



Perylene diimide-thiophene based polymer acceptors for solution-processed all polymer bulk hetro-junction solar cells

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Abstract : Perylene diimide (PDI) and thiophene/bithiophene based polymers such as P-T-PDI-H and P-BT-PDI-H were designed and synthesized by Suzuki coupling method. The polymers exhibited excellent thermal stability with decomposition temperatures of >300 °C with broad and strong absorption in the visible region (300-800 nm). These two polymers showed highest occupied molecular orbital levels of -5.38 and -5.37 eV and lowest unoccupied molecular orbital levels of -3.90 eV, respectively. The non-fullerene PDI polymer acceptor based device, without thermal annealing afforded a maximum power conversion efficiencies of 0.11% and 0.06%, respectively with P3HT polymer donor.

Keywords : Perylene, Suzuki coupling, low band gap, Organic solar cells.

Introduction:

Plastic solar cells (PSCs) based on solution processable semiconducting polymers have been a world-wide budding field of interest as a renewable energy source [1]. The PSCs produced maximum 13.2% power conversion efficiency (PCE) in 2016, it is comparable to the conventional silicon solar cells [2]. The market availability of the PSCs is now also a challenging task due to high production cost of the acceptor materials [3]. Tang reported the non-fullerene acceptors (NFAs) such as perylene diimide (PDI) in 1986 [4]. This historic achievement resulted the synthesis of various NFAs. Various NFAs are available in the PSCs including PDIs, naphthalene diimide (NDI), diketopyrrolopyrrole (DPP), bezodiathiazole (PDT) based polymers or small molecules generally used as an acceptors in PSCs [5-6].

The PDIs showed most potent acceptor in the PSCs field due to low cost, broad and strong absorption, solubility, environmental stability and thermal stability [7]. This leads to more number of papers and review article are published about the PDI based NFAs [8]. Various PDI based acceptors are available such as small molecules, star shaped small molecules, N- or bay bridged polymers [9-10].

In 2011, Zhou et al., reported all polymer PSCs based on six bay substituted D-A type PDI polymers P-1 to P-6 as an acceptor achieved the PCE as follows 0.21%, 0.20%, 0.17%, 0.11%, 0.18%, 0.29%, respectively for P-1 to P-6 with P3HT polymer donor [11]. Zhan et al., reported D-A type PDI polymers with dithienothiophene or N-dodecyl dithienopyrrole (P-7 to P-9) and achieved the PCE of 0.94%, 0.77% and 1.1%, respectively [12]. Kotowski et al., reported polymer PEK-3 with a varying PCE from 0.03% to 1% [13]. In 2015, Dai et al., reported PDI polymer and a PCEs of 1% with a V_{oc} of 0.76 V, J_{sc} 3.29 mA cm⁻² and a FF of 40% [14]. Fascinated by the foresaid result, in this paper we report the synthesis and characterization of bay

substituted D-A type copolymers of PDI and thiophene or bithiophene as an acceptor for the solution processable all polymer BHJ-PSCs.

Material and Methods:

High purity analytical grade (A.R) chemicals were purchased and used as received from the reputed chemical suppliers. N,N'-bis-(hexyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid diimide (Br-PDI-H), thiophene or bithiophenediboronic acid pinacol esters (TDBE and BTDBE) were prepared from the previous reported work [15-16].

Detection Method:

Fourier transform-infrared (FT-IR) spectra were recorded in transmittance mode for the molecules over the range of 500-4000 cm^{-1} by the KBr method using Shimadzu IR Affinity UV-vis spectra in solution and film were measured with the Hitachi U-2910 spectrophotometer. Fluorescence spectra were measured by using Hitachi F-7000 fluorescence spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Bruker 400 MHz and 100 MHz spectrometer respectively using CDCl_3 as the solvent. The electrochemical behavior of the polymers were studied by using CH Instrument workstation in 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6)/DCM as the supporting electrolyte at a scan rate of 25 mV s^{-1} . It contains three electrode system, Platinum (Pt) working electrode, a standard calomel reference electrode, Pt disc as counter electrode. Thermogravimetric analysis (TGA) was conducted under the inert N_2 gas atmosphere with a SDT Q600 instrument in CECRI Karikudi. The sample was heated at a heating rate of 20 $^\circ\text{C min}^{-1}$ in the temperature range from 35 to 800 $^\circ\text{C}$.

