

Synthesis and Characterization of New Dihydroindolo[3,2-*b*]indole and 5,6-Bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole-Based Polymer for Bulk Heterojunction Polymer Solar Cells

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We have designed and developed a new ladder type tetra fused π -conjugated building block such as dihydroindolo[3,2-*b*]indole (DINI) and investigated its role as an electron rich unit. The photovoltaic properties of a new semiconducting π -conjugated polymer, poly[[5,10-bis(octyl)-5,10-dihydroindolo[3,2-*b*]indole-[5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole]], represented by PDINI-OBTC8 are described. The new polymer PDINI-OBTC8 was synthesized in donor-acceptor (D-A) fashion, where fused π -conjugated tetracyclic DINI, and 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl) benzo[*c*][1,2,5]thiadiazole (OBTC8) were employed as electron rich (donor) and electron deficient (acceptor) moieties, respectively. The conventional bulk heterojunction (BHJ) device structure ITO/PEDOT:PSS/PDINI-OBTC8:PCB₇₁M/LiF/Al was utilized to fabricate polymer solar cells (PSCs), which comprises the blend of PDINI-OBTC8 and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) in BHJ network. A BHJ PSC that contain PDINI-OBTC8 delivered power conversion efficiency (PCE) value of 1.68% with 1 vol% of 1,8-diiodooctane (DIO) under the illumination of A.M 1.5G 100 mW/cm².

Key Words : Fused π -conjugated polymer, Dihydroindolo[3,2-*b*]indole, Low band gap polymer, Bulk heterojunction polymer solar cells

Introduction

During the past decade, bulk heterojunction (BHJ) polymer solar cells (PSCs) were given a strong consideration for their potency to convert solar energy to electrical energy. The exceptional merits of BHJ PSCs such as large area devices, light weight, low cost fabrication, and flexibility make them to view as an alternative to inorganic solar cells.¹⁻⁶ BHJ PSCs comprise a photoactive layer, which is an interpenetrating network formed by homogeneous mixture of π -conjugated polymer (electron donor) and fullerene derivative (electron acceptor). Excellent power conversion efficiency (PCE) was achieved using π -conjugated polymer donors in BHJ architecture, in which the polymer donor was synthesized in electron rich (D)-electron deficient (A) fashion, *i.e.*, by copolymerizing D and A units.^{5,6}

Generally, the donor materials should possess few mandatory features like deep highest occupied molecular orbital (HOMO) energy level, broad absorption and high charge carrier mobility to bring out high PCE.^{3,4} Various donor materials were synthesized in order to accomplish the above ideal characteristics and successfully gifted excellent PCE in BHJ network with fullerene derivative as an electron

acceptor.⁷⁻¹⁰ Out of the various donors that are existed, ladder type fused π -conjugated systems have an added advantage such as extended π -conjugation, which results in enhanced delocalization of π -electrons to attain effective π -conjugation length that favors low band gap (LBG).¹¹ The polymers with LBG can harvest more solar flux, there by generating maximum number of excitons, which can dissociate at BHJ interface.¹² So, it is quite obvious that the π -conjugated polymers with planar, fused backbone units exhibit high carrier mobility along with broad absorption spectrum.¹³⁻¹⁵ A precise and thorough investigation is required to gain deep insight into the structural features of fused π -conjugated systems, which can excel the photovoltaic performance.

In this regard, we designed and synthesized a new fused π -conjugated building block namely dihydroindoloindole (DINI) derivatives. The DINI is an electron rich planar aromatic fused structure with two nitrogen atoms, which can be easily substituted with alkyl chains for better solubility of the polymer. These interesting features push us towards the synthesis of π -conjugated polymers using DINI as an electron rich moiety in D-A copolymer system. Though, there have been quite interesting skeletal characteristics for DINI,

a deep exploration of DINI-based polymers is not yet reported for BHJ PSCs application. Owczarczyk *et al.* reported DINI based polymers and shown that the DINI is an effective backbone for PSC applications.¹⁶

In this report, we copolymerized DINI with 5,6-bis(octyl-oxy)-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (OBTC8) and investigated the photovoltaic properties of the BHJ PSCs. By introducing *n*-octyl side chains on two free nitrogen atoms of DINI, better solubility with high molecular weight (M_w) was achieved. The strong π - π interactions among the polymer chains is expected to allow a broad absorption, there by delivering an optimum PCE for corresponding PDINI-OBTC8 based BHJ PSCs. The preliminary PCE results signify that the D-A copolymers consist of DINI as an electron rich unit can be used as an excellent donor unit for realizing high PCE.

