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Study and Analyze the Effect of Polymerization on Device Performance of P3HT: PCBM based Organic Solar Cell

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Abstract: ***This paper gives a comparison of photovoltaic performance of bulk hetrojunction solar cell using blends of P3HT and PCBM in 1:1 ratio using common organic solvents by spin coating technique. Here different regioregular P3HT are used which were synthesised by various techniques. Prior to these processes, fabrication and designing of solar cells, right from the initial steps such as patterning of ITO coated glass, etching, cleaning and subsequent processes were performed. The main advantages of such cells are easy preparation, low process temperature, low cost materials & processing technology and the possibility to produce flexible devices on plastic substrates. Such flexible cells are therefore candidates for gamut of applications, from handheld electronics to commercial power production.***

Keywords: Bulk heterojunction (BHJ) solar cells, Fill Factor (FF), Organic photovoltaic cells (OPV), Power Conversion Efficiency (PCE), Regioregularity.

1. Introduction

Organic solar cell research has attracted scientific and commercial interest in the last decade due to a rapid increase in power conversion efficiencies (PCEs). Today, PCEs in the range of 8-10% have been obtained using conjugated polymers as electron donor materials in combination with fullerene/other acceptors in Bulk heterojunction geometry [1], [2]. However, in order to enable commercial applications, the efficiencies and life time of organic solar cells still need to improve significantly. Among all of these scientific reports, the most-prominent reported material system in Bulk Heterojunction is the mixture of poly(3-hexylthiophene) and (6,6)-phenyl-C61-butyric acid methyl ester (P3HT:PCBM). Despite the enormous research effort that has been expended on the improvement of solar cells, with the P3HT:PCBM cells possessing a various power-conversion efficiencies. The best performing polymeric solar cells are made with regioregular poly(3-hexylthiophene) (P3HT) as donor material and achieve an efficiency surpassing 5% and more than 6% in tandem cell configurations have been reported for this particular system, despite its limited spectral overlap with solar radiation. But the main disadvantage of this polymer is the poor matching of its photon absorbance with the solar cell spectrum [3]–[7]. However, P3HT: PCBM remains of high interest, as it represents a prototypic photovoltaic donor– acceptor system, and more importantly, it is readily available [8]. Although reporting the power-conversion efficiency accurately is not trivial. Scientists are required to use a standard infrastructure, materials, equipments and fabrication etc.

2. Experimental

2.1. Indigenous Synthesis of Regioregular P3HT

In order to demonstrate the OPV performance of indigenous development of P3HT and compared with commercially available P3HT, we obtained the polymer P3HT from commercially available 3-hexylthiophene by adapting literature procedure (Scheme 1). Bromination of compound 1 with NBS in CHCl3 provided dibrormo-compound 2 in 91% yields as an oil. Compound 2 was subjected to polymerization using MeMgCl in presence of catalytic yielded the desired polymer P3HT as presented in Scheme 1 (Figure: 1.1). The resulted polymer was washed with methanol, acetone and hexane and further purified by Soxhlet extraction. Hence a Regioregular P3HT was synthesized.

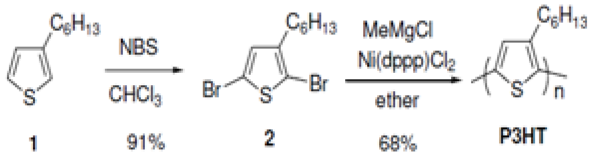
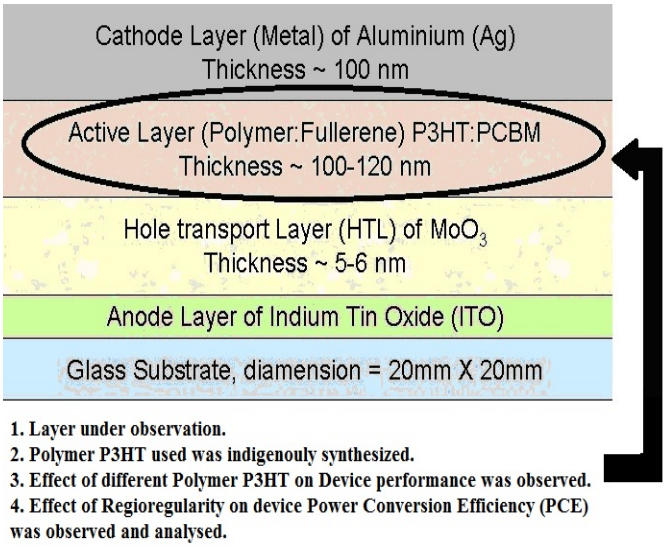