Fabrication and Characterization of Photovoltaic Devices:

The BHJ-PSCs were fabricated by the following configuration:

ITO/PEDOT:PSS/P3HT:Polymers/LiF/Al. Each glass substrate was coated with a transparent ITO electrode (110 nm thick). The ITO-coated glass substrates were ultrasonically cleaned with detergent, distilled water, acetone, and isopropyl alcohol. The 35 nm thick PEDOT:PSS (Clevios PH1000) was spin-coated onto the pre-cleaned and UV ozone treated ITO substrate followed by annealing in air at 150 $^\circ\text{C}$ for 30 min. The P3HT:Polymers blend was prepared in chlorobenzene (CB) or chloroform (CF), at a 1:1 weight ratio with a total blend concentration of 15 mg/mL . The blending solution was filtered with 0.45 μm PTFE (hydrophobic) syringe filter. The active layer was spin-coated and dried at room temperature for 1 h and the thickness of the active layer was 76-82 nm. Lithium fluoride (LiF) (1 nm) and aluminum (Al) cathodes (100 nm) were deposited on top of the active layer under vacuum less than 8.0×10^{-6} kPa. The evaporation thickness was controlled by a quartz crystal sensor. The film thickness was measured with a α -Step IQ surface profiler (KLA Tencor, San Jose, CA). The performance of the BHJ-PSCs were measured using calibrated air mass (AM) 1.5G solar simulator (OrielR SolSM-ITM Class AAA solar simulator, models 9404SM-1) with a light intensity of 100 mW cm^{-2} adjusted using a standard PV reference cell (2 $\text{cm} \times 2$ cm monocrystalline silicon solar cell, calibrated at NREL, Colorado, USA) and a computer controlled Keithley 236 source measure unit [17].

Experimental:

General procedure for the synthesis of polymers:

In a 3 neck round bottom (R. B) flask 0.433 g of Br-PDI-H [15], (0.5 mmol) was dissolved in 30 mL of dry THF and purged with N_2 for half an hour. To this 2 mole % of $\text{Pd}(\text{PPh}_3)_4$ (0) catalyst was added. The temperature was raised to 50 $^\circ\text{C}$ and 5 mL of 2 M aq. K_2CO_3 was added. Finally, to the above reaction mixture 1 mmol of TDBE/BTDBE [16] was added and refluxed overnight under inert N_2 atm and the mixture was extracted with CH_2Cl_2 , dried over Na_2SO_4 , and concentrated. The insoluble impurities were removed by washing the precipitate in hot CHCl_3 (100 mL). The filtrate was concentrated to 20 mL, then dropped into 60 mL acetone. The black precipitate was filtered, and washed with acetone. Finally, the polymers P-T-PDI-H and P-BT-PDI-H were obtained as dark black powder.

Analytical data for the polymer P-T-PDI-H

Black powder, yield-87%. $^1\text{H NMR}$ [400 MHz, CDCl_3 , $\delta=7.26$ ppm, s], 8.56 (b, perylene H), 8.19-8.17 (b, perylene H), 8.00-7.901 (b, perylene H), 7.43-7.42 (b, thiophene H), 7.19-7.12 (b, thiophene H), 4.19-4.09 (m, methylene H), 2.18-0.78 (b, methyl H). Mw, 14,000; Mw/Mn, 1.5.

Analytical data for the polymer P-BT-PDI-H

Dark black powder, yield-59%. $^1\text{H NMR}$ [400 MHz, CDCl_3 , $\delta=7.26$ ppm, s]: 8.59-8.57 (b, perylene H), 8.52-8.50 (b, perylene H), 8.24-8.23 (b, perylene H), 7.22-7.21 (b, thiophene H), 7.18-7.17 (b, thiophene H), 7.13-6.90 (b, thiophene H), 4.19-4.03 (b, methylene H), 1.66 (t, 2H), 1.66-0.75 (b, Hexyl group H). Mw, 11,000; Mw/Mn, 1.8.

Results and Discussion:

The synthesized polymers were freely soluble in most of the organic solvents. Absorption spectra of the polymers were performed in CHCl_3 (1.0×10^{-5} M) and spectra was given in Figure 2 and Table 1. As compared to the, Br-PDI-H, polymers showed the broad and strong UV-vis absorptions. The absorption band appeared at 288-351 nm was due to the $\pi-\pi^*$ transition of the PDI core groups. Second absorption band between 408-483 nm was assigned to the electronic S_0-S_2 transition which confirms the donor thiophene substituents in the bay position. Appearance of the third band between 563-625 nm was attributed to the S_0-S_1 transition of the conjugated thiophene moiety. The optical band gaps of the polymer P-T-PDI-H and P-BT-PDI-H in solution state could be estimated to be 1.73, and 1.59 eV respectively.