Experimental

Materials and Characterization. All chemicals were purchased from Aldrich Chemical Co., TCI, Alfa Aesar, and they were used without further purification unless otherwise noted. The PC₇₁BM was purchased from Solemme BV. The polymerization glassware and syringes were dried at 120 °C for 24 h. Tetrahydrofuran (THF) and toluene were distilled from sodium and benzophenone under N₂ atmosphere. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury Plus 300 and 600 MHz spectrometer in CDCl₃ using tetramethylsilane as an internal reference. The chemical shifts were accounted in ppm related to the singlet of CDCl₃ at 7.26 and 77 ppm and CD₃COCD₃ at 2.09 and 30.60 ppm for ¹H and ¹³C NMR, respectively. The UV-visible absorption spectra were recorded on a JASCO V-570 spectrophotometer at room temperature. Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/SDTA 851e, under N₂ atmosphere at heating rate of 10 °C/min. The weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (PDI) were determined against polystyrene as standard by GPC using PL gel 5 μ m MLXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent. Cyclic voltammetry (CV) studies were carried out in a 0.1 M solution of tetrabutylammonium tetrafluoroborate in anhydrous acetonitrile at a scan rate of 100 mV/s using CHI 600C potentiostat (CH Instruments). A three electrode cell with platinum electrode as the working electrode, Ag/AgCl as the reference electrode and a platinum wire as the counter electrode were used. Thin polymer films were coated on Pt electrode and dried before the experiment.

Device Fabrication of BHJ PSCs. The ITO and glass substrates that have been used for fabrication were ultrasonically cleaned in detergent, water, acetone, and isopropyl alcohol (IPA). Then, a 45 nm thick layer of PEDOT:PSS (Clevious P) was coated on the electrodes by spin coating a solution of PEDOT:PSS diluted with IPA, with the dilution ratio being 1:2. The coated buffer layer was cured at a temperature of 150 °C for 10 min in glove box. A 90 nm

thick active layer of polymer:PC₇₁BM was spin coated using a mixture of polymer:PC₇₁BM (8 mg:16 mg) that was dissolved in 1 mL of chlorobenzene (CB) and further mixed with 1 vol% of 1,8-diiodooctane (DIO). The thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of \pm 1 nm. AFM images were acquired with a XE-100 (park system corp.) in tapping mode.

A 100 nm thick Al cathode with a defined area of 0.36 cm² and 0.7 nm thickness of LiF was deposited via evaporation on the active layer. The performance of BHJ OPV were measured using a calibrated AM1.5G solar simulator (Oriel[®] Sol3A™ Class AAA solar simulator, models 94043A) with a light intensity of 100 mW/cm² adjusted using a standard PV reference cell (2 cm \times 2 cm mono crystalline silicon solar cell, calibrated at NREL, Colorado, USA) and a computer-controlled Keithley 236 source measure unit. Incident photon to current conversion efficiency (IPCE) spectrum was measured using Oriel[®] IQE-200™. All fabrication steps and characterization were carried out in an ambient environment without a protective atmosphere. While measuring the *J-V* curves for OPV, a black mask was used and only the effective area of the cell was exposed to light irradiation. The OPV device data's were reported in this article, which was confirmed for more than 5 iteration under the same condition.

Synthesis of 2,2'-Dinitrotolane (1). Pd(OAc)₂ (0.45 g, 2 mmol), triphenylphosphine (0.52 g, 2 mmol) and cuprous iodide (0.38 g, 2 mmol) were added to mixture of acetonitrile (60 mL) and water (20 mL). 1-Iodo-2-nitrobenzene (10 g, 40 mmol) and triethylamine (16.7 mL 120 mmol) were added to the above mixture. The reaction mixture was purged with 3000 cm³ of acetylene gas and stirred at room temperature for 12 h. The reaction mixture was extracted with methylene chloride MC (250 mL), and organic phase was washed with water and brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure to get crude product. The crude was then purified by column chromatography on silica gel using (hexane:ethylacetate (EA), 9:1, (v/v)) to give 2,2'-dinitrotolane as a dark brown solid (7 g, 65%). ¹H NMR (CDCl₃, 300 MHz) δ 8.17 (d, 2H), 7.86 (d, 2H), 7.70 (t, 2H), 7.58 (t, 2H); ¹³C NMR (CDCl₃, 300 MHz) δ 163.81, 149.48, 135.44, 133.48, 132.16, 125.85, 121.27, 93.89, 62.18, 14.22.