Figure 1.1: Scheme 1 of Synthetic route for polymer P3HT.

Materials: MoO_3 and Commercially available P3HT were purchased from Sigma- Aldrich USA while PCBM was purchased from Nano-C. Indigenous synthesized P3HT. All materials were used as received. Both the polymer (P3HT) is of Regioregular in their chemical structure.

Sample Preparation: For samples the indium tin oxide (ITO) coated glass substrates were patterned by laser etching and subsequently cleaned by an ultrasonic treatment of multiple steps with different solvents. After the initial steps such as patterning of ITO coated glass, etching, cleaning and subsequent processes, the MoO_3 was deposited using vacuum thermal evaporator at the deposition rate of 0.1 Å /sec to form a very thin film of around 5-6 nm. After the deposition of HTL layer the polymer (P3HT:PCBM) was deposited by spin coating technique using a common solvent (chlorobenzene) in both the samples. This layer was also deposited at the speed of 1200 rpm and known as the active layer of thickness around 100-120 nm. Now the last layer also known as cathode was deposited using vacuum thermal evaporation technique at the deposition rate of 10 Å /sec to form a layer of thickness around 100 nm. The pressure of the vacuum chamber should be maintained around 5×10^{-7} torr to ensure good quality deposition. Otherwise without reaching low enough pressure, hot vaporized metal particles react with remaining oxygen molecules and form metal oxide.

Layered structure for the fabricated device is shown below. Figure 1.2, here we have ITO coated glass substrate onto which we deposited various layers to form a solar cell as shown. Active material is a blend of Active material which is a combination of Polymer (Donar) and Fullerene (Aceptor) material. In our device, Polymer is P3HT and the fullerene is PCBM. Here we use both, the commercial available P3HT and the indigenously synthesized P3HT. Both the P3HT are of regioregular in their chemical structure. So we also compared the effect of their regioregularity on the device performance.



1. Layer under observation.
2. Polymer P3HT used was indigenouly synthesized.
3. Effect of different Polymer P3HT on Device performance was observed.
4. Effect of Regioregularity on device Power Conversion Efficiency (PCE) was observed and analysed.

Figure 1.2: Layered structure of an OPV device.

2.2. Characterization Methods

(1) Current - Voltage characteristics

Solar cells are operated between open circuit and short circuit conditions. This is in the fourth quadrant of the current - voltage characteristics, which is shown in Figure 1.3. The current - voltage curve provides a basic for the characterization of the properties of a solar cell. Such a cell is described by several parameters [9]–[11].

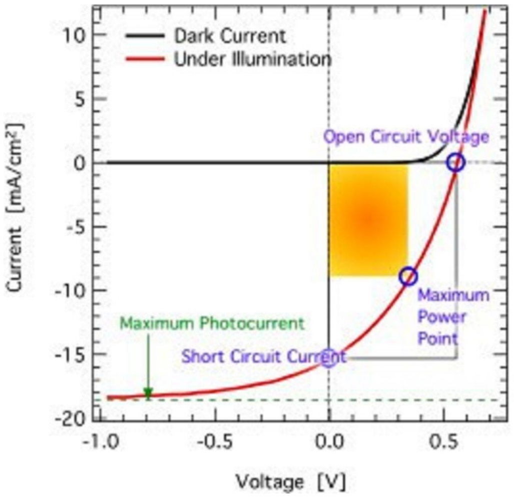


Figure 1.3: Current - Voltage characteristics

Open-Circuit Voltage (Voc): The maximum possible voltage across a photovoltaic cell or the voltage across the cell in sunlight when no current is flowing.

