable model as described above is not possible due to a lack of parameter confinement. However, in case of both solvent annealed films, *ISI* and crystallinity are correlated and show the same time evolution. We used a simple 2 phase model, consisting of a pristine BTR phase proportional to the crystalline donor phase (*RDC*) and a mixed amorphous phase composed of the remaining blend components (including the solvent penetration), to describe the scattering intensity evolution. The required scattering length densities of all compounds were estimated from the known chemical structure and density as $SLD_{BTR} = 1.12 \times 10^{-3} \text{ nm}^{-2}$ and $SLD_{PCBM} = 1.36 \times 10^{-3} \text{ nm}^{-2}$ for the donor and acceptor material, and as $SLD_{CF} = 1.48 \times 10^{-3} \text{ nm}^{-2}$ and $SLD_{THF} = 0.84 \times 10^{-3} \text{ nm}^{-2}$ for the solvents. A detailed description of the modeling can be found in earlier publications. [41] As can be seen in Figure 7b) and c) the overall evolution of the *ISI* is captured quite well by the model, although deviations are present. Allowing for a partitioning of the mixed amorphous phase into two phases with variable degrees of BTR, fullerene and solvent volume fraction did not lead to an increase in fit quality despite the increased number of variables.

The observations above lead to the following interpretations of the processes during post-deposition treatment. In the case of thermal annealing, small crystals are “dissolved” in the amorphous melt as they become more and more unstable with increasing temperature due to

a higher surface energy, hence higher total Gibbs energy. At the same time, "bigger" crystals with more favourable total Gibbs energy grow and the relative volume gained by growth of the "bigger" crystallites compensates the crystal volume loss by the small crystallites. The relatively small increase in *RDC* indicates that the majority of the BTR fraction in the mixed amorphous phase cannot crystallize, suggesting a transport limitation, possibly due to vitrification of the mixed amorphous phase by the high glass transition temperature *T_g* of PC₇₁BM. Simple mixing rules, based on the PC₇₁BM's reported *T_g* of ≈ 163 °C [45] and an estimate of BTR's *T_g* of 38 °C (2/3 of the clearing temperature of 193 °C [5]), place the *T_g* of the amorphous glass around 100 °C to 120 °C for a fully amorphous film assuming 30 % *RDC* of BTR prior annealing respectively. As we expect the morphology to be an inhomogeneous distribution of more or less PC₇₁BM rich regions and thus regions with higher and lower *T_g*, the conducted annealing step leads to fractions of the film which are vitrified and other ones in a molten rubbery or viscoelastic state allowing for diffusion to the surface of existing stable crystallites. However, due to the low annealing temperature of 110 °C, the mixed amorphous blend rapidly vitrifies as the diffusion of BTR molecules to existing crystals increases the *T_g* of the amorphous phase they have left by shifting the volume ratio BTR : PC₇₁BM towards the fullerene. The non-existent *ISI* decrease in early times, indicates that the small crystallites do not necessarily fully "dissolve" into the mixed amorphous matrix, rather exist as amorphous pristine BTR domains within the matrix. This suggests either a low miscibility of PC₇₁BM and BTR within each other or comparably slow diffusion and blending of the two components (vitrification). A low miscibility is supported by bilayer annealing experiments, which show that annealing at 110 °C for 5 min leads to a relatively small inter-diffusion between the materials, see SI. Additionally, differential scanning calorimetry measurements, summarized in the SI, of the melting point depression curve make it clear that the crystalline phase of BTR is highly stable under normal annealing conditions, with the minimum stable temperature being ≈ 155 °C. (Note that the estimated value for the Flory-Huggins interaction parameter for BTR in the presence of PCBM-71 is $\chi \approx 0.86$, further supporting the low miscibility particularly in light of BTR's high crystalline enthalpy). The eventual increase in *ISI* at later times is a result of the growth of the remaining crystallites, which exclude PC₇₁BM from their surroundings.

In the THF and CF annealing cases, the respective vapor acts as a solvent and, depending on the solvent quality, different degrees of crystallite dissolution and regrowth can be observed. In the case of 15 s annealing with a CF vapor, the decrease in *both RDC* and *ISI* suggests small BTR domains are dissolved into the mixed amorphous matrix due to the high solvent quality of CF for BTR and PC₇₁BM. Small crystallites are dissolved as in the case of thermal annealing, while big crystals remain. As the solvent concentration in the vapor phase decreases slowly (at the end of the 15 s period), the remaining large BTR domains allow for crystal growth within their volume due to plasticization. The significant increase in overall crystallinity at the end of the SVA compared to the thermal annealing case indicates that CF must plasticize the mixed amorphous phase allowing BTR transport to the ripening domains. The reduced nucleation density, in the solvated state, results in prolonged crystal growth and larger domains. In the case of THF the solvent quality for PC₇₁BM and BTR is lower than for CF, which in turn reduces the degree of dissolution of small domains. Further, THF is slightly more selective than CF, the ratios of the solubility limits BTR:PC₇₁BM are >

8 and ≈ 4 respectively. As such the decrease in *ISI* and crystallinity is not observed during the short annealing, rather the solvent vapor acts simply as a plasticizer allowing for existing crystallites to grow at the expense of the mixed amorphous phase and cause phase purification and the observed increase in *ISI*. As in the thermal annealing case the nucleation density remains high, set by the morphology in the as-cast film, limiting the crystal size.

