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## The effect of fullerene derivatives ratio on P3HT-based organic solar cells

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### Abstract

The effect of fullerene ratio PCBM and ICBA on the P3HT-based solar cells were investigated under ambient conditions; the ratio was varied in the range of 1-3. The optical, morphological, structural, and electrical characteristics were investigated both in dark and under illumination. The absorption spectra have revealed a decrease in the intensities by increasing the fullerene ratio and the peaks were blue shifted. Moreover, fluorescence spectra demonstrated charge transfer from P3HT to fullerene molecules due to uniform distribution of fullerene domains within the P3HT matrix. XRD patterns have shown a strong reduction in the crystallinity by increasing the ratio of fullerene within the blend. Furthermore, AFM images showed smoother surface corresponding to pinholes with higher ratio while rougher surface with lower fullerene ratio was observed. The best performance was recorded for P3HT:PCBM (3:1) with  $V_{OC} = 0.58$  volt,  $J_{SC} = 9.9$  mA.cm<sup>-2</sup> and PCE 1.82%. The fill factor (FF) was found to be small for all studied samples which could be associated with the preparation conditions where all samples were prepared under normal ambient. Devices which demonstrated best performance were attributed to improved crystallinity and enhanced light absorption of the active layer.

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## 1. Introduction

Organic active layers based on blending electron donor materials with electron accepting molecules has been developed as a promising approach towards low cost and flexible organic solar cell [1]. Polymers and fullerene or fullerene-derivatives combinations are considered as favorable materials in polymer solar cells [2]; the offset between the polymer HOMO molecular level and the fullerene LUMO molecular level is a crucial factor to determine the solar cell performance [1]. Therefore, to achieve high conversion efficiencies, nanoscale interpenetrated bulk heterojunction (BHJ) network of donor and acceptor should be achieved in order to increase the donor and acceptor interfaces, which is essential for exciton dissociation. Generally, P3HT has a strong trend towards creating self-organized thin film which is beneficial for charge transportation [3]. On the other hand, PCBM is one of the most investigated organic acceptor, which is blended with P3HT considering the light harvesting and charge carrier transportation [4]. Recently, PCBM was replaced by another fullerene derivative (ICBA) which has higher LUMO than the PCBM; this was shown to have an impact on the open circuit voltage of the OSC [3]. In this study we have investigated the effect of the blend ratio of P3HT with PCBM and ICBA on the structural, morphological, optical and photovoltaic properties P3HT-based OSCs.

## 2. Experimental

Poly (3-hexathiophene-2,5-diyl) (P3HT), [6,6]-Phenyl C61 butyric acid methyl ester (PCBM), indene-C60 bisadduct (ICBA), Chlorobenzene, Chloroform and Poly (3,4-ethylene dioxythiophene) poly (styrene sulfonate) (PEDOT:PSS) were purchased from Sigma Aldrich and used without any further purification. Different volume ratios of polymer and fullerene derivatives were used to prepare blends of P3HT:PCBM and P3HT:ICBA active layers. P3HT was dissolved in chlorobenzene while PCBM and ICBA were dissolved in chloroform separately. These solutions were sonicated for 30 min in ultrasonic bath followed by hot plate stirring at 45 °C for 3 hours. Next the obtained solutions were mixed with the volume ratios of 1:1, 2:1, 3:1 of P3HT:PCBM and P3HT:ICBA. Moreover, the blended solutions were stirred overnight on a hot plate at 45 °C. Finally, the solutions were filtered by PTFE filter with a pore size of 0.45 μm. ITO coated glass substrates (sheet resistant of 8-12 Ω/□) were cleaned in chloroform, acetone and DI water for 10 min each, respectively and used as substrates. The PEDOT: PSS solution was spin coated on the cleaned ITO with 2000 rpm for 30 sec, and subsequently, the obtained films were annealed on a hot plate at 150 °C for 10 min. The active layers were spin coated on PEDOT:PSS layer at 1000 rpm for 30 sec and annealed on a hot plate at 120 °C for 10 min. Finally, aluminum (Al) contacts were thermally evaporated on the active layers for all samples with 100 nm thickness under vacuum of about 10<sup>-6</sup> mbar using thermal evaporation system. The rate of Al films' deposition of 0.1-0.2 nm/sec and the thickness were monitored quartz crystal film thickness monitor. The active layer thickness was evaluated using M2000 (J.A. Woollam Co., Inc.) spectroscopic ellipsometry.