Synthesis 1,2-Bis(2-nitrophenyl)ethane-1,2-dione (2). Under N₂ atmosphere, 2,2'-dinitrotolane (7 g, 26.1 mmol) was added to ethylene dichloride (200 mL) at room temperature. Aqueous KMnO₄ (20.6 g, 130.5 mmol), ADOGEN 464 (10 mL) and acetic acid (15 mL) were added to above reaction mixture. The reaction mixture was refluxed for 3 h, cooled to room temperature and treated with sodium bisulfate and extracted with MC (200 mL). The organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure. The oily layer was purified by column chromatography on silica gel using MC as an eluent give yellow solid (3 g, 38%). ¹H NMR (CDCl₃, 300 MHz) δ 8.31 (d, 2H), 7.94 (t, 2H), 7.81 (d, 2H), 7.73 (t, 2H); ¹³C NMR

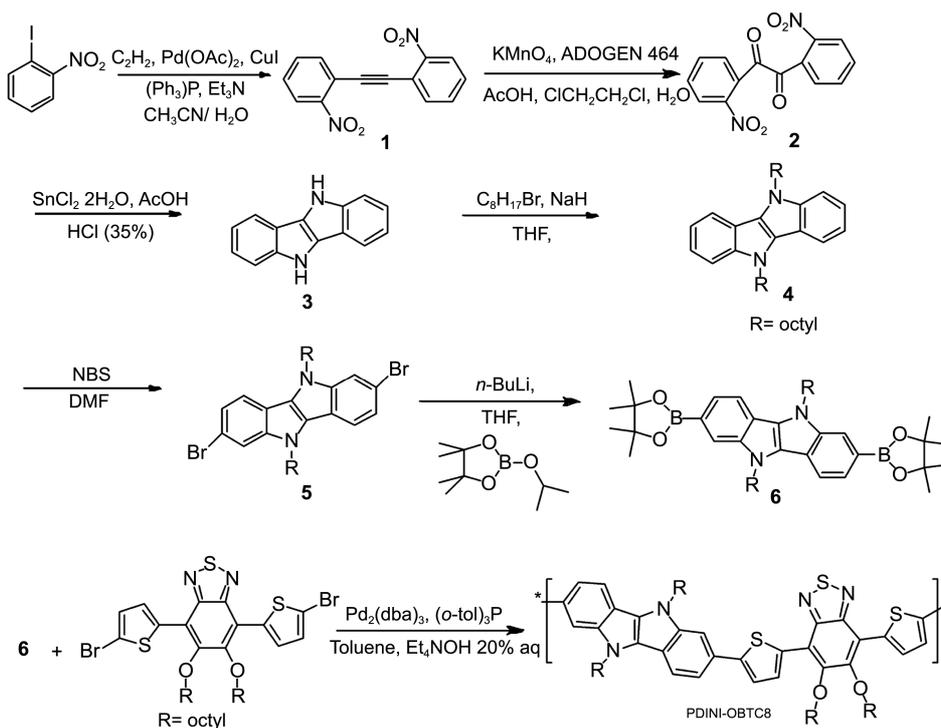
(CDCl₃, 300 MHz) δ 187.53, 147.50, 135.38, 132.38, 132.68, 132.15, 129.39, 124.14.

Synthesis of 5,10-Dihydroindolo[3,2-*b*]indole (3). Stannous chloride dihydrate (22.5 g, 100 mmol) and HCl (14 mL, 1 N) was added to the mixture of 1,2-bis(2-nitrophenyl)ethane-1,2-dione (3 g, 10 mmol) in warm acetic acid (60 mL). Then the reaction mixture was heated to 80 °C and stirred for 5 h at same temperature. Upon completion of the reaction, the fine yellow precipitate was filtered and washed with acetic acid, HCl and ethanol. The resulting solid was dried under reduced pressure to give yellow solid (0.8 g, 39%). ¹H NMR (300 MHz, acetone-*d*₆) δ 7.79 (d, 2H), 7.71 (t, 2H), 7.54 (d, 2H), 7.22 (t, 2H); ¹³C NMR (acetone-*d*₆, 300 MHz) δ 206.29, 205.88, 141.83, 122.54, 119.22, 118.43, 113.00.

