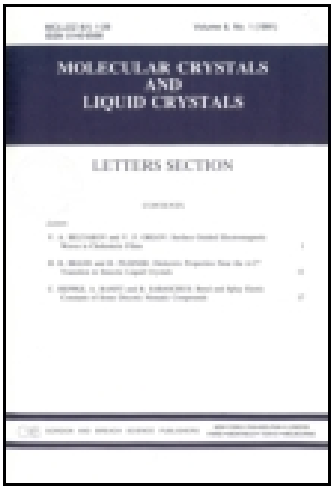

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Synthesis of the Copolymer Based on Diketopyrrolopyrrole with Didecyl Chain for OPVs

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*A new accepter unit, diphenylpyrrolo[3,2-*b*]pyrrole-2,5-dione with didecyl chain, was prepared and utilized for the synthesis of the conjugated polymer containing electron donor-acceptor pair for OPVs. The iDPP, part of the structure of a natural dye found in lichens, is the regioisomer of the known DPP with switched position of the carbonyl group and nitrogen atom. At the 4-positions of the* N*-substituted phenyl groups of 1,4-bis(4-butylphenyl)-pyrrolo[3,2-*b*]-pyrrole-2,5-dione unit in* ***P-butyl****, the butyl group was substituted with decyl group to increase solubility. The absorption spectrum of polymer with diphenylpyrrolo[3,2-*b*]pyrrole-2,5-dione unit exhibit two maximum peaks at about 365 and 542 nm. The spectrum of the* ***P1*** *as the solid thin film shows absorption band with maximum peaks at 370 and 536 nm, and the absorption onset at 703 nm, corresponding to band gap of 1.76 eV. The oxidation and reduction potential onset of the synthesized polymer were estimated to be 0.84 and −1.22 V, which correspond to HOMO and LUMO energy levels of −5.64 and −3.58 eV, respectively. The devices comprising* ***P1*** *with $PC_{61}BM$ annealed at 100°C showed a V_{OC} of 0.79 V, a J_{SC} of 1.75 mA/cm^2, and a* FF *of 0.31, leading to the power conversion efficiency of 0.43% under white light illumination (AM 1.5 G, 100 mW/cm^2).*

Keywords Polymer; photovoltaic cells; pyrrolo[3; 2-b]pyrrole-2; 5-dione

1. Introduction

The research for the achievement of efficient organic photovoltaics (OPVs) has become one of the most popular topics in recent years caused by their potential to be an alternative source of green energy [1–2]. Bulk heterojunction (BHJ) solar cells based on a blend of low band gap materials and PCBM offer promise for the realization of low cost and

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easy fabrication, portable and having the capability to fabricate flexible large-area devices [3–4]. High efficiency low band gap conjugated polymer as donor need to possess broad absorption to provide narrower bandgap, higher hole mobility, and relatively lower HOMO energy level [5]. In order to increase the absorption of the solar spectrum, the copolymer with the electron-rich donor (D) and electron deficient acceptor (A) units can effectively reduce the band gaps ($E_g < 1.8$ eV) of the polymers in BHJ solar cells [6].

Many of the low-bandgap conjugated polymers with excellent efficiencies have electron-deficient heterocycles, such as diketopyrrolopyrrole (DPP) [7]. 2*H*-benzimidazole [1–2], and benzothiadiazole (BT) [8] and electron-rich moieties, such as carbazole [9], and indenoindene [10]. Carbazole was chosen as the donor unit in these two D–A copolymers, due to its good thermal and chemical stability, high charge carrier mobility, and relatively low HOMO energy level [11]. The copolymer based on DPP has been known as the successful low band-gap conjugated copolymer with heat stability and high and balanced hole and electron mobilities in polymer solar cells and field effect transistors [12]. The quinoid character of the DPP core, and its electron-deficient nature and good planarity have been exploited for the synthesis of low band-gap D-alt-A polymers that are used in PSCs with high PCEs [12].