## 3. Results and discussions

### 3.1. UV-visible absorption spectra

Fig.1 shows the UV-visible absorption spectra for pristine P3HT as well as P3HT:PCBM and P3HT:ICBA blends with different volume ratios. Generally, pristine P3HT film shows a maximum absorption around the wavelength of 510 nm which was attributed to  $\pi$ - $\pi^*$  electronic transition, while two shoulders around the wavelength of 560 nm was due to the extended conjugated P3HT, while the shoulder around 610 nm could be related to the interchain stacking of P3HT molecules which suggested an enhancement in the chain ordering of P3HT; this could give good indication of improved chain ordering of the P3HT molecules within the active layer [4]. Moreover, the absorption spectra of both P3HT:ICBA and P3HT:PCBM blends with various ratios have displayed identical broad absorption spectra in the wavelength range between 300-650 nm. These spectra were decreased by increasing the fullerene ratio between 400-650 nm which was associated with the P3HT donor, while increased absorption in the range 300-400 nm can be related to the fullerene molecules [3,6]. It could therefore be concluded that in P3HT-based solar cells doped with fullerene molecules, reduced ratios of fullerene in the blends is favorable for efficient solar cells [7]. Moreover, it is clearly shown that three bands are appearing in the spectra of both fullerene derivatives. Two shoulders around 560

nm and 610 nm accompany the maximum absorption intensity around 500 nm. Furthermore, band A was noticeably blue shifted with the increase of fullerene ratio which could be attributed to the reduction of the interchain interaction between P3HT molecules; it could be assumed that the fullerene molecules are isolating the chains of P3HT from each other and reduce the conjugated length of P3HT backbone [8]. On the other hand, B and C bands were decreased with increasing fullerene ratio which probably gives an indication for further reduction in the usual conjugation length of P3HT [9].

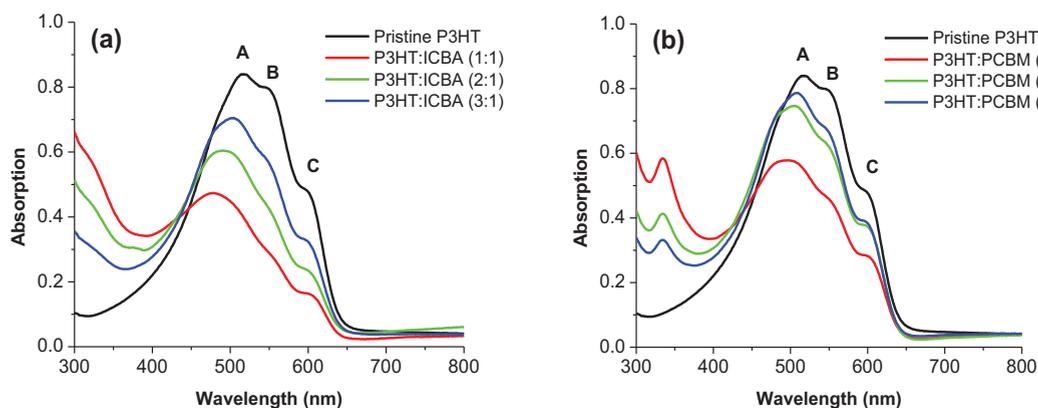


Fig.1. UV-VIS absorption spectra for both P3HT:ICBA (a) and P3HT:PCBM (b) with different ratios.

### 3.2. Fluorescence spectroscopy:

The fluorescence spectra of pristine P3HT and P3HT-based films with different fullerene ratios were investigated in order to determine the intermolecular charge transfer (CT) between the P3HT and fullerene molecules [9].

