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Solvent Vapor Annealing-Mediated Crystallization Directs Charge Generation, Recombination and Extraction in BHJ Solar Cells

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ABSTRACT: Small-molecule (SM) donors that can be solution-processed with fullerene acceptors (e.g., PC₆₁/71BM), or their “nonfullerene” counterparts, are proving particularly promising for the realization of high-efficiency bulk-heterojunction (BHJ) solar cells. In several recent studies, solvent vapor annealing (SVA) protocols have been found to yield significant BHJ device efficiency improvements via structural changes in the active layer morphologies. However, the mechanisms by which active layer morphologies evolve when subjected to SVA treatments, and the structural factors impacting charge generation, carrier transport, recombination and extraction in BHJ solar cells with SM donors and fullerene acceptors, remain important aspects to be elucidated. In this report, we show that – in BHJ solar cells with SM donors and fullerene acceptors – selective crystallization promoted by SVA mediates the development of optimized morphologies across the active layers, setting domain sizes and boundaries. Examining BHJ solar cells subjected to various SVA exposure times, with BDT[2F]QdC as the SM donor and PC₇₁BM as the acceptor, we connect those morphological changes to specific carrier effects, showing that crystal growth effectively directs charge generation and recombination. We find that the SM donor-pure domains growing at the expense of a mixed donor-acceptor phase play a determining role, establishing optimum networks with 10-20nm-sized domains during the SVA treatment. Longer SVA times result in highly textured active layers with crystalline domains that can exceed the lengthscale of exciton diffusion, while inducing detrimental vertical morphologies and deep carrier traps. Last, we emphasize the field-dependence charge generation occurring upon SVA-mediated crystallization and link this carrier effect to the mixed phase depletion across the BHJ active layer.

Introduction

Solution-processable bulk-heterojunction (BHJ) solar cells relying on small-molecule (SM) donors and fullerene (e.g., PC₆₁/71BM) or “nonfullerene” acceptors are gaining attention in the field, mainly because high-efficiency figures are now in reach¹ with the prospects of outperforming the more commonly studied polymer-based BHJ solar cells.^{2,3} Their discrete molecular structure and defined molecular weight, their synthetic accessibility and scalability, and the absence of batch-to-batch variation, are some of the main incentives for using SM donors and acceptors in BHJ solar cells.^{1,4} When combined with fullerene acceptors, SM donor-based BHJ devices can reach power conversion efficiencies (PCEs) >11%,⁵ and swapping fullerenes for “nonfullerene” acceptors yield PCEs >10%.⁶ At the origin of the gradual efficiency improvements seen in the past recent years: (i) the rationalization of material design and (ii) the systematic optimization of film processing conditions and device structure. More often than not, achieving a favorable morphology in SM donor-fullerene BHJ solar cells requires examining several of these parameters: solvent selection,⁷ donor/acceptor ratio,^{8,9} device configuration and interlayer selection,^{10,11} processing additives,^{9,12} thermal annealing,¹³ and – more recently – post-processing “solvent vapor annealing” (SVA).¹⁴ In general, interpenetrating networks with 10-15nm-sized domains are considered optimum for charge generation, transport and extraction, but other structural factors such as domain purity (often

paired with crystallinity),¹⁸ relative molecular arrangements and orientations,¹⁹ and vertical phase-separation patterns are also known to impact BHJ device performance.²⁰

Of all optimization protocols known to influence BHJ morphology, SVA treatments are currently being described as being especially relevant to SM donor-fullerene BHJ solar cells.¹ In those instances, the active layer is exposed to an environment saturated in solvent vapors that diffuse into the organics, inducing a local and/or mesoscale reorganization of the molecular donor and acceptor counterparts. Factors that affect the effectiveness of the SVA treatment include (i) the solubility of the molecular donor and/or acceptor, (ii) the partial pressure of the selected solvent, and (iii) the time of exposure.^{14,16} While SVA protocols are proving useful in the optimization of the SM donor-fullerene BHJ morphologies and efficiencies,²¹⁻²³ a better understanding of the direct correlations between solvent vapor exposure, morphological changes, crystallization, and carrier effects across the active layer (i.e. charge generation, transport, recombination and extraction) should be established in order to continue improving beyond currently reported efficiencies.

