Spectroscopic Investigations of Three-Phase Morphology Evolution in Polymer: Fullerene Solar Cell Blends

Joseph Razzell-Hollis,[a] Saurav Limbu,[a] and Ji-Seon Kim [a,*]

[a] Department of Physics and Centre for Plastic Electronics, Imperial College London, London, SW7 2AZ, United Kingdom

* Corresponding author: ji-seon.kim@imperial.ac.uk +442075947597

Abstract

Nanoscale morphology is critical to determining the device efficiency of bulk heterojunction organic solar cells, and the ideal structure is often described as a three-phase network with one well-mixed phase for efficient charge separation and two purer phases for efficient charge transport. In order to understand such nanoscale morphology, we have performed detailed spectroscopic investigations and identified the three-phase morphology evolution in one of the classic blend systems, P3HT:PCBM. The impact of different phases on polymer molecular (chain conformational) order, blend thermal and optical properties were monitored *in situ* using resonant Raman, absorption and photoluminescence spectroscopy techniques. Semi-crystalline P3HT was found to accommodate up to ~25% PCBM (by weight) in its amorphous phase, with very little impact on either polymer molecular order or aggregation. Higher concentrations of PCBM resulted in a greater proportion of amorphous mixed phase and reduced polymer molecular order and aggregation. On the other hand, the formation of crystalline purer phases via phase separation was evident during *in situ* thermal annealing, revealing a consistent glass transition temperature (T_g) of ~50 °C in blends with up to 50 %wt PCBM. This indicates similar local chemical compositions in the amorphous mixed phase present in blends despite different overall blend ratios. A much higher T_g (80-100 °C) was

observed for blends with >50 %wt PCBM, indicating a stronger impact of PCBM on P3HT molecular order and thermal properties, requiring a higher annealing temperature to ensure formation of the preferred 3-phase morphology.

Introduction

Organic photovoltaics (OPVs) have been subject to a great deal of interest due to their potential as a low-cost, easily-processable alternative to conventional inorganic solar cells. One of the greatest advantages of OPVs is the use of a bulk heterojunction (BHJ) active layer containing a blend of conjugated polymers and fullerenes, which can be fabricated using less-costly and high-throughput solution-based printing techniques.[1–3] The focus of a great deal of research over the past decade, the power conversion efficiency (PCE) of OPVs has risen from below 3% to a certified record of 11.5% as of 2015.[4] A large part of this improvement has been due to the development of a wide range of novel polymers, such as donor-acceptor copolymers like PTB7 and DPPTT-T that have been designed to have small optical band-gaps.[5,6] Yet the complex mixing of polymers with small molecules at the nanoscale means that for every polymer there is a wide range of possible morphologies that can be formed depending on processing conditions, pre-/ post-deposition treatments and the blend composition used.[7–10]

Thin film morphology influences both the efficiency of exciton dissociation, as photo-generated excitons must reach the donor/acceptor heterojunction interface in order to undergo charge separation, and the efficiency of charge transport, as the resulting free charge carriers must travel through different materials to reach their respective electrodes.[11,12] Consequently, an essential part of the optimization of any OPV blend system is controlling the morphology to obtain the best possible efficiency for a particular set of materials.[13,14] This inevitably becomes a trial-and-error process, but one that can be accelerated by a greater understanding of the relationships between processing conditions, thin film morphology and device performance. Here we study and develop a

model of blend morphology for thin films of the semi-crystalline, electron-donating polymer Poly-(3-hexylthiophene) (P3HT) and the electron-accepting, functionalised fullerene [6,6]-Phenyl-C_{61}-butyric acid methyl ester (PCBM). While this blend system can no longer considered to be highly efficient (at best it exhibits a PCE of ~5%)[15] it still serves a valuable role as a model system for studying the general behavior of polymer:fullerene thin films.

The prevailing understanding of morphology in polymer:fullerene blends like P3HT:PCBM is that the two materials can form three different phases: two are the relatively purer phases of the single materials, with a third intermixed phase.[16] This is considered a particularly valuable combination for good OPV performance: the intermixed phase provides a large interfacial area between the donor and acceptor materials, for the dissociation of photo-generated excitons into free charge carriers, while the purer fullerene and purer polymer phases provide efficient transport networks for each charge carrier (electrons and holes respectively).[13] Consequently, BHJ morphology must be controlled to obtain the best possible performance, as the precise balance between the fractions of each phase will depend heavily on inherent molecular properties (such as co-miscibility) and processing conditions (such as blend ratio, deposition technique and choice of solvent).[7–10] Even the choice of substrate can have a detectable effect on the extent of phase separation for BHJ films deposited onto its surface.[17] The existence of an intermixed amorphous phase has been demonstrated by several studies, with a reported miscibility limit of ~25% by weight (%wt) PCBM.[18,19] The as-cast morphology can be altered by post-deposition treatments such as thermal annealing, inducing greater phase separation to increase the fraction of pure, ordered domains that improve charge transport and hence photocurrent.[16,20,21] In this study we will present a detailed description of the phase behavior of P3HT:PCBM blends in terms of the 3-phase morphology evolution, their composition and reorganization during heating/cooling processes.

A large number of characterization techniques are regularly used to study morphology in thin films,[22] and in this work we use three spectroscopic methods that are simple but powerful in their application to *in situ* monitoring of morphology during heating/cooling. Absorption and Photoluminescence spectroscopy techniques offer a direct measurement of the distribution of optical band-gaps and electronic states present within the film through their excitation and emission, providing information on morphology in terms of long-range molecular order and aggregation.[23] Resonant Raman spectroscopy offers a more specific and highly sensitive measurement of short-range molecular order, in terms of chain conformation and planarity, by detecting the vibrational modes of chemical bonds along the conjugated backbone of the molecule. As demonstrated by Tsoi *et al.*, under resonant conditions (excitation energy greater than the optical band-gap) the frequency of the main conjugated backbone C=C stretching mode reflects chain conformation, with more planar polymer chains exhibiting this mode at much lower frequency (~1449 cm^{-1}) compared to more twisted chains (~1475 cm^{-1}). By studying the optoelectronic and conformational properties of P3HT chains when blended with PCBM, we investigate the phase behavior of the blends across a wide range of blend weight ratios. This provides direct evidence of morphological evolution in blends and its impact on polymer molecular order, as well as thermal and optical properties of the blend that are critical to device performance.

