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Structure Formation in P3HT/F8TBT Blends

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Abstract

The structure evolution of all-polymer solar cells based on the blends of poly(3-hexylthiophene) (P3HT) and poly[(9,9-dioctyluorene)-2,7-diyl-alt-(4,7-bis(3-hexylthien-5-yl)-2,1, 3-benzothiadiazole)-2',2"-diyl] (F8TBT) was investigated. The P3HT/F8TBT system exhibits crystallization-driven structure formation similar to the P3HT/Phenyl-C61butyricacidmethylester (PCBM) blend despite the existence of a miscibility gap, which was determined for a blend containing regio-random P3HT. The lamellar crystallization of regio-regular P3HT was not perturbed by the addition of F8TBT. X-ray scattering studies indicate that F8TBT is segregated to the interlamellar amorphous phase,

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establishing a bulk heterojunction framework with the crystalline lamellae of P3HT. The excess F8TBT is accommodated at the film/substrate interface and at amorphous grain boundaries. The structural studies were correlated with the photovoltaic device performance of blend films that consisted of large P3HT spherulites. These device results emphasize the importance of a mesoscopic F8TBT network that separates the P3HT crystal domains. Out results suggest that the nanostructure formation in P3HT/F8TBT blends is determined by P3HT crystallization, resulting both in a 10-nm crystalline morphology and a F8TBT mesoscopic segregation network, both of which are beneficial for exciton dissociation.

Broader Context

Organic solar cells have long been regarded as low-cost alternatives for silicon-based solar cells and new solar-powered products with thin and flexible form factors. With the latest developments of new materials, efficiencies beyond 10% for polymer-fullerene blends and beyond 5% for polymer-polymer systems have been demonstrated. A key issue still remains the nano-morphology of the donor and acceptor material. Employing new materials usually implies the optimization of material processing of the blends to achieve a desirable nano-morphology with sufficiently pure and well interconnected domains. In this manuscript we focus on the crystallinity of a polymer as prevalent in many conjugated polymers. The nano-morphology formation by polymer crystallization in polymer-polymer solar cells is discussed and limitations compared to its fullerene based devices are explored.

Introduction

Organic solar cells based on conjugated polymers as electron donor and fullerene derivatives as electron acceptor are the standard in polymer-based photovoltaics. Since the initial demonstration of polymer/fullerene systems, device efficiencies have substantially improved

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through empirical optimization. While polymer/fullerene systems show good device performance, polymer/polymer blends offer some potential advantages. The variation of the chemical composition of polymers enables the tuning of semiconducting properties such as the bandgap and energy levels, thereby engineering light absorption and open circuit voltages.^{1–4}

The recent performance enhancement of polymer/polymer solar cells, with power conversion efficiencies (PCE) of $\sim 4\%$,^{5,6} is however still relatively poor compared to polymer/fullerene devices. Polymer/polymer systems often suffer from geminate recombination of electron-hole pairs, resulting from charge traps at the donor-acceptor interface, whereas fullerene acceptors show enhanced electron delocalization limiting recombination.⁷ Many polymer/polymer pairs are immiscible because of their high molecular weight, which reduces their effective entropy of mixing.^{8–11} The understanding and control of phase separation in these polymer blends is therefore crucial for the optimization of device performance. The bulk heterojunction concept relies on the high purity of donor and acceptor phases within the characteristic exciton diffusion length, requiring a percolating interconnected network morphology. It is therefore of critical importance to control phase separation at ~ 10 nm length scale compatible with the exciton diffusion length since excitons need to diffuse to and dissociate at donor/acceptor interface to generate charges. To reduce losses by recombination and increase device efficiencies, domain sizes slightly larger than exciton diffusion lengths are beneficial.¹² This morphology has to be embedded in a mesoscopic bicontinuous network that provides charge transport to the two electrodes.

Presently, device optimization is carried out empirically by varying film processing. The morphology is often optimized by using selective solvents for one of the polymers or by adding solvent additives to spin-coating solution.^{13,14} The use of post-fabrication thermal annealing may further alter the film morphology.^{15–18} For the P3HT/F8TBT blend system, a five-fold increase in photocurrent and efficiency has been achieved by thermal annealing.¹⁹ The improvement of device performance is correlated with the growth and purification of the

 ~ 10 nm domains as well as enhanced P3HT crystallization.²⁰ Bulk heterojunction donor and acceptor interface morphologies should have length scales that match the exciton diffusion length, but the processes by which such structures develop in P3HT/F8TBT are not well understood.