Synthesis of 5,10-Di(*n*-octyl)-5,10-dihydroindolo[3,2-*b*]indole (4). Under N₂ atmosphere, NaH (0.65 g, 27.12 mmol) was added slowly to the mixture of 5,10-dihydroindolo[3,2-*b*]indole (1.4 g, 6.78 mmol) in THF (30 mL) at room temperature. *n*-Bromooctane (3.93 g, 20.36 mmol) was added to reaction mixture and refluxed for overnight. Water (30 mL) was added slowly to the solution and extracted with MC (100 mL). The aqueous layer was separated and the organic layer was dried over anhydrous MgSO₄ to get brown residue. The residue was then purified by column chromatography on silica gel using hexane as an eluent to give white solid (2 g, 69%). ¹H NMR (CDCl₃, 300 MHz) δ 7.82 (d, 2H), 7.44 (d, 2H), 7.30 (t, 2H), 7.16 (t, 2H), 4.35 (t, 4H), 1.91 (m, 4H), 1.18-1.44 (m, 20H), 0.86 (t, 6H); ¹³C NMR (CDCl₃, 300 MHz) δ 140.95, 126.17, 121.32, 117.78, 114.56, 109.91, 49.56, 45.40, 31.74, 31.12, 29.26, 29.02, 27.00, 22.53, 14.02.

Synthesis of 2,7-Dibromo-5,10-dioctyl-5,10-dihydroindolo[3,2-*b*]indole (5). Under N₂ atmosphere, a solution of *n*-bromosuccinimide (NBS) (1.48 g, 8.4 mmol) in dimethylformamide DMF (20 mL) was added to a solution of 5,10-di(*n*-octyl)-5,10-dihydroindolo[3,2-*b*]indole (1.8 g, 4.2 mmol) in DMF (20 mL) at room temperature. After stirring for 3 h, the reaction mixture was poured into water and filtered to obtain crude product. The crude was purified by column chromatography using hexane as an eluent to give white solid (1.3 g, 53%). ¹H NMR (CDCl₃, 300 MHz) δ 7.72 (d, 2H), 7.64 (d, 2H), 7.30 (dd, 2H), 4.46 (d, 4H), 1.93 (m, 2H), 1.17-1.36 (m, 48H), 0.88 (m, 12H). ¹³C NMR (CDCl₃, 300 MHz) δ 138.31, 123.00, 118.42, 115.97, 112.39, 110.31, 109.96, 42.62, 28.74, 27.30, 23.89, 19.73, 10.96.

Synthesis of 5,10-Bis(*n*-octyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,10-dihydroindolo[3,2-*b*]indole (6). *n*-BuLi (3.82 mL, 6 mmol) was added dropwise to a solution of compound 5 (1.2 g, 2 mmol) in THF (25 mL) at -78 °C under N₂ atmosphere and resulting mixture was warmed to room temperature for 1 h. Again the reaction mixture was cooled down to -78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.02 mL, 6 mmol) was added. The solution was slowly warmed to room temperature and allowed to stir overnight. Cold water (50 mL) was added to the reaction mixture and extracted with EA (50 mL). The organic layer was dried over anhydrous MgSO₄ and solvent was removed under reduced pressure. Crude was purified by column chromatography on silica gel (hexane: EA, 7:3 v/v) to get a yellowish compound (0.7g, 53%). ¹H NMR (CDCl₃, 600 MHz) δ 7.95 (s, 2H), 7.84 (d, 2H), 7.62 (d, 2H) 4.54 (t, 4H), 1.98 (m, 2H), 1.40 (s, 28H), 1.14-1.50 (m, 18H), 0.8-0.9 (m, 6H); ¹³C NMR (CDCl₃, 600 MHz) δ



Scheme 1. Synthetic route for PDINI-OBTC8.

140.48, 127.17, 124.03, 121.80, 117.21, 116.36, 116.24, 83.58, 45.18, 31.80, 30.38, 29.39, 29.14, 22.58, 14.06.

Synthesis of Poly[5,10-bis(*n*-octyl)-5,10-dihydroindolo[3,2-*b*]indole-5,6-bis octyloxy-4,7-di(thiophene-2-yl)benzo[*c*][1,2,5]thiadiazole] PDINI-OBTC8. Suzuki polymerization condition was employed for the synthesis of new D-A type polymer. Compound 6 (300 mg, 0.43 mmol) and OBTC8 (312 mg, 0.43 mmol) were mixed in of anhydrous CB (15 mL). The reaction mixture was purged with N₂ for 20 min. Pd₂(dba)₃ (15.7 mg, 0.017 mmol) and (*o*-tolyl)₃P (20.9 mg, 0.068 mmol) were added and mixture was purged with again with N₂. Then 2 mL of 20% aqueous tetraethylammonium hydroxide was added and the mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature, poured into methanol (MeOH) and resulting precipitate was filtered and purified by Soxhlet extraction with MeOH, hexane, acetone, and chloroform (CF) until the wash from each extraction was colorless. The CF fraction was concentrated and reprecipitated in MeOH to get dark solid (220 mg, 51%). ¹H NMR (CDCl₃, 600 MHz) δ 8.4-8.6 (m, 2H), 7.3-7.8 (m, 8H), 4-4.6 (m, 8H), 1.8-2.2 (m, 4H), 1-1.6 (m, 48H), 0.6-0.9 (m, 12H). Anal. Calcd. for C₆₀H₈₀N₄O₂S₃: C, 73.12; H, 8.18; N, 5.69. Found C, 74.69; H, 8.03; N, 8.01.