Experimental

All samples were prepared using solutions of RR-P3HT (Sigma-Aldrich, M_W = 37 kDa, 97% regioregularity) and PCBM (Solenne b.v., 99% purity) dissolved separately in Chlorobenzene (Sigma-Aldrich) with concentrations of 20 mg/mL, which were stirred at ~60 °C to fully dissolve all material, then mixed according to the desired weight ratio. Thin films were deposited by spin-coating at 2000 rpm for 120 seconds onto fused Quartz

substrates (Spectrosil, UQG Ltd), which had been cleaned by ultra-sonication in Acetone and Propan-2-ol then baked at 150 °C to remove any solvent.

We used a Renishaw inVia Raman microscope with a 50x objective in a back-scattering configuration to perform both Raman and photoluminescence (PL) measurements, with a Linkam hot/cold stage (THMS600) as the inert sample chamber. To reduce photo-degradation of the samples, the chamber was purged with N_2 gas and the laser-spot was defocused to ~10 μm.[17,21,24] Resonant Raman measurements were done using 488 nm laser excitation (argon ion source, ModuLaser) with a laser power of 0.09 mW and an acquisition time of 30 seconds, and the resulting spectra had a resolution of ± 0.7 cm^{-1}. PL measurements were done using 514 nm laser excitation (argon ion source, ModuLaser) using a power of 5.5 μW and an acquisition time of 3 seconds, with a spectral resolution of ± 3.4 cm^{-1}. PL spectra were recorded between 330 cm^{-1} (522 nm) and 7890 cm^{-1} (865 nm), and measured intensities were corrected for both the instrument response function of the spectrometer and thin film absorption. UV-Vis absorption spectra were obtained using a Shimadzu UV-2550 spectrophotometer with a Quartz reference.

For *in situ* annealing, samples were heated in 10 °C steps at 10 °C/min from ~25 °C to 150 °C, 250 °C or 300 °C, then either cooled in 10 °C steps or directly back to room temperature over several minutes.

Results and Discussion

As-Cast Blend Films

In order to study any morphological changes that take place around the reported 20-25% by weight (%wt) miscibility limit of PCBM in a P3HT matrix, we prepared P3HT:PCBM blend films with a broad range of compositions between 0 and 70 %wt PCBM.

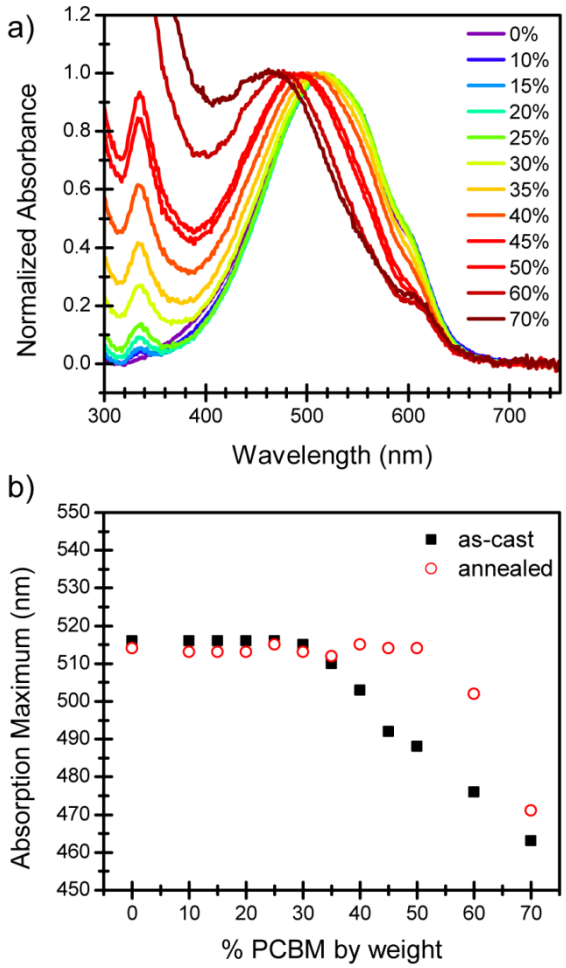


Figure 1: a) Normalized UV-Vis absorption spectra for as-cast blend films of P3HT:PCBM with different %wt PCBM. (b) λ_{max} of P3HT's absorption for as-cast and thermally annealed blends. Spectra are normalized to the P3HT absorption peak.

In Figure 1a, we observe a strong absorption peak from neat P3HT between 400 and 650nm, with a maximum at ~516 nm and a vibronic shoulder at ~605 nm, indicative of relatively high crystallinity.[21] It is important to note that P3HT is semi-crystalline, and even a neat film contains a significant fraction of amorphous phase where polymer chains are disordered (illustrated in Figure 4a), resulting in a broad absorption peak up to 400 nm. With increasing PCBM content, we observe fullerene absorption at short wavelengths (~340 nm) and variation in P3HT absorption: blue-shifted from ~516 to ~460 nm with a decrease in the relative intensity of the vibronic peak at ~605 nm, indicating a shorter

effective conjugation length and reduced crystallinity for the polymer. In Figure 1b, the values of λ_{max} are plotted against PCBM content and reveal that P3HT absorption is almost unchanged from the neat film when blended with up to 30 wt% PCBM (~515 nm versus ~516 nm), but increasing PCBM content beyond 30 %wt results in the characteristic blue-shift of the polymer absorption, reaching ~488 nm for 50 %wt and ~463 nm for 70 %wt. We conclude that blending with low concentrations of PCBM (<30 %wt) appears to have no impact on P3HT crystallinity or conjugation length, but that higher concentrations of PCBM had a deleterious effect on the molecular order of P3HT. The optical absorption technique, however, is not sensitive enough to tell us to what extent the P3HT and PCBM should be intermixed to change the absorption spectrum. For this, we use instead resonant Raman spectroscopy.