The morphology evolution in crystallizing blends is rather complex because of two pathways of polymer-polymer phase separation and crystallization. For many polymer/fullerene blends, structure formation is driven either by polymer crystallization or the aggregation/ crystallization of the fullerene.^{21–23} While this is aided by the typically good miscibility of fullerene derivatives with many conjugated polymers and the lack of kinetic trapping by entanglements, it is unclear in how far crystallization-dominated structure formation also applies to photovoltaic polymer/polymer blends.

In this paper, we present a study of the structure formation in P3HT/F8TBT blends that exemplarily shows the interplay of phase separation and crystallization and its role in photovoltaic device performance.

Results and Discussion

Morphology of P3HT/F8TBT Thin Films

To investigate the miscibility of P3HT and F8TBT, we examined the surface morphology of blend films after melt annealing. Sample series employing three different batches of P3HT were employed, a regio-random polymer with a molecular weight ($M_n = 60 \text{ kg/mol}$ (P3HT-RA), a regio-regular reference material with $M_n = 20 \text{ kg/mol}$ (P3HT-RR1) and the narrowly distributed regio-regular P3HT containing one distributed tail-to-tail defect (P3HT-RR2) with $M_n = 11.8 \text{ kg/mol}.^{24}$ The F8TBT used had $M_n = 49.3 \text{ kg/mol}.^{25}$ Blends with F8TBT:P3HT mixing ratios varying from f = 0.25 : 1 to f = 2 : 1 were studied by atomic force microscopy (AFM). All as-spun films had a homogeneous surface topgraphy (not shown), resulting from a fast quench through solvent evaporation, which suppressed



Figure 1: AFM images of (a-d) P3HT-RA/F8TBT, (e-h)P3HT-RR1/F8TBT, (i-l) P3HT-RR2/F8TBT thin films for various F8TBT/P3HT mixing ratios f after melt annealing.

surface phase separation and crystallization. The samples were then annealed at $230 \,^{\circ}\text{C}$ (above their respective melting point and glass transition temperature of both polymers and slowly cooled to room temperature (rate: $5 \,^{\circ}\text{C/min}$), aiding the thermodynamic equilibration of the samples.

Figure 1 shows AFM height images of 80 to 100 nm thick films after cooling from the melt. P3HT-RA/F8TBT blends show a topography reminiscent of lateral phase separation morphologies which are typical for amorphous/amorphous mixtures in thin films, indicating a limited miscibility of the two polymers.²⁶ With increasing F8TBT content a characteristic

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Figure 2: AFM images of low-f P3HT-RA/F8TBT films after melt annealing.

phase inversion is observed going from f = 0.5 (dark P3HT majority phase) to f = 1 (bright F8TBT majority phase). The loss of contrast in the film with f = 0.1 in Fig. 2 suggests an experimentally accessible miscibility range in the phase diagram which is typical for weakly incompatible polymers.²⁷ The observation of a well-defined spinodal demixing pattern in the P3HT/F8TBT blend is contrast to the observation in P3HT/PCBM blends.^{23,28,29}

Note that the immiscibility of the two components is very weak. The sub-micrometer phase domains in Fig. 1a-d suggest that demixing sets in upon cooling from a homogeneous melt at 230 °C, indicating that the blend has a critical demixing temperature below this temperature. Secondly, P3HT-RA has a much higher molecular weight compared to the two regio-regular batches, which further reduces demixing in these blends.

The films employing the two semicrystalline P3HT batches (P3HT-RR1 and P3HT-RR2) in Fig. 1 did not exhibit a phase morphology for the entire f-range, but instead showed a fibrillar surface texture that is characteristic for semicrystalline polymers.³⁰ The lack of demixing morphologies may arise from suppression of phase separation on the micron scale, a segregation of F8TBT to the substrate surface, or both. Note the distinctive texture in the P3HT-RR2/F8TBT films, which are indicative of longer-ranged crystalline features that form in P3HT-RR2 compared to P3HT-RR1. This may arise from the difference in molecular weight, polydispersity and regio-regularity of the two materials. In both films, the surface

texture is much reduced in the f = 2 films.

A second employed technique quantifying the crystallization in P3HT-RR1/F8TBT blends is UV-Vis spectroscopy. The spectra of as-spun and melt-annealed films are shown in Fig. 3. The annealed films show enhanced absorbance in the 500-625 nm range, accompanied by a characteristic vibronic P3HT peak near 610 nm. The spectrum of F8TBT lacks this vibronic structure and has an additional absorption band centered at ~ 370 nm. As a function of f, there is a smooth cross-over between the two pure compositions with a well-defined isosbestic point at ~ 415 nm in both as-spun and annealed films. To further characterize the spectral response, the UV-Vis spectra of the annealed films in Fig. 3b were integrated over wavelength ranges, in which the absorbance is dominated by P3HT (between $\lambda_1 = 550$ nm and $\lambda_2 = 625$ nm) and F8TBT (between $\lambda_3 = 265$ nm and $\lambda_4 = 375$ nm). The integrated intensities are quantified in terms of the F8TBT volume fraction $\phi = (1 + (\rho_{\text{F8TBT}}/\rho_{\text{P3HT}})/f)^{-1}$, with the densities $\rho_{\text{F8TBT}} = 1 \text{ g/cm}^3$ and $\rho_{\text{P3HT}} = 1.15 \text{ g/cm}^3$.^{31,32}

