Correlating the Phase Behavior with the Device Performance in Binary P3HT: NFA Blend Using Optical Probes of Microstructure

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Abstract

The performance of photovoltaic devices based on blends of conjugated polymers with non-fullerene acceptors depends upon the phase behaviour and microstructure of the binary, which in turn depends on the chemical structures of the molecular components and the blend composition. We investigate the correlation between molecular structure, composition, phase behaviour and device performance of a model system comprising semi-crystalline poly-3-hexylthiophene (P3HT) as the donor polymer and three non-fullerene acceptors, two of which (O-IDTBR/EH-IDTBR) have a planar core with

different side-chains, and one (O-IDFBR) has a twisted core. We combine differential scanning calorimetry with optical measurements including UV-Vis, photoluminescence, spectroscopic ellipsometry and Raman, and photovoltaic device performance measurements, all at varying blend composition. For P3HT:IDTBR blends, the crystallinity of polymer and acceptor are preserved over a wide composition range and the blend displays a eutectic phase behaviour, with the optimum solar cell composition lying close to the eutectic. For P3HT:IDFBR blends, increasing acceptor content disrupts the polymer crystallinity, and the optimum device composition appears to be limited by polymer connectivity rather than being linked to the eutectic. The optical probes allow us to probe both the crystalline and amorphous phases, clearly revealing the compositions at which component mixing disrupts crystallinity.

Introduction

The performance of polymer:small molecule bulk heterojunction (BHJ) solar cells strongly depends on the structural features of the active layer, including the extent of intermixing, vertical phase segregation, domain size and, generally, the phase morphology.¹ Recent studies have shown that in most studied BHJ systems the active layer is not made up of pure donor and pure acceptor domains, but rather contains a number of different phases including crystallites of pure donor and acceptor, and amorphous mixed phases that may be rich in one or other component. The composition of these mixed phases is controlled by the partial miscibility of the polymer:small molecule system.^{2,3} While mixing of the phases assists photoinduced charge separation in BHJ devices, segregation is necessary for efficient charge collection. Miscibility is thus an important parameter, influencing both the phase behaviour of the system and the performance of the solar cell.⁴

Many studies have investigated the relationship between phase behaviour, miscibility of donor and acceptor components and the power conversion efficiency (PCE) of BHJ cells, using methods including differential scanning calorimetry (DSC), optical microscopy and X-

ray diffraction (XRD).^{5–12} For example, a non-equilibrium phase diagram (T, wt%) obtained using DSC displays the effect of mixing on the melting temperature profile of the composite, which indicates the strength of interactions between components. In previous works, DSC measurements of polymer:fullerene blends of different blend compositions revealed a eutectic phase behaviour.^{12–15} The eutectic composition was linked to the optimum composition of the solar cell, with maximum photocurrent being found at a composition slightly to the fullerene-rich side of the eutectic, which could be rationalised by the need for network formation among the fullerene crystals domains to enable electron percolation.¹³ In other studies of polymer:fullerene blends that feature a eutectic nature, the eutectic composition was observed to become more fullerene rich for less crystalline fullerenes, and more polymer rich with lower degrees of order in the polymer.¹⁶ The non-equilibrium phase diagram thus provides a rationale for the optimum composition and is helpful for the effective design of BHJ devices.^{16–22}

However, whilst thermal analysis allows us to extract phase behaviour and estimate optimum composition, it primarily reflects the behaviour of the crystalline phases of the sample and does not provide information related to amorphous-amorphous phase behaviour. Moreover, it consumes a significant amount of material and reflects only the properties of the bulk samples rather than that of thin films similar to those used in devices^{12,23–25} as thin film morphology is likely to be governed more by kinetic factors and processing conditions rather than by thermodynamics. These issues indicate the need for a combination of different techniques to gain a detailed picture of the different phases, in order to control device performance via composition and processing. To date, several techniques other than DSC that have been used to gain insight into the microstructure of donor:acceptor (primarily polymer:fullerene) systems, and to relate those to the performance of the device. For example, the correlation between phase mixing and composition dependent device performance has been previously investigated using near edge X-ray absorption fine structure (NEXAFS) and scanning transmission X-ray microscopy.^{12,26} Further, device studies in parallel

with Raman²⁷ or spectroscopic ellipsometry measurements¹ have shown that the increase in P3HT polymer order achieved during P3HT:PCBM blend thermal annealing is correlated with an increase in device PCE. Optical measurements including luminescence have also shown a direct correlation between fullerene crystallisation and device performance,²⁵ whilst other studies have shown that fullerene domains affect the ordering of the polymer component in polymer:PCBM and related the composition dependent device performance with the percolation threshold in the fullerene phase.²⁸ Optical techniques such as absorption, photoluminescence (PL), Raman spectroscopy and spectroscopic ellipsometry have also proved valuable as probes of the material, composition and process dependent microstructure of polymer:molecules blends.^{1,25,28}

Recently, the introduction of so-called non-fullerene acceptors (NFAs), which offer highly tuneable redox potentials and strong optical absorption in the visible range, has advanced the power conversion efficiency (PCE) of BHJ devices.²⁹ In particular, calamitic acceptor-donor-acceptor structures such as O-IDTBR and ITIC appear to produce favourable microstructure when mixed with commonly used polymers.^{22,30,31} In such systems, small changes to molecular structure design (backbone planarity, conformation torsion, and side chain) can have a large effect on the microstructure and hence the device performance, and optimisation of the microstructure is therefore vital.^{32–34} Identifying the most promising NFAs for solar cells from among all possible designs would thus require not only searching a huge chemical phase space but also exploring a wide range of compositions and processing conditions and their effects on the microstructure. Since exploration of such a large chemical and compositional phase space using device measurements or destructive probes of microstructure is labour intensive, developing non-destructive optical probes that can provide rapid feedback on blend microstructure and phase behaviour, for example as part of a high-throughput exploration process, is highly desirable.