Summary

We have demonstrated that the film morphology evolution during post deposition solvent annealing strongly varies with the solvent vapor quality. A good or excellent solvent like CF leads to rapid film coarsening and high phase purity but less preferable, for OPV bulk-heterojunctions, large domain sizes on the order of and bigger than 60 nm. At early times of the SVA the exposure of the film to CF leads to the dissolution of small imperfect crystallites. It is not until the concentration of CF in the vapor of the annealing chamber is reduced that film crystallization and an increase in phase purity can be observed. The remaining large crystals act as seeds in a solvated mixed amorphous matrix. The decrease in nucleation density due to initial dissolution allows those few crystallites to grow large in size before the solvent vapor completely leaves the SVA chamber. If a moderate solvent like THF is used, the ability to dissolve small crystallites is reduced and the overall nucleation density comparably higher. The increased mobility of small molecules in the mixed amorphous matrix is similarly enabled, allowing for crystallization and the improvement of phase purity, yet the overall crystal sizes remain small and excessive film coarsening is suppressed. This leads to preferably high phase purity with characteristic domain sizes on the order of 30 nm and optimum device performance. The improved morphology of THF vapor annealed films, vs CF and thermally annealed films, is related to the balance between nucleation density set by dissolution and plasticization of the mixed amorphous phase.

Experimental

The small molecule donor benzodithiophene terthiophene rhodanine (BTR) was synthesized as reported in Ref. [5]. PC₇₁BM was purchased from nano-C.* Solutions were prepared in solvent mixtures of chloroform:chlorobenzene 1:1 by volume. The mass ratio of BTR:PC₇₁BM in solution was 1:1, with 60 mg/mL total dissolved solids content. Solutions were prepared at room temperature and allowed to dissolve for 24 h prior to film preparation.

Solvent Vapor Annealing Scheme

A custom-build solvent annealing chamber made of aluminum, with inner dimensions of 36 mm $\times$ 70 mm $\times$ 28 mm (width $\times$ length $\times$ height) was used for all solvent vapor experiments. To enable the acquisition of X-ray scattering data two Kapton windows on each of the long side of the chamber were installed. Film thickness monitoring via normal incidence reflection measurements was enabled using a quartz window on the chamber top. The

*Certain 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.

samples, prepared by blade coating on PEDOT:PSS coated Si substrates as detailed below, were placed in the chamber centre and exposed to solvent vapor generated by flowing dry air through a heated solvent reservoir (40 °C) at a flow rate of 472 cm³/min (1 scfh). We estimate the turn over time for the atmosphere within the 70.56 cm³ chamber to be about 10 s for the SVA and about 2 s for the solvent removal at the end of the SVA. During solvent vapor annealing the SVA chamber was heated to 30 °C in order to prevent vapor from condensing on the sample surface. The procedure and nomenclature for SVA was: (i) allow flow through solvent reservoir and SVA chamber for a defined amount of time – the time period is used as distinguisher between samples. (ii) After this the SVA chamber was isolated from the solvent reservoir and all air flow to the chamber terminated (stagnation). (iii) The SVA is terminated after 5 min from the initial beginning of the air flow through the solvent reservoir by flushing the chamber volume with dry air at a flow rate of 2360 cm³/min (5 scfh).

Solar cell devices

Patterned glass/ITO substrates (≈ 140 nm, 20 Ω /sq, Thin Film Devices) were cleaned subsequently by chloroform, acetone and isopropanol before a 15 min UV-Ozone cleaning. A 30 nm thick PEDOT:PSS (Clevois® P VP Al 4083) layer was spin-coated at $2\pi \cdot 50$ rad/s (3000 RPM) for 60 s and dried at 140 °C for 15 min in air. Still hot device substrates were then transferred into a nitrogen filled glove box for active layer deposition. Films of 200 nm film thickness (determined by spectroscopic ellipsometry) were prepared via blade-coating, depositing ≈ 20 μ L of solution from a glass syringe (at room temperature) under a glass blade which was translated at a height of 300 μ m over the PEDOT:PSS treated glass/ITO substrates. The substrates were held at 45 °C. The film thickness of the active layer was adjusted via variation of the blade velocity.

Films for solvent vapor annealing were then transferred to the above described SVA chamber and exposed to chloroform as well as THF vapors for times between 5 s to 120 s. Devices for thermal annealing were placed on an aluminum hot plate at 45 °C and the temperature gradually increased to 100 °C and held at this temperature for 60 s before allowing the samples to cool down. During thermal annealing the stage temperature was recorded. After annealing, devices were completed by depositing 20 nm Ca followed by 80 nm Al via thermal evaporation through a shadow mask at a base pressure below 2×10^{-4} Pa. The area of completed devices was 0.04 cm² as defined by the overlap of the ITO and metal electrode. Current density-voltage curves were then measured under simulated AM1.5G 100 mW/cm² illumination using a Keithley 2600 SMU in an Ar atmosphere. The OPV device performance was referenced to a KG5 filtered silicon photodiode calibrated by the National Renewable Energy Laboratory (NREL).