The absorbance intensity of P3HT was normalized to pure P3HT ($\phi = 0$) after subtracting the F8TBT absorbance,

$$I_{\rm P3HT}(\phi) = \frac{\int_{\lambda_1}^{\lambda_2} d\lambda \quad [I(\lambda, \phi) - \phi \cdot I(\lambda, 1)]}{\int_{\lambda_1}^{\lambda_2} d\lambda \quad I(\lambda, 0)}.$$
 (1)

The F8TBT absorbance signal was normalized to pure F8TBT ($\phi = 1$) after subtracting the absorbance originating from P3HT,

$$I_{\rm F8TBT}(\phi) = \frac{\int_{\lambda_3}^{\lambda_4} d\lambda \ [I(\lambda,\phi) - (1-\phi) \cdot I(\lambda,0)]}{\int_{\lambda_3}^{\lambda_4} d\lambda \ I(\lambda,1)}.$$
 (2)

The integrated P3HT and F8TBT intensities show a linear variation with volume fraction (Fig. 3c). The two lines intersect at $\phi = 0.5$, which implies that the absorbance signals from these two components are additive. Since the absorbance of crystalline and amorphous P3HT differ around 450 nm, the isosbestic point is evidence that the amorphous/crystalline ratio in P3HT is not strongly affected by the addition of F8TBT. Moreover, the surface morphology



Figure 3: UV-Vis spectra of P3HT-RR1/F8TBT blend films with F8TBT compositions ranging from f = 0 to f = 2; a) as spun and b) after melt annealing. c) Integrated intensities versus F8TBT volume fraction. d) AFM phase image and e) POM image of P3HT-RR1/F8TBT (f = 1) after melt annealing.

of a f = 1 blend film is reminiscent of P3HT lamellar stacks (Fig. 3d). This results form the formation of spherulites that can be seen in the the polarized light microscopy (POM) image in Fig. 3e. Both images support that crystallization of P3HT is not strongly affected by the addition of F8TBT.

Structural Study by X-ray Scattering

The effect of F8TBT addition on the crystallization of P3HT-RR2 was studied by grazing incidence small and wide angle X-ray scattering (GISAXS and GIWAXS, respectively) Measurements were performed for mixing ratios from f = 0 to f = 1.5. P3HT-RR2 was chosen because of its low polydispersity and nearly 100% regionegularity which allows us to resolve the long period of P3HT in GISAXS measurements as we reported earlier.³³ The low polydispersity and lower molecular weight enables the chains to assemble in fully chain-extended crystals, forming a superstructure of amorphous and crystalline domains with a periodicity similar to the contour length of the polymer chains (approx. 14 nm). P3HT-RR2 therefore serves as an ideal model polymer to study the mixing with F8TBT as any changes concerning the crystallinity of P3HT ($q > 0.3 \text{ Å}^{-1}$) or within the amorphous interlamellar domains ($q < 0.06 \text{ Å}^{-1}$) can be tracked. Figure 4 shows the two-dimensional (2D) GISAXS maps of P3HT-RR2/F8TBT films after cooling from the melt. The corresponding integrated profiles along q_y are shown in Fig. 5.

The pure P3HT film shows a lateral scattering signal at $q_y = 0.045 \text{ Å}^{-1}$, corresponding to a long-period of $L_p = 14 \text{ nm}$. P3HT/F8TBT blend films show similar scattering patterns but the peak shifts to lower q_y -values with increasing F8TBT content. This stems from an increase in the long period to 15 nm at f = 0.6 and to 16 nm at f = 1. GIWAXS was performed on the same samples to investigate the crystalline structure of P3HT/F8TBT blends, as shown in Fig. 6. In contrast to the change in L_p , the (100) and (200) P3HT Bragg peaks at $q_z = 0.39 \text{ Å}^{-1}$ and $q_z = 0.78 \text{ Å}^{-1}$ remain constant upon increasing the F8TBT content. The intensity variation of higher order peaks is caused by a relative decrease of the P3HT content. In addition, there is a (020) reflection from the π - π stacked structure of P3HT at $q_y = 1.72 \text{ Å}^{-1}$. This implies that P3HT predominantly adopts an edge-on orientation. Energy & Environmental Science Accepted Manuscript

The F8TBT GIWAXS spectrum, on the other hand, does not show any sharp reflexes arising from main-chain crystallization. The weak signal at $q_z \approx 1.55$ Å⁻¹ is indicative of some face-on π - π -stacking. This signal is absent in the blend spectra, either because oriented F8TBT π - π -stacking is suppressed by P3HT crystallization or because the signal is swamped by the much stronger P3HT reflexes.