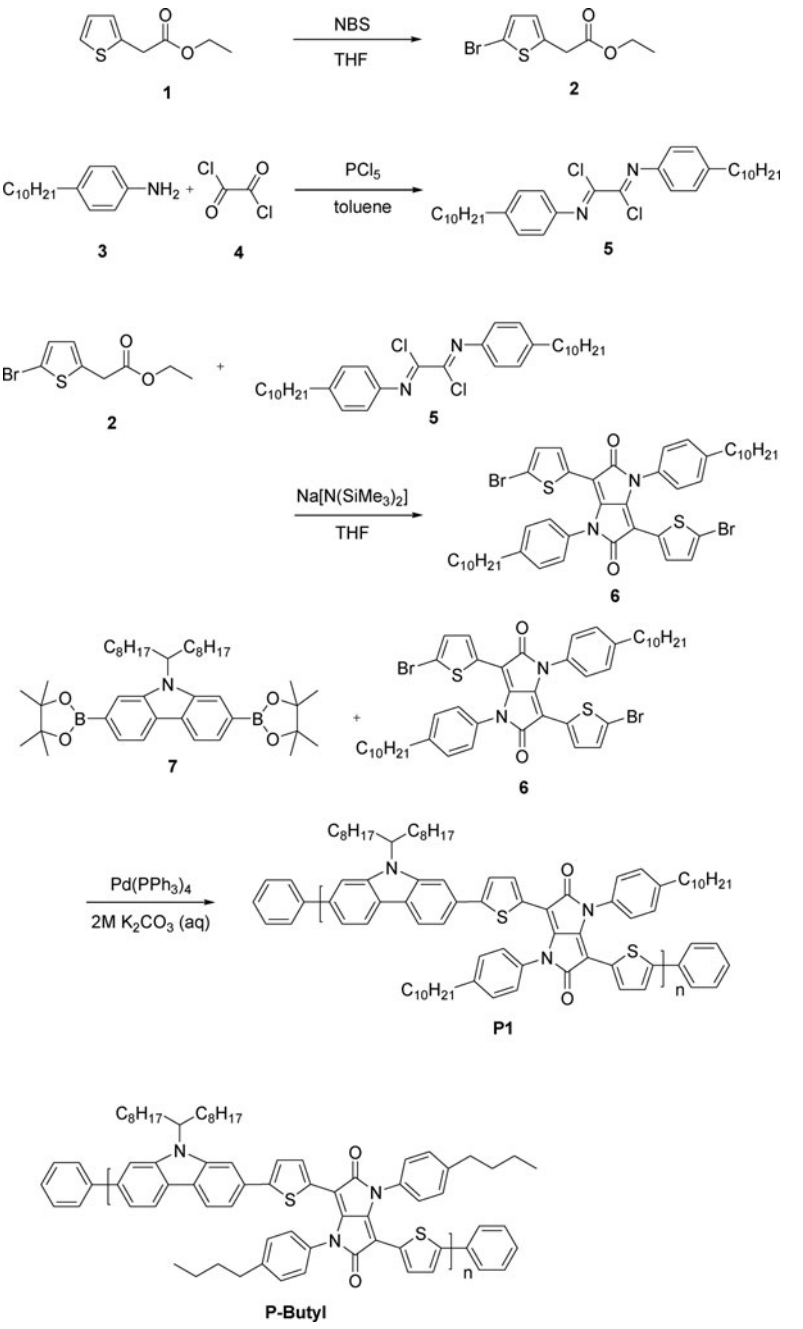
In this paper, we reported the synthesis and characterization of polymer with pyrrolo[3,2-b]pyrrole-2,5-dione (iDPP) [13] for OPV device. To improve the solubility and the film-forming ability of the conjugated polymer with pyrrolo[3,2-b]pyrrole-2,5-dione, two decyl chains were introduced at the 4-positions of the *N*-substituted phenyl groups. The iDPP, part of the structure of a natural dye found in lichens [14], is the regioisomer of the known DPP with switched position of the carbonyl group and nitrogen atom [15]. The low bandgap conjugated polymer was synthesized by Suzuki coupling reaction of **iDPP** as the electron poor unit and carbazole as the electron rich unit with thiophene as the bridge to provide **P1**. The photovoltaic properties of the small molecules were investigated by fabrications of the OPV devices with the configurations of ITO/PEDOT:PSS/polymer:PCBM/Al.

