Differing Impacts of Blended Fullerene Acceptors on the Performance of Ternary Organic Solar Cells

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ABSTRACT:

Organic Photovoltaic (OPV) devices offer the ability to tune the electronic and optical properties of the active layer by selection of a wide range of molecules, however, their power conversion efficiencies currently lag other competing photovoltaic technologies. One method to enhance their performance is to add a further active material into the absorber layer, resulting in a ternary OPV. However, selecting appropriate ternary blend components to yield an improvement in performance is challenging due to the multitude of materials properties and physical processes that ternary blends can display. Here we perform a systematic set of experiments on OPV ternary blends incorporating either of the donor polymers P3HT or PTB7 and the fullerene acceptors PCBM and ICBA. Some combinations of ternary blends are shown to outperform the reference binaries in terms of open-circuit voltage or short-circuit current, however, this was not observed for all combinations. Improvements in IQE of the order of 25% were observed for PTB7-based ternaries compared to the reference binary, which is attributed to a reduction in charge recombination. All blends showed some improvement in open-circuit voltage with addition of ICBA due to alloying

of the fullerene components, but to differing degrees which is argued to be due to molecular morphology. These findings demonstrate that the benefits one can obtain using a ternary OPV approach vary depending on materials system to an extent that depends upon the ternary blend morphology.

KEYWORDS: ternary blends, power conversion efficiency, organic solar cells, organic photovoltaics, fullerene alloy, morphology.

1. INTRODUCTION

Solution processable organic photovoltaics (OPVs) have attracted a considerable amount of attention in the past decade due to its unique advantages as flexibility, large area fabrication and the promise of low-cost printing which makes this technology an encouraging option for renewable PV applications [1-5]. Presently, power conversion efficiencies (PCEs) exceeding 16% have been realized [6,7], which whilst representing a significant improvement on the status quo only a few years ago, are still lower than other competing technologies. One method to address this challenge is to add a further material into the bulk heterojunction (BHJ) donor-acceptor layer to yield a ternary blend [8-10]. The addition of a third component in OPV blends offers the opportunity to optimize the optical and electrical properties beyond which is possible with a binary blend alone [11-13]. From an electrical point of view, ternary blends have been shown to reduce recombination via spatial separation of charges [14-17], whilst blends of fullerenes lead to the formation of an effective alloy which improves open-circuit voltage (V_{OC}) [18-20]. For ternary blends to maximize their usefulness as a methodology to improve OPVs will require better understanding of how materials selection, formulation, and device manufacture impact performance. Here we investigate this question by forming ternary blends in two exemplars binary OPV systems, changing blend composition and

additives to enable control over morphology. We demonstrate that the impact of this approach is substantially different for the two systems examined, with varying impacts on both V_{OC} and short-circuit current density (J_{SC}).

Among the different strategies to fabricate ternary blends, fullerene alloys which include polymers blended with a combination of fullerene acceptors (i.e. PCBM:ICBA) have demonstrated to be an effective route to further improve PV properties [18, 19, 21]. Thompson et al. [18, 19] first proposed the alloy model in P3HT with PCBM:ICBA, where the V_{OC} could be effectively tuned in ternary solar cells by varying the composition of fullerenes. For instance, a ~40 wt% ICBA resulted in a ~64mV increase in V_{OC} compared to the P3HT:PCBM binary blend, however, J_{SC} decreased for all ICBA combinations [18]. These results showed that V_{OC} was not pinned down to the smallest V_{OC} of the binary counterparts but evidenced that ternary OPVs could maximize V_{OC} and exceed binary BHJ efficiencies. Angmo et al. [20] further demonstrated that mixed fullerenes form an alloy in ternary blends of P3HT:ICBA:PCBM with solid-state NMR. Following device optimization, a PCE of 2.37% was realized with the ternary blend alloy exceeding its binary equivalents. Correspondingly, other authors have demonstrated that ternary blends with acceptor alloy and novel polymers can indeed lead to higher performing OPVs [21, 22]. Cheng and co-workers [23] fabricated ternary blends with ICBA:$PC_{71}BM$ and low bandgap PTB7 polymer. Contrarily to P3HT, the enhancement of V_{OC} was moderate with PTB7 as the donor, yet J_{SC} improved until a certain threshold (~20%-30%) prior to reducing. Further, although hole and electron mobilities remained relatively unchanged between the binary and ternary blends, ICBA enhanced the external quantum efficiency (EQE) which was attributed due to a cascade formation. The net result of these effects was a 12% improvement on the PCE. Similarly, Sharma et al. [24] introduced ICBA as a third component in PTB7:$PC_{71}BM$ blend to elucidate critical information for OPV design. In their study, 10 wt%