Short-Circuit Current (Isc): This is the current that flows through an illuminated solar cell when there is no external resistance (i.e., when the electrodes are simply connected or short-circuited). The short-circuit current is the maximum current that a device is able to produce. Under an external load, the current will always be less than Isc.

Fill Factor (FF): The ratio of a photovoltaic cell's actual maximum power output to its theoretical power output if both current and voltage were at their maxima, Isc and Voc, respectively. This is a key quantity used to measure cell performance. It is a measure of the 'squareness' of the *J–V* curve. The formula for FF in terms of the above quantities is:

$$FF = \frac{V_{mpp.}\, I_{mpp}}{V_{OC.} I_{SC}} \qquad (1)$$

Where,
Vmpp = Voltage at Maximum Power Point
Impp = Current at Maximum Power Point

Power Conversion Efficiency (PCE or η): The ratio of power output to power input. In other words, PCE measures the amount of power produced by a solar cell relative to the power available in the incident solar radiation (Pin). Pin here is the sum over all wavelengths and is generally fixed at $100 mW/cm^2$ when solar simulators are used. This is the most general way to define efficiency. The Formula for PCE, in terms of quantities defined above is:

$$\eta = \frac{V_{mpp.}\, I_{mpp}}{P_{in}} = \frac{V_{oc.} I_{SC.} FF}{P_{in}} \qquad (2)$$

(2) Absorption spectrum

Absorption spectra were recorded using a shimadzu UV-2401 UV-Vis spectrophotometer. UV-Vis spectroscopy is the measurement of the wavelength and intensity of absorption of near-ultraviolet and visible light by a sample. Ultraviolet and visible lights are energetic enough to promote outer electrons to higher energy levels. UV-Vis spectroscopy is usually applied to molecules and inorganic ions or complexes in solution. The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law. Since the UV-Vis range spans the range of human visual acuity of approximately 400 –750 nm, UV-Vis spectroscopy is useful to characterize the absorption, transmission, and reflectivity of a variety of technologically important materials, such as pigments, coatings, windows, and filters.

UV–Visible Spectroscopy
Working Principle: A beam of light from a visible and/or UV light source is separated into its component wavelengths by a prism or diffraction grating (Figure 1.4). Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half- mirrored device. One beam, the sample beam, passes through a small transparent container (cuvette) containing a solution of the compound being studied in a transparent solvent. The other beam, the reference, passes through an identical cuvette containing only the solvent.

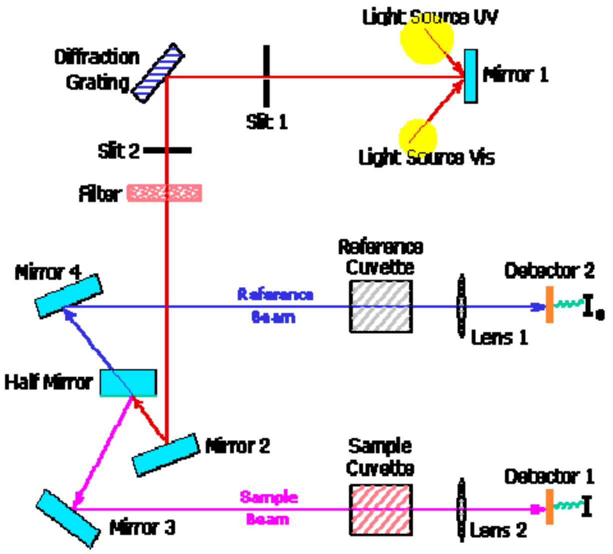


Figure 1.4: Schematic diagram of a dual-beam uv-vis spectrophotometer

The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as Io. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