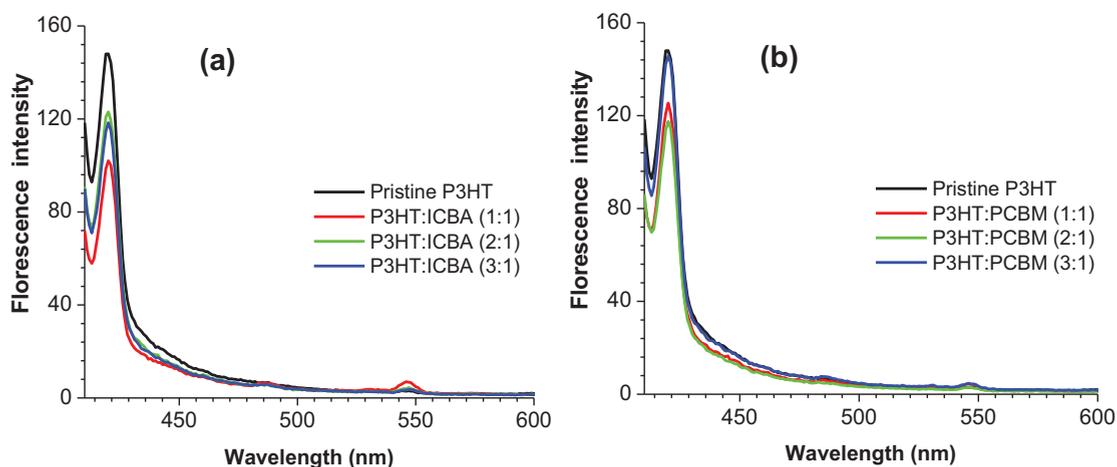


Fig.2. Fluorescence spectra for (a) P3HT:ICBA (b) P3HT:PCBM

Fig.2 displays the fluorescence spectra using an excitation wavelength  $\lambda_{\text{excitation}} = 400$  nm. The maximum emission peaks were found around the wavelength of 420 nm. For pristine P3HT film, the fluorescence spectra have demonstrated strong excitation intensity which is mostly due to the exciton-exciton annihilation [10]. For the blended films, the quenching of the fluorescence spectra gives clear indication of charge transfer from P3HT to fullerene.

molecules [10]. When the blend shows uniform distribution of P3HT and fullerene, the possibility of excitons' separation is high [6].

### 3.3. X-Ray diffraction patterns

The XRD measurement was carried out to investigate the crystallinity of pristine P3HT and P3HT:fullerene films; XRD patterns of the studied films are presented in Fig.3. The main diffraction peaks for the P3HT and P3HT-based films were found to be around  $2\theta^\circ = 5.49 \pm 0.07$  which are correlated with the interchain arrangement in P3HT linked with the interdigitated alkyl chains [11]. P3HT is well known as one of the regioregular polymers, which have several characteristics associated with its self-orientation. The regular P3HT chains structure aid their self-orientation by inter-chain assembling and show highly crystalline features [12]. On the other hand, the fullerene molecules are thought to interrupt the P3HT crystallinity during the film growth [13]. Strong reduction in the XRD peaks was observed with increasing the fullerene ratio. Another visible peak was also observed around  $2\theta^\circ = 10.81 \pm 0.11$  which could be related to the so-called lamellar stacking of P3HT backbones; this could indicate a higher crystallinity of P3HT, which is favorable when the delocalized states are oriented in the transport direction [14].