ICBA increased EQE which was correlated to improved charge dissociation as revealed by transient absorption studies, while higher concentrations of ICBA yielded more recombination. More recently, blends of Non-fullerene acceptors (NFA) have also demonstrated encouraging results in state-of-the art OPVs [25-27]. Lu et al. [28] presented a ternary blend of PPBDTBT donor with ITIC:$PC_{71}BM$ as the acceptor materials, in which ITIC extended the light absorption whilst $PC_{71}BM$ reduced the aggregation of ITIC as seen with TEM images. Despite an increase in J_{SC} and PCE with the ternary blends, V_{OC} progressively decreased with the increasing weight ratio of the fullerene, thus evidencing no intimate acceptor alloy. Notwithstanding, the reductions in V_{OC} were pinned on to be dependent on the composition of the blend, rather than determined by the energy levels of the materials. These papers have given valuable insights into how specific ternary blend systems operate, however, it is not clear how the effects of a ternary component in an OPV generalise to a specific morphology in new systems. The novelty of our approach, is that we seek to provide insights into this question by comparing the performance of two ternary blend systems based on different polymer donors, but with the same fullerene acceptor and ternary components.

We selected the ternary blends PTB7:ICBA:$PC_{71}BM$ and P3HT:ICBA:$PC_{71}BM$ as the reference binary devices (PTB7:$PC_{71}BM$ and P3HT:$PC_{71}BM$) are well known, thus aiding interpretation of our data. Further, ICBA:$PC_{71}BM$ has been shown to form a fullerene alloy under certain circumstances, and hence the selected ternary blend systems may display a wide range of behaviours that may occur in ternary OPV blends in general. The energy levels of these systems are shown in Fig. 1. In both blend systems, the fraction of ICBA was varied from 0% to 30% and devices were fabricated with and without the processing additive 1,8-diiodooctane (DIO). We have showed that increases in V_{OC} occur in both systems when ICBA is added, as is expected due to alloying, but to differing degrees; with P3HT-based ternaries gaining up to 200meV and PTB7-

based ternaries prepared in the same manner, gaining substantially less. Further, we have demonstrated that J_{SC} increases when ICBA is added for PTB7-based ternaries when the processing additive DIO is used, whereas the J_{SC} of other combinations reduces upon addition of ICBA. To the best of our knowledge, this is the first time the utility of a ternary blend is investigated by comparing the J_{SC} and V_{OC} of these blends and then relating it to the morphology. These data therefore demonstrate that nominally similar approaches to forming a ternary OPV blend can result in significantly different results depending upon the donor polymer.

2. RESULTS AND DISCUSSION

The molecular structure of materials used here is presented in Fig. 1a. Two ternary OPV systems were examined, PTB7:ICBA:PC$_{71}$BM and P3HT:ICBA:PC$_{71}$BM the energy levels for which are shown in Fig. 1b [29]. In all cases the active layer was incorporated into OPV devices with the layer structure glass/ITO/PEDOT:PSS/Active layer/Al, as shown in Fig. 1c. We note that as no interlayers (e.g. LiF or Ca) were used, this will result in lower V_{OC} values than that reported elsewhere in device which do [30, 31]. Ternary BHJ active layers were fabricated with a 1:1.5 donor and fullerenes acceptor ratios for PTB7-OPVs and 1:1 for P3HT-OPVs since these have been observed to be the optimum ratios for each type of blend [32-36]. Details of the materials, fabrication and measurements are given in the supporting information. A total of 8 nominally same repeats were prepared for each blend system yielding 96 OPV devices; 48 for each ternary blend system in which the wt% of ICBA was increased from 0% (i.e. a binary blend) to 30%. The impact of morphology was examined by fabricating the series of devices both with and without the processing additive DIO with a 3% concentration. Previous investigations with solvent additives have demonstrated that 3 vol% DIO when used as a co-solvent in PTB7 and P3HT blends can assist in achieving higher performances when compared to controls, other additives and different

volume concentrations [37-39]. The devices reported hereafter were chosen as typical examples of that composition, rather than 'champion' devices.
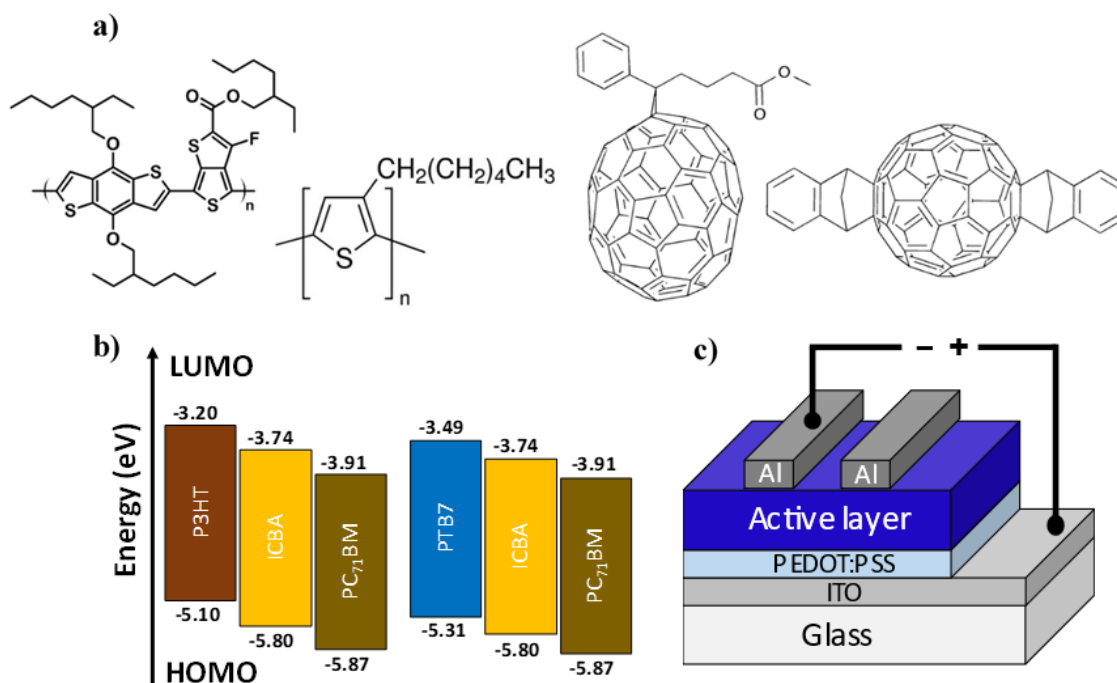