Results and Discussion

Synthesis and Characterization. The synthesis of monomers described in experimental section was followed from previously published literature.¹⁶⁻¹⁹ Sonogashira Pd-catalyzed crosscoupling of *o*-iodonitrobenzene with acetylene yielded 2,2'-dinitrotolane, after oxidation of 2,2'-dinitrotolane to dione, followed by ring closure, *N*-alkylation with NaH and bromination with NBS resulted DINI monomer. After borylation of DINI, the resulted monomer was copolymerized with OBTC8 by using Suzuki polycondensation reaction conditions to obtain PDINI-OBTC8 with high molecular weight (30000 g/mol) and good solubility.

In the process of synthesis of new polymers with DINI, we have tried to substitute two nitrogen atoms with 2-ethylhexyl, *n*-octyl and *n*-decyl present in backbone. By brominating DINI backbone on 2- and 7-positions three different monomers were obtained and by copolymerizing with 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole results polymers with poor solubility in common organic solvents and shown poor device performances. Further, we decided to introduce alkyl chains in acceptors, and it is well known that by introduction of alkoxy substituents on the benzothiadiazole results in good solubility. By implementing this idea, *n*-octyl substituted DINI and octyloxy substituted BT with thiophene π -bridge were copolymerized using Suzuki polycondensation reaction conditions. Fortunately, we ended up with high molecular weight of (30000 g/mol) along with good solubility in organic solvents like CF, THF and CB.

The UV-visible absorption spectra of PDINI-OBTC8 in solution and film state are shown in Figure 1. The absorption spectrum in CF exhibits two characteristic peaks; one rang-

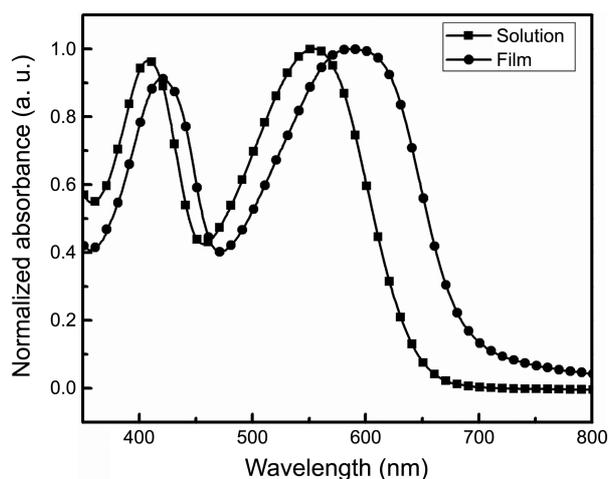


Figure 1. UV-visible absorption spectra of PDINI-OBTC8 in CF solution and thin film.

ing from 350 to 450 nm, other from 500 to 700 nm. The shorter wavelength band is attributed to π - π^* transition of polymer backbone and longer wavelength is due to intramolecular charge transfer (ICT) between DINI and OBTC8. The thin film state absorption spectrum showed a bathochromic shift (36 nm) along with the broader ICT compared to solution, which is attributed to more aggregated arrangement in solid state. The absorption maxima for PDINI-OBTC8 in solution and film state are at 406 and 551 nm, 418 and 587 nm, respectively. The optical band gap ($E_{g, opt}$) of PDINI-OBTC8 was determined by absorption edge of film state absorption spectrum and was found to be 1.73 eV. Sufficient interchain π - π stacking between polymer backbones leads to enhanced absorption intensity, reduced optical band gap, and improved charge mobility,⁸ broad absorption. LBG of PDINI-OBTC8 revealed that DINI-based polymers can be used as efficient materials for BHJ PSC applications.

The thermal stability of PDINI-OBTC8 was measured by TGA. It shows 5% weight loss temperature at 328 °C. This indicates that thermal stability of PDINI-OBTC8 was good enough for the BHJ PSC applications.