2. Results and Discussion

2.1 Synthesis and Characterization

The general synthetic routes of the monomer and polymer are outlined in Scheme 1. In the first step, ethyl 2-thiopheneacetate (**1**) was brominated with *N*-bromosuccinimide (NBS) to generate ethyl 2-(5-bromo-2-thienyl)acetate (**2**). The 4-decylaniline (**3**) was treated with oxalyl chloride (**4**) and PCl_5 in toluene to provide *N,N′*-bis(4-decylphenyl)ethanediimidoyl dichloride (**5**). Ethyl 2-(5-bromo-2-thienyl)acetate (**2**) and compound **5** were coupled using $Na[N(SiMe_3)_2]$ to form 1,4-bis(4-decylphenyl)-3,6-(bis-(5-bromo-2-thienyl)-pyrrolo[3,2-*b*]pyrrole-2,5(1*H*,4*H*)-dione (**6**). Compound **6**, as electron-accepting moiety, and 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-*N*-9″-heptadecanylcarbazole[8] (**7**), as electron-donating unit, were co-polymerized through Suzuki coupling reaction with Pd(0)-catalyst to yield poly[*N*-9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(1,4-bis(4-decylphenyl)-3,6-(bis-(2-thienyl)-pyrrolo[3,2-*b*]pyrrole-2,5(1*H*,4*H*)-dione)] (**P1**). The structures and purities of the monomers were confirmed by ^{1}H-NMR, ^{13}C-NMR, and HRMS. The synthesized polymer was soluble in various organic solvents such as chloroform, chlorobenzene, tetrahydrofuran (THF), dichloromethane and *o*-dichlorobenzene (ODCB).

The thermal properties and summarizes the polymerization results including molecular weight and polydispersity index (PDI) are summerized in Table 1. The number-average molecular weight (M_n) of 12400 and weight-average molecular weight (M_w) of 35400



Scheme 1. Synthetic route for the synthesis of the monomer and polymer.

with PDI value of 2.84 were determined by gel permission chromatography (GPC) for **P1**. The thermal properties of the polymer were characterized by both differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). TGA was performed with TGA 2950 in a nitrogen atmosphere at a heating rate of 10°C/min to 600°C as shown in

Table 1. Polymerization result and properties of polymer

Polymer	M_n[a]	M_w[a]	PDI[a]	TGA (T_d)[b]	λ_{max} (sol.)	λ_{max} (film)	
P1	12400	35400	2.84	439	365, 542	370, 536	2.45×10^{-5}
P-Buthyl	10100	19300	1.91	428	368, 545	374, 548	2.38×10^{-6}

[a]Molecular weight (M_w) and polydispersity (PDI) of the polymer were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. [b]Onset decomposition temperature (5% weight loss) measured by TGA under N_2.

Figure 1. The DSC analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 2920 at heating rate of 10°C/min. The polymer showed good thermal stability with onset decomposition temperature (T_d, 5% weight loss) of 439°C. The DSC performed on P1 shows no phase transitions in the temperature range 30∼250°C caused by longer alkyl chain. The high thermal stability of the synthesized polymer prevents the deformation of the morphology and is important for OPV device applications.

2.2 Optical Properties

The solution was prepared using chloroform as a solvent and the thin film by spin-coating on quartz plates from the solution in chloroform at room temperature. The UV-vis absorption spectra of the polymer in solution and as thin filmr are shown in Figure 2 and summarized in Table 1. The solution of **P1** presents two absorption band with maximum peaks at 365 and 542 nm. The spectrum of the **P1** as the solid thin film shows absorption band with maximum peaks at 370 and 536 nm, and the absorption onset at 703 nm, corresponding to band gap of 1.76 eV. The absorption maximum peaks in film were red shifted as compared to that of solution caused by the increased π-π^* stacking of polymer backbone in solid film. The short-wavelength absorption peaks have been ascribed to a delocalized excitonic π-π^* transition in the conjugated chains and the long-wavelength absorption peaks attributed to the intramolecular charge transfer (ICT) between the electron rich unit and BTI unit [16]. The absorption peaks of P1 in film was blue shifted about 12 nm as compared with that of

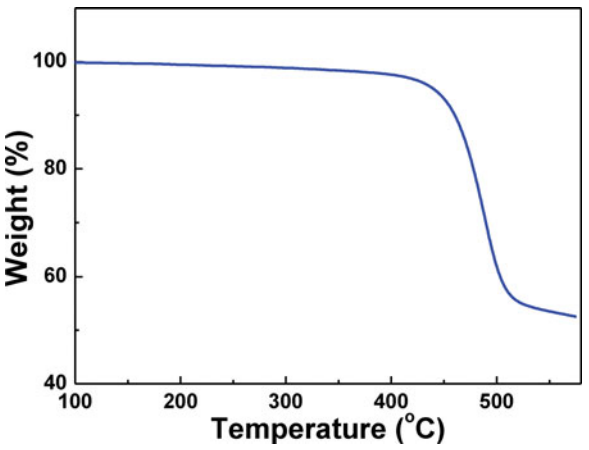


Figure 1. Thermogravimetric analysis of the polymer under N_2.