In our initial work, we described the rational design approach that led to the development of the SM donor BDTQdC (Chart 1) – a particularly efficient material system in BHJ solar cells with the fullerene acceptor PC₇₁BM.²⁴ When subjected to SVA conditions, BDTQdC-based BHJ solar cells see their PCE increase from a

modest *ca.* 2.5% (“*as-cast*” values) to >8%, with some important apparent morphological changes.²⁴ In the present contribution, we examine the systemic influence of the SVA protocol based on chloroform vapor employed in the optimization of BHJ device performance for the model system BDT[2F]QdC:PC₇₁BM and, more specifically, the impact of SVA exposure time –which is shown to mediate the selective crystallization of the SM donor (BDT[2F]QdC) with respect to the fullerene acceptor (PC₇₁BM), and sets the lengthscale of the phase-separated network. As the morphology evolves across the active layer, we demonstrate that SVA-mediated crystallization effects direct charge generation, recombination and extraction in the SM donor-fullerene BHJ solar cells, to which connects device performance figures. Our systematic examinations combine a large span of characterization techniques that provide direct insight into morphological and carrier effects, including: in-situ UV-vis absorption, high-resolution transmission electron microscopy (HR-TEM), atomic force microscopy (AFM), photoluminescence (PL) quenching analyses, transient photocurrent (TPC) measurements, X-ray diffraction (XRD) and time-delayed collection field (TDCF).

Results and Discussion

Material Properties

The solution and thin film UV-vis spectra overlaid in Figure 1a show a significant bathochromic shift on going from solution to the thin film –an observation indicating that aggregation, typically promoted by π – π interactions, takes place upon solidification of the SM donor in films.^{25, 26} The absorption of the thin films have two main spectral features, an absorption band at high energy (centered around 430 nm) and a lower-energy band consisting of three apparent “peaks” (convoluted) respectively at *ca.* 575 nm, 630 nm and 688 nm. Referring to previous work,^{5, 27, 28} we assign the 688 nm peak to the A₀₋₀ transition and the 630 nm peak to the A₀₋₁ transition. Figure 1b emphasizes the temperature-dependent spectral variations observed in thin films of BDT[2F]QdC as the layer is subjected to a gradual elevation of temperature (up to 180°C) (cf. experimental details in the SI). Looking at the intensity ratio of the 2 vibronic peaks A₀₋₀ and A₀₋₁: while the film temperature increases, the ratio I_{A0-0}/I_{A0-1} decreases, and a blue-

Chart 1. Molecular Structures of the SM Donor BDT[2F]QdC and the Fullerene Acceptor PC₇₁BM.

shift of the A₀₋₀ maximum intensity is observed. The evolution of the ratio I_{A0-0}/I_{A0-1} combined with the blue-shift observed is consistent with the fact that thermal heating induces molecular disorder and weakens π – π stacking interactions.²⁸⁻³⁰ Considering the remarkable variation in UV-vis absorption patterns shown in Figure 1c for the BDT[2F]QdC:PC₇₁BM blend films (1:1) subjected to solvent vapors (SVA), it is evident that molecular reorganization effects are occurring across the films. Compared to the neat film, the spectrum of the BDT[2F]QdC:PC₇₁BM blend in “*as-cast*” film shows only weak vibronic features and the 0-0 peak around 680 nm is absent. In other words, the presence of PC₇₁BM in the blend films suppresses the propensity of ordered BDT[2F]QdC aggregates to form. This behavior is consistent with prior reports depicting a reduction in overall crystallinity with the incorporation of fullerenes (commonly referred to as “vitrification” process), resulting in the formation of disordered mixed phases within the donor-acceptor blends.³¹⁻³³ In contrast, upon solvent exposure for 20s, the features observed in the UV-vis spectrum of the blend film are common to those of the neat film: prominent A₀₋₀ and A₀₋₁ peaks. Those observations are consistent with the occurrence of pronounced morphological changes during the SVA process. In light of those analyses, we turned to a more involved study of the aggregation kinetics, performing in-situ UV-vis absorption measurements on the BDT[2F]QdC:PC₇₁BM blend films during the first 120 seconds of solvent exposure. The outcome of this study is presented in Figure 1d (full spectrum in Figure S1). In this experiment, the blend film was placed inside the Petri dish saturated in solvent vapor, and the transmission of a white light passing through the films was measured with a time resolution of two spectra per second (cf. further experimental details in the SI, section 2; for consistency, the setup used was the same as that later employed in the later device sections). Here, we note that SVA time is provided on a logarithmic scale because most morphological changes occur during the first 20 seconds.

Figure 1. (a) Superimposed solution and thin-film UV-vis absorption spectra for BDT[2F]QdC (normalized). (b) Temperature-dependent thin-film UV-vis absorption for BDT[2F]QdC subjected to increasing temperatures over the range 25–180 °C. (c) UV-Vis absorption of BDT[2F]QdC:PC₇₁BM blend films (1:1), “as-cast” and after 20s chloroform (CF) vapor exposure. (d) In-situ absorbance of BDT[2F]QdC:PC₇₁BM blend films (1:1) vs. solvent vapor annealing (SVA) exposure time.