In particular, in contrast to the case of polymer:fullerene blends, the relation between chemical structure, phase behaviour and device performance in polymer:NFA blends is there-

fore as of yet relatively unexplored. Previously, the effect of P3HT molecular weight (MW) on the device performance of P3HT:O-IDTBR and P3HT:EH-IDTBR binaries has been explored, showing maximum PCE at an intermediate MW (34 kg/mol for 1:1 weight ratio). In the case of P3HT:O-IDTBR, the eutectic composition becomes increasingly rich in O-IDTBR as the molecular weight of P3HT increases, while for EH-IDTBR the eutectic composition is insensitive to molecular weight.²² However, whilst that study reported blend microstructure as a function of polymer MW, there was no investigation into the structural details as a function of composition. One previous study of ternary devices where a second acceptor component (O-IDFBR) was added to the P3HT:O-IDTBR binary showed that O-IDFBR is more miscible with the P3HT polymer whilst O-IDTBR forms a more phase-separated morphology with P3HT.³⁵ Further optimisation of both binary and ternary devices requires an analysis of the blend phase behaviour as a function of composition, and its relation to device behaviour.

In this work, we select a set of three chemically related acceptors that differ in their backbone or side chain structure and study their blends with P3HT. The acceptors are O-IDTBR, which has a planar backbone and linear side chains and is known to crystallise strongly; EH-IDTBR, whose more bulky side chains are expected to affect the molecular packing, and O-IDFBR whose twisted backbone is likely to affect the crystallisation and mixing behaviour compared to O-IDTBR. By studying the correlation between molecular structure, composition, phase behaviour and device performance for this model system we probe the structural and chemical factors that control the optimum composition for maximum device performance. We use DSC to study the phase behaviour of each P3HT:NFA binary by mapping the temperature as a function of composition, and compare the results with the composition dependent device performance. Additionally, we complement the thermal characterization with a series of non-destructive optical probes, namely linear absorption, steady-state photoluminescence, spectroscopic ellipsometry (SE), and Raman spectroscopy. Such probes can be applied with spatial resolution in combinatorial approaches for rapid ex-

perimental screening of blend systems. An important goal of this work is to establish which combination of such optical techniques are best suited to examine the composition dependent microstructure, which we achieve by comparing the structural information obtained from the optical characterization with the information obtained by thermal analysis. Finally, as well as establishing the eutectic nature of the blend films, we establish the conditions under which the composition of a blend layer can be deduced from optical (SE or Raman) measurements along with information about the optical properties of the individual components.

Experimental Methods

Materials and solutions: O-IDFBR, O-IDTBR, and EH-IDTBR ($M_w = 1326$ g/mol, 1314 g/mol, and 1314 g/mol respectively) were synthesised as described elsewhere.²⁹ P3HT was purchased from Ossila ($M_w = 34$ kg/mol, $RR = 94.7\%$). All other chemicals were purchased from Sigma-Aldrich and used as received. Thin films for spectroscopy were spin-coated at 2500 r.p.m for 1 min from chlorobenzene solution (concentration of 25 mg/mL⁻¹) onto quartz substrates. The substrates were cleaned by sonication in acetone, and isopropanol before ozone plasma treatment for 10 min. The solutions were heated to 70 °C overnight and the substrate was also kept at 70 °C. P3HT and NFAs were mixed at different weight percentages.

UV-Vis measurements: Absorption spectra were measured using a commercial UV-Vis spectrophotometer.

Differential Scanning Calorimetry: Samples for differential scanning calorimetry (DSC) were prepared by drop-casting of chlorobenzene homogeneous solutions (150 μ L of 25 mg mL⁻¹) onto glass slides followed by evaporation of the solvent at room temperature. The films were held under vacuum over the night then scraped off, and ~ 2 - 3 mg were transferred into hermetic DSC pans, which were sealed with punctured lids. The measurements were performed under Nitrogen using a Mettler Toledo DSC 800. Two heating and two cooling cycles were recorded at a 5 °C min⁻¹ rate. The first heating cycles were used to construct

the liquidus curves, for which the endotherm onset temperatures were used.

Variable Angle Spectroscopic Ellipsometry: We performed variable angle spectroscopic ellipsometry (VASE) measurements using a SOPRALAB GES5E rotating polarizer ellipsometer installed within a clean room that uses a Xe lamp as a light source and a CCD detector to record optical spectra from 1.2 eV to 5.6 eV. Three incidence angles were typically recorded for each sample, varying between 55 and 75 degrees.

Photoluminescence (PL) measurements: We performed PL measurement with an Andor SR-163 spectrometer and a CCD array (Andor i-DUS). The excitation source (model) provided the excitation wavelength of 532 nm (2.33 eV photon energy) and to attenuate incident beam reflection a low pass filters were put in place, 550 nm for λ_{ex} = 530 nm. The emitted light was collected perpendicular to excitation focused into an optical fiber. The spectra were measured at 100 accumulated exposures of 0.1 s. The spectra were calibrated by subtracting the constant background and accounting for the detector response, all measured in the same optical configuration.

Raman spectroscopy: We performed Raman spectroscopy in air, and at room temperature using a WITec alpha 300 RA⁺ setup coupled to a 2.54 eV (488 nm) solid-state laser line. We obtained the Raman spectra using a 10 X magnification objective while measuring on-the-fly an area of 500 × 500 microns squared defined as an array of 25 × 25 points. Laser power and integration time were adjusted such that to avoid fast photodegradation of the sample; typical values selected were 3 mW (measured in free-beam after filtering) and 136 ms per spectrum. Spectra were background-corrected and then fitted according to the solid-state Raman cross-section of the binary blends. Raman cross-sections were obtained fabricating thickness gradients and fitting the experimental trends using a transfer matrix model as reported elsewhere.³⁶

Atomic Force Microscopy: Atomic force microscopy (AFM) measurements were carried out to study the surface morphology of various blend films spin cast on a quartz glass substrate using an Agilent 5500 AFM system in a tapping mode. We used the same film that

we previously used for other measurements. The cantilever had an approximate resonant frequency of 270 kHz and a force constant of 40 nm^{-1} . The topography and phase data of the films were recorded using PicoView scanning probe microscopy control software, and information on the surface roughness were extracted from the analysis of $5 \mu\text{m} \times 5 \mu\text{m}$ and $1 \mu\text{m} \times 1 \mu\text{m}$ AFM images using Gwyddion software.