Figure 1. a) Molecular structure of materials used: PTB7, P3HT, PC$_{71}$BM and ICBA (from left to right), b) energy levels and c) OPV device configuration. Energy levels from [23, 40].

2.1 Open circuit voltage

Fig. 2 shows variation in PV parameters for the two ternary blend systems as a function of ICBA composition. Most notable is an increase in V_{OC} as ICBA composition increases. P3HT based blends show the greatest increase in V_{OC}, with the 25 wt% ICBA devices with DIO having an additional 100mV. PTB7-based blends also show an increase in V_{OC} over the majority of the ICBA composition range, but by contrast, the magnitude of increase is much smaller, with the 25 wt% ICBA devices with DIO having only an additional 20mV. Our results therefore also show

that V_{OC} appears to be determined by an effective fullerene alloy, rather than having the V_{OC} pinned to the lowest acceptor energy level [18-20, 41]. The improvement in V_{OC} for the DIO based P3HT ternary blend lead is sufficient to yield a net improvement in PCE compared to the equivalent binary.
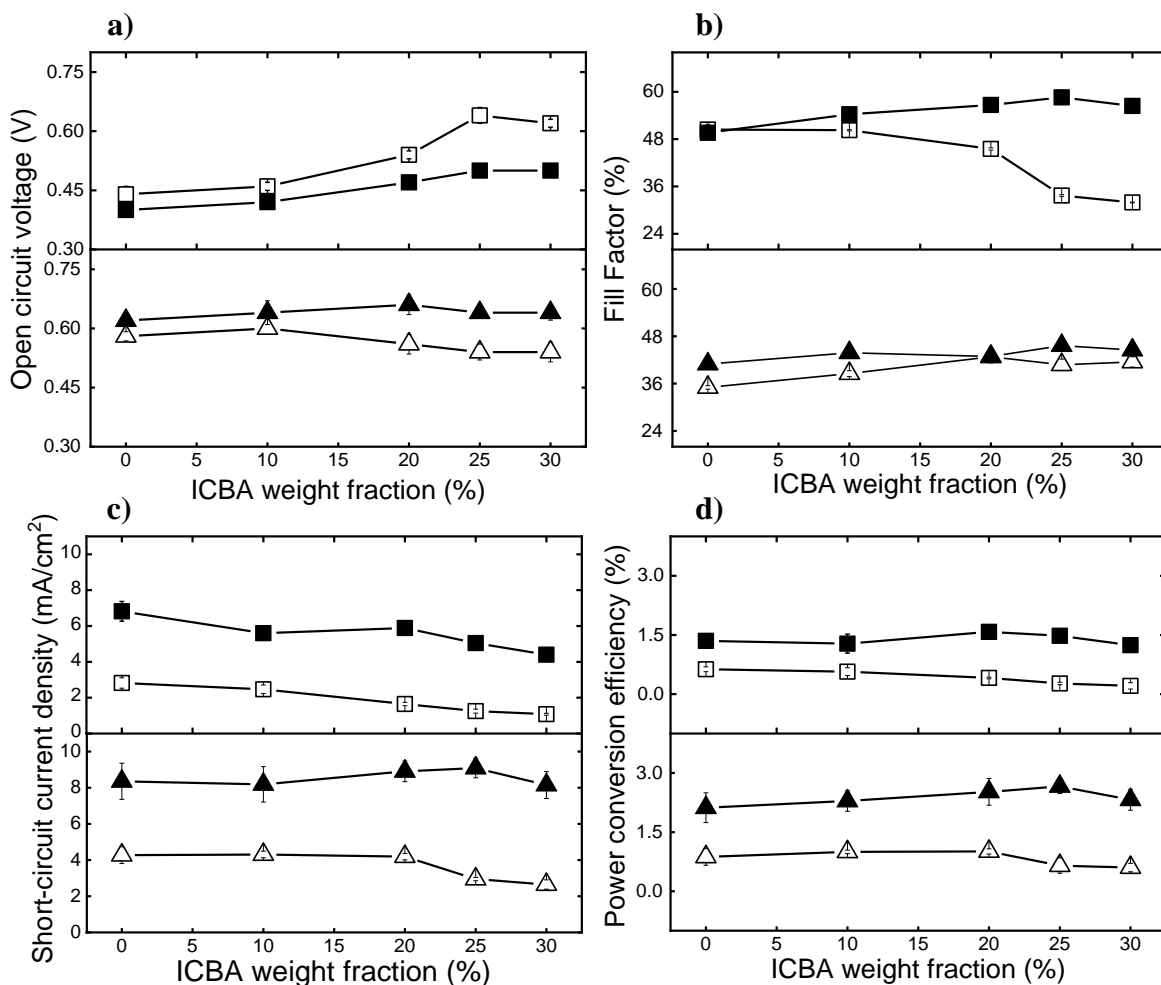