Within the first 20s, the 0-0 peak emerges, and its maximum peak intensity red-shifts to some extent upon solvent exposure. Since the intensity of the 0-1 peak increases only slightly during this time, the overall ratio I_{A0-0}/I_{A0-1} increases substantially, indicating that structural order is developing in the film, along with π - π aggregation. From 20 to 120 seconds, the UV-vis spectrum of the BDT[2F]QdC:PC₇₁BM blend film shows only minor changes over time, suggesting that any further crystallization may be occurring from the merging of existing crystallites.

Device Examinations

Solution-processed thin film BHJ solar cells were fabricated using the conventional device architecture ITO/PEDOT:PSS/BDT[2F]QdC:PC₇₁BM/Ca/Al (device area: 0.1 cm²), and were tested under simulated AM1.5G illumination (100mW/cm²); the detailed experimental protocol is provided in the SI (see section 1). Table 1 summarizes the figures of merit of the BHJ devices made from BDT[2F]QdC and PC₇₁BM, where the active layers are treated with various SVA times (up to 120 seconds); the *J-V* curves of the corresponding devices are shown in Figure 2a. As shown in Table 1, the reference “as-cast” device shows an open-circuit voltage (V_{oc}) of 0.96 V and only modest short-circuit current (J_{sc}) and fill-factor (*FF*) values of 6.9 mA/cm² and 33%, respectively. Within the first 20s of SVA treatment, both the J_{sc} and *FF* increase significantly, reaching 11.4 mA/cm² and 66%, respectively. The power conversion efficiency (PCE) upon optimal solvent annealing time

Figure 2. (a) Characteristic *J-V* curves of BHJ solar cells made from BDT[2F]QdC:PC₇₁BM active layers subjected to various SVA times. (b) Photocurrent (J_{ph}) vs. effective applied voltage $V_{eff} = (V_0 - V)$. (c) J_{sc} vs. light intensity of BDT[2F]QdC:PC₇₁BM. The solid lines correspond to fits to the data according to $J_{sc} \propto I^{\alpha}$. Analyses performed via a white LED with a maximum irradiance of 200 mW/cm². In accounting for spectral mismatch, 70% of the maximum irradiance of the white-light LED was used to reproduce the J_{sc} values achieved under standard AM1.5G solar illumination (100mW/cm²).

Table 1. Summary of PV device performance parameters for BDT[2F]QdC:PC₇₁BM active layers subjected to various solvent vapor annealing (SVA) times.

SVA time	V_{oc}	J_{sc}	<i>FF</i>	Avg. PCE ^a	Max. PCE
[s]	[V]	[mA/cm ²]	[%]	[%]	[%]
0	0.96	6.9	33	2.2	2.3
5	0.95	9.5	38	3.4	3.7
20	0.94	11.4	66	7.1	7.2
60	0.94	5.5	58	3.1	3.2
120	0.94	2.1	36	0.7	0.9

^aAdditional device statistics are provided in Table S1 in the Supporting Information.

peaks to 7.1% (Avg.; 7.3% Max.). Upon longer solvent exposure times, the J_{sc} decreases and drops to 5.5 mA/cm² after 60s, and down to 1.8 mA/cm² after 120s. The *FF* also decreases from 66% for “optimized” devices to 36% after 120 s. It is worth noting that the *FF* remains as high as 58% after 60s. After 120s of SVA treatment, the PCE drops to 0.7%, and longer solvent annealing times result in partial active layer deterioration, leaving partially uncovered areas across the substrate. Clearly, the SVA treatment plays a determining role, setting the conditions for high J_{sc} and *FF* values, but can also be detrimental to device operation. Assuming that the SVA exposure times directly impacts active layer morphology, an

Figure 3. Bright-field TEM images of the BHJ thin-film morphologies for various SVA times: (a) 0s, (b) 20s, (c) 30s, (d) 60s and (e) 120s. The scale bar is 500nm. (f) Photoluminescence quenching (PLQ) of SM:PC₇₁BM blend films obtained from various durations of SVA exposure. Excitation at 630nm. (g) Specular XRD of the neat SM donor (neat film). Intensity plotted on a log scale. (h) Specular XRD of the SM donor (neat film) and that of the blend with PC₇₁BM for various SVA times (up to 120s). Intensity plotted on a linear scale.

indirect examination of the internal electric field across the BHJ solar cells should reveal significant variations in active layers exposed to various SVA times.

