Controlling intercalations of PBDTTT-EFT side chain to initiate suitable network for charge extraction in PBDTTT-EFT:PC71BM blended bulk heterojunction solar cell

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**Abstract**

Electrical, optical and structural properties, based on blend of PBDTTT-EFT:PC71BM bulk heterojunction solar cell is investigated. We have shown the presence of PC71BM in the blend facilitates interfaces for charge transfer mechanisms leading to PCEs of ~ 9.38%. GIXRD line profile obtained reveals that quantitative presence of PC71BM initiates a change in preferred orientation. It is proposed that PC71BM facilitates polymer alkyl side chain intercalations causing reduced *d*100 spacing, leading to larger π-π stacking of the back bone. The data obtained from *d*200 plane associated with PC71BM, reveals correlation between increased vertical stacking and PC71BM loading, suggesting a bicontinuous network for electron transport. Raman spectroscopy results provides evidence of PC71BM impact on frequency shift associated with C = C stretching mode of side chain thiophene rings responsible for of π-πspacing. Correlations between AFM surface roughness and blend ratio reveals migration of PC71BM to the film surface.

**Keywords:** (copolymer solar cell, power conversion efficiency, side chain intercalations, XRD)

1. Introduction

Organic solar cells have been the subject of extensive investigation for more than three decades owing to properties such as: high optical absorption coefficient, ultrafast electron transfer, solubility, flexible substrate, room temperature and lower fabrication costs [1-4]. Whilst OPV devices manufactured from blend of acceptors and relatively large band gap polymers were identified as promising active material for future generation of solar cells [5,6], nonetheless, substantially lower associated PCEs are disappointing when compared to its inorganic counterparts. Several communications associated with the impact of thermal and vapour annealing [7-11], buffer materials [12-14], Nano-structuring [15,16] is reported to incrementally increase PCEs but not substantially to manifest in breakthrough in solar cell manufacturing. Recent advances in material synthesis paved the way for realisation of narrow band gap polymers such as PBDTTT-EFT, PTB7, PBDTTT-CT and PBDTTT-CF, resulting in PCEs of 7-9% [17-20]. To improve PCE of narrow band gap devices, researchers focused their attention on processes applied for enhancing performance of large band gap devices [21-23]. Whilst some processes such as thermal annealing of large band gap material had positive impact on PCEs, it was proved to be detrimental in the case of narrow band gap polymer PBDTTT-EFT [24-26]. The presence of different acceptors in blended solution with large band gap polymers proved to be crucial in open circuit voltage value and exciton dissociation leading to higher PCEs [27]. Recently the impact of PC71BM percentage loading on narrow band gap polymer PBDTTT-EFT was investigated, giving supporting evidence that, fullerene concentration regime plays an important role in exciton dissociation and charge transport [28,29]. We propose that the role of PC71BM and its quantitative presence in blended solution with PBDTTT-EFT is multipurpose processes which some results in improved PCEs whilst, some having opposing effects. To this end the role of PC71BM and its quantitative presence in blended solution with PBDTTT-EFT is investigated to elucidate the Nano-structural formation and its subsequent impact on thin films electrical behavior.