Device fabrication: We fabricated an inverted architecture, ITO/ZnO/P3HT:NFA/MoOx/Ag, with ZnO and MoOx as the electron and hole transport layer, respectively. Pre-patterned ITO substrates were cleaned by sonication in acetone, detergent, deionized water, and isopropanol, after which dried by nitrogen gas gun, and then oxygen plasma treated for 5 min before ZnO deposition. 30 nm ZnO thin films were deposited via spinning coating. ZnO precursor solution made from zinc acetate (219.5 mg) dihydrate in 2-methoxyethanol with (2 ml) monoethanolamine (60 ml), followed by 150°C thermal annealing for 10-15 min. Active layers made from various D/A compositions were then deposited on top of ZnO film by spin coating from solution in chlorobenzene (25 mg/ml^{-1}), giving layers of $70 \pm 5 \text{ nm}$. Finally, 10 nm of MoOx followed 100 nm of Ag layers were deposited on top of active layer by evaporation with a mask area of 0.045 cm^2 . Current-voltage (J-V) characteristics were measured by a Keithley 2400 source-measurement unit under the AM 1.5 G spectrum from a solar simulator (Oriel Instruments).

Results

The chemical structures of the three NFA acceptors used in the study, O-IDFBR, O-IDTBR and EH-IDTBR, are shown in Figure 1 (a,b). All three acceptors are blended with the polymer P3HT to fabricate binary donor-acceptor systems.

To gain an initial understanding of the phase behaviour of the three polymer:NFA blend systems, we carry out DSC on the blends to plot non-equilibrium phase diagrams (T , wt%) of the binaries and compare the phase diagram with their OPV device short circuit current

(Jsc) as a function of composition (see Figure 1 (c-f)). The devices have the inverted structure ITO/ZnO/P3HT:NFA/MoOx/Ag with further details in the supporting information at Figure S1. Note that, to be consistent with the optical measurements on the films, will be discussed later, we studied devices where the active layer was not thermally annealed.

We present the thermograms of binary P3HT:NFA blends in Figure S2-S4, displaying the data up to 250 °C as there are no further features above that temperature (see Figure S5). Based on the thermograms, we confirm that P3HT is a semicrystalline polymer with a melting point T_m of about 245 °C, and O-IDFBR, O-IDTBR, and EH-IDTBR are crystalline with melting temperatures of 195.6 °C, 231.4 °C, and 225.7 °C, respectively. We define the melting temperature as the end values of the endotherms observed in the first heating thermograms. Note that the thermograms also exhibit an exothermic peak for the NFAs, probably due to cold crystallisation upon heating, with temperatures of 132.2 °C, 115.1 °C, and 188.4 °C, for O-IDFBR, O-IDTBR, and EH-IDTBR respectively. We observed a significant melting point depression for P3HT upon mixing the semi-crystalline polymer with different amounts of diluent NFAs.

For the cases of the O-IDTBR and EH-IDTBR, we have a eutectic phase diagram where the eutectic composition and eutectic temperature can be defined. At the eutectic point of a binary, phase-pure crystals of both polymer and acceptor form, surrounded by a fine matrix containing both components.¹³ We find a eutectic composition of 40 wt% O-IDTBR (223.4 °C) in P3HT:O-IDTBR and 50 wt% EH-IDTBR (223 °C) in P3HT:EH-IDTBR. The eutectic composition of the more crystalline O-IDTBR is therefore lower (less NFA rich) than that of EH-IDTBR, in agreement with trends in eutectic composition for blends of polymer with fullerenes of different crystallisation tendency.¹⁶

Figure 1: Chemical structure of O-IDFBR (a), O-IDTBR and EH-IDTBR (b), phase diagram of P3HT:O-IDFBR (red squares) (c), P3HT:O-IDTBR (blue circle), P3HT:EH-IDTBR (green triangle) (d) binary blends obtained on the basis of the first heating DSC thermograms. O-IDFBR initially prefers to mix with P3HT compared to O-IDTBR, and EH-IDTBR based on the melting point depression. The phase diagram of binary P3HT:O-IDFBR exhibits a composition window of 40-80 wt% O-IDFBR where O-IDFBR displays no melting point depression, while the P3HT melting point is depressed up to 70 wt% O-IDFBR. The eutectic composition of 40 wt% O-IDTBR, and 50 wt% EH-IDTBR shows that the pure primary crystals of O-IDTBR start to develop earlier and at lower composition of O-IDTBR compared to EH-IDTBR, that is consistent with more planar (potentially crystalline) chemical structure of O-IDTBR compared to EH-IDTBR. e), (f): measured device short-circuit current density, J_{sc} , as a function of composition for non-annealed blend devices of P3HT:O-IDTBR and P3HT:O-IDFBR. J_{sc} peaks around the eutectic composition i.e. 40-50 wt% whereas J_{sc} of P3HT:O-IDFBR peak far below the possible eutectic composition of 80 wt%.

In the case of P3HT:O-IDFBR, a different phase behaviour is observed where the melting temperature of P3HT is suppressed by O-IDFBR addition, indicating interaction between

the materials, whilst the O-IDFBR melting temperature is affected only slightly. We observe a composition window of 40-80 wt%, where O-IDFBR displays no melting point depression, while the P3HT melting point is depressed up to 70 wt% O-IDFBR. This behaviour is not consistent with simple eutectic phase behaviour, and whilst the underlying behaviour may be consistent with a solid solution or a monotectic at 40 wt% O-IDFBR followed by a eutectic at 80 wt%, the available data are insufficient to specify the precise phase behaviour. Furthermore, in accordance with previous studies of the phase behaviour of NFAs where evidence was found of polymorphism,³⁷ it is possible that O-IDFBR may form different polymorphs.