As mentioned above, the well-defined P3HT-RR2 forms chain-extended lamellae and the increase in L_p is directly correlated with the incorporation of F8TBT into the amorphous



Figure 4: 2D GISAXS maps of P3HT-RR2/F8TBT films showing a scattering signal at $q_y \approx 0.045 \text{ Å}^{-1}$ arising from a lateral structure corresponding to the long period L_p in P3HT. The GISAXS image of F8TBT is shown for reference. The horizontal lines in the top-left GISAXS image delimit the region used to construct the 1D intensity profiles along q_y . The F8TBT to P3HT weight ratio f is given in the images.

interlayers. Unlike P3HT/PCBM in which the swelling of amorphous interlamellar regions saturates around f = 0.185,²³ P3HT/F8TBT shows a continuous increase in L_p up to a F8TBT loading of f = 1. A 2 nm increase in L_p corresponds, roughly estimated, to a volume fraction of 14% in P3HT. Assuming similar densities, it is therefore unlikely that all the F8TBT that was expelled from the P3HT crystalline lamellae is accommodated within the interlamellar amorphous P3HT regions.



Figure 5: a) Integrated GISAXS intensity profiles along q_y from the 2D GISAXS maps of P3HT-RR2/F8TBT films with increasing F8TBT content. The curves are vertically shifted for clarity.

While Figs. 1,2 show phase separation for blends containing RA/F8TBT, macroscopic demixing was neither observed, microscopy images nor in the GISAXS maps for blends containing regio-regular P3HT. This might either arise from the lower molecular weight of the RR/P3HTs, rendering them miscible with F8TBT, or from a suppression of demixing by the quick onset of P3HT crystallisation.

The F8TBT distribution in the film along the surface normal was probed by X-ray reflectometry (XR), which resolves the vertical composition of a P3HT-RR2/F8TBT film with f = 1, shown in 7a. The XR data was analyzed by comparing it to a simulated multilayer model that incorporates several variable parameters including film thickness, layer compo-

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Figure 6: a) 2D GIWAXS maps show the characteristic P3HT scattering signal. The vertical alignment of the (h00)-reflections indicates an edge-on orientation of P3HT. F8TBT shows a face-on orientation of π - π stacking at $q_z \approx 1.55 \text{ Å}^{-1}$. The lines in the top-left image indicate the sectors used for the radial integration of the scattering peaks (see the Supporting Information). The additional scattering feature adjacent to the (100) peak for f = 0.06 arises from the scattering setup and not the sample.

sitions, and interfacial roughnesses. The scattering length densities (SLDs) of pure P3HT of $1.28 \times 10^{-5} \text{\AA}^{-2}$ and F8TBT of $0.85 \times 10^{-5} \text{\AA}^{-2}$ were first determined by measurements of pure films. The SLD of a homogeneous P3HT/F8TBT blend with f = 1 is therefore expected to be $1.07 \times 10^{-5} \text{\AA}^{-2}$. Fitting the model to the data also yielded the substrate parameters of Si and SiO_x, with SLD of $2.2 \times 10^{-5} \text{\AA}^{-2}$ and $2.3 \times 10^{-5} \text{\AA}^{-2}$, respectively, and a thickness of the SiO_x layer of 2 Å. Based on these parameters, a fit of the simulated profile to the XR data of the blend film yielded a significant depression in SLD in the film adjacent to the substrate surface, corresponding to an interfacial segregation of a pure F8TBT layer



Figure 7: a) Measured XR and b) simulated SLD profile of a melt-annealed P3HT-RR2/F8TBT film with f = 1.

with a thickness of $\sim 20\,\mathrm{nm}.$

This 20 nm thick F8TBT layer corresponds to ~ 40% of the overall F8TBT content, resulting in the blend ratio in the film-interior of $f \approx 0.6$, much less than the initial value of f = 1, which is confirmed by the SLD plateau in Fig. 7 of $\approx 1.1 \times 10^{-5} \text{ Å}^{-2}$. When compared to the GISAXS results of Figs. 4 and 5, estimating a F8TBT ratio of $f \approx 0.16$ in the interlamellar amorphous region of P3HT crystals (which averages to $f \sim 0.1$ over the entire crystalline regions), it becomes evident that about one-half of the F8TBT is accommodated within the interior of the film, but outside of P3HT crystal stacks, i.e. at grain and spherulitic boundaries, and crystal defects.