To understand the role of the internal electric field on the device current we analysed the photocurrent as a function of the effective voltage;^{34,35} data presented in Figure 2b. The photocurrent J_{ph} is given by the current measured under light minus the current measured in the dark. The effective applied voltage V_{eff} is defined as the voltage V_0 for $J_{ph}=0$ minus the applied voltage V . For BHJ devices subjected to 20s and 60s SVA, J_{ph} increases rapidly at low voltages and saturates at an effective voltage of *ca.* 0.3 V. The early onset of saturation of the photocurrent observed in those devices indicates that the internal electric field plays a minor role during charge extraction, and that charges are efficiently extracted at the electrodes. The distinct values of saturated current reflect the difference in J_{sc} between the two devices (see Table 1). In contrast, “*as-cast*” devices do not show this saturation regime as the photocurrent keeps increasing with applied voltage. Interestingly, at significantly higher effective voltage (>3V), the “*as-cast*” device and the optimized devices have similar photocurrents, indicating that the modest J_{sc} measured for the *as-cast* device does not originate from charge generation issues, but rather from a poor extraction of carrier at the electrode interfaces. If not assisted by a strong electric field, the charges recombine before reaching the electrodes. The photocurrent measured for the BHJ devices subjected to 120s SVA also show a continuous dependence on voltage, with no visible saturation regime. In this instance, the photocurrent remains low at high voltages (3–4 mA cm⁻²), even though the electric field increases charge collection to some extent.

In order to quantify the extent of bimolecular recombination occurring in active layers subjected to varying SVA times, we tested

the BHJ solar cells under various light illumination intensities. It has been shown that the extent of bimolecular recombination can be estimated looking at the dependency of different illumination conditions on the device J_{sc} .³⁶ The dependence of the J_{sc} is described by $J_{sc} \propto I^\alpha$. Here, a value of α close to unity indicates a regime where bimolecular recombination losses can be considered negligible, whereas smaller α values indicate a competition between recombination and carrier extraction.³⁷ Figure 2c shows the J_{sc} versus light intensity data for various SVA times, (all J - V curves are provided in Figure S2). For the *as-cast* device (no SVA treatment) the fit yields $\alpha = 0.81$, indicating substantial bimolecular recombination losses. After SVA exposure for 20s and 60s, $\alpha = 0.97$, suggesting that bimolecular recombination gets significantly reduced. Longer SVA treatments of 120s result in $\alpha = 0.85$, indicating that bimolecular recombination significantly limits device efficiency for longer exposure times as well.

In several prior studies,^{14, 16, 23} SVA treatments have been described as inducing crystallization and changing the morphology of the BHJ blend films. Thus, one may assume that crystallization effects occurring in BDT[2F]QdC:PC₇₁BM active layers subjected to SVA may also be at the origin of significant macroscopic changes in thin-film morphology. Here, active layer morphologies were analyzed via bright-field transmission electron microscopy (TEM) and atomic force microscopy (AFM); results shown in Figure 3. Figure 3 shows the blend morphologies obtained upon exposure to SVA treatments of varying duration. Donor- and acceptor-rich domains (bright and darker regions, respectively) appear rather intermixed in the *as-cast* films (Figure 3a), and domain sizes can be inferred as <10 nm. During solvent exposure, the BHJ reorganizes and the size of the domains increases. After 20s, time after which the “optimized” thin-film condition is obtained, the size of the do-

mains increases to 15–20 nm –a favorable domain size range allowing excitons to reach D/A interfaces, and favoring carrier generation and percolation required for efficient transport and extraction. Upon further solvent exposure, the donor-rich domains form needle-like morphologies across the active layer. By direct imaging, the widths of these apparent crystalline features can be inferred as ca. 35, 95 and 600 nm (avg. widths) for SVA-treated films exposed for 30, 60 and 120s respectively. Large domains (>30nm) are not desirable from a charge generation standpoint, as excitons tend to decay before reaching the donor-acceptor interface. After 120s of solvent exposure, the SM donor crystallites are overly grown (as large as film thickness) and the active layers no longer form BHJ networks. These severe aggregation patterns obtained upon prolonged solvent exposure have commonly been held responsible for the loss of photocurrent.²¹ AFM images and root mean square (RMS) roughness estimates are provided in Figure S3. *As-cast* BHJ thin films are smooth RMS estimates of ca. 0.5 nm. RMS values then gradually increase for active layers exposed to longer SVA times. For films said “optimized”, RMS values remain low at ca. 1.3 nm. RMS estimates then rise quickly to values as high as 19.8 and 45.6 nm for SVA times of 60 and 120s, respectively. Those increases in RMS roughness are consistent with the TEM data indicative of a substantial growth of the SM donor-rich domains.