In P3HT:O-IDFBR and P3HT:O-IDTBR binaries the J_{sc} peaks around 40-50 wt% NFA, shown in Figure 1, which corresponds to the eutectic composition in the P3HT:O-IDTBR and is also the composition where the crystallinity of P3HT becomes suppressed in P3HT:O-IDFBR binary blend.

Whilst the behaviour of the O-IDTBR blend is consistent with previous analysis suggesting that photocurrent generation should peak at a composition that is slightly acceptor-rich relative to the eutectic, the behaviour of the O-IDFBR blend device series is not so easily explained. Further evidence of reduced P3HT crystallinity upon O-IDFBR addition appears in the enthalpy of fusion of the P3HT fraction in P3HT: O-IDFBR blends which, as shown in Figure S6, is greatly reduced relative to the value for pure P3HT at NFA contents of 40 wt% O-IDFBR and above.

Based on these results, it is therefore evident that there is a need to further investigate the microstructure, and in particular the amorphous phase of the blends, using a wider range of techniques. Given that techniques such as DSC and grazing-incidence wide-angle X-Ray scattering (GIWAXS) only help to characterize the crystalline part of the sample, we inspect how the details of the microstructure are reflected in the optical properties of the blends.

To this end we measure composition dependent absorption and PL to obtain information on the microstructure of the thin films based on how the positions and strength of optical transitions are affected by molecular interaction and mixing.

Figure 2 (a,b) shows the normalized UV-Vis spectra of binary P3HT:O-IDFBR and O-IDTBR blends for various blend compositions as well as for the pristine materials.

Figure 2: normalized UV-Vis absorption spectra for blend films of binary (a) P3HT:O-IDFBR, and (b) P3HT:O-IDTBR, absolute PL spectra for binary (c) P3HT:O-IDFBR, and (d) for P3HT:O-IDTBR blends across the whole composition of NFAs under 2.33 eV and 1.96 eV excitation respectively. The red-shifted absorption of O-IDTBR relative to O-IDFBR indicates the planarization and greater tendency of O-IDTBR to crystallise. PL measurements suggest a higher propensity of P3HT and O-IDFBR to mix at the molecular level.

The pristine P3HT film shows a maximum absorption range of 2.2-2.4 eV, along with a strong absorption shoulder at ~ 2.05 eV indicating the ordered phase of semi-crystalline P3HT. O-IDFBR has a broad featureless absorption spectrum with a maximum observed at 2.41 eV while O-IDTBR exhibits an absorption maximum at 1.75 eV with a second well defined vibronic peak at 1.82 eV which can be correlated to the O-IDTBR crystal phase.

The red-shifted absorption of O-IDTBR relative to O-IDFBR reflects the more stabilized π system of O-IDTBR that results partly from the more planar conformation of O-IDTBR and its greater tendency to crystallise.^{29,30}

As can be seen, P3HT absorption overlaps significantly with O-IDFBR absorption, which limits the contrast in that system. It is easier to distinguish the contributions of O-IDTBR and P3HT in P3HT:O-IDTBR blends, although there is also some overlap. The overlapping absorption spectra make interpretation of absorption spectra significantly harder than in the case of P3HT: fullerene blends.

After blending with O-IDFBR, the P3HT contribution to the film absorption does not show any significant changes in spectral shape up to 40 wt% O-IDFBR. For higher O-IDFBR content, the absorption spectra reveal a sharp reduction in the shoulder of P3HT at 2.05 eV and in addition the absorption maxima of the blend are slightly blue shifted in comparison with those of both pure P3HT and pure O-IDFBR. The change in spectral shape as well as the blue shift can be explained by the amorphisation of the P3HT due to the disruptive effect of O-IDFBR. Upon blending P3HT and O-IDTBR, there is no evidence of change in the spectral shape of the contributions from the two components, indicating little impact on the packing of the materials by the presence of the other component.

Figure 2 (c,d) shows PL spectra of P3HT:NFAs blends. Note that we excite P3HT:O-IDFBR at 2.33 eV (530 nm) and P3HT:O-IDTBR at 1.96 eV (630 nm) where the respective NFAs absorb strongly. Unlike in P3HT: fullerene blends, the PL of the NFAs are stronger than that of P3HT in the measured range.

Upon addition of P3HT to O-IDFBR, and O-IDTBR, quenching of the NFAs is observed. However, we observe that O-IDFBR emission quenching upon P3HT addition is relatively efficient (i.e. stronger quenching at lower P3HT content) in comparison with O-IDTBR PL quenching. By contrast, upon addition of 10 wt% NFAs to P3HT the P3HT PL is efficiently quenched for both O-IDTBR and O-IDFBR addition. Given that both blends present a significant energetic offset for photoinduced exciton dissociation, any differences in quenching ability are likely to be due to microstructure rather than energetics. The more efficient O-IDFBR PL quenching upon addition of P3HT relative to O-IDTBR can therefore be related to a greater propensity of P3HT to mix with O-IDFBR at the molecular level in

comparison with O-IDTBR.

Taken together, the UV-Vis absorption and PL spectra suggest a stronger tendency for P3HT and O-IDFBR to mix at the molecular level and hence indicate a stronger interaction between O-IDFBR and P3HT compared to between O-IDTBR and P3HT. The absorption and PL spectra of binary P3HT:EH-IDTBR blends exhibit similar trends to that of O-IDTBR with P3HT, Figure S7.

We next evaluate the composition-dependent Raman spectra of the binary blends to identify the extent of conformational disruption under mixing. The Raman spectra of the three pristine NFAs, shown in Figure S8, are consistent with previous studies in the literature.^{30,38} The Raman spectra of pristine O-IDFBR, O-IDTBR and EH-IDTBR films are characterized by peaks at 1530 cm^{-1} , 1550 cm^{-1} which correspond to vibrations of the benzothiadiazole (BT) unit and 1600 cm^{-1} to the phenyl rings of the indacenodithiophene (IDT) core, respectively. The thiophene peaks present at $(1380\text{--}1450\text{ cm}^{-1})$ for O-IDTBR and EH-IDTBR, are not observed for O-IDFBR.³⁰ These modes can be used to track the conformational order and chain planarity in pristine O-IDFBR, O-IDTBR and EH-IDTBR films.³⁰ Similarly, the peaks around $1350\text{--}1450\text{ cm}^{-1}$ in the vibrational Raman spectrum of P3HT can be used to probe the state of order in the polymer.²⁷

Figure 3(a,b) shows the normalized Raman spectra of three selected compositions of P3HT:O-IDFBR, and P3HT:O-IDTBR respectively, excited at 2.54 eV (488 nm) in the $1200\text{--}1700\text{ cm}^{-1}$ spectral range, while the normalized Raman spectra of P3HT:EH-IDTBR are shown in Figure S9.