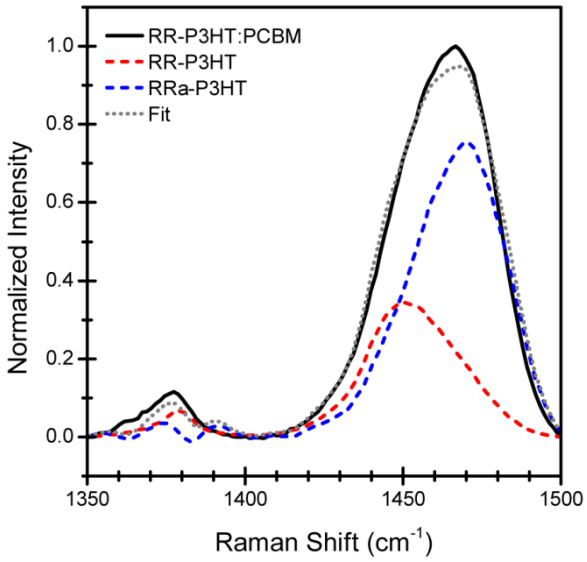


Figure 2: Resonant Raman spectrum of a 1:1 P3HT:PCBM blend film, fitted using RR-P3HT and RRa-P3HT spectra to represent ordered and disordered phases respectively.

Under resonant conditions, Raman spectroscopy selectively probes the molecular vibrations associated with specific electronic excitations, namely the C=C and C-C bonds of the conjugated backbone.[25,26] The Raman spectrum of P3HT, shown in Figure 2,

contains two major vibrational modes: the C=C symmetric stretching mode (1450 cm^{-1}) and the intra-ring C-C symmetric stretching mode (1380 cm^{-1}). As reported previously,[17,21] the Raman shift and full-width-half-maximum (FWHM) of the C=C mode, as well as the relative intensity of the C-C mode, are highly sensitive to the planarity of the conjugated polymer backbone; demonstrated by the difference in Raman shift between highly ordered regioregular-P3HT (~1450 cm^{-1}) and highly disordered regiorandom-P3HT (~1470 cm^{-1}). The overall spectrum between 1350 and 1500 cm^{-1} can thus be fitted using reference spectra from regioregular and regiorandom-P3HT polymer films to represent the two extremes of ordered (crystalline) and disordered (amorphous) phases. By deconvoluting of the P3HT spectrum into ordered and disordered components, it is possible to estimate the relative degree of molecular order for a given blend film (i.e. the fraction of ordered phase relative to that of a RR-P3HT reference film) using Equation 1 (see ESI). Calculating the degree of molecular order by fitting is preferable to simply reporting a single property of the C=C peak (such as Raman shift or FWHM) as a measure of molecular order; modelling has shown that variations in these properties are not always consistent with changes in order (illustrated in the ESI).

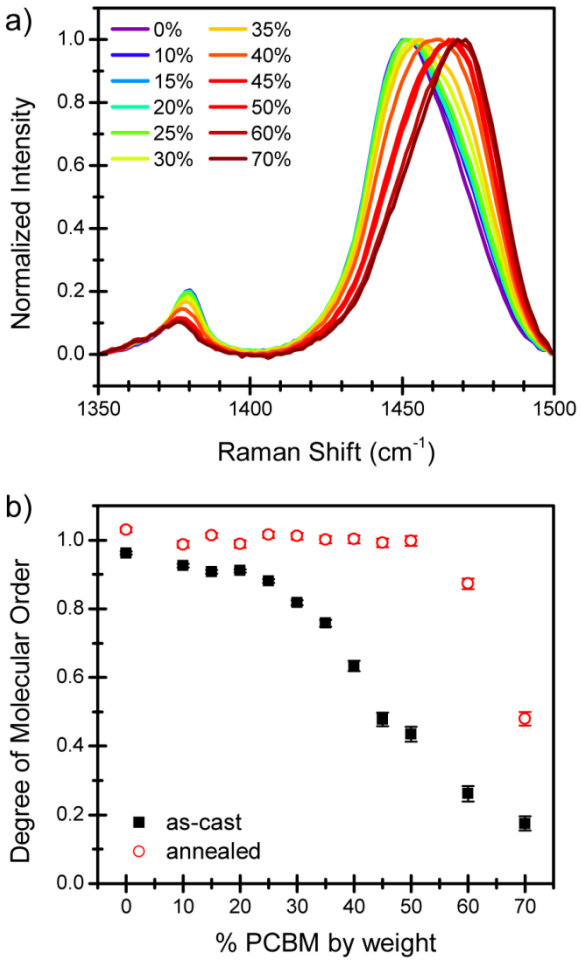


Figure 3: a) Normalized resonant Raman spectra for blends with 0-70 %wt PCBM, normalized to the P3HT C=C peak at 1450-1470 cm^{-1}. b) Estimated degree of P3HT molecular order for each film, based on the relative fraction of ordered phase obtained by Raman fitting of the C-C and C=C peaks. Raman excitation λ was 488 nm.

Raman spectra for the as-cast blend films (Figure 3a) reveal a large variation in C=C peak position and molecular order between different blend compositions. There was a ~16 cm^{-1} shift in C=C peak position towards higher frequency between neat P3HT (~1451 cm^{-1}) and the 70 %wt PCBM blend (~1467 cm^{-1}). The calculated relative degree of molecular order confirms the extreme nature of these two films: the neat P3HT has a high value of 0.96, indicating a film only slightly less ordered than the RR-P3HT reference, which has a defined degree of 1.0, while the 70 %wt blend was dominated by disorder,

with a low value of 0.17. Low concentrations of PCBM proved to have little impact on P3HT conformation compared to the neat film: blending with up to 25 %wt PCBM resulted in a mere ~1.0 cm^{-1} up-shift of the C=C peak (to ~1452 cm^{-1}) and a small decrease in the corresponding degree of order, from 0.96 to 0.88. Further loading of the blend with a higher PCBM content caused the C=C peak to up-shift dramatically, from 1453 cm^{-1} (for 30 %wt PCBM) to 1466 cm^{-1} (for 50 %wt), with a significant decrease in the degree of molecular order from 0.82 to 0.43 respectively. This provides clear evidence of PCBM hindering the organization of P3HT that correlates with the change in P3HT effective conjugation length observed by UV-Vis absorption spectroscopy (Figure 1).

