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POLYMER-FULLERENE BASED BULK HETEROJUNCTION P3HT:PCBM SOLAR CELL: THE INFLUENCE OF PTU AS A CHEMICAL ADDITIVE ON PHOTOVOLTAIC PERFORMANCE

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Abstract

The polymer-fullerene based bulk heterojunction (BHJ) polymer solar cells (PSCs), which contain the blends of poly (3-hexylthiophene) (P3HT) and [6, 6] phenyl C_{61} butyric acid methyl ester (PCBM) with different concentrations of propylthiouracil (PTU) additive were fabricated and characterized in the open air. The current density-voltage characteristics were measured in the dark and under the white light illumination at an illumination intensity of 80 mW/cm^2. The consistency of optical absorption and incident monochromatic photon to current conversion efficiency (IPCE) of the PSC with and without additive were studied and compared. Different optimizations were prepared by varying the concentrations of PTU from 0.75% (w/w) to 1.5% (w/w). It has been observed from photovoltaic studies that the PSC with 1% (w/w) of PTU shows the best photovoltaic performance among the other concentrations of PTU and without PTU; with a short circuit current density (J_{SC}) of 5.69 mA/cm^2, open circuit voltage (V_{OC}) of 0.648 V, fill factor (FF) of 40%, and power conversion efficiency (PCE) of 1.8%. The PSC with 1% (w/w) of PTU shows the IPCE of 62% at 480 nm. In addition, it has also been observed from the studies that the IPCE spectra of each PSC match the corresponding optical absorption spectra. The results in general show that the addition of 1% (w/w) PTU additive to P3HT:PCBM bulk heterojunction solar cell improves the PCE from 1% to 1.8%.

Keywords: polymer solar cell, bulk hetero-junction solar cell, chemical additive, photovoltaic performance of solar cell, efficiency of solar cell.

I. INTRODUCTION

A promising approach towards low cost production of photovoltaic device is fabrication of solar cells based on polymer organic materials [1]. The interest in polymer solar cells has risen strongly in recent years due to their interesting properties in terms of low cost synthesis, flexibility, easy manufacture of solution cast technologies [2] and high absorption coefficients exceeding 10^5 cm^{-1} [3]. The bulk heterojunction concept has been employed to overcome the short exciton diffusion distance. The photoactive film of heterojunction forms from the donor and acceptor materials, which are phase separated on the nanometer length scale, to facilitate the photo, induced charge transfer as well as create a percolating pathway for charge transport to the electrodes [4]. Therefore, the nanomorphology of polymer solar cells plays a crucial role for the performance of the devices. Various methods have been tested and employed to control the nanomorphology of the blends, namely use of solvents with different boiling points (choice of solvent), reduction of drying speed (rate of drying and vapor annealing), changing the solubility of materials, and the use of processing additives [5]. The later method has received great academic interest as it removes the need for postproduction treatment while at the same time allowing fine control of the nanomorphology in various donor acceptor blends [6]. Many researchers have studied the polymer-fullerene based P3HT (poly 3-hexylthiophene):PCBM ([6, 6]-phenyl C_{61} butyric acid methyl ester) solar cells and much of it is devoted on the effect of blend composition and morphology on the device performance, the

stability enhancement, the relation between the efficiency and the morphology, the influence of post deposition thermal treatment on the efficiency, the relation between morphology and the electro-optical characteristics [7-10] etc. However, there is no research on how the concentration of the chemical additive propylthiouracil (PTU) influences the photovoltaic performance of the bulk heterojunction P3HT:PCBM solar cells. In view of this, it is aimed in this work and studies were made to report the influence of chemical additive PTU on various photovoltaic characteristics of the polymer-fullerene based bulk heterojunction P3HT:PCBM solar cells.

II. EXPERIMENTAL SECTION

2.1 Chemical Preparation

0.75 mg, 1 mg and 1.5 mg of PTU were dissolved separately in 10 ml chlorobenzene and stirred overnight. The photoactive solutions were prepared by dissolving P3HT (10 mg) and PCBM (10 mg) in 1 ml chlorobenzene (without additive), and with the addition of 0.75% (w/w), 1% (w/w), and 1.5% (w/w) PTU. The mixtures were thoroughly stirred overnight. Figure 1 shows the chemical structures of the substances used in this work.