We select 2.54 eV (488 nm) as the excitation wavelength in order to avoid the large photoluminescence background that arises at longer wavelengths, which would prevent an accurate analysis of peak positions and intensities.

Figure 3: normalized Raman spectra of the binary P3HT:O-IDFBR (a) and P3HT:O-IDTBR (b) blends. The experimental data (dots) was fitted (solid line) using Gaussian and Lorentzian (dashed lines), at 2.54 eV excitation, with deconvolution of the relative contribution of semi-crystalline P3HT (Lorentzian) and amorphous P3HT (Gaussian).

In addition, 2.54 eV (488 nm) as the excitation wavelength enables us to probe both crystalline and amorphous parts of the P3HT fraction, both of which absorb leading to Raman resonant conditions. While both NFAs also absorb at 2.54 eV, they show a low Raman cross-section compared to P3HT, at this excitation wavelength.

The Raman spectra in Figure 3 (a,b) first indicate that the Raman cross-section of the NFAs is substantially lower than that of P3HT at the probing wavelength, which is consistent with the reported values.³⁹ This fact results in large uncertainties in the quantitative analysis of their characteristic peak intensities and shifts as a function of blend composition, which makes it difficult to infer composition dependent trends. For this reason, we focus on the spectral range ranging between 1350-1500 cm^{-1} that encompasses the characteristic, most intense Raman bands of P3HT, i.e. 1380 cm^{-1} (C-C intra-ring stretch) and 1450 cm^{-1} (symmetric C=C stretch mode).²⁷ The main 1450 cm^{-1} band (C=C mode) of P3HT is known to have contributions from both crystalline and amorphous P3HT domains that coexist in the

film, such that C=C mode softening (hardening) is associated with an increase (decrease) of the conjugation length, thus indicating higher (lower) degree of crystallinity.²⁷ The relative intensity of these contributions changes when the polymer is blended with some (partially) miscible material therefore it can be used to infer the nature and extent of polymer:molecule mixing. The normalized Raman spectra of P3HT:O-IDTBR, and P3HT:O-IDFBR across the whole composition are shown in Figure S10.

In order to qualitatively assess the extent of the polymer's crystallinity disruption upon blending with the corresponding NFA we compare the relative strength of the Raman signals associated with the crystalline and amorphous parts of the P3HT, adapting a previous approach.²⁷ We model the main C=C stretching band of P3HT (1450 cm^{-1}) as a convolution of two line shapes: a Lorentzian and a Gaussian function. The Lorentzian is centred at 1448 cm^{-1} (FWHM= 26 cm^{-1}), which corresponds to the crystalline fraction of the P3HT; while the amorphous counterpart is ascribed to a Gaussian function centred at 1455 cm^{-1} (FWHM= 36 cm^{-1}). These peak positions are close to those reported for regioregular- and regiorandom-P3HT films²⁷ while the corresponding line shapes were selected to minimise the fitting error throughout the whole composition range. By looking at the ratio of the fitted peak intensities, we gain information regarding the crystalline fraction of P3HT in the film and the extent of the miscibility with the NFA, which is expected to break polymer's conjugation and induce its amorphisation.

Figure 4 illustrates the crystalline-to-amorphous fraction intensity obtained from the ratio of the Lorentzian to the Gaussian peak intensities at each blend composition. The general trend observed suggests that when the NFA wt% is increased the crystalline-to-amorphous fraction decreases accordingly, which indicates a more disrupted conjugation in the polymer domains upon NFA addition. Moreover, the trends indicate that the crystallinity of P3HT is more easily disrupted by mixing with O-IDFBR than by the equivalent mass of O-IDTBR or EH-IDTBR, with the largest depression in crystallinity occurring precisely beyond 40 wt% O-IDFBR, compared to beyond 70 wt% O-IDTBR and EH-IDTBR addition.

Figure 4: Raman intensity of crystalline relative to amorphous phases of P3HT:O-IDFBR (pink square), P3HT:O-IDTBR (blue circle), and P3HT:EH-IDTBR (green triangle). Crystallinity of P3HT is more easily disrupted when mixed with O-IDFBR (beyond 40 wt%) than when mixed with O-IDTBR or EH-IDTBR (beyond 70 wt%).

We next carried out variable-angle spectroscopic ellipsometry on pristine films, with Figure 5 showing the refractive index, n , and extinction coefficient, k , of O-IDFBR, O-IDTBR, and EH-IDTBR pristine thin films calculated using the standard critical point (SCP) model (note that the refractive index of P3HT from ellipsometry has been reported previously¹ and is reproduced here, as shown in Figure S11). The results clearly show a lower extinction coefficient of O-IDFBR compared to O-IDTBR and EH-IDTBR. This lower extinction is expected given the higher absorption energy of O-IDFBR, whose absorption peaks at 2.4 eV, while O-IDTBR and EH-IDTBR show absorption maxima at 1.80 eV and 1.83 eV, respectively. Note that the feature at 2 eV is not present in the extinction coefficient of the solution,²⁹ see Figure S12.

To then provide insight into how the structure of each component changes by blending with the other one, we present a detailed analysis of the VASE data corresponding to the three binary blends using SCP, and Bruggeman effective medium approximation (EMA) methods. The former method treats each blend as a completely new material, with new properties relative to its constituent compounds. Since we cannot infer the degree of interaction between

components using the SCP model, we employ the Bruggeman model in which a homogeneous mixture of the two non-interacting materials is represented using a combination of their optical constants. This approach minimises the number of fitting parameters.

