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Optoelectronic Properties of 4,6-Dihydro-5H-Thieno [2,3-B]Pyrrol-5-One Based Conducting Polymers for Photovoltaic Applications

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Abstract

Energy materials have great demand in the global energy market today. Renewable sources of energy materials are sustainable sources of energy materials that have many advantages over traditional materials. Metal-based solar cells are first-generation materials that are commercialised due to their high efficiency. However, the high cost of these materials hinders their wide applications. In recent times organic polymers have attained a lot of interest due to their low cost, flexibility and broad absorption. This research reports a new polymer (4Z)-4-(thiophene-2- ylmethylidene)-4,6-dihydro-5H-thieno[2,3-b] pyrrole-5-one synthesised using Aluminium substituted catalyst which achieved high yield at ambient temperature. Separate polymerisation of the produced monomer was done using thiophene functionalised with bis (trimethylstannyl) to get polymer P1 which showed broad absorption in UV-visible region between 620 to 625nm showing Highest Occupied Molecular Orbital (HOMO) energy levels that are low lying. The heterojunction solar cells based on the new polymers were fabricated and tested. Based on the novel polymer, the solar cell devices demonstrated a remarkably high power conversion efficiency of 6.6%, an open circuit voltage (VOC) of 0.63, a fill factor of 0.52 and a short circuit current density (Jsc) of 6.3. For Polyvinyl Chloride (PVC) applications, the produced polymers are hence promising candidates. Furthermore, future studies involve doping of suitable metals like copper and samarium to the polymer to enhance the efficiency of the photovoltaic cells.

Keywords: *Aluminum Chloride, I-V Curve, Optical Properties Stille Coupling*

1.0 Introduction

Due to globalisation, the requirement of energy for various industrial utilisation has increased in the past decades. Fossil fuels are the major source of non-renewable sources and currently depletion of fossil fuels has led to a shift towards renewable sources of energy[1]. Among these photovoltaic cells are the best alternative source of energy. Silicon metal-based photovoltaic cells were first-generation cells which are commercialised. Due to their fabrication cost effectiveness, first-generation photovoltaic cells are replaced by organic polymer-based photovoltaic cells[2]. An enormous amount of work has been put into developing organic solar cells during the last