**2. Material and methods**

Pre-fabricated ITO/glass substrates were first cleaned using ultra sonic bath with three step process; deionised water, acetone, isopropanol and left to dry in nitrogen environment. PEDOT: PSS purchased from Ossila was filtered and then spin coated onto the substrate at a speed of 5,000 rpm for 30s and then baked on a hotplate at 120ºC for 10 minutes. A DektakXT thickness profiler accurately measured the film to be 30 – 40 nm. The substrate was then transferred to a nitrogen glove box maintained at 0.1 ppm for O2 and H2O level left for 30 minutes before fabricating the active layer. PBDTTT-EFT: PC71BM (1-Material, used as received) with concentration of 25mg mL-1 in 1,2-dichlorobenzene but with blend ratios of 1:0.5, 1:1, 1:1.15, 1:2 and 1:3 were produced. The pre-tested PBDTTT-EFT: PC71BM spin-casted at 600 rpm for 18s resulted in a film thickness of ~100 nm. After fabrication of the active layer, substrates then vacuum dried for 5 min at -100 kPa ready for surface washing with 60µL of Ethanol purchased from Sigma Aldrich and drop cast at 4000 rpm for 30s. For fabrication of top electrodes, substrate was transferred to a metallisation rig (Auto 500) via an interconnecting chamber. First 10 nm of Calcium (sigma Aldrich) was fabricated at a rate of 0.1nm s-1 using mask aligner. After a delay time of 5 minutes 100 nm of Aluminium was then deposited through the mask aligner at a rate of 0.1nm s-1 for the first 20 nm and then at a rate of 0.5nm s-1 for the remaining 80nm. A microbalance quartz crystal monitor (Intellmetrics IL 150) was used to measure the deposition rate as well as the Aluminium thickness. During the deposition, the chamber vacuum was maintained below 10-6 Torr. For Raman, PL and GIXRD studies similar processes were followed apart from metallisation stage.

The active area for each device was 0.13 cm2, illuminated through a shadow mask under 1 SUN condition using 1.5 AMG filter (LOT-LSZ389) and xenon arc lamp solar simulator (LOT-LS0306). I-V characteristics were collected using Keithley 2400 source meter. To test the accuracy of solar simulator, silicon reference solar cell (LOT-LS0041) which its accuracy is certified by National renewable energy laboratory was used to adjust the input power.

The GIXRD data were collected using Bruker D8 Advance in out-of-plan XYZ stage mode. Optical absorption data were collected using (Varian Cary 50-Bio). Raman and PL measurements were collected using (Renishaw inVia) with 685, 785nm excitation laser. The device morphology was performed using Agilent AFM 5400 series.

**3. Results and Discussion**

 **3.1 Optical and electrical characterisations**

PBDTTT-EFT: PC71BM blend with ratios 1:0.5, 1:1, 1.15, 1:2 and 1:3 were fabricated either for optical and structural investigations or electrical characterisations. PBDTTT-EFT is a narrow band gap copolymer used as donor material in our devices structure [30,31]. The optical absorption spectrum and the impact of PC71BM in the blend is fundamentally important to this investigation. For this reason, optical absorption spectroscopy based on blended films with increasing PC71BM loading is investigated and the results are presented in figure 1a. As is evident upon introduction of PC71BM and subsequent increase in its ratio, a redshift in the peak associated with π-π stacking of PBDTTT-EFT backbone unit is observed [32]. Furthermore, the onset of optical absorption is found to shift towards the longer wavelength with increasing PC71BM blend ratio. This could initiate a change in optical band gap and result in variation of open circuit voltage as suggested in the literature[29]. To verify the impact of PC71BM on open circuit voltage, electrical characterisations were performed and graphically shown in figure 1b. Results presented in table 1, indicate that the power conversion efficiency, peaks at blend ratio of 1:2 with further increase leading to the deterioration of this parameter. An interesting observation made is that increasing PC71BM loading has no impact on open circuit voltage in contrast to the increase of this parameter previously reported [29]. This is explained to be the result of PC71BM aggregation when its percentage loading is increased, initiating reduction of tail state in the density of states (DOSs) leading to higher VOC [29]. We believe this may be the result of solvent used and film drying process facilitating PCB71M aggregation. Furthermore, the short circuit current density peaks at 1:1.5 blend ratio but relatively lower value of fill factor results in PCEs of approximately 8.08%. However, this parameter further improves to 9.38% upon increasing PC71BM loading to 1:2 at the expense of improved fill factor even though a reduction in the short circuit current density is observed. To gain insight to the trend of electrical parameters presented in table 1 and to elucidate the trade-off between short circuit current density and FF for 1:1.5 and 1:2 PC71BM loading, photo luminescence measurements were performed on thin films devices with the same blend ratios. As shown in figure 2a the PL intensity quenches by introducing PC71BM resulting from a fast charge transfer [9,33-35]. Upon further PC71BM loading the quenching efficiency improves as shown in figure 2b and peaks at 1:1.5 ratio which corresponds to the highest short circuit current density observed. Similar observations indicate that the best quenching is obtained at 1:15 PBDTTT-EFT:PC71BM ratios [28]. We believe 1:1.5 blend ratio provides domains suitable for efficient exciton dissociation resulting in enhanced short circuit current density. However, further increase in PC71BM above 1:1.5 leads to higher PL intensity yielding lower short circuit current density [28]. We suggest increasing PC71BM above 1:1.5 ratio could facilitate opposing processes initiating lower exciton dissociations at the same time as providing suitable networks for charge extractions. Figure 3 shows correlation between the device fill factor and shunt resistance as a function of blend ratio. As is evident, both these parameters peak at 1:2 ratio as presented in table 1. We believe improved value of fill factor is due to better charge carriers transport network and lower device leakage current. Previous work by Foster et-al [36] suggests that the improved value of fill factor is initiated from increased PC71BM loading, providing suitable network and leading tohigher electron mobility. Further work on other polymers also suggests similar behaviour upon PC71BM loading [37].