Figure 5: Refractive index, and extinction coefficient of O-IDFBR (pink-dashed line), and O-IDTBR (blue-solid line), and EH-IDTBR (green-dotted line) using the SCP modelling. The extinction coefficient spectra closely resemble the absorption spectra of the NFAs shown in 2. The less visible vibronic structure in the extinction coefficient of O-IDFBR can be assigned partly to the lower degree of crystallinity of O-IDFBR compared to O-IDTBR and EH-IDTBR.

Figure 6 shows the refractive indices (n, k) calculated for P3HT:O-IDFBR (a), and P3HT:O-IDTBR (b) binaries using the Bruggeman EMA, where the inferred mass fraction of NFA is obtained by fitting the model to the experimental data for the given binary blend. Note that the resulting mass fraction, $\phi_{inferred}$, is not necessarily equal to the actual value used in preparing the binary. Figure S13 shows the refractive indices (n, k) obtained with SCP model and Bruggeman EMA when the actual compositions are used with the (n, k) spectra obtained using the more flexible SCP model, which can be considered a best estimate of the (n, k) of the blend. This differs from the results of the Bruggeman EMA shown in Figure 6, where the compositions were inferred from a best fit to the experimental data, which would be a relevant procedure if the composition of a blend were not known. The Bruggeman spectra deviate slightly from the SCP fits and do not exactly reproduce the amplitude, position

and width of the vibronic peaks in the binaries. The difference between (n,k) of the blends determined by SCP and Bruggeman EMA indicates that there is some degree of mixing between the two constituents which depends on the relative composition of the mixture.

Figure 6: Refractive indices (n,k) of a) P3HT:O-IDFBR, and b) P3HT:O-IDTBR binaries of compositions 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 wt% NFA obtained using the Bruggeman EMA. For each blend, the spectra are obtained by varying the composition to obtain the best fit to the experimental data. This inferred composition is in general different to the actual one, shown in Figure S13 (c,d). As shown the extinction coefficient (k) of the O-IDTBR is significantly stronger than O-IDFBR.

In order to evaluate the effect of blend composition on (n,k) deviation and hence on mixing, we compare the NFA wt% inferred from the Bruggeman EMA with the actual one. We first consider the NFA wt% $\phi_{inferred}$ extracted from a binary Bruggeman model, containing only the optical constants of the pristine P3HT and pristine NFA (spectra in Figure 6) where film thicknesses extracted from the transparency region using the Cauchy law, cross-checked with profilometer, have been used as a first guess in the model. The results of the analysis using a binary model including P3HT and NFA, are shown in Figure 7 a.

The results from the Figure show that according to the VASE analysis based on the Bruggeman EMA, the binary Bruggeman EMA significantly overestimates the O-IDFBR wt% in the composition range beyond 40% O-IDFBR. However, the wt% of both O-IDTBR and EH-IDTBR is slightly underestimated beyond 40 wt%, and more significantly beyond 70 wt% O-IDTBR and EH-IDTBR. Deviation from the direct proportionality line indicates the extent of mixing and molecular interaction in the binary.⁴⁰ Note that the *volume* fraction

was determined by fitting the ellipsometric data and to calculate the inferred weight fraction we use the densities of P3HT and NFAs, taken as 1.1 gr/cm^3 for P3HT according to Prosa et al.⁴¹ and 1.314 gr/cm^3 and 1.244 gr/cm^3 for O-IDFBR, and O-IDTBR and EH-IDTBR respectively. The deviation between the inferred and actual NFA wt% can be assigned, to some extent, to the miscibility of the NFAs within the P3HT semi-crystalline matrix, which would contribute to a third mixed blend phase that is not included as a constituent in the standard (i.e. binary) Bruggeman EMA model.

Figure 7: Inferred wt% of NFAs via Bruggeman EMA of the three binaries, a) using a binary and, b) a ternary approach. The ternary approach using regio-random P3HT helps improve the matching between the inferred, and the actual wt% of O-IDFBR, and using air in the ternary compensates for the roughness of the film including P3HT, O-IDTBR and EH-IDTBR, and improves the matching.

Therefore, a more detailed EMA is needed to identify the optical properties of the binary blends, and provide insight into the extent to which we can infer the blend content from the optical properties. Hence, we analyse the data further using a Bruggeman EMA with a third component to fit the binary data. We include, in a first attempt, a third component based on regiorandom (RRa) P3HT as well as semicrystalline P3HT and the NFA. The RRa P3HT is intended to represent P3HT whose crystallinity has been disrupted by mixing with NFA. This approach leads to an improvement in the matching between the inferred, and the actual weight fraction as well as the goodness of fit in only P3HT:O-IDFBR binary,

Figure 7b. Note that the inferred wt% of NFA for each ternary is relative to the wt% of semicrystalline P3HT.

Raman analysis showed that P3HT becomes rather amorphous in the presence of O-IDFBR. Including RRa P3HT as a third component did not assist the fit of the spectra for the O-IDTBR and EH-IDTBR blends. The fact that the optical properties of RRa P3HT overlap strongly with O-IDFBR may help to explain why this ternary works better for O-IDFBR than O-IDTBR and EH-IDTBR blends.

In our second attempt we included air (as free volume) as a third component to the binary of semi-crystalline P3HT and NFA. For this ternary, P3HT:O-IDFBR fitting did not improve, and the matching between the inferred and the actual NFA weight fraction as well as the goodness of fit improved only for P3HT:O-IDTBR and P3HT:EH-IDTBR binary blends. Air is able to account for the roughness of a polymer film such as blend including semi-crystalline P3HT and large fraction of crystalline O-IDTBR or EH-IDTBR. The greater roughness of these films is verified by the atomic force microscopy (AFM) shown in Figure 8 and S14. The AFM images of the P3HT:O-IDFBR and P3HT:O-IDTBR blends are shown in Figure S15-S16. Moreover, in both the binary and ternary approach the Bruggeman EMA appears to be a more effective model to infer the true NFA wt% of P3HT:O-IDTBR or P3HT:EH-IDTBR than P3HT:O-IDFBR. This observation can be assigned to the more phase separated P3HT:O-IDTBR and P3HT:EH-IDTBR compared to P3HT:O-IDFBR, which means the properties of the binary are better represented by a combination of the properties of the pristine components, than in the case of a strongly mixed blend.