To examine the effect of domain size on charge generation and device photocurrent, we analyzed the propensity of excitons to reach the donor-acceptor interfaces via photoluminescence quenching (PLQ) measurements. Figure 3f shows the PLQ data for films exposed to various SVA times (raw data provided in Figure S4). The high PLQ value of 93% measured for the *as-cast* BHJ thin film is consistent with the short domain lengthscale observed for the same films via high-resolution TEM (Figure 3), and indicates that excitons are effectively reaching the interface. With longer SVA times, the SM donor-rich phases grow and the PLQ values drop to some extent. It is worth noting that “optimized” films undergo a slight reduction in PLQ value of 5–10% compared to *as-cast* films, but here we note that the corresponding devices still show increased current density, suggesting that the somewhat increased exciton quenching process does not significantly affect charge generation at this stage. However, longer solvent exposure times lead to significantly larger domain sizes, which in turn substantially decrease the PLQ values to 58 and 53 % for 60 and 120s SVA times, respectively. These low PLQ values are consistent with pronounced exciton decay reflected in reduced charge generation (in agreement with the device current densities of < 3 mA/cm²). Correlated with the TEM analyses (Figure 3), the PLQ data is also pointing to the high purity of the SM donor crystallites forming on longer SVA times (needle-like domains).

Earlier grazing incidence wide-angle X-ray scattering (GIWAXS) experiments showed that the SM donor BDT[2F]QdC tends to crystallize in neat films, adopting edge-on orientations with respect to the substrate with intermolecular π - π spacings of ca. 3.68 Å.²⁴ However, in blends with PC₇₁BM, the SM donor does not maintain the same degree of structural order and crystallites with mixed orientations prevail.²⁴ Solvent exposure induces more crystallinity, as reflected by the higher-order lamellar reflections and more pronounced π - π stacking arcs visible in the GIWAXS spectra. In Figure 3g,h, we use specular X-ray diffraction to provide further insights into the aggregation pattern of the SM donor in both neat

and blend films with PC₇₁BM subjected to various SVA times. In the specular reflection data, out-of-plane diffraction peaks are observed where the (100), (200) and (300) reflections are resolved. The specular data is also consistent with the fact that BDT[2F]QdC tends to adopt an edge-on configuration, and from the data a lamellar spacing of 1.70 nm can be inferred. Figure 3h shows that the high crystallinity of the neat films is not maintained as BDT[2F]QdC is mixed with PC₇₁BM in *as-cast* active layers, with only a relatively broad first-order reflection showing on the X-ray pattern, while the corresponding diffraction peak intensity is greatly reduced (“vitrification” process). This observation is consistent with the features described earlier from the absorption spectra of the BDT[2F]QdC:PC₇₁BM blend films (Fig. 1c). Upon solvent annealing of the active layer, the intensity of the first-order lamellar peak increases and its intensity rises, indicating the coherence length of the SM donor gradually increases during the first 40s. After 60s SVA time, the XRD patterns become comparable to that of the neat SM donor with high-intensity higher-order reflections indicative of the significantly higher structural organization achieved in the BHJ blend films.

Important morphological differences between films often correlate with distinct charge transport patterns and, in SM-based BHJ solar cells with fullerene acceptors, the occurrence of crystalline aggregates –in which carrier transport proceeds by intermolecular charge transfer events– only exacerbates the morphological dependence. The carrier mobilities of the various active layers subjected to distinct SVA treatment durations were determined from the MIS-CELIV method;³⁸ results reported in Figure 4 (see experimental details in the SI, section 7). As shown in Figure 4, the hole and electron mobilities of *as-cast* devices

Figure 4. Hole- and electron-only MIS-CELIV mobility of the active layers exposed to various SVA times. The error bars represent the standard deviations (estimated from at least 3 devices). MIS-CELIV dark-current transients are provided in Figure S5 (electrons) and Figure S6 (holes).

are rather modest: 6.5×10^{-7} and 5.0×10^{-6} cm²V⁻¹s⁻¹, respectively. However, those figures increase rapidly within the first 20s of SVA treatment. Beyond 20s, the hole and electron mobilities reach 2.8×10^{-5} cm²V⁻¹s⁻¹ and 6.3×10^{-4} cm²V⁻¹s⁻¹, respectively –representing significant increases of ca. x40 and x140 (respectively) compared to the *as-cast* films. The slight mobility reductions estimated for active layers subjected to longer SVA exposure times are likely the result of the less continuous BHJ networks as pronounced crystalline aggregation takes place in the films. Low and/or unbalanced

mobilities correlated to morphological factors can induce space-charge effects that impact BHJ solar cell performance.^{21,39}