The reduction of effective conjugation length and increase in disorder that have been observed for films above the critical composition of ~25 %wt PCBM indicate that this is the threshold between two morphologies (illustrated in Figure 4): below ~25 %wt, the fullerene is sufficiently dilute to dissolve in the P3HT matrix without hindering the formation of crystalline ordered P3HT domains during deposition (4b), but >25 %wt PCBM can only be accommodated by reducing the crystalline fraction of P3HT in order to dissolve the additional fullerene molecules (4c). This implies that PCBM must be dissolved as individual molecules selectively in the amorphous matrix. However, based on Raman and UV-Vis absorption observations alone we cannot prove that the dilute PCBM molecules are dispersed within the amorphous domains, rather than forming their own separate aggregates (4d). Raman peaks from PCBM were not observed under 488nm excitation, even in the 70 %wt blend, due to their relatively weak vibrations and spectral overlap with the significantly more intense Raman modes of P3HT.

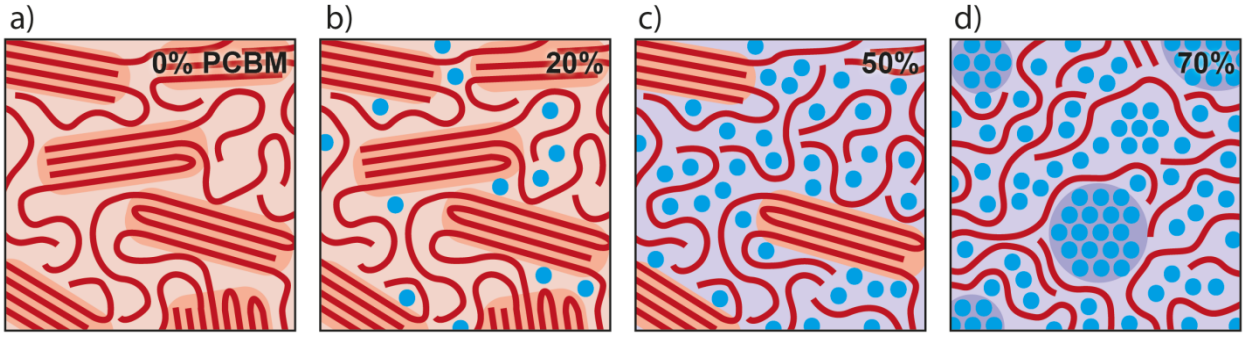


Figure 4: Schematic diagram of P3HT:PCBM blend morphologies with different blend compositions. From left to right: a) the neat P3HT film, b) the dilute PCBM regime, c) the disordered regime, d) the PCBM-rich regime. Polymer chains are depicted as red lines, PCBM molecules as blue circles. Representative PCBM fraction in each regime is also indicated.

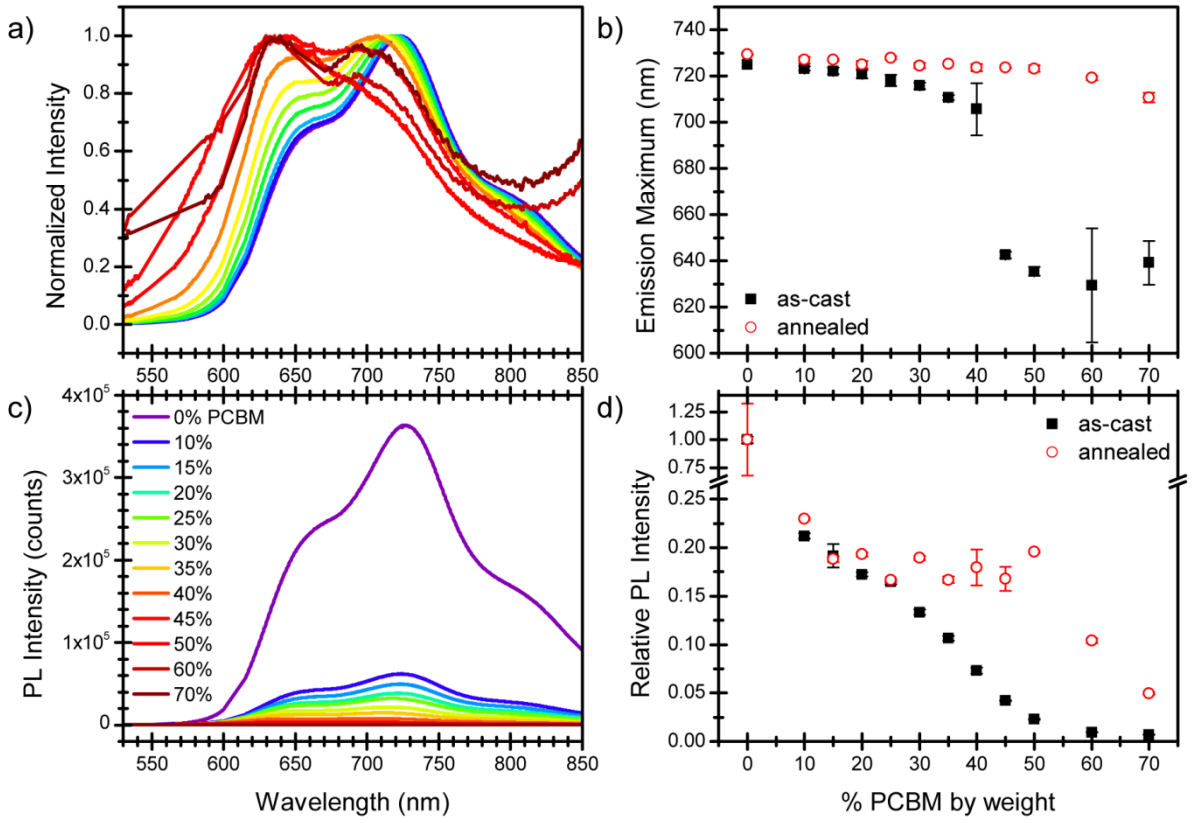


Figure 5: Normalized (a) and absolute (c) photoluminescence spectra for as-cast P3HT:PCBM films of different %wt PCBM under 514 nm excitation. Corresponding maximum PL peak positions (b) and integrated PL intensities relative to that of neat P3HT

(d) for as-cast and annealed films. Note truncated y-axis values for blends with > 10 %wt PCBM.