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three decades, even though photovoltaics, the process of converting sunlight into electricity, usually uses inorganic materials[3]. Small organic compounds (pigments) were initially used in the sector and as semiconducting polymers advanced, these materials were combined into organic solar cells, leading to notable advancements in recent years. Because of the sp^2 hybridisation of carbon atoms, semiconducting organic materials can conduct electricity and absorb light in the Ultraviolet (UV)-visible area of the solar spectrum. These electrons become delocalized due to the isomeric effect, which leads to a high level of electronic polarisability[4]. The relatively poor mobility of charges in these materials has a significant impact on the architecture and effectiveness of organic semiconductor devices and is almost distinct from inorganic solid-state semiconductors[5]. Another factor is exciton's short diffusion length especially in these organic materials is comparatively different from crystalline and inorganic semiconductors[6]. Substantial electric fields are typically needed to separate these excitons to become free charge carriers, which are desired end products for photovoltaic conversion, as they constitute a key intermediate in the process of solar energy conversion[7]. In the case of inorganic semiconductors, exciton binding energies are often higher[8]. The majority of organic semiconductors exhibit optical band gaps of about 2 eV, which are comparatively higher than those of silicon and severely restrict solar spectrum harvesting[9]. When it comes to organic photovoltaic solar cells, initially the two metal electrodes with various work functions were placed between a single organic layer[10]. Although low power conversion efficiency of 0.7% was reported in the early days for merocyanine dyes which was remarkabe[11]. The next innovation was the bilayer heterojunction concept, which included sandwiching two organic layers with distinct electron or hole-carrying characteristics between the electrodes[12]. In the interim, conjugated polymers developed into a mature field and the first single-layer devices based on these recently created materials were exhibited, but they also only displayed a power conversion efficiency of less than 0.1% in these polymer single-layer devices[13,14]. The development of bulk heterojunction devices with the incorporation of C60 and its derivatives has a great impact on solubility and was prompted by photoinduced electron transfer from optically excited conjugated polymers to the C60 molecule[15]. By coupling of polymers with Donor (D) and Acceptor (A) leads to the concept of bulk heterojunction[16]. To produce Bulk Heterojunction (BHJ) polymer solar cells, a mixture of electron-donating polymers and electron-accepting fullerene derivatives such as [6,6]-phenyl-C61-butyric acid methyl ester8 (PCBM), is used[17]. Both synthesis and manufacturing have a great role in the development of solar cell devices[18]. The donor-acceptor bilayer planar heterojunction concept can be utilised to increase the Power Conversion Efficiency (PCEs) of Organic Photovoltaic (OPVs) by reducing the bandgap energy between the Lowest Unoccupied Molecular Orbital (LUMO) of the donor and the HOMO of the acceptor. The n-type OPV devices were constructed using azo dyes of [6,6]-phenyl-C61-butyric acid methyl ester8 (PCBM)[19]. The fusion of thiophene and benzothiophene rings with various substitutions led to a series of new core structures with a wide range of biological activity[20]. They also have excellent optical, electrical, and mechanical properties, as well as solution processability and stability. When coupled with a conjugated polymer scaffold, major industrial dyes and pigments like diketopyrrolopyrrole or naturally occurring isoindigo have developed materials that work well for use in organic photovoltaics[21]. Wudl *et al*., created one of the first Organic Photo Voltaic cells (OPVCs) using two poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylenevinylene] (MEH-PPV). Additionally, PCEs were increased to 4-5% by using poly(3-hexylthiphene) (P3HT)26; this marked the introduction of novel OPVs to the worldwide market. The polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b'] dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) increased the efficiency of power conversion by 3% [22], Poly[N-9"-hepta-decanyl2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] yielded a PCE of 3.6% (PCDTBT). Isatin and related chemicals are widely used in chemical synthesis and come in a variety of natural hues that can be chemically created[23,24]. Since iso-indigo is the precursor of isatin, it has been sufficiently studied to be directly incorporated into functional fragments for organic electrical applications or OPV[25]. Formally, the isatin structure is formed by an amide that is connected to the aromatic ring paired with a ketone that withholds electrons. This donor-acceptor structure gives the chemical its vivid red hue. With the carbonyl amide, the ketone demonstrates orthogonal

reactivity and derivatisation was not too difficult[26]. To coordinate and enhance solar photon harvesting, narrow band gap molecules for OPVs are being constructed using alternating electron donor and electron-deficient units in the form of the donor-acceptor (D-A) technique[27,28]. Among these, the most promising polymers are Bbenzodithiophene (BDT) and thieno[3,4-b]-Thiophene (TT) with PCE of 7.7% [29]. The efficient synthesis of simple structures for the development of photovoltaic polymers has become an important research topic[30]. Prominent utilisation of exciton and free charges lead to PCE 19.2% by using a double-fibril network in single junction solar cells[31]. D-A combination generally plays a promising role in enhancing the efficiency of an Organic Solar Cell (OSC). The addition of covalent organic frameworks into the D-A structure incorporated excellent stability and humidity for solar cells with PCE 23.19% [31]. The lifetime of the photovoltaic device is important for practical applications, in addition to the efficiency of power conversion.

In simple terms, the concept of conjugated polymers for OPV applications needs to be designed using Density Functional Theory (DFT) calculations to attain narrow bandgap energies of monomers to increase the PCEs and other parameters like solubility, stability, flexibility and easy fabrication etc., should be considered. Upon designing, the monomers can be synthesised with a donor-acceptor approach. The optoelectronic characteristics of a completely π-conjugated chalcone, where the satin core is bonded with a thiophene ring, are presented in this study. The synthetic polymers' optoelectronic characteristics point to these materials as a viable option for use in organic solar cells.