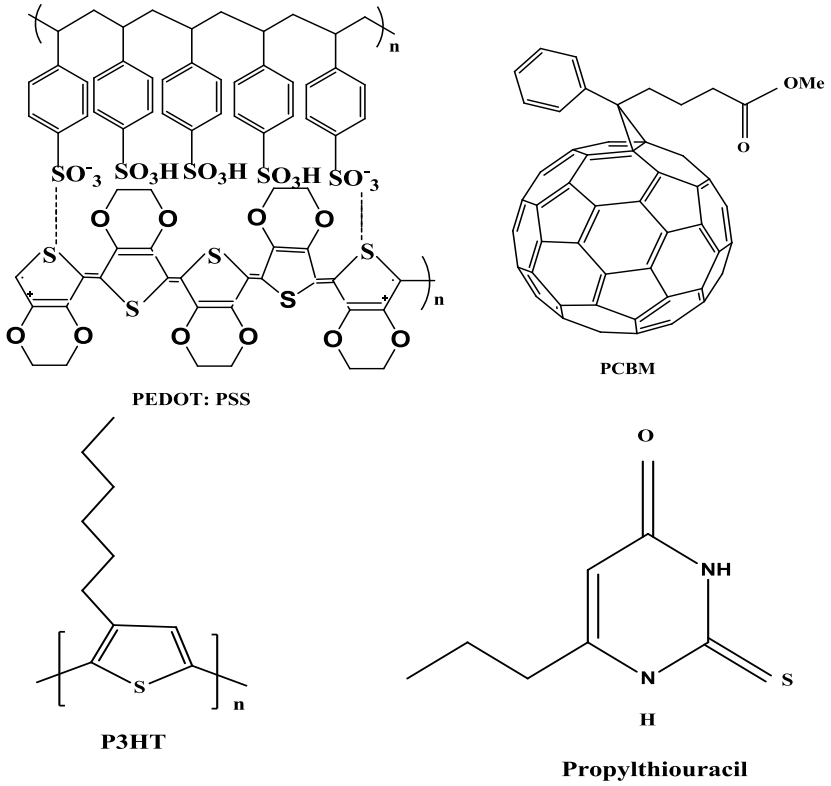

Figure. 1 Chemical structures of the substances used in this work

2.2 Fabrication of Solar Cell

Indium doped tin oxide (ITO) coated glass substrates were cleaned sequentially by using acetone, isopropanol, and ethanol for 20 min in an ultrasonic bath. After cleaning, the PEDOT:PSS was spin coated on top of the cleaned ITO coated glass substrate at spin rate of 4000 rpm for 46 s. This was followed by annealing of the film at 150 ^{o}C for 10 minutes, leaving a dried thin film. The surface roughness of the ITO is minimized and the electric contact to the active layer is improved. Then, P3HT:PCBM solution with different concentration of PTU additive was spin coated on top of PEDOT:PSS at 800 rpm for 41 s yielding thin film spread over the whole plate as active layer. Spin coating was done by using SCS 6800 spin coater series. For electrical contact some part of the polymer film is removed from the etched part using toluene. Finally, the low work function metal aluminum (Al) is thermally deposited partly on the active area film and partly on the clean glass using a mask. The deposition was done using Edward Auto 306 vacuum evaporator, at pressure in

the chamber of the evaporator is reduced about 4×10^{-6} mbar. As a source, tungsten boat was used. After aluminum is evaporated, the device was taken out of the chamber for characterization. The final sandwich type devices of bulk heterojunction solar cell of ITO/PEDOT:PSS/P3HT:PCBM/Al is depicted in Figure 2.