In order to study the extent of mixing between P3HT and PCBM, we examined the impact that the fullerene has on the polymer's photoluminescence (PL) properties. Under resonant conditions, electronic excitation leads to the formation of excitons that eventually decay radiatively, producing PL as a fluorescence background in resonant Raman measurements (see Figure 5). The emission from P3HT is distinctly vibronic, with a weak 0-0 transition (at ~650 nm) and a strong 0-1 transition (at ~725nm) that are typical of a predominantly H-aggregated material like P3HT, where the 0-0 transition is suppressed by weak intra-chain coupling.[23,27] Introducing up to 20 %wt PCBM by weight resulted in a blue-shift in P3HT emission of only ~4 nm (to λ_{max} of ~721 nm), indicating only a small reduction in effective conjugation length due to blending with low concentrations of PCBM that agrees well with absorption measurements. Further PCBM loading up to 50 %wt resulted in a significant blue-shift of emission by ~86 nm (to ~635 nm) with a marked increase in the relative intensity of the shorter-wavelength 0-0 transition. Such changes can be attributed to disturbed P3HT molecular order, leading to a reduced effective conjugation length and less H-aggregation.

When P3HT is blended with PCBM, there is a significant decrease in the polymer's PL intensity (i.e. quenching) as excitons are dissociated across the donor/acceptor heterojunction to form free charge carriers, rather than decaying radiatively to produce photoluminescence.[19] The exciton diffusion length in organic semiconductors is reported to be on the order of ~10 nm, and consequently only excitons generated within this distance of a PCBM molecule will be able to diffuse to the heterojunction before decaying via emission.[28] This distance dependence allows us to use PL quenching as a measure for the degree of intermixing in P3HT:PCBM blend films. Figures 5c and d demonstrate that

blending with just 10 %wt PCBM reduced P3HT's PL intensity by ~79%, despite having no impact on the effective conjugation length or the molecular order of P3HT (according to Raman, PL and absorption spectra). This leads us to an important conclusion that small amounts of PCBM can dissolve preferentially in the amorphous disordered domains of P3HT, where it has very little impact on the polymer chain conformation, as shown in Figure 4b. The possibility of the fullerene dissolving in the ordered P3HT domains without disrupting them can be dismissed, as the intercalation of PCBM between a polymer's alkyl side-chains to form a bi-molecular crystal has been reported for other conjugated polymers but not for P3HT.[29] Higher concentrations of PCBM resulted in further quenching of PL intensity, down to a mere ~0.45% for the 50 %wt PCBM blend, suggesting that nearly all excitons generated on the polymer are undergoing dissociation rather than radiative decay. This corroborates our earlier conclusion that when PCBM content exceeds the 25 %wt miscibility limit, a greater fraction of the amorphous mixed phase is formed; exhibiting greater quenching, a significant reduction in effective conjugation length (according to λ_{max} of absorption and PL) and loss of polymer molecular order (according to Raman).

Annealed Blend Films

Thermal annealing is a well-known method for restoring a longer effective conjugation length in P3HT and other polymers; crystallinity and high molecular order in blend systems, and is commonly understood to be a result of induced phase separation (a spinodal decomposition of the disordered mixed phase into purer, separate phases in blends) towards a thermodynamic equilibrium morphology. Therefore we expect to see a 'standardization' of P3HT properties upon thermal annealing, regardless of PCBM content.

After annealing at 150 °C, films of 0-50 %wt PCBM exhibited similar absorption, Raman and PL spectra (see ESI). Figures 1b and 5b demonstrate that these annealed films had λ_{max} values of ~513 nm and ~729 nm for absorption and PL respectively, indicative of restoring an effective conjugation length comparable to that of the neat

polymer. In terms of Raman, we observed a consistent C=C peak position of 1450 cm^{-1} (varying by ± 0.3 cm^{-1}) and FWHM of 33.6 cm^{-1} (± 0.6 cm^{-1}), resulting in the maximum possible degree of molecular order: ~1.0 (± 0.014, see Figure 3b). We consider that the thermodynamic equilibrium morphology is one comparable to the neat polymer. When blends with 'dilute' PCBM (<25 %wt) were annealed, the improvement in conjugation length and molecular order was comparable to that observed for the neat polymer, suggesting no real difference in their reorganization despite the presence of some PCBM. This was corroborated by a small increase in PL intensity (an average of 0.7% ± 1.1%, see Figure 5d), which demonstrates that little to no change in phase separation was involved. For films with greater PCBM loading (>25 %wt), there was a significant improvement in the P3HT's effective conjugation length (Figures 1 and 5) and molecular order (Figure 3) due to the as-cast films possessing a more disordered structure further from the equilibrium. Furthermore, Figure 5d demonstrates that PL intensity had increased significantly after annealing (by 5.6 to 17.3%), suggestive of a large reduction in exciton quenching as a result of greater phase separation and increased aggregation. We note that P3HT predominantly forms H-aggregates, which are associated with a lower quantum yield for PL, and thus the increase in PL for all films of >30%wt PCBM after annealing must be indicative of phase separation and an overall reduction in PL quenching. J-aggregation is indeed possible for P3HT, but is usually only observed in large, highly crystalline structures such as nanofibres, or blends with polarising PEO.[30,31]

Consequently, we propose that the 'dilute' blends are morphologically stable, having a similar degree of P3HT molecular order to the neat polymer, and a PCBM content below the miscibility limit means that there is no thermodynamic pressure for PCBM to separate out from the amorphous P3HT matrix. Thus, spinodal decomposition (phase separation) only occurs when the concentration of PCBM exceeds the miscibility limit and thus the as-cast film has a significantly higher proportion of disordered mixed phase

(further away from the thermodynamic equilibrium). When heated, these disordered blends phase-separate until the proportion of mixed phase is reduced back to the ‘standard’ for the polymer and P3HT molecular order is restored; in other words the P3HT morphology evolves from that depicted in Figure 4c to that of Figure 4b, with the excess fullerene forming its own pure phase.