2.0 Materials and Methods

2.1 Optoelectronic Properties of Polymers

The author has designed, synthesised and characterised the monomer along with polymer by Still polycondensation[32]. The synthetic polymer was employed in the creation of the solar cell application study. The absorption spectra of synthesised molecules were studied by using a UV-2600 (Shimadzu) Spectrophotometer. Indium Tin Oxide (ITO) glass plates measuring 250mm × 250mm x 1mm thickness and having an 80–100 resistance were bought from ultra-nanotech Private Limited in Bengaluru. De-ionised water, acetone (purity 99.5%) and Isopropanol (purity 99%) were used for cleaning the ITO substrates. Nitrogen filled glove box was used for the fabrication process. A spin coater was used for coating the active layer on the ITO substrate. Using Tauc plots and a Shimadzu UV-2600 spectrophotometer, the band gap energy was determined. New sport solar simulator Keithley 2400 digital source meter under 1.5G illumination with intensity at 100 $mWcm^{-2}$. The cyclic voltammetry of the thiophene-based polymers was measured using a CHI Company USA (Austin) type D630 electrochemical analyser with a scan rate of 100 mV s^{-1} and a current resolution of 80 nA. The preferred fluids were a nitrogen-saturated solution of 0.1M tetrabutylammonium hexafluorophosphate in acetonitrile, with glass carbon electrodes serving as the working, reference and counter electrodes, respectively and Ag/AgCl electrode and platinum electrode. K-Lyte software was used to create the graphs.

2.2 Molecular Design and Computational Details

The proposed monomer was subjected to DFT calculations along with the donating group. Gaussian 09 software was used to perform DFT calculations. Without any symmetry restrictions, optimizations of the geometry were made and frequency computations on the resulting optimised geometries revealed no erroneous frequencies.

2.3 Fabrication of Polymer Solar Cell Device

A solar cell device was fabricated to get polymer P1 with thiophene as the donating group was tested. The arrangement of the device was ITO/PEDOT: PSS/P1/MoO_3/Al. The photoprotective layer was removed from glass substrates coated with ITO by first washing them in acetone. After that, the substrates were immersed in an ultrasonic bath for five minutes in both acetone and 2-propanol. They were then dried for ten minutes at 80 °C and treated for twenty minutes with ozone. A layer of PEDOT-doped PSS was coated on an ITO substrate and heated at 160°C for 15 minutes. Further, fabrication was carried out in a glove box. To finish the device manufacturing, the active layer was treated with 10mg mL^{-1} of chlorobenzene and then MoO_3/Al was thermally deposited as the top electrode. A Keithley 2400 digital

source meter was used to characterise solar cells at 100mWcm^{-2} under 1.5G light.

3.0 Result and Discussion

3.1 UV-Visible Spectral Analysis for Polymers

The UV-visible spectral analysis of polymerP1 (BTMTTP) along with monomer TMTP were recorded in the range 350 to 700nm. For the monomer, a strong intense band was recorded at 419 nm. Product P1 (BTMTTP) was created by polymerising 2,5-bis (tributylstyannyl) thiophene while the monomer and donor group were still condensed. This resulted in a broad absorption peak at 663nm, which was caused by the prolonged conjugation of π-π* of the donating and withdrawing groups. These outcomes were similar to those of the donors who were reported for various acceptors[33].

3.2 Optical Properties of Polymers

The Tauc equation, presented in Equation 1, which Tauc provided in 1968, can be used to compute the bandgap energy.

$$(\alpha h\nu)^{\gamma}=A(h\nu-E_g) \qquad \text{Equation 1}$$

The monomer showed an absorption peak at a wavelength of 419nm. In the present work polymer P1 showed the Tauc plot with maximum absorption at 663nm and energy disparity (Eg) at 2.050eV. The introduction of

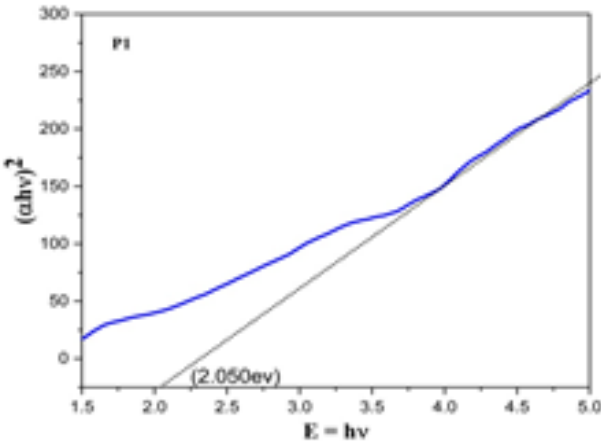


Figure 1. Tauc plots of P1.

cyclised moieties like thiophenes donating group resulted in the λ_{max} moving in the direction of the red region, which lowers the energy needed for the electrons to go to a higher excitation state and reduces the band gap energy. Figure 1 shows the polymer Tauc graphs.