Previous studies show that blending polymer with fullerene changes the degree of polymer crystallinity, and the degree of anisotropy such that the film anisotropy increases when the film thickness decreases.⁴² We found that the fitting to the transparency region, which can be modeled with a Cauchy law, did not improve when including anisotropy.

Discussion

In this study, we have made a number of observations regarding the microstructure of P3HT:NFA blend systems studies as follows and shown in Figure 8:

First, that the P3HT:IDTBR blends looks eutectic, while the P3HT:O-IDFBR blend shows a rather different behaviour, requires a higher NFA fraction before NFA crystallization and may have an amorphous composition window. Second, as shown by UV-Vis, PL and Raman, O-IDFBR disrupts the packing of P3HT more easily than O-IDTBR or EH-IDTBR. Third, in analysis of the optical functions n and k , blends of P3HT with O-IDTBR resemble the combination of the pristine components while those of P3HT with O-IDFBR do not. Some of these observations may be expected from the molecular conformations of the different molecules and their resulting tendency to crystallise. Here we consider the question of how well the optical measurements could be used to predict the microstructure, and the relevance of the phase behaviour to PV device performance. First we review the key results in detail.

The DSC of P3HT:O-IDTBR follows the familiar behaviour for a eutectic mixture due to the interplay of crystallisation of the constituents. P3HT:EH-IDTBR also shows a eutectic structure but one where pure primary NFA crystals develop at higher EH-IDTBR content, suggesting that the less crystalline chemical structure of EH-IDTBR hinders its crystallisation in the blend.

A previous study on P3HT: fullerene adduct binaries showed that the eutectic composition becomes increasingly rich in fullerene as the crystallisation tendency of the fullerene decreases.¹⁶ A similar trend is observed here, where the acceptor with the greater tendency to crystallise (the more planar O-IDTBR) forms a eutectic at a lower concentration in the blend than the less crystalline EH-IDTBR. The blend formed with the least crystalline acceptor, the twisted core O-IDFBR, displays a different phase behavior and shows polymer melting point depression at the highest NFA fraction of the three, consistent with the trend.

Moreover, a significant jump in the melting point depression observed in the phase diagram for P3HT:O-IDFBR (70-80 wt% O-IDFBR) may be assigned to the blend forming a

mainly amorphous mixture in that composition window, or to the formation of crystals that are too small (nanometer size) to be detected by DSC, see Figure S17.

Figure 8: Composition dependence of the phase behaviour, microstructure and device properties of the O-IDFBR and O-IDTBR blends: Phase diagram (a,b), PCE (c,d), J_{sc} (e,f) from JV (open squares/circles) from EQE (filled squares/circles), IQE (g,h), Raman intensity of crystalline relative to amorphous phases (i,j), PLQE (k,l) and surface roughness (m,n) of P3HT:O-IDFBR (left panel) and P3HT:O-IDTBR (right panel).

As a further probe of the mixing tendency of the three binaries, we analyse the DSC data to extract the Flory-Huggins interaction parameter (χ), following polymer-diluent mixture melting point depression theory,⁴³ Figure S18 and Table S1. All interaction parameters observed here are positive, indicating that the small molecules cannot mix completely with P3HT and tend to phase separate to some extent. The value of χ increases from P3HT:O-IDFBR ($\chi = 0.99$) to P3HT:EH-IDTBR ($\chi = 1.15$) and P3HT:O-IDTBR ($\chi = 1.26$) binaries. The increase in χ , representing a decrease in miscibility, can be assigned to the increasingly planar chemical structure of the acceptor, which leads to a more phase-separated morphology in P3HT:O-IDTBR due to segregation of the acceptors and ordering of P3HT and crystalline O-IDTBR. We note that O-IDFBR is comparable with PCBM in terms of extent of mixing in the bulk, given the reported value of $\chi = 0.86 \pm 0.09$ for P3HT:PCBM.⁴⁴

The conclusion from the DSC studies that O-IDFBR mixes more easily with P3HT than O-IDTBR or EH-IDTBR is supported by the series of optical measurements. The greater tendency of O-IDFBR to mix with P3HT is consistent with the loss of the P3HT red shoulder at 2.06 eV (600 nm) in UV-Vis and PL spectra (Figure S19-S20) at $\phi \geq 40\%$ O-IDFBR while the same shoulder persists up to $\phi = 70\%$ in O-IDTBR and EH-IDTBR (Figure S21). It is also evidenced by the blue shift in the absorption spectra of P3HT:O-IDFBR binary upon increasing the O-IDFBR content, which indicates loss of crystalline order in the polymer, and by the loss in crystallinity in the polymer, as shown by Raman peak analysis, at a much lower fraction of O-IDFBR than O-IDTBR or EH-IDTBR. The trend can be rationalised in terms of the chemical structure of the acceptor with the more twisted O-IDFBR showing a weaker tendency to crystallise than the planar IDTBR molecules, and hence a greater tendency, at any composition, to mix into the polymer and so disrupt the polymer's crystallinity. Similar optical trends of binary P3HT:O-IDTBR and P3HT:EH-IDTBR blends demonstrate that the interactions of acceptors with P3HT are not strongly affected by the side chain but more by the chemical structure of the core. Consistently the optical methods (absorption, PL, Raman and spectroscopic ellipsometry) indicate the onset of amorphisation of P3HT at

around 40 wt% O-IDFBR compared to 70 wt% O-IDTBR or EH-IDTBR in the blend, with a greater degree of mixing indicated by an earlier onset of amorphisation. Beyond these critical compositions, the further addition of the NFA to P3HT increases and/or encourages formation of NFA clusters.