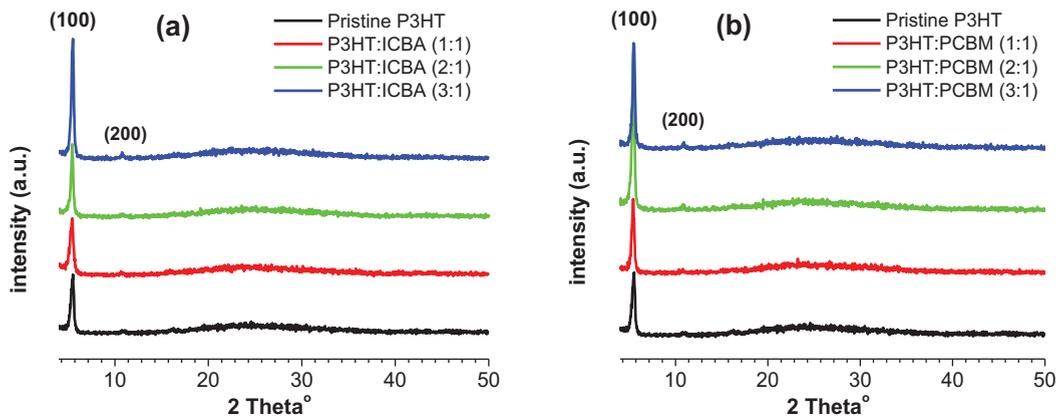


Fig.3. XRD curves for (a) P3HT:ICBA (b) P3HT:PCBM

### 3.4. AFM images

The surface morphology of film blends of P3HT:fullerene derivatives was examined by AFM. Fig.4 shows the AFM images of P3HT:PCBM and P3HT:ICBM active layers with different blend ratios. It is clear that the films morphology were considerably affected by the fullerene ratio. The films with higher fullerene proportions exhibited lower surface roughness, while films with lower fullerene ratio have displayed higher roughness; the root mean square (rms) roughness of the investigated films are listed in Table 1. Although the variation in films' surface roughness was small, the images show very fine features of phase separation. In addition, 1:1 P3HT:PCBM film was exhibited more pinholes compared to films incorporating ICBA, this may cause leakage current that reduce the fill factor and overall power conversion efficiency (PCE) of the OSCs based on such blend [15]. On the other hand, rougher surface is thought to be an advantage for increasing contact area with the top metal contact, hence increasing the short circuit current density  $J_{SC}$  [11].

Table 1. The films thicknesses and the rms surface roughness of the P3HT:PCBM and P3HT:ICBA

Samples	Film thickness (nm)	Rms (nm)
P3HT:ICBA (1:1)	164.019	0.47
P3HT:ICBA (2:1)	163.054	0.55
P3HT:ICBA (3:1)	169.463	0.64
P3HT:PCBM(1:1)	167.089	0.47
P3HT:PCBM(2:1)	168.89	0.63
P3HT:PCBM(3:1)	168.104	1.35

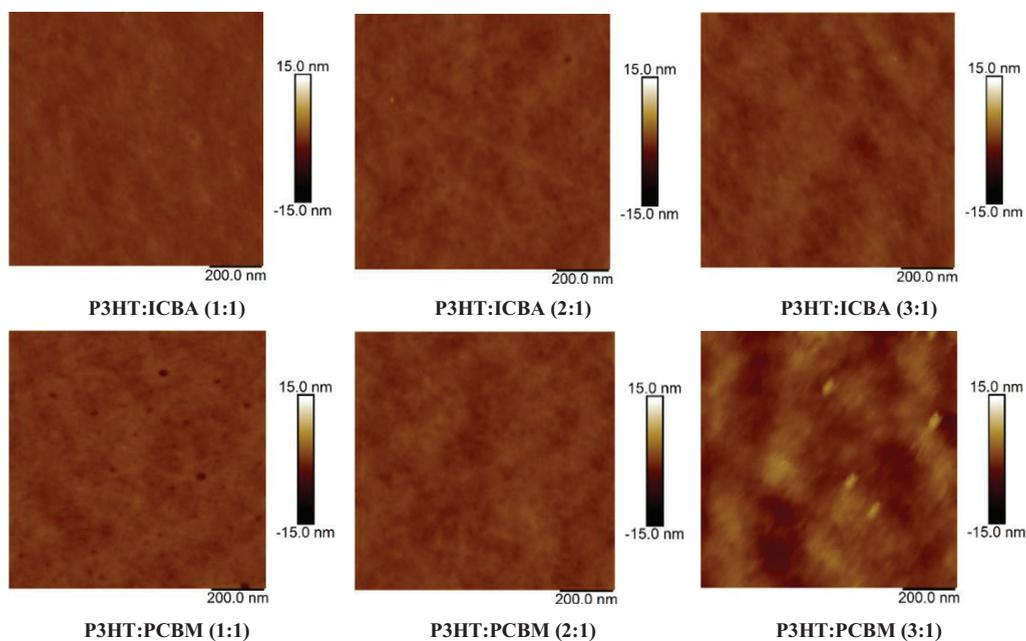


Fig.4. AFM images for P3HT:PCBM and P3HT:ICBA with different blend ratios

Table 2. The electrical parameters for the devices under study.