3.3 Electrochemical Properties of Polymers

The redox behaviour of all three polymers was measured using cyclic voltammetry. Figure 2 indicates the Coefficient of Variation (CV) curve for each polymer was used to calculate the HOMO-LUMO energy levels using the empirical relation as shown in equations 1 and 2. Ferrocene was used as an external reference with E1/2 as 0.41V due

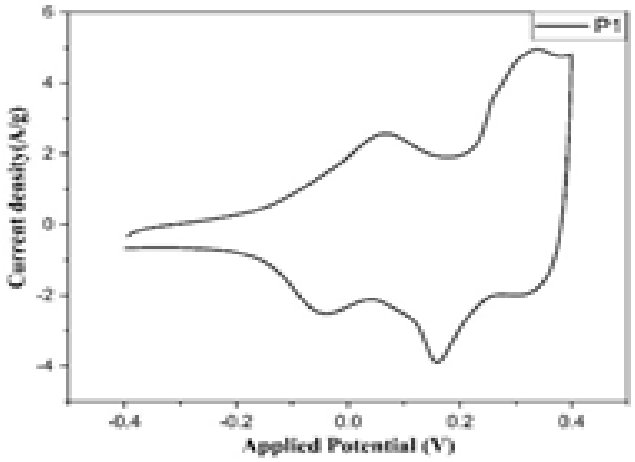


Figure 2. CV plots of P1.

to two peaks at 0.37 v and 0. 44 V [35,36]. Polymer 1 showed the onset oxidation at -0.1064 V and on-set reduction at -0.1762 V. The calculated HOMO and LUMO energy levels were at 4.28 eV and 4.21 eV respectively. Further, the band gap energy was calculated using the equation 7[37]. In equation 8, the λ onset corresponds to the longest wavelength of the exciton absorption band obtained from the UV-visible spectrophotometer. The calculated Eg is shown in the Table 1S. There is good agreement between the bandgap energy and the optical band gap energy that was obtained using cyclic voltammetry data. As a result, it was shown that continuous conjugation (π-π* and n-π*) aids in lowering the HOMO-LUMO energy levels, increasing the conductivity of the polymer[38].

$$E\,(HOMO) = -\,e\,[E_{oxd}^{onset} + 4.4] \qquad \text{Equation 6}$$

$$E\ (LUMO) = -\ e\ [E_{red}^{onset} + 4.4] \qquad \text{Equation 7}$$

$$E_g = 1240/\lambda_{onset} \qquad \text{Equation 8}$$

3.4 DFT Calculations

Gaussian 09 ab initio quantum chemistry software was used to do DFT calculations for the TMTP-based polymer P1 to comprehend the generated molecule's optical and electrical characteristics better. The Hartee unit (1 Hartee unit = 27.2114 eV) is used to express the HOMO-LUMO energy levels, which are then converted to eV. Theoretically, the monomer TMPT was found to have a bandgap of 3.1 eV, which indicates that its highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO) energies are -0.08319 and -0.19731, respectively[39,40]. The HOMO-LUMO energy for P1 BTM-TTP was found to be -0.18743 and -0.09279 respectively with a band gap of 2.57 eV. This indicates that as the electron donors donated the electron towards the acceptor thereby increasing the π-π* and n-π* conjugation augmented the HOMO energy levels while decreasing the LUMO energy levels. The absorbance spectra were expanded due to a substantial intramolecular charge transfer from the donor to the acceptor type and decreasing the bandgap energy leading to form more efficient conducting materials. A similar trend was observed in the literature[41,42].