3. Results and Discussions

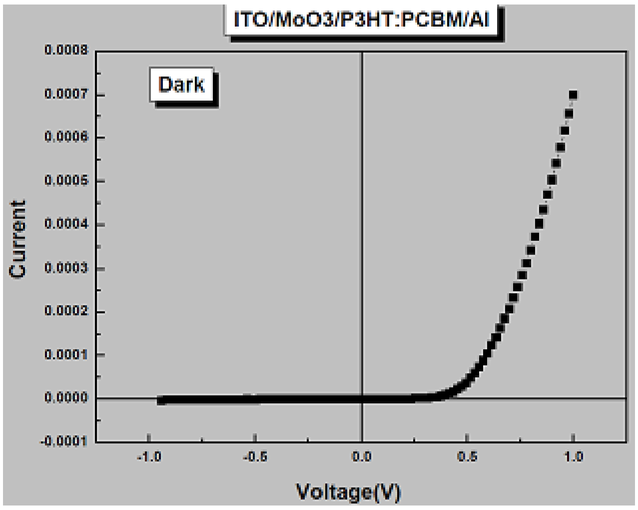
3.1. Photovoltaic Characteristics

Bulk heterojunction solar cells with blends of both regioregular polymers (P3HT) with PCBM were prepared and characterized. Typical current density-voltage (*J-V*) characteristics of a P3HT:PCBM (1:1) blend solar cell measured under illumination with a AM1.5G spectrum at 100 mW/cm^2. The *J-V* characteristics of the both the samples were recorded using Keithley 2420 Source Meter unit interfaced with computer is shown in Table 1.1. The Power conversion efficiency (PCE) of the device using commercial P3HT was found to be 1.29% with a fill factor of FF = 47.4%, an open circuit voltage of Voc = 0.50 V and a short-circuit current density of Jsc = 5.52 mA/cm^2. However the Power conversion efficiency (PCE) of the device using synthesized P3HT was found to be 1.26% with a fill factor of FF = 37.1%, an open circuit voltage of Voc = 0.514 V and a short-circuit current density of Jsc = 6.58 mA/cm^2.

Table 1: Observations

P3HT	*Rotation speed*	*Voc (volts)*	*Jsc (mA/cm^2)*	*Fill Factor (FF)*	*Power Conversion Efficiency (PCE)*
Commercial	1200 rpm	0.50	5.52	47.4 %	1.29 %
Synthesized	1200 rpm	0.514	6.58	37.1 %	1.26 %

Figure 1.5 shows the J-V characteristics of sample using commercial P3HT and Figure 1.6 shows the J-V characteristics of sample using synthesized P3HT. We realize that as such the fabrication conditions have not yet been entirely optimized as can be deduced from the lower fill factor and lower short-circuit currents of our cells compared to literature reports showing record efficiencies for P3HT:PCBM bulk heterojunction solar cells. However, a trend towards reproducible power conversion efficiencies of about 3.0% with P3HT:PCBM solar cells seems to have been established in recent literature [12]–[16].



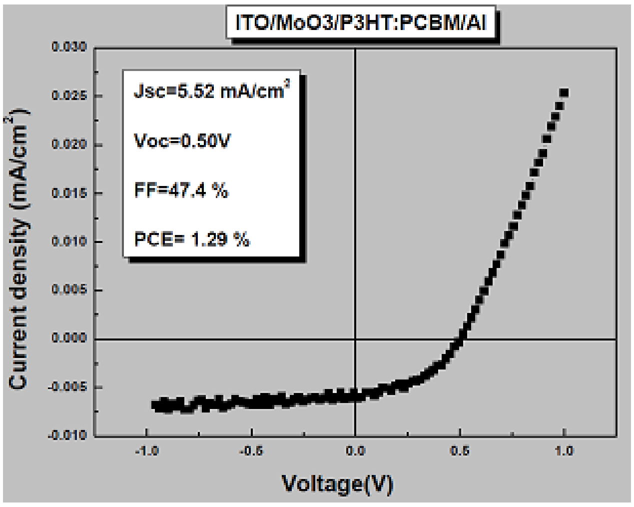


Figure 1.5(a), (b): J-V characteristics of commercially available P3HT based organic solar cell.