Figure 2. Variation of a) V_{OC}, b) *FF,* c) J_{SC} and d) PCE as a function of the amount of ICBA added to the P3HT:PC$_{71}$BM (black square) and PTB7:PC$_{71}$BM blends (black triangle) in 0%, 10%, 20%, 25% and 30%. Open figures denote OPVs without DIO and solid figures with 3% of DIO respectively.

The difference in the degree of V_{OC} shift for the same change in fullerene composition is not explained in the literature. To explain why, we begin by reasoning that the formation of an alloy implies intimate mixing of the two fullerene components somewhere in the blend. If so, the differing morphology of the two blend systems may hold some clues as to why the alloying behaviour is different. Whilst PCBM has been shown to be miscible in PTB7 [42] and in amorphous P3HT [43], resulting in an amorphous polymer:fullerene phase in both blend systems, we note that the side-chain density of P3HT is high compared to many donor:acceptor polymers [44]. An outcome of this high side-chain density is that PCBM does not intercalate into P3HT crystalline regions [36, 43]. Consequently, we propose that fullerene molecules do not readily interpose between P3HT side-chains in either the crystalline or amorphous phases, and that as a consequence, fullerenes are excluded to other regions in the blend where they form an alloy. Conversely, we argue that the impact of alloying is less strong in the PTB7 blends as fullerenes can more easily interpose between the side-chains, which we term molecular intermixing. There is indirect evidence of molecular intermixing in PTB7:fullerene blends as optimised blends require an excess of fullerene [36], side-chains have weak orientational uniformity [45, 46], and that PCBM molecules disrupt π-π stacking in PTB type polymers generally [47].

To further investigate this hypothesis, we investigated literature ternary blend systems utilising an ICBA/PCBM fullerene alloy (Table S1 in the Supplementary Information) and whether the polymer donors supported molecular intermixing with fullerenes (Table S2 in the Supplementary Information). Interestingly we found that polymer donors which did support molecular intermixing (i.e. PTB7 and PBTTT-C14) all had similar small increases in V_{OC} when 30-40wt% of ICBA was added into the acceptor fraction compared to the binary control, in agreement with our hypothesis [21, 23, 24], which is consistent with our hypothesis. We note that PBTTT-C14 is an

interesting comparison to the current data as it is both crystalline (as P3HT) and has a structure that permits PCBM molecules to site between side-chains (as argued for PTB7) [48], and shows more modest increases in V_{OC} when ICBA is added (like that observed for PTB7) [21]. P3HT was the only example of a polymer donor that was not favourable to molecular intermixing which has been used in ICBA/PCBM ternary blends, but what data has been reported also agrees with our observation of a larger V_{OC} when ICBA is added as compared to non-intercalated blends [18, 19]. Thus, it may be the case that the degree of molecular mixing is a key element in whether the full benefit to V_{OC} provided by a fullerene alloy is observed. Further experiments on donor:acceptor blend systems that do, or do not, support molecular intermixing would be useful to test this assertion. However, we note from our review shown in Table S2, that P3HT is unusual in its high side-chain density, as many other blend systems (e.g. PTT, PQT, PBTTT, PCDTBT, and PFBT-T20TT) do intercalate to some degree [36, 49, 50].