Thermal annealing was notably less effective at reducing disorder in the PCBM-rich (60 and 70 %wt) blends: although there was a red-shift in λ_{max} for both absorption and emission spectra, indicative of an increase in effective conjugation length, they fell short of the ‘standard’ values of ~514 nm (absorption) and ~729 nm (emission), as shown in Figures 1 and 5. Raman spectra demonstrate that although the maximum positions of C=C peaks for the 60 and 70 %wt PCBM blends were both down-shifted in frequency with respect to the as-cast films, a significant contribution from the disordered component at high frequencies (~1475 cm^{-1}) is still retained. Consequently, the relative degree of molecular order achieved by annealing was only 0.87 for 60 %wt PCBM, and 0.48 for 70%wt, rather than ~1.0 as with all the other blend films (see Figure 3b). With a limited increase in PL intensity observed for both, we consider that the PCBM-rich blends failed to achieve the equilibrium morphology, that the polymer was not able to phase-separate fully from PCBM within the short annealing time (<5 min). This was later found to be a result of kinetic hindrance limiting reorganization, according to *in situ* observations.

In Situ *Thermal Annealing*

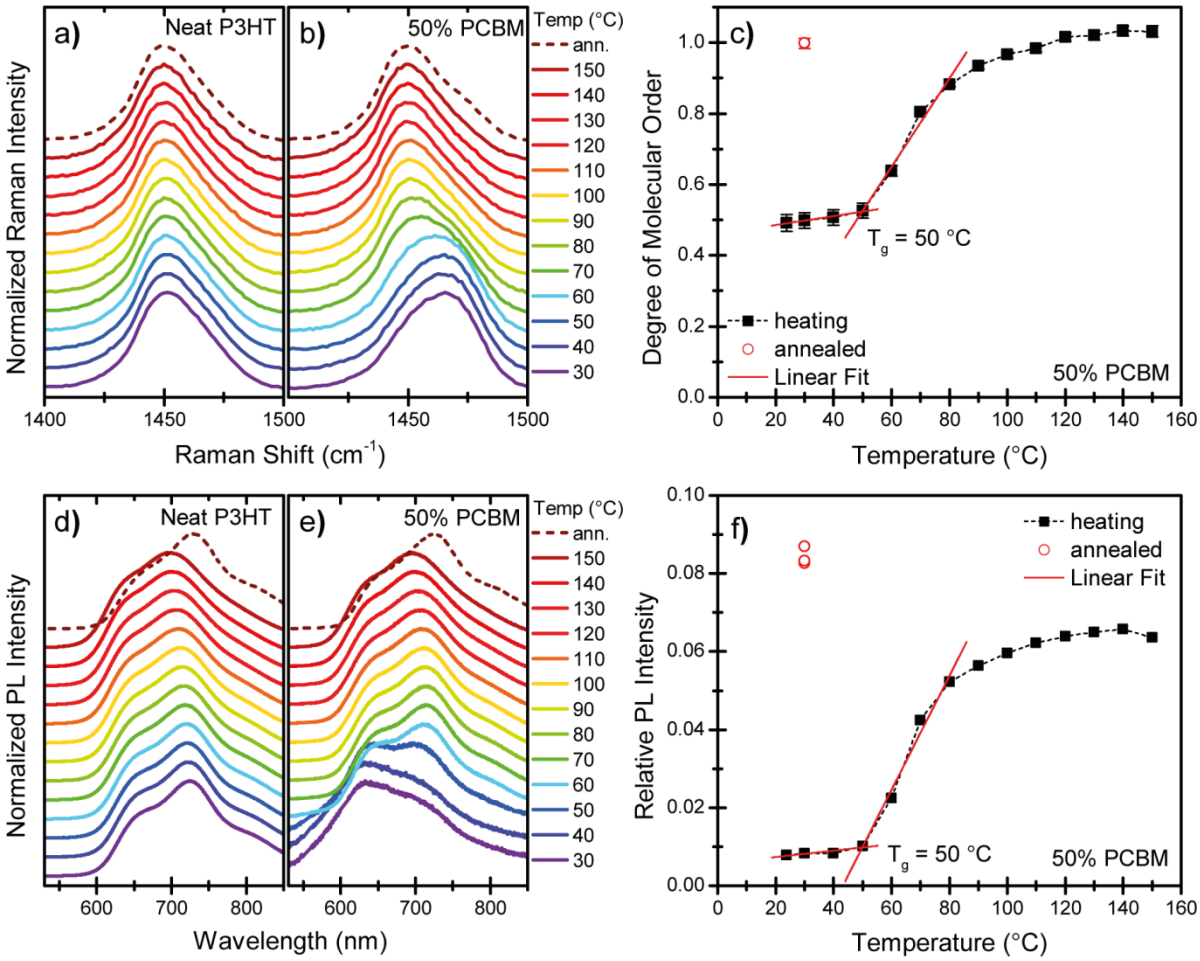


Figure 6: Evolution of resonant Raman spectra (a,b) and PL spectra (d,e) for films of neat P3HT and 1:1 P3HT:PCBM during stepped heating to 150 °C and after annealing. c) Evolution of the blend's relative degree of P3HT molecular order during heating, as calculated by Raman fitting, and f) evolution of integrated PL intensity during heating, relative to the intensity of a neat P3HT film. Excitation λ were 488 nm for Raman, 514 nm for PL.

As we have reported previously, temperature-induced changes in molecular order can be studied by the *in situ* annealing of samples within a Raman microscope.[17,25] When an as-cast film of P3HT:PCBM (1:1 by weight) is heated up to 150 °C *in situ*, the distinctive reorganization of P3HT chains from disordered conformational states towards more ordered states occurs above a particular temperature, which we can associate with the

glass transition temperature (T_g) of the blend. Below this temperature, polymer chains lack the thermal energy necessary for collective motion and cannot reorganize themselves into more energetically stable, planar conformations.[32]