Table 1 UV-vis, FL and CV data for the PDI polymers.

Polymers	λ^{abs} (sol) nm ^a	E_g^{opt} (eV) e sol ^a	E_{onset}^{red} e V	E_{onset}^{ox} eV	HOMO (eV) ^b	LUMO (eV) ^c	E_g^{ele} (e V) ^d
Br-PDI-H	255, 386, 520	2.25	-	-	-	-	-
P-T-PDI-H	288, 408, 563	1.73	-0.23	1.25	-5.38	-3.90	1.58
P-BT-PDI-H	351, 483, 625	1.59	-0.20	1.28	-5.37	-3.90	1.47

a. $E_g^{opt} = (1240/\text{absorption edge})$ eV b. HOMO = $-(4.8 - E_{1/2, \text{Fc}/\text{Fc}^+} + E_{onset}^{ox})$ c. LUMO = $-(4.8 - E_{1/2,$

$\text{Fc}/\text{Fc}^+ + E_{onset}^{red})$ d. $E_g^{ele} =$

HOMO-LUMO.

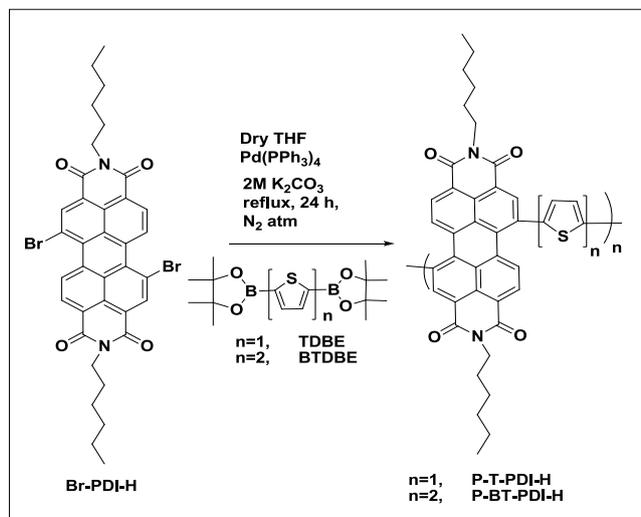


Figure 1 Scheme for the synthesis of P-T-PDI-H and P-BT-PDI-H polymers.

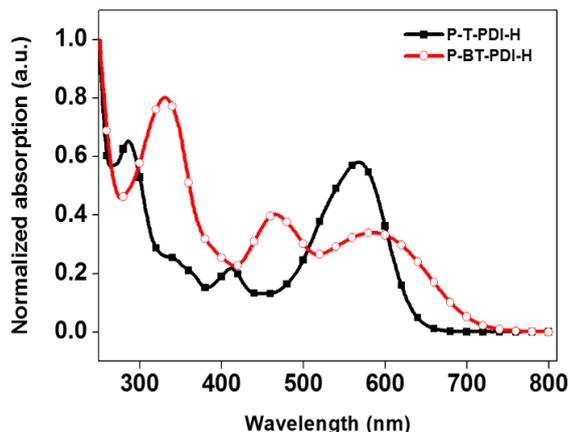


Figure 2 UV-vis spectra of polymers P-T-PDI-H and P-BT-PDI-H in CHCl_3 solution.

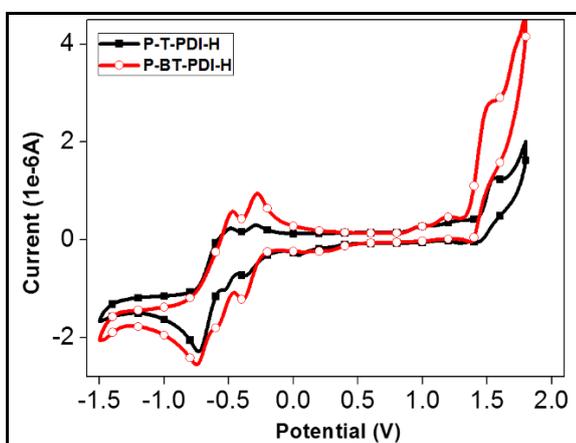


Figure 3 CV graph of polymers P-T-PDI-H and P-BT-PDI-H in DCM with 0.1 M Bu_4NPF_6 as a supporting electrolyte at a scan rate of 25 mV s^{-1} .