2.2 Fill Factor

Returning to the PV characteristics reported in Fig 2, we observed that the fill factor (FF) is largely unaffected by the addition of ICBA in all cases with the exception of the P3HT ternary where DIO is not used. The devices with DIO maintained a similar FF to the binary control. The reduction in FF for P3HT-based ternaries with more than 20 wt% ICBA may be due to poor charge transport, as TEM and AFM imaging shown in Fig 3 show that DIO promotes an extensive P3HT network of fibrils in high ICBA wt% devices, whilst devices without DIO do not show such structure. However, it is also possible that P3HT-based ternaries with more than 20wt% ICBA are impacted by a poor interface between the film surface and cathode, as the J-V curves for these devices have an S-shaped characteristic.
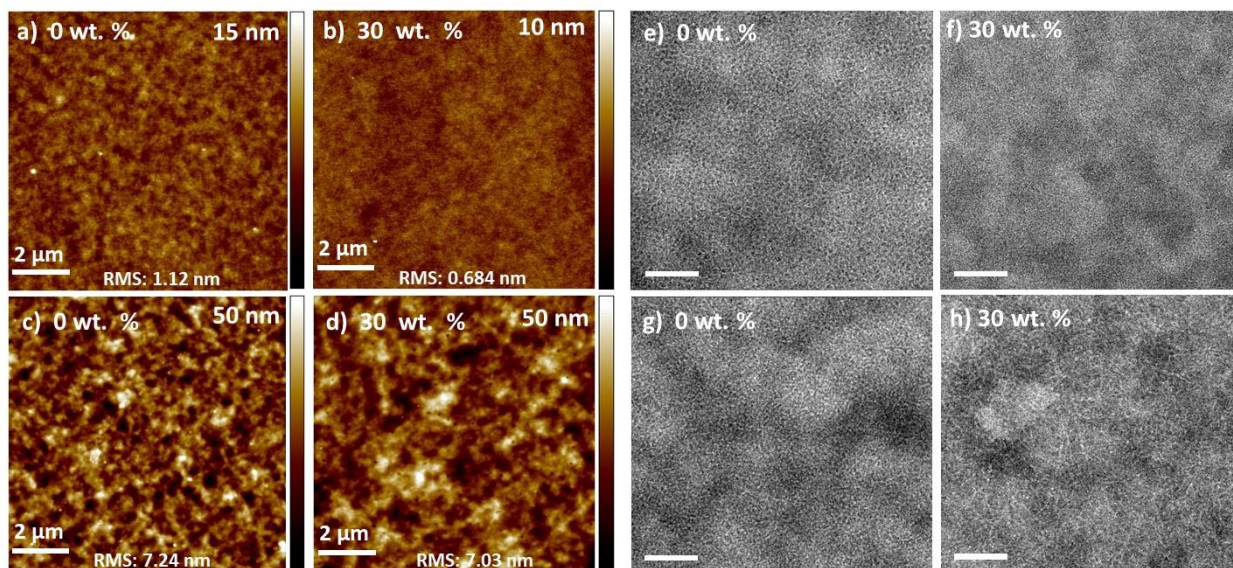
Figure 3. AFM topography and TEM morphology images of P3HT:PC$_{71}$BM binary blends without (a, e,) and with (c, g,) DIO, and ternary P3HT:ICBA:PC$_{71}$BM (30 wt%) without (b, f) and with (d, h) DIO. On TEM images, scale bar represents 200 nm.

2.3. Short-circuit current

Fig. 2 also shows that increasing ICBA wt% reduces the J_{SC} for all devices except for PTB7-based devices with DIO, for which the improvement in J_{SC} is sufficient to increase PCE as compared to the equivalent binary. To examine in more detail the changes in J_{SC}, Fig. 4 shows EQE measurements for PTB7:ICBA:PC$_{71}$BM and P3HT:ICBA:PC$_{71}$BM OPVs with ICBA content varying from 0 to 30%, both with and without the processing additive DIO. Here we observed that PTB7-based OPVs with added ICBA and DIO have an EQE enhanced by an order of 20% compared to the reference binary, whereas EQE is reduced for other device types.
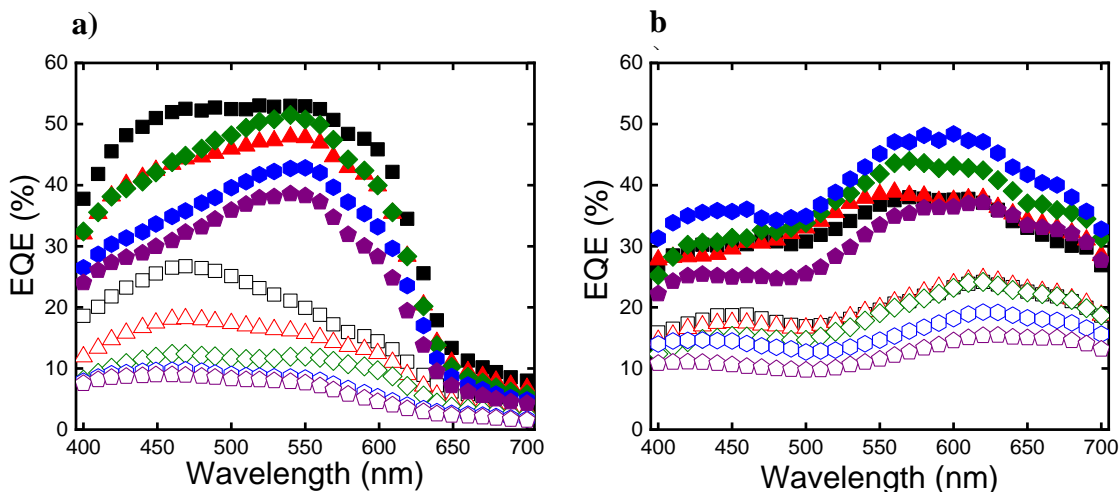
Figure 4. EQE spectra of a) P3HT:PC$_{71}$BM and b) PTB7:PC$_{71}$BM prepared with 0% (black) and

an additional 10% (red), 20% (green), 25% (blue) and 30% (purple) concentration of ICBA with

and without 3% of DIO. Solid figures represent OPVs with DIO and open figures represent

OPVs without DIO.