To examine the role of morphology-related limiting factors on space-charge effects, we turned to transient photocurrent (TPC) measurements. In recent work, TPC measurements have been used to investigate space-charge effects, carrier trapping and de-trapping in polymer-fullerene,^{40, 41} “all-polymer”⁴² and hybrid⁴³ BHJ solar cells. During the measurement, devices held in the dark are subjected to a long light pulse (200 μ s) allowing the short-circuit current to reach its steady-state value, and various light intensities are scanned (the LED intensity corresponding to “one sun equivalent” produces a device current equivalent to the one obtained upon illumination via solar simulator). In general, the rise/fall behavior of the photocurrent is described with respect to two components, a fast initial rise/fall component followed by a second component of slower dynamics. Figures 5a-d (normalized at 190 μ s) and Figure S7 (raw data) show the transient short-circuit current for the devices subjected to the various, aforementioned SVA times. In the *as-cast* active layers, the rise time (defined as the time taken to go from 10 to 90% current intensity) drops from 39 to 1.2 μ s when the light intensity increases from 0.14 to 1.43 sun. With increasing light intensity, the fast rise of the current evolves into a transient peak before leveling off to the steady state J_{sc} . In parallel, the slow component gets suppressed as light intensity increases –an observation that can reflect the filling of trap states at higher intensities⁴⁴ and/or charge density-dependent carrier mobility.⁴⁵ The transient photocurrent peak observed at higher light intensities can be attributed to space-charge effects, whereby an accumulation of one carrier type occurs under the effect of mobility ratio imbalance after a few μ s, thus reducing charge generation and increasing recombination.⁴⁶ In contrast, active layers exposed either to SVA treatments for 20s and 60s exhibit fast rise/fall times almost independent of light intensity, indicative of a favorable device behavior for which modest mobilities, carrier traps and space-charge effects are not significant limiting factors. For 120s SVA treatments, the TPC data shows a prominent transient peak within the first 50 μ s; broad and weak at low intensities, the photocurrent peak sharpens and becomes more

pronounced with increasing light intensity (*i.e.* as the number of carriers increases across the device). Vertical phase segregation and carrier-blocking layers forming at interfaces can induce this behavior.⁴⁷ Here, we think that trapped electron populations in the PC₇₁BM-rich domains (higher mobility phase) steadily build up, inducing trap-mediated space-charge characteristics that promotes recombination and suppresses charge generation.

The origin of the space-charge effects and the occurrence of charge build-ups can be confirmed by examining the voltage dependence of the transient current. By applying a voltage bias, the internal field in the device varies; if the internal field increases, the drift of the charges is promoted (reverse bias) and if the internal field gets reduced, the open-circuit condition is approached and carrier recombination increases (forward bias). Figure 5e-h shows the corresponding data for 1 sun equivalent (normalized in Figure S8); the applied bias being scanned from -0.75V to +0.75V. As illustrated in Figure 5, the *as-cast* device sees its current vary greatly (from 2mA to 10mA) upon scanning of the applied bias – observation consistent with the low FF of the device indicative of a notable recombination regime. Given the low carrier mobilities estimated earlier for the *as-cast* device, a large reverse bias effectively promotes the drift of the charges and favors hole collection (suppressing the space-charge effects seen at short-circuit). In contrast, near the open-circuit voltage, the internal field is low and carrier collection becomes less effective. As holes accumulate (space-charge), the transient peak becomes more pronounced and the collection current is suppressed. On the other hand, devices subjected to 40s and 60s SVA treatments show minimal-to-no dependence on the applied voltage. For those devices, the shape of the transient current is practically independent of the applied voltage (also see Fig. S8 b-c). Importantly, Figure 5h shows that active layers exposed to longer SVA times (here, 120s) suffer from a dependence on the applied bias that resembles that of *as-cast* devices. Those results can be correlated to those discussed earlier from Figure 3, showing the occurrence of overgrown crystallites with domain sizes far greater than

Figure 5. Transient J_{sc} (normalized) in response to a 200 μ s white light (LED) pulse for various light intensities (given in sun equivalent) and for BHJ active layers subjected to varying SVA exposure times: (a) “as-cast” (0s), (b) 20s, (c) 60s, and (d) 120s. Transient current in response to the 200 μ s white light (LED) pulse at 1 sun equivalent, for various voltage biases applied and for BHJ active layers subjected to varying SVA exposure times: (e) “as-cast” (0s), (f) 20s, (g) 60s, and (h) 120s.

the diffusion length of excitons. In this case (120s SVA time), the phase-separation lengthscale is such that trapped carriers cannot be efficiently extracted even under large reverse voltages. Those accumulate in the active layer, changing the local electric field, increase recombination effects and suppressing charge generation.