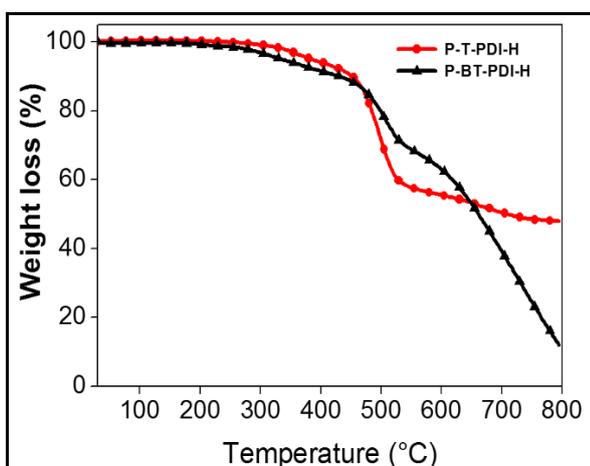


Figure 4 TGA graph of polymers P-T-PDI-H and P-BT-PDI-H.

CV analysis for the polymers P-T-PDI-H and P-BT-PDI-H were given in Figure 3 and the data were presented in the Table 1. The calculated HOMO and LUMO values of the polymers P-T-PDI-H and P-BT-PDI-H were -5.38, -5.37 eV, and -3.90 eV respectively by assuming that the energy of Fc/Fc^+ was -4.8 eV. The electrochemical band gaps of the polymers P-T-PDI-H and P-BT-PDI-H were 1.58, and 1.47 eV respectively

Thermogravimetric analysis (TGA) graph of the polymers were given in Figure 4. TGA confirmed the good thermal stability of the P-T-PDI-H and P-BT-PDI-H polymers. The 5% weight losses of the polymers on heating were found 392 °C, and 330 °C respectively. So that the polymers were stable up to 300 °C.

The current-voltage (I–V) graph for the polymers P-T-PDI-H and P-BT-PDI-H in BHJ-PSCs with P3HT donor was shown in Figure 5, and the corresponding open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), and the PCE were shown in Table II. The photovoltaic study exposed that J_{sc} of polymers P-T-PDI-H was maximum, which resulted the highest PCE of 0.11%. The J_{sc} follows the order of P-T-PDI-H ($\sim 1 \text{ mA cm}^{-2}$) > P-BT-PDI-H (0.73 mA cm^{-2}). The polymers P-T-PDI-H and P-BT-PDI-H were showed the V_{oc} of 0.36V and 0.42V respectively. The ultrafast self-aggregation of small molecules resulted the poor FF of 21-34%.

Aforesaid reasons, were resulted the poor performance of BHJ-PSCs. The PCE of the small molecules was comparable with the other D-A-D type PDI small molecules [11].

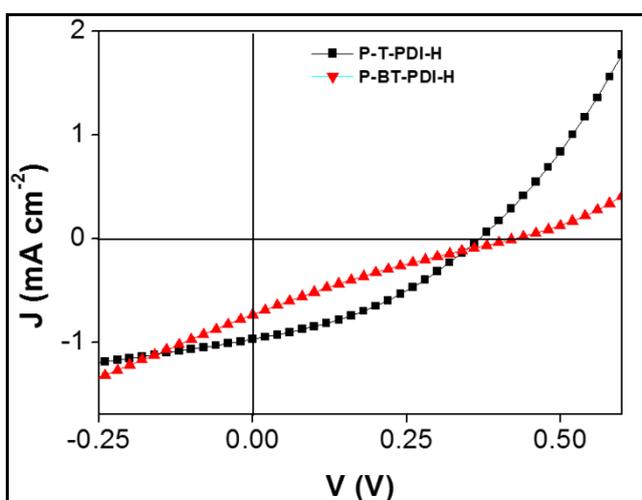


Figure 5 I-V graph of PDI polymers with P3HT polymer donor in BHJ-PSCs.

Table 2 Photovoltaic property of P3HT: Polymers (w/w; 1:1) in conventional BHJ-PSCs device structure under 1.5G illumination with an intensity of 100 mW cm^{-2} .

Polymers	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
P-T-PDI-H	0.36	0.98	34	0.11
P-BT-PDI-H	0.42	0.73	21	0.06

Conclusions:

New bay substituted, D-A type PDI polymers namely, P-T-PDI-H and P-BT-PDI-H were synthesized by Suzuki coupling method and characterized by FT-IR, ^1H NMR, and UV-vis studies. The polymers showed broad and strong absorption extended up to 800 nm which ultimately reduced the band gap value to $< 2 \text{ eV}$. The polymers showed excellent thermal stability above 300 °C. The polymers P-T-PDI-H and P-BT-PDI-H showed a maximum PCE of 0.11% and 0.06% respectively in BHJ-PSCs device structure with P3HT polymer donor.

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