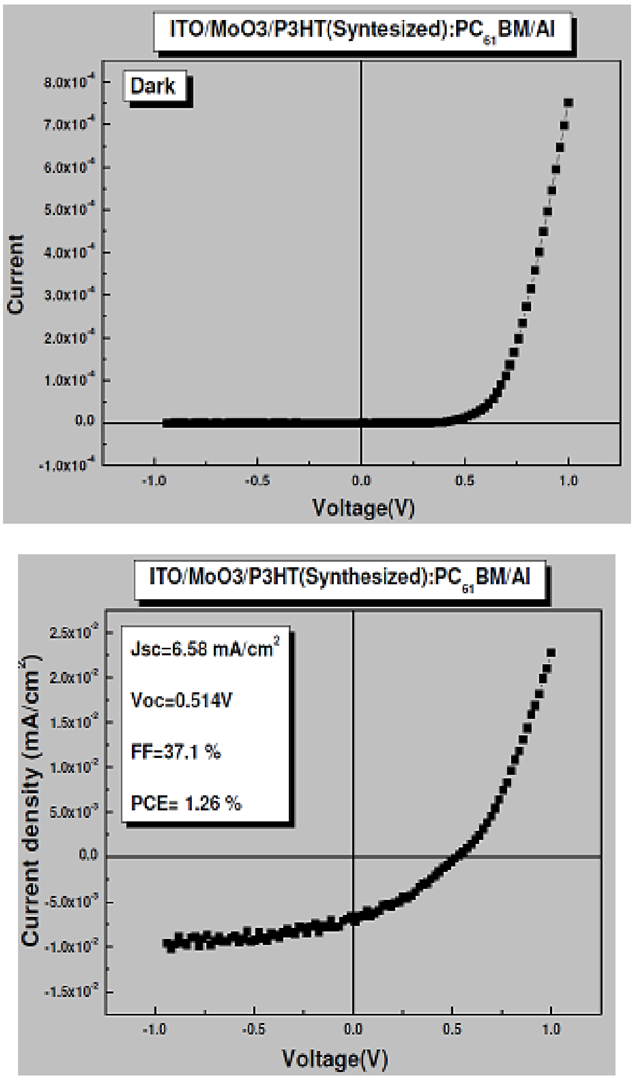


Figure 1.6(a), (b): J-V characteristics of synthesized P3HT based organic solar cell

Devices prepared with different P3HT exhibited lower short-circuit current densities and higher open-circuit voltages but they had comparable fill factor resulting in similar power-conversion efficiencies for both blend systems. The above results show that our lab synthesized P3HT based solar cell is also having PCE comparable to the commercially available P3HT based solar cell. Hence, the observed difference in various properties described above only results in small changes in device performance and does not seem to play a very crucial role in the measured range of power-conversion efficiencies. A tendency towards lower open-circuit voltages at higher polymer regioregularities had already been reported by others [17]. Veldman et al. [18] found that in donor–acceptor blends like P3HT:PCBM the opencircuit voltage is linearly dependent on the energy level difference between the highest molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor with a slope close to one. Also, Kirchartz et al. [19] suggested that under certain conditions, for instance through non-ideal recombination of charge carriers at the electrodes or an energetic distribution of charge-transfer states at the heterojunction, an increase in charge-carrier mobility could lead to a reduction of the open-circuit voltage.