To examine the impact of the electric field on geminate recombination and charge generation, we turned to time delayed collection field (TDCF) experiments. In prior studies using TDCF experiments to probe the influence of the electric field on charge generation: Knipert et al. described a charge generation process independent of the electric field in “as-cast” and optimized P3HT:PC₇₁BM blend films;^{48, 49} considering various polymer:PC₇₁BM systems, Albrecht et al. emphasized an apparent interdependence between chemical structure, optimization protocol and dependence of charge generation on the electric field;^{50, 51} Foerzig et al. correlated the use of the processing additive DIO, morphological changes in the blend films, and an apparent suppression of the dependence of charge generation on the electric field;⁵² and Proctor et al. related the use of DIO to the reduction of geminate recombination in a SM-based blend system.⁵³ In TDCF analyses, the devices are subjected to a pre-bias (V_{pre}) and illuminated with a short laser pulse. After a certain delay time (t_d), a large reverse bias is applied to the solar cell to collect all the remaining carriers. The transient current is integrated to determine the total of collected charges (Q_{tot}). The fluence of the laser pulse is low enough that non-geminate recombination remains negligible while geminate recombination represents the main loss channel. Measuring Q_{tot} as a function of the pre-bias can be seen as a direct measurement of the voltage dependence of geminate recombination. First, the pulse fluence was varied from 0.02 to 1.5 μ J·cm⁻² in order to determine the regime where the relation between light intensity and the col-

lected charges is linear (Figure S9). The excitation wavelength was chosen to be 532 nm, noting that at this wavelength the absorption of the blend does not change during the SVA treatment. The measurements were performed with a delay time of 10ns and a V_{coll} of -4V; results shown in Figure 6. Interestingly, for the non-optimized as-cast device, Q_{tot} is independent of V_{pre} . The charge generation is independent of the pre-bias voltage. Devices for which the active layer was subjected to 20s SVA exposure time show a weak dependence of the charge generation on the pre-bias V_{pre} . Geminate losses at open-circuit condition are 8% higher than the losses incurred at -2.5V. For active layers exposed to 60s SVA times, the dependence is even stronger with geminate losses 18% higher at open-circuit condition compared to the loss incurred at -2.5V. Here, it is worth noting that these results differ from those obtained earlier by Proctor et al. who found that geminate recombination in as-cast devices can be strongly voltage-dependent, whereas “optimized” devices cast using DIO as the processing additive did not show the same dependence.⁵³ In their study, the reduced field dependence was correlated to the highly ordered crystalline domains obtained in active layers cast with DIO. Since the solvent vapor annealing process also increases domain sizes while promoting phase crystallinity, a similar trend could have been expected. In light of those differing outcomes, we conclude that the relative crystallinity of the domains alone cannot explain the voltage-dependence of charge generation. Other factors difficult to probe and beyond the scope of this study could have a contribution to the voltage-dependence: (i) molecular orientation at the donor-acceptor interface, (ii) the concomitance of ordered and disordered domains, and (iii) the presence of the so-called “mixed” phase. In BDT[2F]QdC:PC₇₁BM active layers, the presence/absence of mixed phase may be at the origin of the behavior observed. Based

on direct TEM imaging and considering the crystallization process of BDT[2F]QdC mediated by SVA treatment, the interface between the donor

Figure 6. *J-V* curves (left axis) and voltage dependence of the total charge extracted as probed by TDCF experiment (right axis) for BHJ active layers subjected to varying SVA exposure times: (a) "as-cast" (0s), (b) 20s, (c) 60s. (d) Total extracted charge data normalized to Q_{tot} at -2.5V. The right axis provides the percentage of photogenerated carriers lost due to geminate recombination relative to the loss incurred at -2.5V.

and the acceptor domains is expected to be sharp and abrupt – a situation likely to result in the reduction of mixed-phase at those interfaces. The mixed phase is known to be beneficial to charge separation and to suppress carrier recombination in BHJ solar cells.^{19, 54, 55}