In-situ X-ray Scattering

In-situ 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. [41] 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. X-ray data were recorded with a 0.5 s integration and period during SVA. The

same custom-built solvent annealing chamber and annealing procedure as described above were utilized to remotely control the exposure of as-cast samples to solvent vapor. During all scattering measurements normal incidence reflectometry data (50 ms integration) was recorded with a custom-built fiber-spectrometer based system. It was ensured that the reflectance data was taken at the same area as the X-ray scattering data. The reflectometry was analyzed using a commercial ellipsometry code (JA Woollam WVASE32), GIXD and GISAXS data reduction was performed with the Nika software package.[46]

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Chemical structure of benzodithiophene terthiophene rhodanine (BTR, not shown are ethylhexyl side chains “EH”), and phenyl C₇₁ butyric acid methyl ester (PC₇₁BM).

Figure 2.

(left) Current-voltage characteristics of blade-coated BTR/PC₇₁BM devices, for an as-cast film, as well as films after 30 s SVA annealing with THF vapor, 15 s SVA annealing with CF and 60s thermal annealing at 110 °C. Traces correspond to the average of 4 devices, the 95 % confidence interval is indicated by an shaded area. (Right) Also shown are corresponding absorbance spectra acquired on reference areas on solar cell devices without aluminum electrode.

Figure 3.

Topographic atomic force microscopy images (top) and STEM LAADF Imaging (bottom) of blade coated BTR/PC₇₁BM films. Shown are: a, e) As-cast BHJ; b, f) BHJ after 60 s thermal annealing at 100 °C; c, g) BHJ after 30 s SVA with CF; d, h) BH after 60 s SVA with THF. The scale bar in the AFM and STEM images 4 μ m and 500 nm respectively.

Figure 4.

GIXD detector image for (a) an as-cast BTR/PC₇₁BM BHJs, (b) after thermal annealing at 100 °C, (c) after 15 s SVA with CF and (d) after 30 s SVA with THF. Also shown are (e) vertical line profiles near $q_{xy} \approx 0$, (f) the extracted (01-1) pole-figures and (g) relative degree of crystallinity. Vertical profiles have been offset by multiples of 10 for clarity. The broken line in graph (f) corresponds to an isotropic crystal distribution. All data was normalized to the probed film volume.

Figure 5.

(a–c) In-situ GIXD false color images constructed from vertical line profiles near $q_{xy} \approx 0$, as well as the evolution of (d) the (01-1) position, (e) (01-1) coherence length and (f) relative crystallinity. Shown are films during thermal annealing at 100 °C (a), 15 s SVA with CF (b) and 30 s SVA with THF (c). The solvent flow into the chamber began at $t = 1$ s. Broken lines indicate the end of air flow through the bubbler (15 s SVA with CF, 30 s SVA with THF) as well as the flush of the solvent annealing chamber with dry air (in both SVA cases at 5 min). Also shown are the evolution of the film thickness during SVA at 30 °C. In the case of

thermal annealing no thickness change could be detected. Also shown is the temperature profile during thermal annealing.

Figure 6.

Evolution of the q^2 -weighted background corrected GISAXS intensity near the sample horizon ($q_z \approx 0$, a–c). The data corresponds to a BHJ during thermal annealing (a), during 15s SVA with CF (b) and during 30 s SVA with THF (c). The background corrected scattering intensity after annealing is shown in (d).

Figure 7.

Integrated scattering intensity (*ISI*) and integrated pole figure during annealing. Shown are thermal annealing (a), 15 s SVA with CF (b) and 30 s SVA with THF (c). Shown in red broken lines are fits of the *ISI* using a two phase model consisting of pristine BTR and a mixed amorphous phase of non-crystalline BTR, amorphous PC₇₁BM and solvent vapor.

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Table 1

Summary of the prepared device characteristics. Given are the average short circuit density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency of 4 devices. The uncertainties correspond to the 95 % confidence limit.

	J_{sc} [mA/cm ²]	V_{oc} [mV]	FF [%]	PCE [%]
As-cast	7.1 ± 0.7	980 ± 4	36 ± 2	2.5 ± 0.3
60s thermal annealing @ 110C	9.5 ± 1.1	952 ± 5	43 ± 1	3.9 ± 0.4
15s SVA with CF	10.6 ± 1.5	863 ± 4	59 ± 2	5.4 ± 0.6
30s SVA with CF	9.8 ± 1.0	847 ± 8	60 ± 1	5.0 ± 0.6
30s SVA with THF	12.2 ± 1.0	911 ± 9	57 ± 1	6.4 ± 0.5
60s SVA with THF	9.4 ± 0.8	814 ± 12	62 ± 1	4.7 ± 0.4