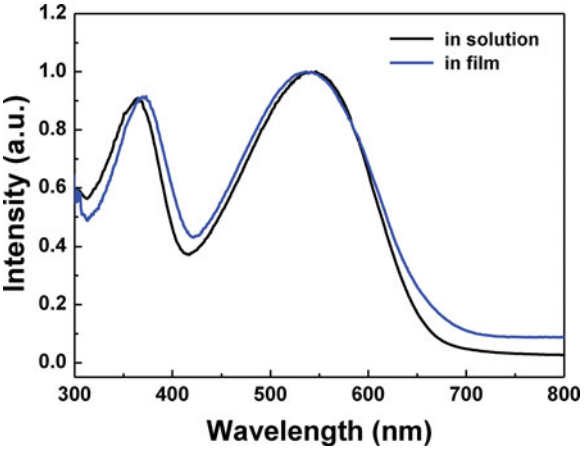


Figure 2. UV-visible absorption spectra of polymer in chloroform solution and the solid state.

the polymer based on pyrrolo[3,2-b]pyrrole-2,5-dione (iDPP) with buthyl chains (P-Butyl) because of long alkyl chain to prevent π-π^* stacking of polymer backbone.

2.3 Electrochemical Properties

The electrochemical property of the polymer was determined from the bandgap estimated from the absorption onset wavelength, and the HOMO energy level which was estimated from the cyclic voltammetry (CV). The CV was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (0.10M) in acetonitrile at a scan rate of 100mV/s at room temperature under argon atmosphere. A platinum electrode ($\sim$0.05 cm^2) coated with a thin polymer film was used as the working electrode. Pt wire and $Ag/AgNO_3$ electrode were used as the counter electrode and reference electrode, respectively. The energy level of the $Ag/AgNO_3$ reference electrode (calibrated by the Fc/Fc^+ redox system) was 4.8 eV below the vacuum level. The CV spectra is shown in Figure 3, and the oxidation potential derived from the onsets of electrochemical p-doping is summarized in Table 3. HOMO and LUMO level was calculated according to the empirical formula ($E_{HOMO} = -([E_{onset}]^{ox} + 4.8)$ eV) and ($E_{LUMO} = -([E_{onset}]^{red} + 4.8)$ eV), respectively. The polymer exhibited the absorption onset wavelength of 703 nm in solid thin film, which corresponds to band gap of 1.76 eV.

Table 2. Electrochemical potentials and energy levels of the polymer

Polymer	Optical band gap[a] (eV)	HOMO[b] (eV)	LUMO[c] (eV)	E_{ox}[d] (V)	E_{red}[d] (V)	Chemical band gap[e] (eV)
P1	1.76	−5.64	−3.58	0.84	−1.22	2.06

[a]Optical energy band gap was estimated from the onset wavelength of the optical absorption.
[b]Calculated from the oxidation potentials.
[c]Calculated from the reduction potentials.
[d]Onset oxidation and reduction potential measured by cyclic voltammetry.
[e]Calculated from the E_{ox} and E_{red}.

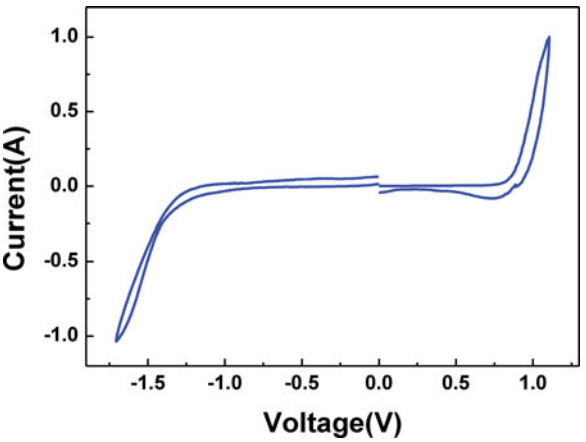


Figure 3. Electrochemical properties of polymer.