For neat P3HT, reported T_g values are typically 12-20 °C, suggesting there is a degree of mobility for the neat polymer even at room temperature, but T_g is known to increase upon mixing with a vitrifying agent like PCBM (which has a T_g of ~130 °C).[33,34] Figure 6 demonstrated, when heated from room temperature to 50 °C, that were was little change in the resonant Raman spectrum of P3HT for a 1:1 blend, resulting in only a small increase in the relative degree of order from 0.49 to 0.53, as shown in Figure 6c. Further heating to 90 °C produced a marked shift of the C=C peak to lower wavenumbers, increase in order up to 0.93, reaching a maximum of ~1.0 by 120 °C. Fitting of the trends in Figure 6c above and below the onset of this reorganization allows us to estimate the blend's T_g to be at 50 ± 7.8 °C, in good agreement with what we have reported previously.[17] These observations were consistent with *in situ* PL spectra, which showed a marked change in shape when heated above 50 °C (Figure 6e), namely a red-shift of 0-1 emission and increase in overall intensity. According to Figure 6f, between 50 and 80 °C there was a 6-fold increase in PL intensity (from ~0.8% to ~5.2%, relative to the intensity from a neat P3HT film). We have attributed this increase to enhanced phase separation of the dominant mixed phase into distinct P3HT- and PCBM-rich phases, resulting in a less interfacial area between the two materials for exciton dissociation and emission quenching. The onset of phase separation was estimated from Figure 6f to be at 50 ± 9.2 °C, in good agreement with the observed onset of reorganization based on Raman. Therefore, we conclude that restoration of P3HT's lost molecular order occurs simultaneously with the decomposition of the as-cast blend into separate phases. We also find that our value for T_g agrees well with reported values (40-55 °C) for similar 1:1

P3HT:PCBM blends measured using other techniques such as ellipsometry and MTDSC.[33,34]

Continued heating of the 1:1 blend film from the 120 to 150 °C, the standard annealing temperature for P3HT:PCBM blends, provided no real improvement in P3HT molecular order (with the relative degree of molecular order remaining at ~1.0), but we observed a gradual increase in PL intensity (saturating at ~6.4% by 140 °C). In fact, the profile of evolving PL intensity with temperature presented in Figure 6 appears to be a good match for the *in situ* short-circuit current measurements done by Treat *et al.* for a device based on P3HT:PCBM (1:1 by weight).[20] Despite our observation that exciton quenching across the P3HT/PCBM interface is reduced by increasing phase separation above ~50 °C, Treat *et al.* observed a significant increase in photo-current at the same temperature and attributed it to an increase in the number of neat P3HT and PCBM crystallites within the blend, which provide more efficient charge transport pathways. This agrees with our understanding that thermal annealing serves not just to improve P3HT molecular order but also encourages the formation of an interpenetrating network of purer domains essential to good and balanced charge transport.

However, as the length scale of spinodal decomposition is determined entirely by molecular diffusion, higher temperatures can result in excessive phase separation, where P3HT- and PCBM-rich domains become much larger than the exciton diffusion length,[28] and thus charge generation (i.e. exciton quenching) is significantly reduced. While we did not observe the formation of micron-scale PCBM aggregates during annealing in situ, this is likely a result of a relatively short anneal time (<5 min at 150 °C), as prolonged annealing (~30 min) typically results in the appearance of large aggregates as the PCBM-rich phase coalesces into larger and larger domains.[35] Interestingly, as we have observed that this particular 1:1 blend is only morphologically stable below 50 °C;[36] we expect that even an annealed film would only be meta-stable at temperatures below T_g; molecular

diffusion at higher temperatures resulting in a gradual increase in domain size and loss of charge generation over time, limiting the working lifetime of OPV devices that can be expected to operate at elevated temperatures under constant illumination.[16]

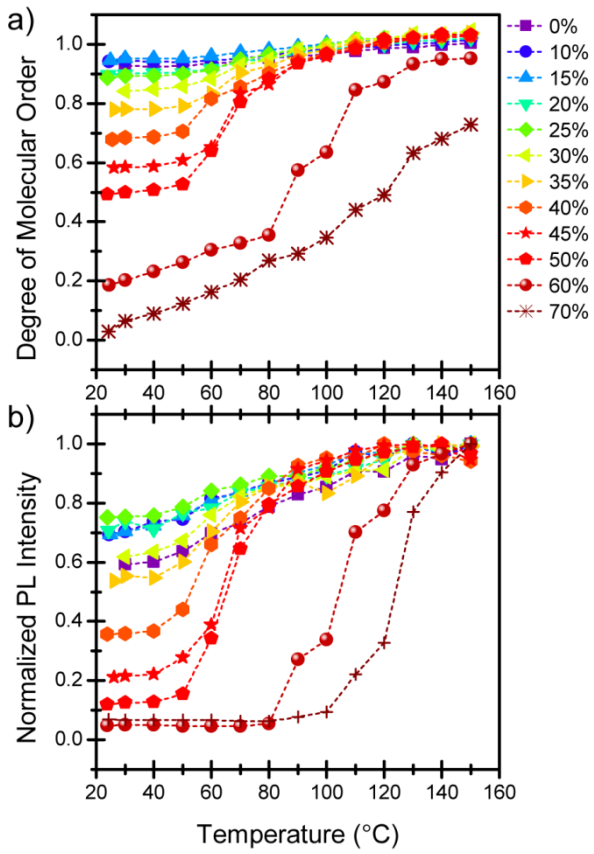


Figure 7: For as-cast P3HT:PCBM blend films of different %wt PCBM, the evolution of relative P3HT molecular order (a) and integrated PL intensity (b) during stepped heating up to 150 °C. PL intensities are normalized to the maximum value achieved during heating for each film.

When blend films with different compositions were subjected to the same *in situ* annealing process, we observed that most underwent the characteristic increase in degree of molecular order and PL intensity during heating (Figure 7, see ESI for *in situ* spectra) that we have associated respectively with P3HT reorganization and phase separation of the blend. However we found that blends of <20 %wt PCBM, which started with a high degree of molecular order (~0.94), exhibited a gradual and monotonic increase in both

molecular order and PL intensity between 30 and 150 °C, more likely as neat P3HT than the 1:1 blend. The lack of a definable onset temperature for either reorganization or phase separation meant that it was not possible to reliably estimate T_g for these films. We consider that these dilute blends are indeed morphologically stable, exhibiting behavior during heating similar to that of the neat P3HT film, by virtue of having a PCBM content below the miscibility limit and a near-equilibrium as-cast morphology, and thus are incapable of forming the PCBM domain network required for efficient electron transport.