Figure 4a reveals the AFM topography and phase images of PBDTTT-EFT:PC71BM blended films. When AFM surface roughness (Sq) is measured, it appears that there is correlation between this parameter and series resistance presented in table 1 and figure 4b. As can be observed the lowest series resistance corresponds to lowest value of Sq. We believe this stems from better surface contact, resulting in lowering Rs. Similar trend has been reported for other polymers/fullerene blended devices [38,39]. Furthermore, when surface roughness for pristine PC71BM, PBDTTT-EFT and all the blend ratios are examined, it appears that the surface roughness is influenced by the quantity of PC71BM present in the blend. In another word, it provides evidence of PC71BM formation at the top surface upon increase in blend ratio. As is evident the deviation from this trend appears after 1:2 ratio as the roughness increases slightly. Previously we reported on the formation of PCBM cluster as a percentage of its loading with P3HT blend [40]. We propose, the size of these clusters is dependent on the amount of PC71BM present at the film air boundary. Therefore, there must be a mechanism for assisting migration of PC71BM to the surface.

 **3.2 Structural characterisations**

To elucidate the impact of PC71BM in the blended film, careful consideration on structural properties of these blends becomes essential. Figure 5 represents OOP GIXRD pattern for thin films of pristine PBDTTT-EFT, as well as PBDTTT-EFT: PC71BM blend with different percentage loading. As PC71BM percentage loading is increased a peak at 2θ = 4.15˚ associated with alkyl side chain appeared and its intensity enhanced with further PC71BM loading. To accurately measure the impact of PC71BM on PBDTTT-EFT structural parameters a computer model based on Gaussian & Lorentzian curve fit is used to analyse figure 5 and the outcomes are presented in table 2. The *d*-spacing presented in table 2a corresponds to the edge on orientation or *d*100 associated with PBDTTT-EFT. It is interesting to note that previous reports have revealed the existence of this peak for IP GIXRD only and furthermore, upon increasing PC71BM percentage loading a reduction in peak intensity is observed in contrast to our OOP data presented in table 2a. It is also worthwhile mentioning that there are no peaks at 2θ = 4.16˚ associated with pristine PC71BM line profile and therefore, its presence must be initiated when PC71BM is introduced to the blend. Also, OOP GIXRD line profile reveals a strong peak at 2θ = 22.69˚ corresponding to face on orientation (*d*010). Furthermore, as the percentage loading is increased, the peak intensity is reduced and shifts towards lower 2θ value. In a simple term, there seems to be a sea sore action between face on and edge on orientation initiated by PC71BM loading. It is reported that, PBDTTT-EFT has preferred face on orientation whilst, randomly edge on orientation may also be formed during the fabrication processes [41]. It appears that increasing PC71BM percentage loading could initiate a change in preferred orientation, revealing the edge on orientation line profile which otherwise could not have been observed. The change in preferred orientation could facilitate vertical segregation of PC71BM towards the film surface. Table 2(c) presents data for *d*200 associated with PC71BM. It provides evidence that the coherent length increases with increased loading initiating system of bicontinuous network assisting electron transport leading to a higher electron mobilities [36]. Furthermore, data presented in table 2a reveals that quantitative increase in PC71BM loading results in reduced *d*100 spacing, suggesting that side chains are intercalated leading to the dihedral angle change of thiophene rings attached to BDT unit. Using DFT modelling it was shown that narrow band gap polymer PBDTTT with three different side chains namely EFF, EFT, and EFS have different dihedral angles (34º, 60º and 60º). The spacing between the π-π back bone is shown to increase with increasing dihedral angle change [42]. As is evident