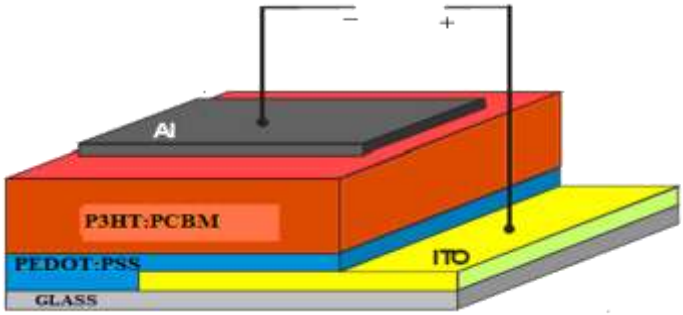

Figure. 2 Basic device structure of bulk heterojunction solar cell used in this study

2.3 Device Characterization

The current-voltage (I-V) characteristic in the dark, as well as under illumination was measured by using HP 4140B pA meter/DC voltage source, together with HP 16055A-test fixture. The measurement was taken by continuously sweeping the voltage applied from -2 V to 2 V at 10 mV steps with hold time and step delay time of 1 s. The I-V measurement under illumination was carried out by mounting inside the sample holder under a standard sun illumination, using a solar simulator model SS-50AA the intensity of light incident on the cell was about 80 $mWcm^{-2}$. IPCE characterizations of the solar cell were performed using a computer controlled CHI630A instrument. A 150 W Xenon lamp regulated by an Oriel power supply (Model 68830) was used to illuminate the solar cells. A grating monochromator (Model 77250) placed into the light path was used to select a wavelength manually between 300 nm and 800 nm at an interval of 10 nm. The measured photocurrent spectra were corrected for the spectral response of the lamp and the monochromator by normalization to the response of a calibrated silicon photodiode (Hamamatsu, Model S-1336-8BK) whose sensitivity spectrum was known. No correction was made for the reflection from the surface of the sample. The white light intensity was measured in the position of the sample cell with Gigahertz-Optik (model X1-1) Optometer. The intensity of the incident light was 100 mW/cm^2. Optical absorption measurements were carried out using UV-VIS Spectrophotometer (Spectronic GENESIS, USA).

III. RESULTS AND DISCUSSION

3.1 Absorption Spectra Measurement

Figure 3 shows the absorption spectra of P3HT:PCBM with different concentration of PTU blends spin coated onto glass substrates from chlorobenzene solutions.

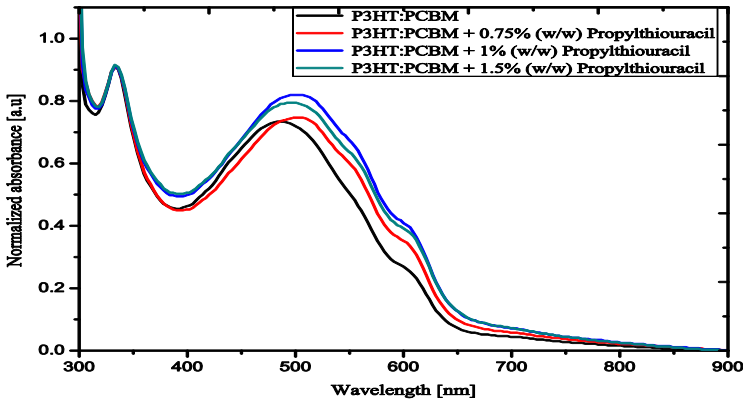

Figure. 3 Normalized absorbance of thin films of P3HT:PCBM with different concentrations of PTU

For each blend, the absorption spectrum has been normalized to the PCBM peak (around 330 nm). The results show that the absorption edge is red shifted and that the vibrational structure of the P3HT absorption band is more pronounced when PTU is added to the blend. This implies better stacking/ordering of P3HT because a closer π stacking of P3HT chains can lead to a lower band-like energy [11]. Closer π-stacking of P3HT chains can contribute to an enhancement in short circuit current density, J_{SC} due to a lower resistance to the hopping of carriers between P3HT backbones. From the chemical structure of PTU and PCBM the common carbonyl functional group leads to higher miscibility of PTU additive in PCBM than P3HT. The addition of additives with a selective miscibility in one of the components of BHJ films is known to improve the morphology of the photoactive layer for charge separation and transport, which ultimately improves device characteristics [12]. The relatively better miscibility of PTU additive with PCBM molecules in the bulk resulted in a phase separation between P3HT and PCBM, which can contribute to the formation of larger PCBM domains. Thus, the existence of PTU is considered to lead to the formation of slightly larger PCBM domains, while most PCBM in the device without additive is molecularly dispersed within a P3HT matrix [13]. Hence, the selectively dispersed PTU additive facilitate the formation of bicontinuous phase separation between P3HT and PCBM to provide better bicontinuous pathways for the holes and electrons. The higher stacking/aggregation also plays an important role in increasing charge transport in the active layer, contributing to the high current density of the device.