The polymer exhibit irreversible process in an oxidation scan. The oxidation onset of the synthesized polymer was estimated to be 0.84 V, which correspond to HOMO energy level of −5.64 eV. The reduction potential onset of synthesized polymer is −1.22 V, which corresponds to LUMO energy level of −3.58 eV. The electrochemical bandgap, calculated from cyclic voltammetry data, is about 2.06 eV, somewhat higher than the optical bandgap estimated from the onset wavelength of the absorption spectrum.

2.4 FET and Polymer Photovoltaic Properties

The field-effect carrier mobilities of the polymers were measured by fabricating thin-film field-effect transistors (FETs) using the top-contact geometry. Hole mobilities of the polymers were calculated from the transfer characteristics of the OFETs. The field-effect hole mobility of **P1** without and with thermal treatment (100°C, 10 min) were determined to be 2.4×10^{-6} and 1.7×10^{-6} cm^2/Vs, respectively.

The OPVs was fabricated by spin-casting of chlorobenzene solution of $PC_{61}BM$/polymer. The polymer was applied as donor into a conventional BHJ type OPV device with $PC_{61}BM$ as acceptor, which has been widely used for this purpose. Typical *J-V* characteristic of device with the configuration of ITO/PEDOT:PSS (40 nm)/polymer:PCBM (80 nm)/ Al (100 nm) under AM 1.5G irradiation (100 mW/cm^2) is depicted in Figure 4. The photovoltaic parameter of all the polymer, including open circuit voltage (V_{OC}), short

Table 3. Photovoltaic properties of the polymer

Ration	Annealing	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
1:2	w/o	1.59	0.40	0.30	0.19
	100	1.75	0.79	0.31	0.43
1:2(70)	w/o	1.54	0.50	0.34	0.26
	100	1.67	0.65	0.35	0.38
1:4	100	0.75	0.66	0.35	0.17

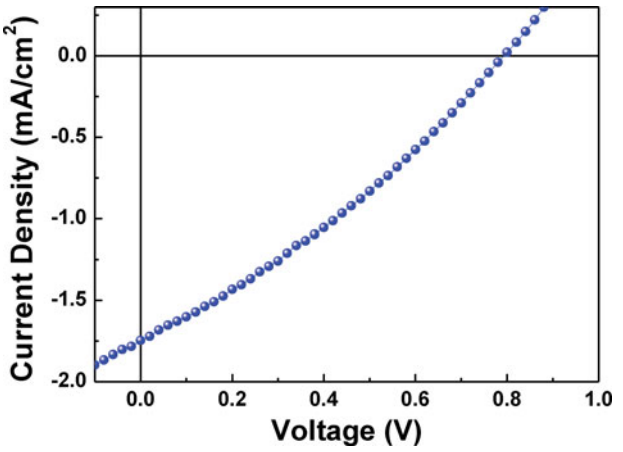


Figure 4. Current density-potential characteristics of the polymer solar cell under the illumination of AM 1.5, 100 mW/cm^2.

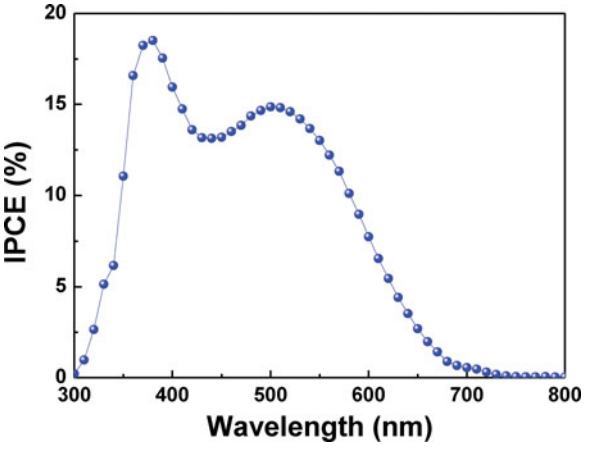


Figure 5. IPCE curve of the polymer solar cells under the illumination of AM 1.5, 100 mW/cm^2.