X-ray photoelectron spectroscopy (XPS) is a complementary technique for the analysis of the sample surface composition. The fibrillar texture in the AFM image of Fig. 3d suggests the formation of a P3HT surface layer which is too thin to be resolved by XR. The existence of a P3HT surface layer was previously confirmed by XPS depth profiling.³⁴ Here, we have investigated the composition of the film on the device-relevant poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) substrate surface (Fig. S3). P3HT/FHTBT films were prepared in an identical fashion as for the XR experiments. After annealing, they were floated-off the PEDOT:PSS surface and inverted for XPS measurements. The detection of the binding energies of thiophene and benzothiadiazole groups allowed the quantification of chemical composition of the film-substrate interface. Depending on the annealing protocol, F8TBT volume fractions between 60-80% were found within 10 nm (the sensitivity range of XPS) of the PEDOT:PSS surface. While this confirms the enrichment of F8TBT at the substrate surface, this enrichment layers seems to be much reduced at the PEDOT/PSS interface compared to the more polar silicon oxide. A 20 nm thick pure hole-blocking layer covering the anode surface in a solar cell would severely limit charge extraction from such a device.

These results allow to draw a qualitative picture of the P3HT/F8TBT phase structure in the films. Crystalline P3HT constructs a framework on the 10-nm length scale where the structural size is determined by the lamellar crystals. Some of the F8TBT is enriched in the interlamellar P3HT regions but the majority is segregated to the substrate surface and to regions within the film. It is likely that these film regions include the boundaries of the P3HT crystalline domains, which form a 3D percolating network on mesoscopic (micrometer) length scales.

Spherulitic Crystallization of P3HT/F8TBT

To correlate the structural studies with device performance, we fabricated solar cells with P3HT-RR1/ F8TBT photoactive layers that were equilibrated by solvent vapor annealing (SVA). SVA enhances chain mobility in crystalline polymers at room temperature. This is often used for improving the self-organization of conjugated polymers and the performance of corresponding electronic devices.³⁵ SVA has recently been used to control the nucleation density in P3HT and relatively large (up to 100 μ m-wide) P3HT spherulites of



Figure 8: POM images of P3HT/F8TBT films crystallized by SVA at different $P_{\text{vap}}^{\text{cryst}}$ for 30 min after initial swelling at 95% for 10 min. a) As spun, b) 80% (SVA1), c) 70% (SVA2), and d) 60% (SVA3).

P3HT were obtained in thin films.³⁶ In the present work we have applied the same method to P3HT/F8TBT blends. Films with the composition f = 1 were investigated as this corresponds to the composition of optimized photovoltaic devices. Carbon disulfide (CS₂) is a good solvent for both P3HT and F8TBT, enabling sufficient mobility for the blend to reorganize its morphology towards thermodynamic equilibrium. CS₂ is also one of the few solvents which alows the complete dissolution of P3HT crystalls upon swelling through solvent vapor. The careful adjustment of the initial vapor pressure and quench conditions allow to control the nucleation density of spherulites in the film and and thereby their final size.³⁶

The as-spun films were first swollen in CS_2 vapor to dissolve most of the initial crystal nuclei. By using *in-situ* UV-Vis spectroscopy, we found that at a vapor pressure of 95% all P3HT aggregates were dissolved. At this stage the film is a semidilute mixture of predominantly amorphous P3HT and F8TBT chains. The growth of P3HT spherulites was

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Figure 9: TEM images of P3HT/F8TBT films prepared via a, b) SVA crystallization at $P_{\text{vap}}^{\text{cryst}} = 60\%$, and c) melt-annealed.

performed at a constant recrystallization vapor pressure $(P_{\text{vap}}^{\text{cryst}})$ for 30 min after equilibration at a vapor pressure of 95% for 10 min.

Figure 8 presents typical POM images of P3HT/F8TBT films, obtained by varying $P_{\rm vap}^{\rm cryst}$ from 80% to 60%. Similar to the isothermal crystallization from the melt, the crystallization rate is increased by higher "undercooling" (i.e. lower $P_{\rm vap}^{\rm cryst}$), leading to a larger number of initial nuclei, which grow into a large number of small spherulites. The as-spun P3HT/F8TBT film shows no birefringence (Fig. 8a), but after the SVA cycle, films show distinct Maltese cross patterns (Figs. 8b-d). The films exhibit clear spherulitic morphologies with sizes on the order of 10 µm. A weak anisotropic texture is only observed in films prepared with $P_{\rm vap}^{\rm cryst} = 60\%$, which stems from a high nucleation density. In all cases, the films were macroscopically homogeneous and showed no phase separation, in agreement with the AFM images of Fig. 1. This again indicates that structure formation in the blend is dominated by P3HT crystallization rather than the phase separation of the two polymers.