3.2 Current Density-Voltage (J-V) Characteristics

Figure 4 shows the dark current density-voltage (J-V) characteristic curves of the different solar cells made at different concentrations of PTU. The characteristics for all these devices exhibit three distinct regimes: at low voltage, the measured current is dominated by local leakage currents due to weak spots in the film, giving rise to Ohmic behaviour, which is symmetric for reverse bias. An exponential behaviour at intermediate positive voltages where the current is controlled by the diode and at high voltages where the current is limited by the serial resistance R_S.

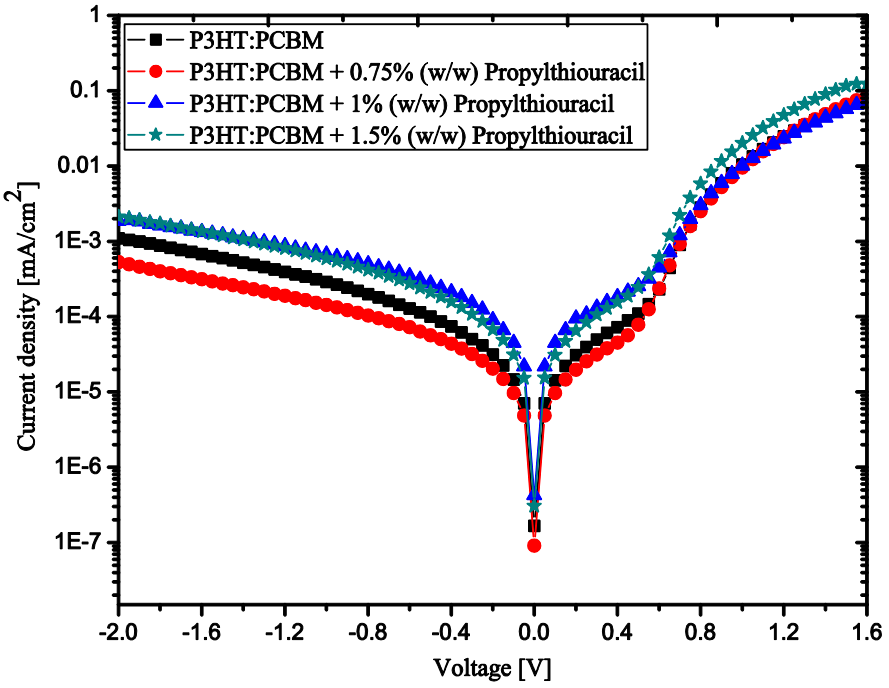

Figure. 4 Semi-logarithmic dark current density-voltage characteristics of P3HT:PCBM with different concentrations of PTU

Figure 5 and 6 show the current density (J)-voltage (V) curves of the solar cells constructed at different concentrations of PTU additives. For comparisons, the device without additive is also included. Table 1 summarizes the data obtained from the curves shown in Figure 5 and 6.

Table 1 The typical photovoltaic performance parameters of P3HT:PCBM with different concentration of PTU additive at illumination intensity of 80 mw/cm^2

Active Layer	R_S (Ω-cm^2)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	Efficiency (%)
P3HT:PCBM	15	0.660	3.43	35	1.0
P3HT:PCBM + 0.75% (w/w) PTU	20	0.610	3.20	37	0.9
P3HT:PCBM + 1% (w/w) PTU	8	0.648	5.69	40	1.8
P3HT:PCBM + 1.5% (w/w) PTU	14	0.623	4.47	41	1.4