We now evaluate the ability of the studied optical properties obtained from spectroscopic ellipsometry to indicate the degree of mixing in binary blends. The mixing behaviour controls the extent to which the composition of a blend can be inferred optically. In the case of P3HT:O-IDTBR and P3HT:EH-IDTBR blends, P3HT and O-IDTBR or EH-IDTBR largely resemble their pristine form in the blends, provided that the optical model used in fitting compensates for the roughness, and do not disrupt each other much in the blends. Therefore, upon blending both materials are able to keep their optical properties unaffected to a larger extent and the Bruggeman EMA is a good model for the microstructure of films. In the case of P3HT:O-IDFBR, the significant deviation of inferred from actual NFA weight fraction for $\phi \geq 40\%$ indicates disruption of blend optical properties relative to a simple combination of constituents. The study shows that the true blend composition can be extracted fairly reliably by a fit of the Bruggeman model to experimental spectroscopic ellipsometry data using optical constants of the pristine components in cases where the components do not mix strongly, but cannot be extracted so reliably when the components mix strongly enough to disrupt their crystallinity. Therefore Bruggeman optical modelling can be used as a probe of composition reliably only for binaries with limited degree of molecular scale mixing.

We now address the relationship of phase behaviour to the performance of photovoltaic devices. As noted above, the behaviour shown by the phase diagram was not sufficient to explain the composition-dependent behaviour of the J_{sc} for P3HT:O-IDFBR.

We therefore further examine the relationship between the blend microstructure and the photovoltaic devices' characteristics, as shown in Figure 8(c-h) and S1&S22. We find that the trend in PCE, Figure 8(c,d), with composition is dominated by the trend in short circuit current density (J_{sc}) for each blend, Figure 8(e,f). We observe that the PCE of

P3HT:O-IDTBR peaks at the eutectic composition where crystals of both donor and acceptor form and, based on the optical measurements, both components retain their pristine microstructure. This is consistent with previous discussion of composition dependent device performance of eutectic binaries.¹³ Surprisingly, we observe the maximum of the PCE of P3HT:O-IDFBR to lie around 30-50 wt% O-IDFBR, which is not aligned to any feature in the phase diagram. It suggests that some other factors, possibly deteriorating electronic properties due to the loss of P3HT crystallinity, could be limiting the device performance.

Since J_{sc} results from the combined efficiencies of light absorption, charge separation and charge collection, we eliminate the effect of the different absorption spectra of the two acceptors on J_{sc} by calculating the internal quantum efficiency (IQE) from the measured EQE, together with a calculated absorption based on the (n,k) values obtained from ellipsometry using the Bruggeman EMA method (ternary approach), as shown in Figure S22. IQE should reflect only the product of charge generation and charge collection efficiency.

Figure 8 (g,h) shows the calculated IQE values taken at two different wavelengths, one where the NFA and the other where the polymer dominates the absorption. We find that the O-IDTBR contribution to IQE at NFA concentration higher than the eutectic composition is notably larger than that of O-IDFBR. This can be assigned to the higher crystallinity of O-IDTBR compared to O-IDFBR, which assists with collection efficiency. However, both sets of IQE data follow a similar trend as a function of NFA content, with IQE decreasing with NFA wt% after reaching a maximum at around 40 wt% NFA in both cases. The decreased IQE in P3HT:O-IDTBR blends coincides with the reduced PL quenching efficiency at higher NFA fraction ($\geq 40\%$ wt%) see Figure 8l and so could be due to reducing the interfacial area for charge pair generation. In the case of P3HT:O-IDFBR PL quenching remains efficient to higher NFA fractions, which indicates that the decreased IQE in P3HT:O-IDFBR must be due to either fast CT exciton decay or free charge recombination rather than the charge pair formation efficiency. Moreover, as shown in Figure 8 (g,h), while the P3HT contribution in IQE peaks at 40 wt% O-IDTBR content in P3HT:O-IDTBR it peaks at only 30 wt% O-

IDFBR content in P3HT:O-IDFBR followed by a drastic reduction which is substantially faster than that observed in P3HT:O-IDTBR devices. That can be attributed to the effect of the NFA content on P3HT crystallinity and hence on hole transport. Whereas, as measured by Raman spectroscopy, for the IDTBR blend the P3HT remains crystalline up until 70 wt% of IDTBR, for the IDFBR blend the P3HT crystallinity appears to be disrupted from 40 wt% of IDFBR, see Figure 8 (i,j).

Conclusion

To conclude, from this study we find that, among the set of acceptors studied here, the more planar acceptor molecules retain their crystallinity better and are less likely to mix into the polymer. More crystallisable molecules require a smaller volume fraction to form a eutectic mixture and then to enable percolation. Further, more crystalline materials retain their optical properties in blends and consequently the composition of blends of such materials can be inferred from spectroscopic ellipsometry measurements using Bruggeman analysis. By contrast, blends based on less crystalline acceptors lose their original optical properties when blended, meaning that composition cannot be worked out accurately from the optical response. However, the optical probes do provide a good indication of the point at which one material's crystallinity is disrupted by the other. In terms of device performance, optimum photocurrent generation requires both large interfacial area and network formation. In crystalline-crystalline blends the optimum composition occurs close to or slightly to the acceptor-rich side of the eutectic point. When the added molecule is less crystalline or mixes well with the polymer, more of it is required to achieve conducting network formation, pushing the expected optimum composition out to higher acceptor concentrations. However, if good mixing has also disrupted the packing in the polymer, this will compromise hole transport and prevent an optimum J_{sc} being reached at the point of simultaneous crystallisation and push the optimum towards the point of balanced transport. Too strong mixing can thus

compromise the achievement of good conductivity simultaneously in both components and limit the J_{sc} and PCE of the device.

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Supporting Information

The attached supporting information includes the open circuit voltage and fill factor, DSC thermograms, P3HT enthalpy of fusion, absorption and PL of EH-IDTBR, Raman spectra of pristine materials and all samples, refractive indices of P3HT, extinction coefficient of the solutions, refractive indices of all samples, AFM images, microscopy images, Flory-Huggins equations as well as the calculation of the interaction parameters inferred from DSC measurements, and device characteristics figures.

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Graphical TOC Entry