These results confirm the scattering study that the crystallization of P3HT is not strongly affected by the presence of F8TBT and spherulitic growth in blends is therefore possible. From the GISAXS and XR results, we conclude that F8TBT is predominantly expelled from the spherulites and should significantly enrich at the spherulite boundaries. In Fig. 9, we have attempted to resolve this by transmission electron microscopy (TEM). Interestingly, the



Figure 10: a) UV-Vis and b) PL spectra of P3HT/F8TBT (f = 1) films prepared by different annealing protocols.

SVA film in Fig. 9a,b shows a very different nanomorphology compared to the melt-annealed film in Fig. 9c. The crystalline lamellae are clearly resolved in Fig. 9b, accompanied by a dark pattern on a larger length scale. The presence of the dark network-like pattern in Fig. 9a,b (and possibly c) is curious and may have several possible causes. It may arise from a second, bundle-like P3HT crystal morphology; local, crystallization-induced film thickness fluctuations; or the localization of F8TBT at the spherulitic grain boundaries. The latter would confirm our conjecture of F8TBT meso-morphology formation by F8TBT segregation during P3HT crystallization.

Figure 10 compares the UV-Vis and photo-luminescence (PL) spectra of differently prepared P3HT/F8TBT films. Since all SVA samples have similar UV-Vis and PL spectra, only one representative sample crystallized at $P_{\rm vap}^{\rm cryst} = 60\%$ is included. While amorphous P3HT shows only broad absorbance at 500 nm, crystalline and well-ordered P3HT exhibits distinct vibronic absorbance features up to 610 nm. Compared to the as-cast film, the SVA and melt-annealed samples exhibit enhanced red-shifted absorbance originating form the more pronounced vibronic progressions, indicating improved P3HT order.³⁷ The strong anisotropy in crystalline P3HT and a slightly different in-plane alignment can lead to the further difference in the two differently annealed films.

PL spectra were used to study the efficiency of exciton dissociation in P3HT/F8TBT



Figure 11: Device characteristics of P3HT/F8TBT solar cells. a) EQE spectra. b) J-V curves measured under a solar simulator. The inset shows a schematic drawing of the device architecture.

blends. The PL spectra of homopolymers and their blends are shown in Fig. 10b. F8TBT shows strong luminescence with a peak centered at 650 nm, and P3HT has much lower emission with vibronic features at 650 nm and 720 nm. The PL intensities of blend films show a significant decrease in comparison to pure F8TBT, indicating enhanced exciton quenching at donor-acceptor interfaces. Created excitons are efficiently quenched during their life time, that is, they find a donor-acceptor interface within the range of the exciton diffusion length. The peaks at 650 nm and 720 nm in the PL spectra of the blends match those of the pure components.

The decrease in PL intensity of the melt-annealed film as compared to the as-spun state is due to the low emissive characteristics of crystalline P3HT.³⁸ This indicates that thermal annealing improves the crystallinity of P3HT without significant phase coarsening. In comparison, SVA films show less quenching of F8TBT emission. This may be caused by a higher degree of phase separation of P3HT and F8TBT or improved phase purity, with fewer excitons reaching the interface and thus recombining radiatively. The PL intensity of SVA films remains far below that of F8TBT, suggesting P3HT and F8TBT are largely intermixed within the exciton diffusion range.

	$J_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}$ (V)	\mathbf{FF}	PCE (%)
As spun	0.5	0.85	21.7	0.10
SVA1	0.9	0.91	37.7	0.32
SVA2	1.3	0.98	42.9	0.54
SVA3	1.4	0.98	40.4	0.56
melt-annealed	2.2	0.98	33.8	0.87

Table 1: Device parameters of P3HT/F8TBT solar cells presented in Fig. 11.

Figure 11 presents the device characteristics of P3HT/F8TBT photoactive layers prepared using different protocols. All devices were fabricated on PEDOT:PSS-coated indium tin oxide (ITO) substrates and Al top electrodes. P3HT/F8TBT films with different spherulite sizes (Fig. 8) were investigated. These devices were further annealed at 140 °C after Al deposition to ensure a good contact between the active layer and the electrode. As-cast and melt-annealed devices are included as references. Figure 11a shows a significant improvement in the measured external quantum efficiency (EQE) upon annealing, with an increase in the maximum EQE from 5% to 18% upon melt-annealing of the as-cast device. SVA devices have a maximum EQE in the range of 8-10%, which decreases with increasing spherulite size.