We note that the data also show the positive impact of DIO of EQE in both P3HT- and PTB7-

based blends in agreement with the literature [38, 51-54]. In the case of P3HT based blends, DIO has

been shown to improve the formation of P3HT fibrils [39, 55], in agreement with TEM and AFM

images in Fig. 3. By contrast, PTB7-based blends are improved by the addition of DIO as it limits

the size of PCBM aggregates that would otherwise reduce exciton dissociation [42, 56]. Again, our

AFM and TEM analysis in Fig. 5 is in agreement with these literature data, however, we

additionally show that DIO also suppresses the size of ICBA aggregates more generally.
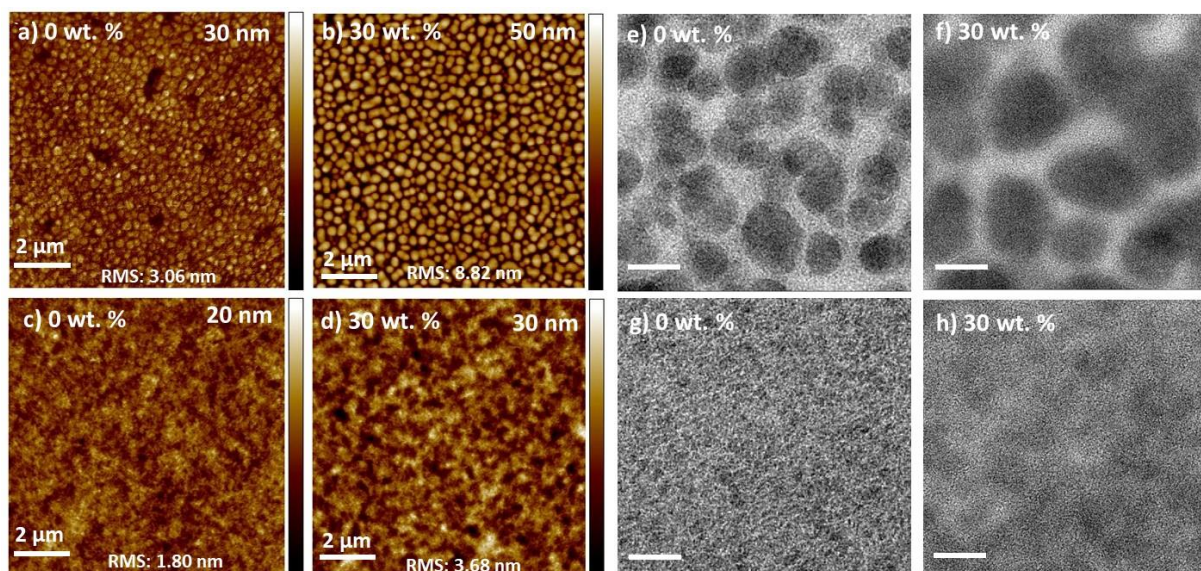
Figure 5. AFM topography and TEM morphology images of PTB7:PC$_{71}$BM binary blends without (a, e,) and with (c, g,) DIO, and ternary PTB7:ICBA:PC$_{71}$BM (30 wt%) without (b, f) and with (d, h) DIO. On TEM images, scale bar represents 200 nm.

Returning to the impact of the ternary blend on EQE, we note that the changes in EQE shown in Fig. 4 should be viewed in the context of reducing absorption as wt% of ICBA increases, shown in Fig. 6. In all cases the addition of ICBA reduced absorption as expected due to the weaker absorption in ICBA (Fig. S2) compared to the other active components [18, 24, 57].
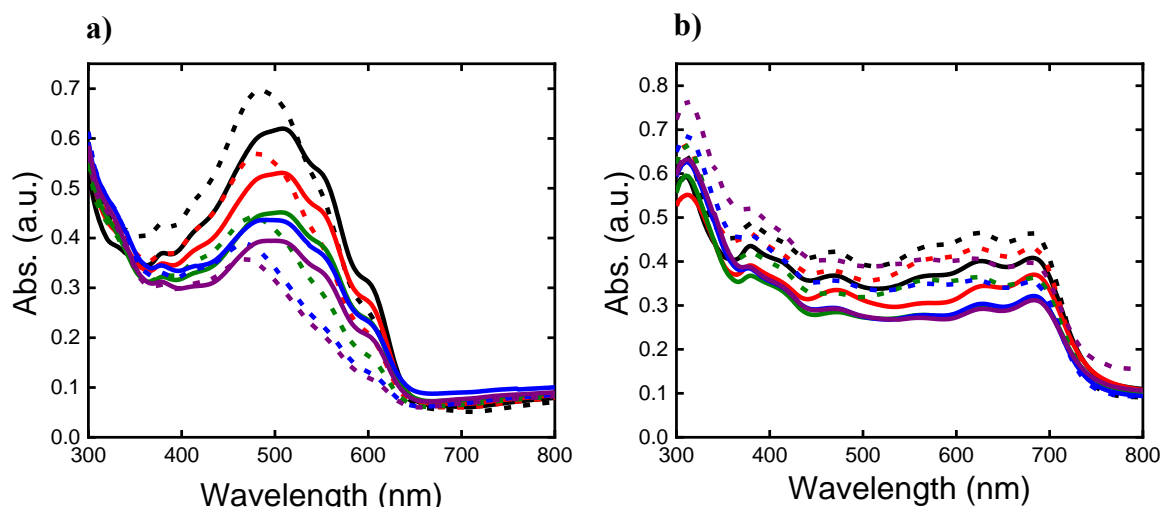
Figure 6. Optical absorption spectra of a) P3HT:PC$_{71}$BM and b) PTB7:PC$_{71}$BM blends with 0% (black), 10% (red), 20% (green), 25% (blue) and 30% (purple) ICBA loading, with and without 3% of DIO. Solid lines denote OPVs with DIO and short-dash lines denote OPVs without DIO.