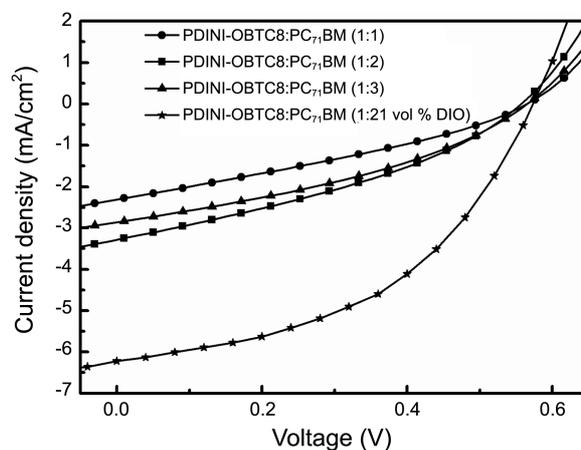


Figure 2. Current density-voltage characteristic curves of PDINI-OBTC8.

Table 1. Molecular weights, thermal, optical and electrochemical properties of PDINI-OBTC8

Polymer	M_n (g/mol)	M_w (g/mol)	PDI	T_d^a (°C)	E_g^b (eV)	HOMO ^c (eV)	LUMO ^d (eV)
PDINI-OBTC8	17350	30000	1.73	328	1.73	-4.96	-3.22

^aDecomposition temperature at 5% weight loss with a heating rate of 10 °C/min under N₂ atmosphere. ^bCalculated from absorption onset in the thin film. ^cCalculated from onset oxidation potential of cyclic voltammogram. ^dCalculated from $E_{g, opt}$ and HOMO level.

The electrochemical properties of PDINI-OBTC8 thin film was measured by cyclic voltammetry (CV). And their results are summarized in Table 1. The onset oxidation potential was observed at 0.685 eV and the calculated HOMO energy level of PDINI-OBTC8 is -4.96 eV. The lowest unoccupied molecular orbital (LUMO) energy level of PDINI-OBTC8 was calculated from the $E_{g, opt}$ and HOMO energy level obtained from CV. The LUMO energy level of PDINI-OBTC8 was found to be -3.22 eV. The calculated LUMO energy level was higher than that of PC₇₁BM (-4.30 eV) to ensure energetically favorable electron transfer from donor to acceptor in the photovoltaic device.

The photovoltaic properties of PDINI-OBTC8 were investigated with the device configuration of ITO/PEDOT:PSS/PDINI-OBTC8:PC₇₁BM/LiF/Al. PC₇₁BM was used as an electron acceptor material due to its stronger light absorption in the visible region.²⁰ The active layers were spin coated from CB. The PDINI-OBTC8-based BHJ PSCs were characterized with diverse donor and acceptor weight ratios of 1:1, 1:2 and 1:3 in CB solvent with the active layer thickness of 90 nm. The current density-voltage ($J-V$) curve of the above different donor and acceptor weight ratios were shown in Figure 2 and the related photovoltaic parameters are summarized in Table 2. The PCE of BHJ PSCs at three different weight ratios (1:1, 1:2 and 1:3) of donor and acceptor were found to be 0.42, 0.65 and 0.58%, respectively. Among the three different ratios, blend made from 1:2 ratio of donor and acceptor showed superior photovoltaic parameters such as open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (FF) with 0.56 V, 3.21 mA/cm² and 35.71 %, respectively. It has been reported that selective solubility of PCBM in solvent additives results in more ordered film morphology by aggregation of polymer.²¹ In order to study the effect of additive on PDINI-OBTC8:PC₇₁BM system, the optimized 1:2 blend ratio was spin coated with 1 vol% of DIO. Surprisingly, a pronounced PCE of 1.68% was accomplished, which is 2.5 times more than pristine film, which is attributed to increased J_{sc} as shown in Figure 2 and photovoltaic parameters are summarized in

Table 2. Solar cell performance of PDINI-OBTC8

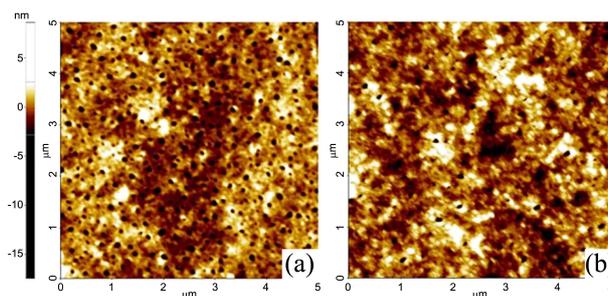
PDINI-OBTC8: PC ₇₁ BM	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
1:1 (wt %)	0.56	2.32	32.03	0.42
1:2 (wt %)	0.56	3.21	35.75	0.65
1:3 (wt %)	0.57	2.87	35.71	0.58
1:2 (wt %) ^a	0.57	6.23	46.49	1.68

^a1 vol% of DIO was used.