The J-V characteristics of P3HT/F8TBT solar cells demonstrate a significant improvement in device performance with annealing, as shown in Fig. 11b. The performance parameters are summarized in Table 1. The power conversion efficiency increased five-fold upon solvent annealing (SVA3), from 0.10% for as-spun to 0.56%, due to changes in the shortcircuit current (J_{sc}) and fill factor (FF). J_{sc} directly correlates with the trend in EQE, with a highest value of 2.2 mA cm⁻² for the melt-annealed device. In the SVA devices, J_{sc} increases from 0.9 to 1.4 mA cm⁻² with decreasing spherulite size. The low photocurrent is probably partially connected to the low PL quenching, indicating that charge generation inside the spherulitic structures in not very efficient, and partially arises from the F8TBT anodic holeblocking layer. Secondly, the XPS measurements showed an increased F8TBT segregation at the PEDOT:PSS interface compared to the melt annealed film. This hole-blocking layer may strongly limit charge extraction from the device, contributing to the reduced EQE and $J_{\rm sc}$ values.

Despite the lower J_{sc} of the SVA devices compared to the melt-annealed device, spherulitic P3HT/F8TBT devices show improved fill factors, which reflects a reduction in recombination losses at the bulk heterojunction interface. This is attributed to a higher hole mobility in crystalline P3HT phase, resulting in more balanced hole and electron mobilities.

The performances of spherulitic solar cells suggest that a bulk heterojunction morphology is formed in P3HT/F8TBT blends with a structure that is determined by the lamellar crystallization of P3HT. While a high degree of P3HT crystallinity is clearly important, large semi-crystalline domains are not beneficial for device performance. This indicates that charge generation and/or extraction from the spherulites is necessarily not efficient in polymer-polymer solar cells. This further emphasizes the role of the spherulitic grain boundaries and interfaces between crystalline domains.

Conclusion

We have investigated structure formation in P3HT/F8TBT blend films using a range of complementary experimental techniques. While the polymeric nature of the two components is reflected in characteristic demixing patterns for regio-random P3HT, structure formation in samples containing regio-regular P3HT is surprisingly similar to P3HT blends containing the globular C₆₀-derivative PCBM. P3HT/F8TBT structure formation is driven by P3HT crystallization that gives rise to crystalline P3HT lamellae separated by amorphous interlamellar regions. The P3HT crystallization process segregates F8TBT into these interlamellar spaces, to the boundaries of P3HT crystallites and to the substrate interface (Fig. 12). Material balance arguments based on GISAXS and XR measurements suggest that >50% of F8TBT is accommodated at grain and inter-spherulitic boundaries where it probably forms a percolating F8TBT network, which is possibly evidenced by TEM.

The comparison with an earlier study on the P3HT/PCBM blend²³ allows interesting



Figure 12: Sketch illustrating a a) top and b) side view of P3HT/F8TBT structure formation, with F8TBT (red) segregating into P3HT (black) interlamellar spaces and to the boundaries of P3HT crystallites. F8TBT further tends to segregates towards the substrate interface.

conclusions. In both systems the strong crystallization of P3HT provided the structure forming motive that determines device performance. It creates an interdigitated binary morphology on the 10-nm scale that is embedded in mesoscopic network of the acceptor phase. The present study shows that this principle extends also the polymer-polymer bends. The design rules in both systems include the combination of a strongly crystallizing polymer with one that only weakly aggregates, and good compatibility of the two components.

Having established function of P3HT crystallization in film structure formation, it becomes possible to tune P3HT crystal morphologies by a carefully conducted quench of solvent swollen films. Device measurements comparing solvent-vapor annealed P3HT/F8TBT blend films with different spherulite sizes show a reduction in device efficiency with increasing spherulite size. This suggests that the charge generation and/or extraction from the inter-lamellar P3HT/F8TBT is at least partially determined by the overall size of the P3HT crystallites. While more work is required, this result is in agreement with a recent study that links the device efficiency with the presence of a phase allowing extended electron delocalization in fullerene-based systems⁷ and might therefore be one of the mechanisms that limit the performance of polymer-polymer blends. Future spectroscopic studies of photovoltaic blends with well-defined morphologies should be able to confirm this.