Thus to account for the effect of changing absorption the internal quantum efficiency (IQE) is estimated by dividing EQE by the simulated absorption of the active layer using the transfer matrix method described by Burkhard et al. [58] as outlined in the supplementary information. Estimated IQE are shown for P3HT- and PTB7-based OPVs in Fig. 7a and 7b respectively. Focussing our attention on the impact of ICBA on the IQE for the reported blends, we observed that the IQE for the PTB7-based ternaries with DIO increase by as much as 25 wt% for when DIO is used. Hence, although absorption changes with composition, the IQE data suggest that ICBA is acting to improve recombination in the PTB7-based blend with DIO. We now consider possible explanations as to why the IQE of PTB7-based ternaries with DIO are improved by ICBA, whilst it is reduced for the other systems examined. Understanding the underpinning physics is critical should lessons be learned for the design of future ternary OPV devices.

First, we consider the possibility of changing exciton dissociation. TEM imaging (Fig. 3, 5) suggests fine intermixing of the donor and acceptors (<20nm) for P3HT based blends with and without DIO, and PTB7 blends with DIO, even with the addition of 30 wt% ICBA. By contrast, PTB7-based devices without DIO show large (>150nm) fullerene domains which increase in size with addition of ICBA (Fig 5e, f) which would be expected to reduce IQE through reduced exciton dissociation efficiency, as is observed in the data. Whilst changing exciton dissociation efficiency appears to explain reducing IQE as ICBA composition is increased for the PTB7-based ternaries without DIO, we note that the reduction in IQE up to 25 wt% ICBA is only slight (~4%), which contrasts to an increase in fullerene-rich domain size (~100nm) which is many times larger than the exciton diffusion length (~10nm) [59-62].
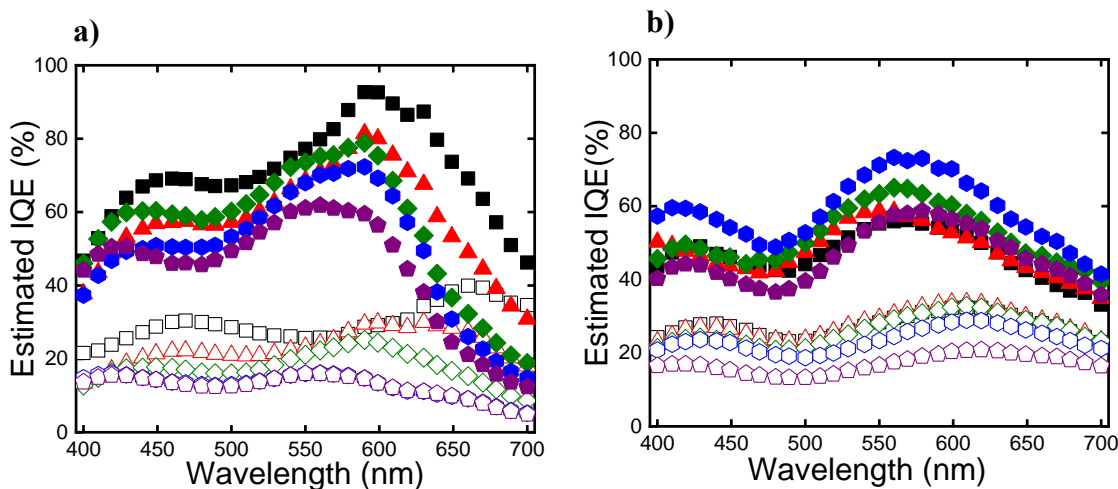

Figure 7. Estimated IQE curves of a) P3HT:PC$_{71}$BM and b) PTB7:PC$_{71}$BM prepared with 0% (black) and an additional 10% (red), 20% (green), 25% (blue) and 30% (purple) concentration of ICBA with and without 3% of DIO. Solid figures represent OPVs with DIO and open figures represent OPVs without DIO.