Sample	Voc (V)	Jsc (mA.cm <sup>-2</sup> )	FF %	PCE %
P3HT:ICBA (1:1)	0.53	7	29.4	1.1
P3HT:ICBA (2:1)	0.53	7.3	29.6	1.144
P3HT:ICBA (3:1)	0.53	8.5	30.7	1.41
P3HT:PCBM (1:1)	0.58	7.7	29.1	1.3
P3HT:PCBM (2:1)	0.58	8.7	30.3	1.53
P3HT:PCBM (3:1)	0.58	9.9	32.4	1.86

### 3.5. Electrical properties:

J(V) measurements were carried out under illumination using a solar simulator source AM1.5 of 100 mWcm<sup>-2</sup>. Table 2 summarises the photovoltaic parameters of the OSCs with active layers produced from different blending ratios of P3HT and fullerene derivatives. As revealed in Fig.5, an increase in J<sub>SC</sub> and fill factor (FF) was evident, which was the main reason for increasing PCE up to 1.86% in the P3HT:PCBM in the ratio (3:1). However, V<sub>OC</sub> for P3HT:ICBA films exhibited lower values (~0.53 Volt) than the P3HT:PCBM films (0.58 Volt); no change in V<sub>OC</sub> as

a result of blend ratio variation was recorded. These results were in contradiction with previous literatures [16,17]. Boyuan and co-workers have revealed that higher LUMO of ICBA could result in higher  $V_{OC}$ . On the other hand, several characteristics could affect the  $V_{OC}$  [18]; bearing in mind that these devices were fabricated in ambient air, it is expected that the active layers could be oxidized leading to increased traps density. Furthermore, recombination could also result the loss in  $V_{OC}$ , as well as the work function of the electrode which could influence  $V_{OC}$  if the contact is not ohmic [19]. Other factors such as microstructure, morphology and crystallinity of the blend, which could also have an impact on the  $V_{OC}$  [20]. The interaction between P3HT polymer chains is interrupted by PCBM molecules; this could reduce the charge carrier mobility thereby decreases the efficiency of the OPVs [21]. The best device performance was recorded the P3HT:PCBM (1:1) blend with PCE=1.86%, FF=32.4,  $J_{SC}$ =9.9 mA.cm<sup>-2</sup> and  $V_{OC}$ =0.58V.

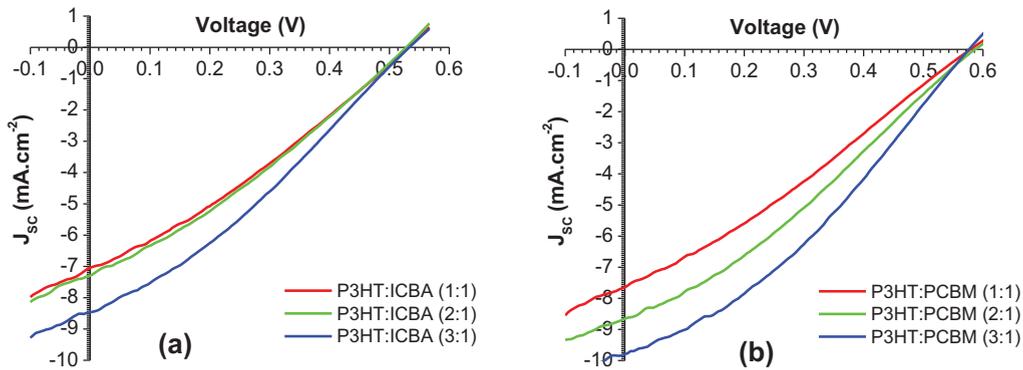


Fig.5. Current density-voltage under 1.5 illumination for P3HT:PCBM and P3HT:ICBA with different ratio

## Conclusion

OSCs based on P3HT polymer was studied by adding PCBM or ICBA with different blending ratios. Optical absorption spectra displayed reduction in their intensities by increasing fullerene ratio correlated by blue shift in the main peak. This was attributed to a decrease in the interchain interaction of the main polymer. These results were further confirmed by XRD results and AFM images. On the other hand, fluorescence spectra have demonstrated efficient quenching by increasing the fullerene ratio. The best solar cells performance was obtained for P3HT:PCBM prepared in the 3:1 with PCE=1.86% whereas P3HT:ICBA (3:1) exhibited a PCE of 1.41%.  $V_{OC}$  on the other hand has given lower values in the case of devices made with ICBA in comparison to devices used PCBM; this was attributed to the morphology, microstructure as well as effect of contact with the electrodes, bearing in mind that all the samples were fabricated in ambient air.

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