Experimental

Materials: P3HT-RR1 (P200, >98% regioregular, molecular weight $M_n = 20 \text{ kg/mol}$, polydispersity index PDI = 1.69) was obtained from Rieke Metals Inc. P3HT-RR2 ($M_n = 11.8 \text{ kg/mol}$, PDI = 1.13, >98% regioregular) was synthesized by M. Sommer.²⁴ P3HT-RA (4007, regiorandom, $M_w = 60 \text{ kg/mol}$, PDI = 1.78) was obtained from Rieke Metals Inc. F8TBT($M_n = 49.3 \text{ kg/mol}$, PDI = 2.41) was synthesized at the Melville Laboratory, University of Cambridge.²⁵

Melt and Solvent Annealing: Blend solutions of P3HT/F8TBT were prepared with a total concentration of 15 mg/mL in chlorobenzene. The weight ratios of F8TBT to P3HT $(f = m_{\rm PCBM}/m_{\rm polymer})$ were varied from f = 0 to f = 2. Films were prepared by spin coating either on quartz glass for AFM and UV-Vis, on silicon substrates for X-ray scattering measurements, or on PEDOT:PSS-coated indium tin oxide (ITO) substrates for photovoltaic device fabrication. Melt annealing was carried out on spin coated films by first heating on a hotplate at 230 °C for 3 min, followed by cooling to room temperature at a rate of 5 °C/min. Solvent annealing was performed using a previously reported protocol.³⁶ The solvent and samples were kept at 21 °C by a water thermostat and the gas flow into the annealing chamber was regulated by two MKS mass flow controllers, one gas line carrying nitrogen and the other saturated CS_2 . The relative vapor pressure (P_{vap}) in the annealing chamber was controlled by adjusting the relative gas flow in the two lines. Blend films with spherulitic features were achieved by first creating a population of nucleation seeds at a vapor pressure of 95% for 10 min followed by crystallization at a fixed value of P_{vap} . A Vecco (Bruker) Dimension 3100 system was used in the tapping mode for atomic force microscopy imaging. UV-visible absorption spectroscopy was performed using the Hewlett Packard 8453 UV-vis spectrophotometer. Photoluminescence spectra were taken using a Varian fluorimeter and samples were excited with a 470 nm laser.

X-ray Scattering: P3HT-RR2/F8TBT films were used for the x-ray structural studies. GISAXS and GIWAXS measurements were performed at beamline D1, at the Cornell High

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Energy Synchrotron Source (CHESS) at Cornell University, U.S.A. The wavelength was $\lambda = 1.15$ Å. A beam stop for the primary beam was employed for GISAXS measurements. A CCD detector with a pixel size of $46.9 \times 46.9 \,\mu\text{m}^2$ was used with a sample-detector distance of $1.81 \,\text{m}$ (GISAXS) and $0.1 \,\text{m}$ (GIWAXS). Scattering maps were then taken at an incident angle of 0.13° for GISAXS and 0.15° for GIWAXS. Both values are slightly higher than the critical angle of the polymer film and lower than that of the substrate. Therefore the entire film was penetrated by the X-ray beam, and internal film structures could be detected with the beam fully reflected from the sample/substrate interface. The q-space calibration was performed by fitting the characteristic scattering signal arising from silver behenate. X-ray reflectivity (XR) measurements were performed *in-situ* using the collimating slits, goniometer and sample environment of the GISAXS experiment. The detector was an ion chamber with an $50 \times 13 \,\text{mm}^2$ aperture. A blade placed in front of the ion chamber screened the detector at low angles from the direct beam. The measuring time was 1 s per point. The electronic background was measured and subtracted from the data. XR-data fitting was carried out by model calculations using the Parratt formalism (HMI, Berlin).

X-ray photoelectron spectroscopy: The XPS samples were transferred to an ultrahigh vacuum chamber (ESCALAB 250Xi) for XPS measurements. The measurements were carried out using a XR6 monochromated AlK α x-ray source ($h\nu = 1486.6 \text{ eV}$) with a 900 µm spot size and 20 eV pass energy.

Device Fabrication: Photovoltaic devices were fabricated in the standard PEDOT:PSS|ITO| P3HT/F8TBT|Al layer sequence. ITO on glass anodes were first cleaned with acetone and isopropanol, followed by oxygen plasma treatment. A ~ 50 nm thick PEDOT:PSS was spincoated onto the plasma-treated substrates and annealed at 150 °C for 30 min and transferred into a nitrogen glovebox for the subsequent fabrication steps. The commercially available P3HT-RR1 was blended with F8TBT at f = 1. P3HT/F8TBT photoactive layers were processed using different annealing protocols. Solvent vapor annealing (SVA) was used to produce spherulitic P3HT/F8TBT films. Melt annealing was performed at 140 °C for 10 min after Al deposition.

Device Testing: Device EQE was measured using a tungsten lamp with a monochromator at intensities of $\sim 1 \,\mathrm{mW/cm^2}$. Short circuit currents were recorded using a Keithley 237 source meter. The current-voltage characteristics of the device were measured under simulated 100 mW/cm² AM 1.5 illumination using an Abet Technology solar simulator. The spectral mismatch of the simulator was calibrated to a silicon reference cell.

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