3.5 Photovoltaic Properties

The PCE for the P1-based solar cell devices was 6.6%. The PCEs for P1 were attained at 6.6mA cm^{-2}. 0.63V stands for both the short circuit and open voltage currents and 0.52 for the fill factor. The synthesised monomer has the potential to be a novel building block for high-performance solar applications, according to the obtained results. Solar cell devices and their performance based on three different polymers with 6 varying resistances are represented in Figure 3 and Table 1.

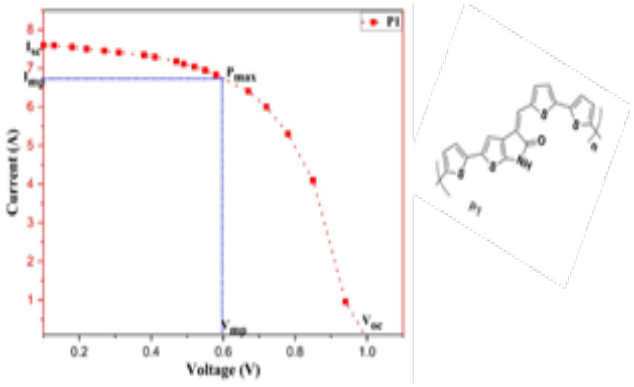


Figure 3. I-V curves of PSC's of P1.

4.0 Discussions

According to report 32, the polymer was synthesised by still polycondensation of the monomer thieno[2,3-b] pyrrole-5-one with a donating group in the presence of MOF RIT 62-Cu/Pd, as illustrated in Figure 1S. The polymer's structure was verified by 1H NMR and GPC. The P1's 1H NMR results are included in the supplemental data. Using gel permeation chromatography, the polymer's Polydispersity Index (PDI), weight-average Molecular Weight (Mw)40, and Number-average Molecular weight (Mn) were investigated. Figure 2S displays the results of the polydispersity index, weight-average Molecular Weight (Mw), and Number-average Molecular weight (Mn). The thermal stability of the polymer was investigated using

Table 1. PCE and I-V parameters of the 150 µM thick polymer P1

Sample	I_{mp} (mA cm^{-2})	V_{mp} (V)	FF	PCE [η] expressed in %
Polymer P1	7.5	0.31	0.30	3.8
	7.3	0.39	0.37	4.7
	6.8	0.44	0.39	4.9
	6.5	0.54	0.46	5.85
	6.3	**0.63**	**0.52**	**6.6**
	6.0	0.69	0.46	5.9

thermogravimetric analysis. The thermograms of the polymer are shown in Figure 3S. The results show that the polymer was stable beyond 460°C and that no discernible thermal transition was seen until 220°C. Polymer weight loss is compiled in Table 2S.

5.0 Conclusions

Finally, we have described the TMTP-based polymer that uses thiophene as a donating group to produce the appropriate conjugated molecules. To create polymers P1, the new monomer was polymerised independently using bis(trimethylstannyl) functionalised thiophene. The synthesised polymer exhibited low-lying HOMO energy levels and wide absorption in the UV-visible range. The heterojunction solar cells were made and tested using the new polymers. The solar cell devices exhibited a 6.3 short circuit current density (Jsc), 0.63 open circuit voltage (Voc), 0.52 fill factor, and 6.6% power conversion efficiency, all of which were based on the new polymer P1. The results show how crucial it is to choose the right donor/acceptor material to create high-performance PSCs. Additionally, this work offers a fresh perspective on the characteristics of TMTP-based polymers and how well they function as semiconductors in solar energy applications. Currently, the energy efficiency by selective doping of metals such as copper, zinc and samarium is also being enhanced. Pilot studies have shown that the use of metals along with this polymer will undoubtedly have a significant impact on solar cell performance, including variations in concentration, film thickness, donors, etc.

6.0 Acknowledgements

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7.0 Authors Contribution

Mrs. Maya Pai has carried out the synthesis of monomers and polymers. Dr. Basappa C. Yallur has contributed to the characterisation of polymers. Dr. Vinayak Adimule has carried out the photovoltaic applications of polymers. Dr. Sheetal Batakurki has contributed to the draft of the manuscript.

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