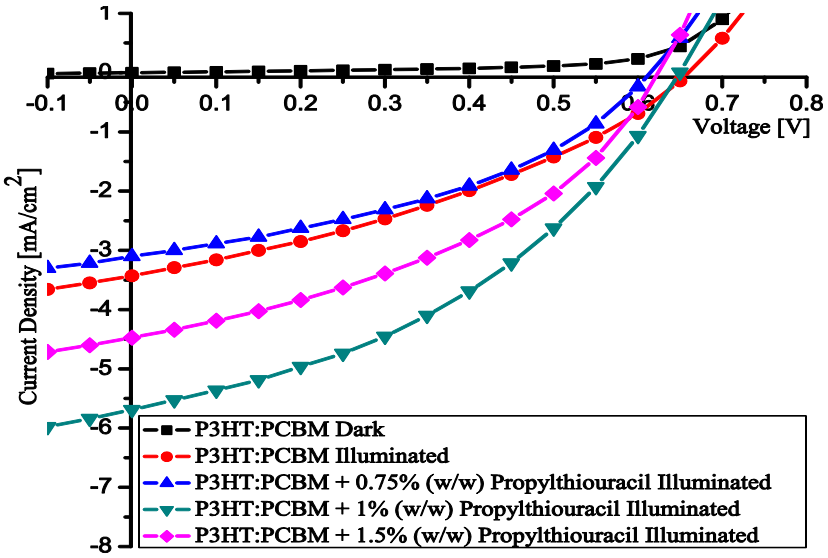

Figure. 5 The J-V characteristics of P3HT:PCBM with different concentrations of PTU additives in the dark and under white light illumination with incident light intensity of 80 mW/cm^2

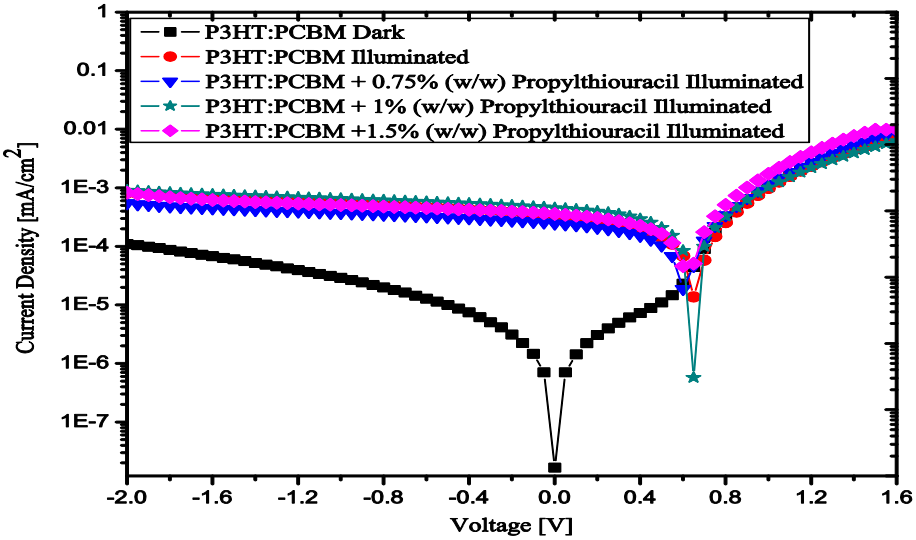

Figure. 6 Semi-logarithmic J-V characteristics of P3HT:PCBM with different concentrations of PTU additives in the dark and under white light illumination with incident light intensity of 80 mw/cm^2