Table 2.

The AFM images of blend films of PDINI-OBTC8-PC₇₁BM (1:2 wt %) and PDINI-OBTC8:PC₇₁BM (1:2 wt %) with 1 vol% of DIO as shown in Figure 3. Since 1:2 ratio of PDINI-OBTC8:PC₇₁BM has shown better device performance, we have studied the effect of 1 vol% of DIO as an additive in the blend of the active layer of the devices to enhance further photovoltaic performance. As we expected, upon addition of 1 vol% of DIO to the optimized blend of active layer, the PCE is elevated from 0.65% to 1.68%. This is due to the fact that the generation of smooth morphology by DIO, the root mean square (rms) roughness of the film is reduced to 0.95 nm from 1.38 nm for the pristine film as shown in the Figure 3. This can be explained that upon addition of additives like DIO selectively dissolves the PCBM in the blend that lead to dissolve the aggregates of PC₇₁BM. Generally, in the absence of DIO, the PC₇₁BM aggregates are large enough that hinder its inter penetration into the polymer network during film formation, which led to lesser device performance. Thus, upon addition of DIO as additive increases the device performance by generation of good PDINI-OBTC8/PC₇₁BM phase separation. In addition, additives have a higher boiling point than the processing solvent, CB that led to allow sufficient time for the PC₇₁BM molecules to integrate into the polymer aggregates resulting in a greater PDINI-OBTC8/PC₇₁BM interface density and smaller domains.^{22,23} These facts are the main reason behind the improvement in device performance in the presence of DIO.

The external quantum efficiency (EQE) studies as a function of wavelength were characterized to examine accuracy of the newly synthesized polymer. EQE curves of the active layer with (1 vol% DIO) and without DIO are shown in Figure 4. The EQE curves of PDINI-OBTC8-based devices cover a broad wavelength range from 300 to 800 nm and show a maximum EQE value of 17% at 400 nm and 18% at 500 nm for the BHJ PSCs without additive. A maximum EQE value of 40% at 400 nm and 39% at 600 nm were

**Figure 3.** AFM images of (a) PDINI-OBTC8:PC₇₁BM (1:2 wt %) and (b) PDINI-OBTC8:PC₇₁BM (1:2 wt %) with 1 vol% DIO.

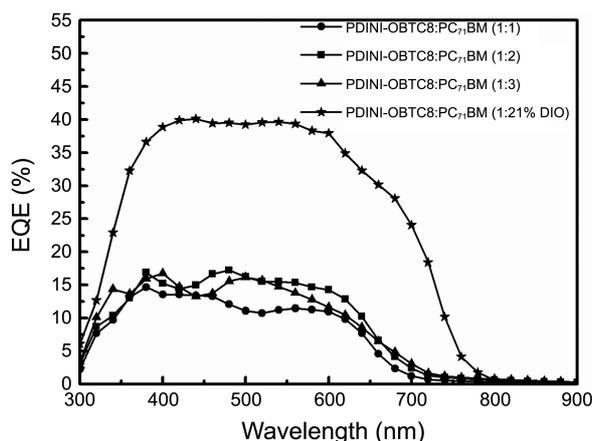


Figure 4. EQE curves for BHJ PSC film based on PDINI-OBTC8:PC₇₁BM.

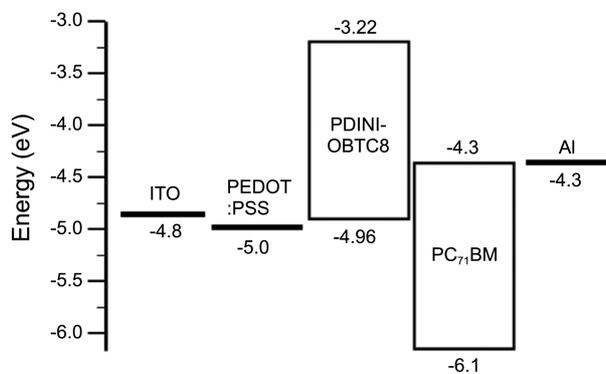


Figure 5. Energy band diagram for BHJPSC device.

observed upon adding 1 vol% of DIO.

Conclusion

In summary, a new D-A ladder type fused π -conjugated polymer PDINI-OBTC8 was synthesized by palladium catalyzed Suzuki polycondensation reaction for BHJ PSCs application. The synthesized polymer PDINI-OBTC8 showed high molecular weight, solution processability, thermal stability, and broad absorption in visible region. A BHJ PSC device showed a PCE of 0.65% and it reached 1.68% with 1 vol% of DIO. These preliminary PCE results strongly suggest that PDINI-OBTC8 is a good choice to use it for BHJ PSC applications. We envisage that the improvement in PCE of PDINI-OBTC8 based BHJ PSCs is achievable by optimization of molecular engineering and the device processing conditions.