It may therefore be the case that charge recombination reduces in the PTB7-based device without DIO as well as the PTB7-based device with DIO. However, without a detailed morphological model of the PTB7-based blend without DIO as ICBA is increased it is not possible to quantitively examine the competition between exciton and charge further. Next, we consider the possible impact of changing charge transport. In other studies of ternary blends, changes in IQE have been shown to be due to improvements or otherwise in charge transport through the blend [63, 64]. When considering the current data, adding ICBA increases the overall fraction of acceptor and reduces the fraction of donor. Recalling the literature, P3HT:PCBM devices are susceptible to being limited by hole transport [65], whilst thick PTB7:PCBM devices are susceptible to being limited by electron transport [66]. Thus, it is possible that increasing ICBA content may be more detrimental to the performance of P3HT based blends rather than PTB7 based blends as the former is more sensitive to poor hole transport. We observe hallmarks of this hypothesis in the data, as dark forward diode current increases with ICBA for PTB7-based devices (Fig. S1c), whilst it reduces for P3HT-based devices (Fig. S1a). However, we point out that the reference binary devices have the optimal polymer:PCBM ratio, thus one may expect that the addition of ICBA would push the blend away from this optimum and so reduce efficiency from a charge transport point of view. To investigate this balance further, we performed drift diffusion modelling using the General-Purpose Photovoltaic Device Model (GPVDM). This software has been used to evaluate in detail a number of different OPV devices [67-69]. For interested readers, complete details on how the model operates are presented here [70]. In brief, GPVDM solves drift-diffusion equations for electrons and holes along with Shockley-Read-Hall capture/escape on a finite difference mesh. The transfer matrix method and Poisson's equation are solved for optical and electrostatic effects respectively. With this approach, the model describes the distribution of carriers in position and energy space, as well

as simulate J-V characteristics. In this work, the modelled architecture of devices was ITO (100nm) / PEDOT:PSS (30nn) / Active layer (150nm) / Al (100nm). In the supplementary information (Fig. S3a), we fit to dark J-V curves for PTB7-based blends for the range of ICBA compositions by changing the electron mobility alone. Whilst we could recreate the increase in diode current observed with increasing ICBA content, this approach did not recreate the observed increase in photocurrent (Fig S3b). Hence, we view it unlikely that the improvement in IQE observed for the PTB7-based blends with ICBA is due to changing mobility alone.

Finally, it has been proposed that ternary blends can act to reduce recombination if the energy levels of the constituent materials form a 'staircase' in which separation of the charge pair is energetically favoured [14, 15, 71, 72], in much the same manner as photosynthesis. This 'cascade' effect, and a consequent reduction in recombination has been observed directly in some evaporated systems [73-75]. The question remains, however, as to why we observe an increase in IQE for PTB7 based blends with increasing ICBA, but not for P3HT based blends. We propose that this difference can be attributed to the alloying effect discussed previously. In P3HT based blends, fullerene alloying appears to occur readily, and as such, we may expect that any possible advantage from a cascade heterojunction to be lost. Contrastingly, PTB7 based blends appear to show fullerene alloying to a lesser degree, suggesting that electronically distinct fullerene domains may be more prevalent, in turn leading to the possibility of cascade heterojunctions.

3. CONCLUSIONS

In this paper we have analysed the performance of two ternary OPV blend systems, PTB7:ICBA:$PC_{71}BM$ and P3HT:ICBA:$PC_{71}BM$, and compared them to reference binary OPVs

(PTB7:$PC_{71}BM$ and P3HT:$PC_{71}BM$) to better understand the contrasting impacts of a ternary approach to optimising performance on OPVs. The impact of the ICBA ternary component was shown to be different for the two donor polymers. P3HT-based ternaries showed the largest increase in V_{OC} as compared to PTB7-based ternaries, notwithstanding the same concentrations of ternary and acceptor components in each series. Further, the EQE of the PTB7-based devices with DIO was shown to increase by 20% upon addition of ICBA, whilst the EQE reduced for all other investigated systems. We hypothesise that the observed differences are rooted in the molecular morphology of the systems examined, with the fullerene compounds being able to interpose in between the side-chains of PTB7, but not in the case of P3HT. This is argued to lead to larger V_{OC} shifts for the P3HT-based devices, due to greater molecular mixing of the fullerene components; and greater reduction in recombination due to a cascade effect in the PTB7-based devices that arises due to more electronically distinct fullerene molecules. These data demonstrate both that ternary blends can have differing impacts upon the physical operation of the OPV, and that the behaviour observed depends upon the donor polymer. More speculatively, the data may point to a common cause to the differing impacts of adding a ternary component to an OPV blend, namely the degree of intermixing between the ternary component and other constituents. This motivates further experiments of ternary OPV systems to investigate whether choice of acceptors that can, and cannot, interpose between donor side-chains can control the effects of ternary blends.

ASSOCIATED CONTENT

Supporting information:

More details on the characterization of materials, OPV fabrication, UV-vis of neat films, dark/light J-Vs, PV table, AFM, TEM and modelling fits are available in the supporting information.

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The manuscript was written by contributions of all authors. All authors have given approval for the final version of the manuscript.

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