The device without additive shows V_{OC} of 0.660 V, J_{SC} of 3.43 mA/cm^2, FF of 35%, and power conversion efficiency, (PCE) of 1%. At addition of 0.75% (w/w) of PTU, V_{OC} decreased from 0.660 V to 0.610 V, J_{SC} decreased from 3.43 mA/cm^2 to 3.20 mA/cm^2, which in turn reduces the PCE from 1% to 0.9%. The reason might be due to the insufficient concentration of PTU that do not lead to phase separation rather increases the serial resistance from 15 Ω cm^2 to 20 Ω-cm^2. But as concentration of PTU increases to 1% (w/w), the current increases as a result of good phase separation as confirmed from the decrease in serial resistance to 8 Ω-cm^2. When we further increase the concentration of PTU to 1.5% (w/w) still J_{SC} increases but as compared to 1% (w/w), it is decreasing due to the increase in serial resistance from 8 Ω-cm^2 to 14 Ω-cm^2. Thus, the most effective PTU content is 1% (w/w), where the BHJ solar cell device exhibits the best performance, this shows that the concentration of PTU at around 1% (w/w) is the optimum that leads to decrease in serial resistance and increase in J_{SC}. Another possible reason might be the increased dielectric constant of the matrix, due to polar nature of PTU that increases the screening of photo-generated electrons and holes and, thus, facilitates the charge separation. The low V_{OC} in additive processed devices is attributed to the upward shift in the HOMO level of P3HT as a result of its aggregation [14]. The photovoltaic performance parameters of the device before addition of PTU additive shows V_{OC} = 0.660 V, J_{SC} = 3.43 mA/cm^2, and FF= 35%. The corresponding power conversion efficiency (PCE), η is found to be 1%. With the addition of 1% (w/w) PTU additive, the J_{SC} increased from 3.43 mA/cm^2 to 5.69 mA/cm^2 and the FF from 35% to 40%, which lead to an enhancement of PCE from 1% to 1.8%.

3.3 Spectral Response

The dependence of the photovoltaic performance on the PTU content was further confirmed by the incident monochromatic photon to current conversion efficiency (IPCE) measurement of the devices, as shown in Figure 7.

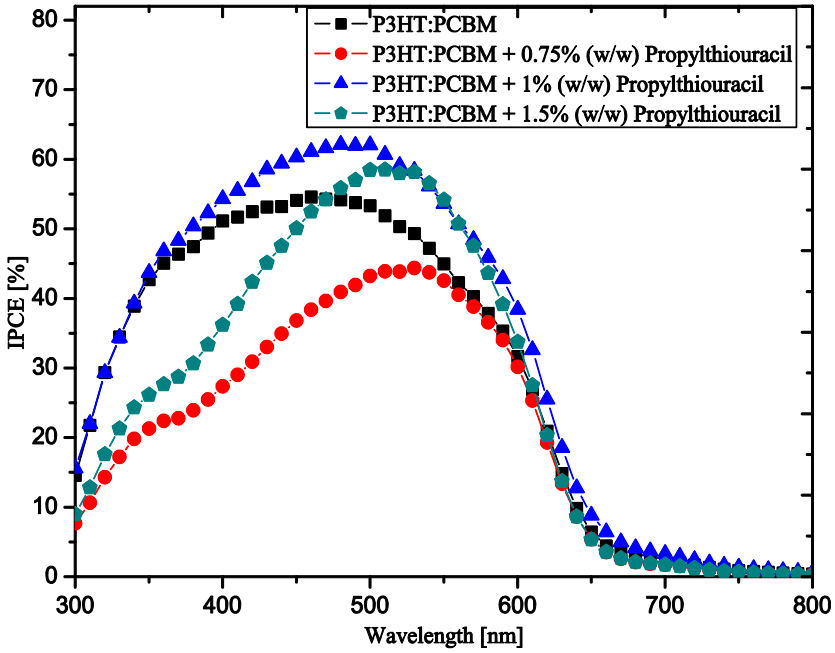

Figure. 7 IPCE spectra of P3HT:PCBM with different concentrations of PTU additives

The IPCE curves of the devices with different PTU contents show maximum IPCE around 62% in the wavelength range of 480-510 nm, corresponding to the absorption maxima of the blend. With increasing the PTU content from 0% (w/w) to 0.75% (w/w) to 1% (w/w) then to 1.5% (w/w), the IPCE maximum decreased from 55% to 44%, and then increased to 62%, finally decreased to 59%. The IPCE profile varying with the PTU content is consistent with that for J_{SC} and PCE. Comparing the spectral response of the solar cells and the optical absorption spectra of the devices, information on the charge-generation mechanism can be obtained [15]. Figure 8 shows comparison

between the IPCE and absorption spectra of bulk heterojunction solar cells which are investigated in this study.