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References

- Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photon.* **2009**, *3*, 297.
- Huo, L.; Hou, J.; Zhang, S.; Chen, H.-Y.; Yang, Y. *Angew. Chem. Int. Ed.* **2010**, *49*, 1500.
- Zhou, H.; Yang, L.; You, W. *Macromolecules* **2012**, *45*, 607.
- Li, Y. *Acc. Chem. Res.* **2012**, *45*, 723.
- Li, G.; Zhu, R.; Yang, Y. *Nat. Photon.* **2012**, *6*, 153.
- Dou, L.; Gao, J.; Richard, E.; You, J.; Chen, C.-C.; Cha, K. C.; He, Y.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2012**, *134*, 10071.
- Dou, L.; Chang, W.-H.; Gao, J.; Chen, C.-C.; You, J.; Yang, Y. *Adv. Mater.* **2013**, *25*, 825.
- Min, J.; Zhang, Z.-G.; Zhang, S.; Li, Y. *Chem. Mater.* **2012**, *24*, 3247.
- Duan, R.; Ye, L.; Guo, X.; Huang, Y.; Wang, P.; Zhang, S.; Zhang, J.; Huo, L.; Hou, J. *Macromolecules* **2012**, *45*, 3032.
- Hendriks, K. H.; Heintges, G. H. L.; Gevaerts, V. S.; Wienk, M. M.; Janssen, R. A. J. *Angew. Chem. Int. Ed.* **2013**, *52*, 1.
- Cheng, Y.-J.; Wu, J.-S.; Shih, P.-I.; Chang, C.-Y.; Jwo, P.-C.; Kao, W.-S.; Hsu, C.-S. *Chem. Mater.* **2011**, *23*, 2361.
- Chen, Y.-L.; Chang, C.-Y.; Cheng, Y.-J.; Hsu, C.-S. *Chem. Mater.* **2012**, *24*, 3964.
- Zhang, Y.; Zou, J.; Yip, H.-L.; Chen, K.-S.; Davies, J. A.; Sun, Y.; Jen, A. K.-Y. *Macromolecules* **2011**, *44*, 4752.
- Tsai, J.-H.; Chueh, C.-C.; Lai, M.-H.; Wang, C.-F.; Chen, W.-C.; Ko, B.-T.; Ting, C. *Macromolecules* **2009**, *42*, 1897.
- Zhang, M.; Guo, X.; Wang, X.; Wang, H.; Li, Y. *Chem. Mater.* **2011**, *23*, 4264.
- Owczarczyk, Z. R.; Braunecker, W. A.; Garcia, A.; Larsen, R.; Nardes, A. M.; Kopidakis, N.; Ginley, D. S.; Olson, D. C. *Macromolecules* **2013**, *46*, 1350.
- Jin, Y.; Kim, K.; Song, S.; Kim, J.; Park, S. H.; Lee, K.; Suh, H. *Bull. Korean Chem. Soc.* **2006**, *27*(7), 1043.
- Murry, M. M.; Kaszynski, P.; Kaisaki, D. A.; Chang, W.; Dougherty, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 8152.
- Ding, P.; Chu, C.-C.; Liu, B.; Peng, B.; Zou, Y.; He, Y.; Zhou, K.; Hsu, C.-S. *Macromol. Chem. Phys.* **2010**, *211*, 2555.
- Wienk, M. M.; Kroon, J. M.; Verhees, W. J. H.; Knol, J.; Hummelen, J. C.; Van Hal, P. A.; Janssen, R. A. J. *Angew. Chem. Int. Ed.* **2003**, *42*, 3371.
- Graham, K. R.; Mei, J.; Stalder, R.; Shim, J. W.; Cheun, H.; Steffy, F.; So, F.; Kippelen, B.; Reynolds, J. R. *ACS Appl. Mater. Interfaces* **2011**, *3*, 1210.
- Lee, J. K.; Ma, W. L.; Brabec, C. J.; Yuen, J.; Moon, J. S.; Kim, J. Y.; Lee, K.; Bazan, G. C.; Heeger, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 3619.
- Zhang, M.; Gu, Y.; Guo, X.; Liu, F.; Zhang, S.; Huo, L.; Russel, T. P.; Hou, J. *Adv. Mater.* **2013**, *25*, 4944.