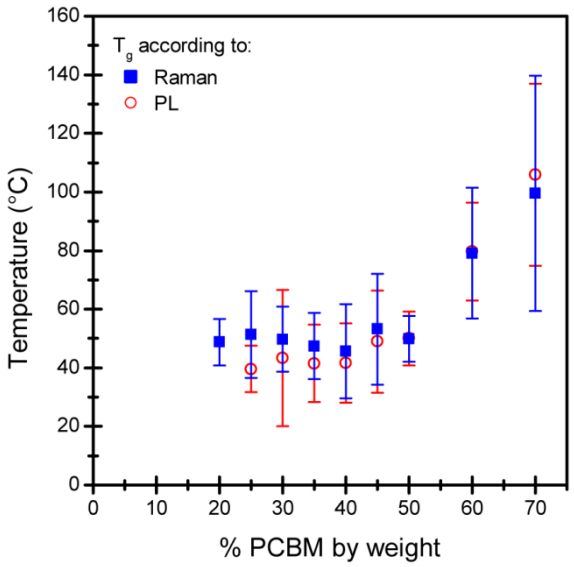


Figure 8: The estimated glass transition temperature T_g for blend films of different %wt PCBM, based on both Raman and PL measurements.

For blends in the disordered regime (> ~20 %wt PCBM), we can observe the distinctive reorganization of P3HT from disorder towards higher order during heating (see Figure 7a). Based on the onset temperature of this reorganization, and for the increase in PL intensity (Figure 7b), we were able to estimate two T_g values for each blend (plotted in Figure 8). There was a good correlation between the two measurements, although the onset of phase separation (according to PL) occurred at slightly lower temperatures than the onset of reorganization (according to Raman) for most films, the difference is well

within the margin of error. Unexpectedly, we did not observe an obvious threshold in T_g at ~25 %wt PCBM, which we earlier identified as the critical concentration for disrupting P3HT order. With increasing the fraction of amorphous phase by adding more PCBM (up to 50 %wt), instead these blends all exhibited fairly similar changes in molecular order and PL intensity during heating, and we estimated T_g values between 40 and 55 °C for all blends between 20 and 50 %wt PCBM. The lack of a clear linear relationship between T_g and blend composition does not follow what was reported by Pearson and Zhao *et al.* using other techniques such as ellipsometry and DSC.[33,34] Our understanding is that, unlike those methods (which probe average properties of the bulk blend), under resonant conditions we measure changes occurring mostly within the amorphous mixed phase: its spinodal decomposition (PL) and reorganization (Raman); and as such we believe that our resonant techniques are powerful for specifically probing the local properties of the amorphous mixed phase within the blend, rather than the average properties of the whole film.

We propose that the mixed phase has a similar composition (and similar properties) across the 20-50 %wt range of composition, as determined by the miscibility limit of PCBM in the amorphous disordered phase of P3HT, and that the only variation is the proportion of amorphous phase in the entire blend (illustrated in Figure 4c). Therefore, while the average T_g of the entire blend (as measured by ellipsometry or DSC) will change with the proportion of mixed phase and overall composition, the local T_g of the amorphous phase we measure does not. Interestingly, a notable deviation was observed for PCBM-rich blends, which only exhibited an improvement in molecular order and PL intensity at relatively high temperatures (shown in Figure 7). Consequently, the estimated T_g values for these blends were markedly higher: 80 and 110 °C for 60 and 70 %wt PCBM respectively. This suggests that P3HT chains in the PCBM-rich blends is not only highly disordered but also kinetically hindered, such that the collective motion of polymer chains

is not possible at the same temperatures as it was in the amorphous mixed phase of the more dilute blends. This kinetic hindrance presumably prevents the as-cast blend from phase-separating at room temperature, despite the high concentration of PCBM within the film. The reduced improvement in P3HT molecular order and effective conjugation length obtained for these PCBM-rich films after a standard thermal annealing cycle is likely a result of their higher T_g values, which reduce the amount of time these films spend at temperatures sufficient to enable phase separation and reorganization.

Despite the complex interplay between the three morphological phases in P3HT:PCBM thin films, its history as a classic polymer:fullerene blend and the depth of study done over the years make it a model system for understanding and interpreting newer, more efficient semi-crystalline materials such as PBTTT and DPPTTT.[25]

Conclusion

In conclusion, we have found two critical changes in the thin film morphology of P3HT:PCBM bulk heterojunctions using a combination of spectroscopic techniques including resonant Raman, absorption and photoluminescence. First, in as-cast films, there is ~25 %wt miscibility limit of PCBM in P3HT, below which PCBM is sufficiently dilute to be dissolved well in the amorphous disordered phase of semi-crystalline P3HT without affecting the chain conformation or optoelectronic properties of P3HT. Between 25 and 50 %wt PCBM, the blend films become more amorphous by dissolving additional fullerenes, which compromises the overall molecular order of P3HT resulting in a distinctive frequency up-shift of the polymer's C=C Raman peak and a blue-shift of absorption/ emission spectra. Above 50 %wt PCBM, the phases of blend films become dominated by PCBM, exhibiting no evidence of an ordered P3HT polymer phase, concomitantly producing significantly higher glass transition temperatures of blend thin films. Second, after thermal annealing we found an excellent degree of consistency in P3HT chain conformation and effective conjugation length between neat P3HT films and blends of up to 50 %wt PCBM.

This indicates that even a short thermal annealing (<5 min) can induce a high degree of phase separation, being able to restore the molecular order (crystallinity) of P3HT. These observations justify the importance of thermal annealing at 150 °C which ensures that the blend is sufficiently phase separated to form an interpenetrating network of purer and more ordered P3HT domains for the efficient charge transport regardless of original blend morphology or compositions.

Our work demonstrates the use of relatively simple but powerful spectroscopic techniques such as resonant Raman and PL, with the flexibility to monitor the evolution of thin film morphology *in situ*, we can develop a detailed understanding of the relationships between processing conditions, thin film morphology and final device performance.

Supporting Information

Resonant and non-resonant Raman spectra for RR- and RRa-P3HT, equation 1 for calculation of molecular order, blend film thicknesses, absorption spectra and optical densities for blend films before and after annealing, Raman and PL spectra for blend films during *in situ* heating and after annealing, evolution and fitting of spectral properties during *in situ* heating for all blends.

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