3.2. Absorption and Visible Spectrum of P3HT

The UV-Vis spectra of commercially and indigenously synthesized polymer P3HT were measured in chloroform as presented in Figure 1.7. The UV-vis spectra of commercially available P3HT (Figure 1.7; left) consist of three absorption peaks, whereas indigenously obtained P3HT has broad absorption spectra. The optical band gap for these polymers are very similar and are found to be around 640nm (1.92 eV) and 650nm (1.90 eV) respectively calculated from the onset of those spectra. This shows that the synthesized P3HT is of high regioregularity, which means that broad absorption spectra is typically attributed to well-ordered regions of P3HT polymer chains with lamellar structures [20]. In contrast, the spectrum of synthesized P3HT does not show the signatures of any vibronic structures and instead exhibits one featureless absorption peak with its maximum at 460nm (2.74 eV). This in turn resembles the absorption of a highly diluted solution of regioregular P3HT, that is, under conditions that suppress intermolecular interactions that lead to ordering of polymer chains and interchain interactions [20]

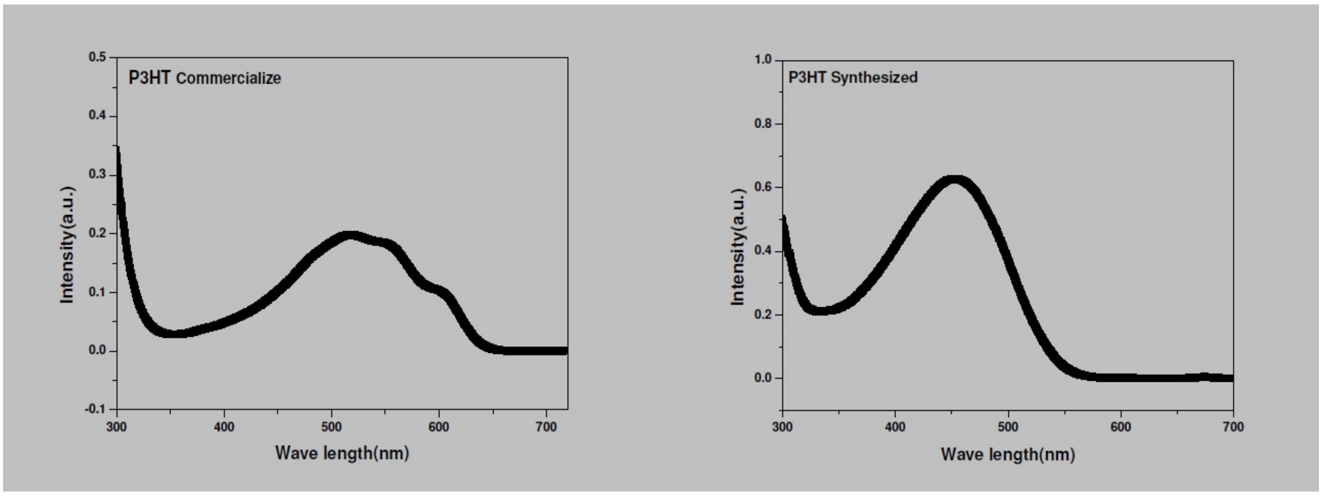


Figure 1.7: UV-Vis absorption spectra of P3HT in chloroform commercial (left) Synthesized (right)

We conclude from these observations that a substantial fraction of the polymer chains in films of commercially available P3HT and indigenously synthesized P3HT form well-ordered structures, and show the characteristics that are more towards regioregular P3HT.

4. Conclusion

We have been able to fabricate several OPV device based on commercially available P3HT and finding average PCE in the range of 1.0% to 1.30% in the device geometry of ITO/MoO3/P3HT:PCBM/Al in ambient condition. We have also fabricate the OPV device with PCE 1.26% using indigenous development of P3HT in the device geometry of ITO/MoO3/P3HT:PCBM/Al in ambient condition. We demonstrated that PCE (1.26%) of indigenous synthesis P3HT is comparable to commercial available P3HT (1.29%). In spite of the differences caused by the different polymers, solar cells prepared from both regioregular polymers in combination with PCBM showed comparable power-conversion efficiencies of around 1.26% to 1.29% without any major variation in the device parameters. The optical band gap for commercial polymer and synthesized polymer are very similar and are found to be around 640nm (1.92 eV) and 650nm (1.90 eV) respectively calculated from the onset of those spectra. This shows that the synthesized P3HT is of high regioregularity, which means that broad absorption spectra. It, thus, appears that regioregular P3HT films by using very high regioregular polymers give almost similar device performance.

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