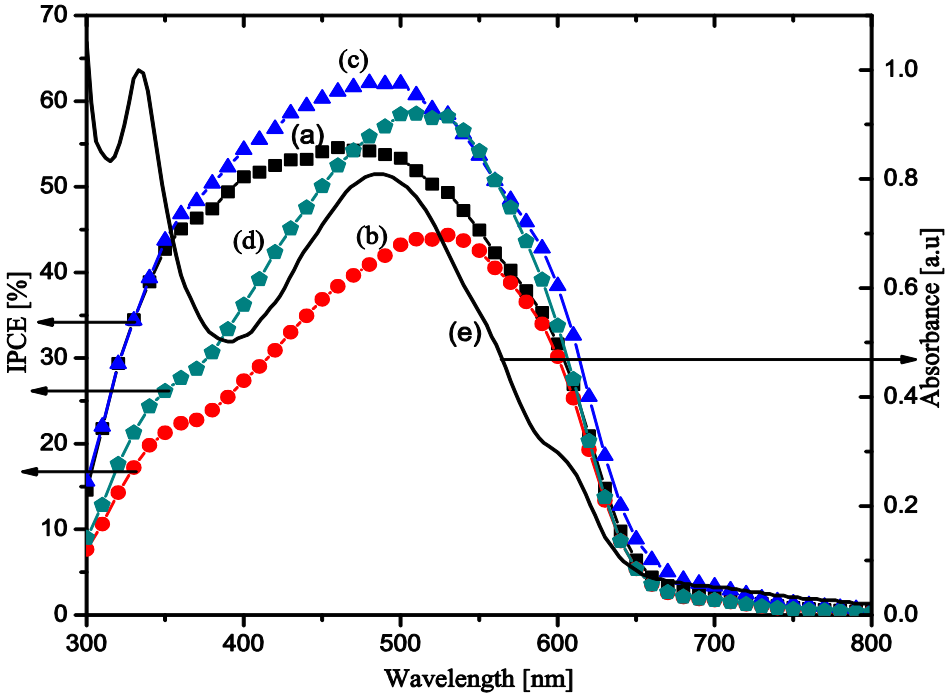

Figure. 8 IPCE spectra of P3HT:PCBM (a) without PTU (b) with 0.75% (w/w) PTU (c) with 1% (w/w) PTU (d) with 1.5% (w/w) PTU (e) absorption spectra of P3HT:PCBM.

Increased J_{SC} is mainly related to more exciton and charge generations and more effective charge transport. To probe the role of PTU in this system, effect of PTU on absorption spectra of P3HT:PCBM films was examined to have an insight into the generations of excitons and charge carriers. The film with 1% (w/w) PTU content exhibits stronger absorption than that without PTU, while when 0.75% (w/w) and 1.5% (w/w) of PTU was added, a drop in absorbance was observed. The stronger absorption partially contributed to higher J_{SC} and IPCE of the device processed with 1% (w/w) PTU compared to the others. It can be seen clearly that optical absorption matches the IPCE spectra.

IV. CONCLUSIONS

Bulk heterojunction P3HT:PCBM solar cells without and with different concentrations of PTU additives were fabricated. The effect of different PTU concentrations on the optical performance of the solar cells were studied and reported. Short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and power conversion efficiency of the solar cell without additive are found to be respectively, 3.43 mA/cm^2, 0.66 V, 35%, and 1%. While the same parameters in the same respective order for 1% (w/w) PTU additive are found to be 5.69 mA/cm^2, 0.648 V, 40%, and 1.8%. In addition, the IPCEs of 62% at 480 nm and 55% at 460 nm are found for devices with 1% (w/w) PTU and without PTU, respectively. Studied showed the relatively best photovoltaic performance for the device containing 1% (w/w) PTU among all other solar cell devices with (0.75% (w/w) PTU and 1.5% (w/w) PTU) and without PTU additives. The optical absorption results clearly indicated that the absorption edge is red shifted and that the vibrational structure of the P3HT absorption band is more pronounced when PTU is added to the blend. Finally, the results from the studies showed that the addition of 1% (w/w) PTU additive to the device improves the efficiency of the device from 1 to 1.8%.

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