Additional Remarks

As-cast active layers show a high degree of intermixed donor- and acceptor-rich domains – a situation that can lessen the level of interconnection within donor and acceptor phases through molecular intercalation (e.g. fullerenes isolating SM donors and disrupting their packing/aggregation propensity) and, in turn, disfavor efficient percolation pathways for charge transport. As the UV-Vis data (Fig. 1) lacks the footprint of structural order through aggregation, the XRD pattern of the *as-cast* blend (Fig. 3h) indicates that the structural order present in the neat films of SM donor is not preserved in the blend film. In contrast with polymer-fullerene BHJ solar cells, where charge transport occurs mainly through π -conjugated main-chain conduction pathways (including tie-chains interconnecting distant domains), carrier transport in SM donor-fullerene systems is dominated by intermolecular charge transfer processes and relies on molecular interconnects. With the low degree of structural order seen in *as-cast* devices, the carriers mobilities are at their minimum, $\sim 10^{-7}$ and $\sim 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and electrons, respectively. In the meantime, the small domain sizes (<10nm) provide a high density of D/A interfaces, favoring charge separation processes across the active layer. In those devices, charge generation is efficient and shows no sign of voltage-dependence. Nevertheless, those same devices suffer from low charge collection yields. Given the limited mobilities and the non-

ideal bulk morphology lacking percolation pathways, free carriers are not efficiently reaching the electrode interfaces, and tend to recombine non-geminately instead. The modest and unbalanced mobilities in *as-cast* devices cause an accumulation of holes (space charge effect) across the active layer that further promotes recombination and suppresses charge generation. In contrast, in SVA-treated active layers, solvent exposure induces the crystallization of the SM donor, and both domain size and crystallinity increases, impacting device performance. Upon 20s of SVA exposure, the morphology transitions from overly mixed to a favorable co-continuous network with domains sizes of 15-20 nm that are adequate for charge generation and charge collection processes. As packing and structural order increase, carrier mobilities improve, promoting charge transport and charge collection. Bimolecular recombination is greatly reduced in parallel. This condition yield the best device efficiency figures, comprising the highest J_{sc} and FF values achievable with BDT[2F]QdC:PC₇₁BM active layers.

On the other hand, exposing the active layer to the solvent for more extended periods of time results in a deterioration of device performance. In those instances, the SM donor forms larger-sized crystals of high purity (needle-like structures) and the morphology evolves towards domain sizes larger than the exciton diffusion length, affecting charge generation. A significant extent of excitons decay before they can reach a D/A interface and the J_{sc} plummets. Thus, in 60s-SVA treated devices, while the high FF, high mobilities, fast transient behavior and low bimolecular recombination characteristics can be maintained, higher yields of exciton quenching (PLQ data, Fig. 3f) result in an overall drop in efficiency. Beyond 120s-SVA times, new morphological effects take place and the interpenetrating network model is no longer valid. SM donor domains are now sufficiently extended that their lengthscale matches the thickness of the active layer, hindering electron collection at the cathode (amongst other issues). In turn, PC₇₁BM can be expected to segregate in the vertical direction across the BHJ and/or accumulate at the wrong interface (*i.e.* anode). Poor charge generation and extraction are at the source of the more modest efficiencies estimated for those devices, which show lower photocurrents and the characteristics of charge-trapping effects.

Conclusions

In summary, our examinations of the time-dependence of solvent vapor annealing (SVA) on SM donor-fullerene BHJ solar cell efficiency via a combination of direct morphology imaging and spectroscopy techniques establish a fundamental understanding of this important device optimization protocol. As SVA treatments induce a reorganization of the BHJ morphology from a highly intermixed blend with limited structural order to a structurally ordered, co-continuous network, with crystalline domains sizes of 15-20 nm (20s-SVA condition), charge generation and collection patterns dramatically improve. However, our analyses indicate that extended SVA times (>60s) can promote excess crystallization and undermine device performance, as significant impediments arise from larger domain sizes: specifically, increased exciton quenching and detrimental extent of phase segregation between SM donor and fullerene acceptor. Since SVA treatments tend to reduce the density of mixed phase across the active layer, our findings show that it is critically important to control SVA exposure times. Over-

all, SVA protocols represent a particularly useful tool in the optimization of SM donor-fullerene BHJ solar cells, but our study also shows that they are an efficient method to examine morphology-charge dynamics relationships in BHJ solar cells in general independently of intrinsic molecular characteristics when comparing two or more molecules.

ASSOCIATED CONTENT

Supporting Information

Experimental methods, characterization, and additional figures and tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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Solvent Vapor Annealing-Mediated Crystallization Directs Charge Generation, Recombination and Extraction in BHJ Solar Cells

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TOC Figure