from table 2b, the *d*010 is enhanced upon increasing PC71BM loading. We propose that PC71BM plays a similar role in influencing dihedral angle change and subsequently π-π back bone spacing as the side group EFF, EFS and EFT do. To further support the above interpretation, Raman spectroscopy using 685 and 785 nm excitation lasers were performed on thin film samples of PBDTTT-EFT:PC71BM blend. As we are interested in the impact of the PC71BM loading on PBDTTT-EFT, our interpretation of the data is mainly focused on 785 nm excitation laser because the onset of optical absorption for PBDTTT-EFT is around 780 nm revealing more detail structures associated with PBDTTT-EFT. The result of Raman signal for 685nm excitation laser is presented in the Supporting Information. Figure 6 (a) shows vibrational mode associated with pristine PBDTTT-EFT as well as blended structure with corresponding molecular structure shown in figure 6(b). As expected upon increasing PC71BM loading the intensity of the peaks drop indicating less vibrational mode associated with EFT. However, the detail analysis of the individual peaks using Gaussian and Lorentzian curve fit indicates that there are no frequency shift and noticeable FWHM for peaks 2 and 3 shown in figure 7. Previous report [43] assigns peaks 2 and 3 to the central back bone and increasing PC71BM content may not be an influential factor to initiate a frequency shift or substantial change in FWHM as shown in figure 7. Our observation here correlates well with OOP GIXRD FWHM results obtained for *d*010 plane, which indicates that there are no significant changes in this parameter, further supporting that PC71BM does not compromise the integrity of the backbone structure. On the contrary, a noticeable change in frequency shift and FWHM in peak 1 and similar trend but not as prominent in peak 4 is observed and graphically shown in figure 7. It is reported [44,45] that P1 is associated to C = C stretching mode of thiophenes ring attached to BDT unit. As discussed earlier upon increasing PC71BM loading the lamella or *d*100 spacing reduces resulting in intercalation of the side chains. This in turn initiates dihedral angle rotation between the thiophene and backbone benzene rings. The rotation of thiophene rings is therefore more likely to impact the vibrational mode associated with P1 and P4 as shown in figure 6(b).

**4. Conclusion**

In conclusion, we are reporting on the power conversion efficiency of blended copolymer/ fullerene derivative bulk heterojunction solar cell. It is identified that PC71BM as well as its well-known role for exciton dissociations, can facilitate electron transport networks. The AFM data presented here reveals correlation between surface roughness and series resistance and its dependent on blend ratio. The result of surface roughness for pristine PC71BM, PBDTTT-EFT and blended film indicates that, the film morphology is dependent on blend ratio and for higher loading the surface roughness value is predominantly closer to that of PC71BM. This could therefore be used as a measure for PC71BM presence at the film surface. Our GIXRD line profile data suggests that, PC71BM loading can assist PBDTTT-EFT side chain intercalations leading to preferred orientation change. Subsequently this could remove obstruction of PC71BM vertical segregation and enhance its quantity at the surface. Furthermore, longer coherent length associated with *d*200 plane for PC71BM stems from increased loading, creating a system of bicontinuous network suitable for electron transport. The Raman signal also supports our suggestions for intercalations leading to dihedral angle change. Based on electrical characterisations results we are reporting an average power conversion efficiency of 9.38% for 1:2 blended ratios. Correlation between fill factor and shunt resistance as a function of blend ratio provides sufficient information to suggest, that the charge carriers transport network can be influenced by the quantitative presence of PC71BM leading to lower leakage current.

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