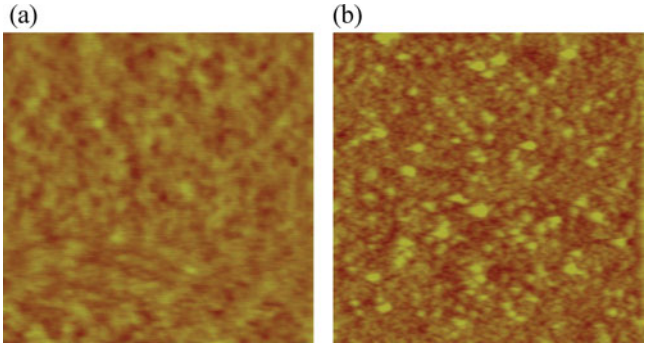


Figure 6. Atomic force microscopy images of **P1**/PCBM (a) and **P-Buthyl** /PCBM (b).

circuit current density (J_{SC}), fill factor (*FF*), and power conversion efficiency (PCE) is summarized in Table 4. The device of **P1** with $PC_{61}BM$ showed V_{OC} value of 0.40 V, J_{SC} value of 1.59 mA/cm^2, and *FF* of 0.30, giving PCE of 0.19%. The devices comprising **P1** with $PC_{61}BM$ with thermal treatment showed a V_{OC} of 0.79 V, a J_{SC} of 1.75 mA/cm^2, and a *FF* of 0.31, giving PCE of 0.43%. In case of device with thermal treatment, the device has higher efficiency due to the increasing V_{OC}. as compared to the device without thermal treatment. The devices based on P1 with $PC_{71}BM$ (without/with thermal treatment) showed power conversion efficiencies of up to 0.26 and 0.38%. The devices had an open-circuit voltage (V_{OC}) of 0.56 and 0.65 V, a short-circuit current density (J_{SC}) of 1.54 and 1.67 mA/cm^2, and a fill factor (*FF*) of 0.35 and 0.35%, respectively. The efficiency of **P1** results from the lower mobility as compared to the cases of **P-Buthyl** (w/o: 2.45×10^{-5} , 2.51×10^{-5}). The devices using $PC_{71}BM$ have higher FF values as compared with the devices using $PC_{61}BM$. The device using $PC_{71}BM$ with thermal treatment has lower PCE from lower V_{OC}. as compared to the device using $PC_{61}BM$. The incident photon-to-current efficiency (IPCE) spectra of the photovoltaic devices from polymer:$PC_{61}BM$ blends are presented in Figure 5. The IPCE spectra of the polymers show maxima of 18.5 % at 380 nm for P1.

Atomic force microscopy (AFM) studies of polymer blends (polymer:$PC_{71}BM$ = 1:2 w/w) revealed that the morphology of the polymer/$PC_{61}BM$ blend film exhibited very fine domains and no large phases can be found in figure 6, where the images were obtained in a surface area of 2.5 × 2.5 μm^2 by the tapping mode. In comparison with blended **P-butyl** (0.660 nm), the solid film of blended **P1** revealed very smooth surface with rms roughness of 0.303 nm.

3. Conclusions

The conjugated copolymer utilizing a new accepter unit, diphenylpyrrolo[3,2-*b*]pyrrole-2,5-dione with didecyl chain, was synthesized to show good solubility at room temperature in organic solvents. At the 4-positions of the *N*-substituted phenyl groups of 1,4-bis(4-butylphenyl)-pyrrolo[3,2-*b*]-pyrrole-2,5-dione unit in **P-butyl**, the butyl group was substituted with decyl group to increase solubility. The absorption spectrum of polymer with diphenylpyrrolo[3,2-*b*]pyrrole-2,5-dione unit exhibit two maximum peaks at about 365 and 542 nm. The spectrum of the **P1** as the solid thin film shows absorption band with maximum peaks at 370 and 536 nm, and the absorption onset at 703 nm, corresponding to band gap of 1.76 eV. The oxidation and reduction potential onset of the synthesized polymer were estimated to be 0.84 and −1.22 V, which correspond to HOMO and LUMO energy levels of −5.64 and −3.58 eV, respectively. The devices comprising **P1** with $PC_{61}BM$ with thermal treatment showed a V_{OC} of 0.79 V, a J_{SC} of 1.75 mA/cm^2, and a *FF* of 0.31, giving PCE of 0.43%.

Experimental Section

General. All reagents were purchased from Aldrich or TCI, and used without further purification. Solvents were purified by normal procedure and handled under moisture-free atmosphere. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini-300 (300 MHz) spectrometer and chemical shifts were recorded in ppm units with TMS as the internal standard. The NMR acronyms are as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), sextet (sex) and septet (sep). Flash column chromatography was performed with Merck silica gel 60 (particle size 230-400 mesh ASTM) with ethyl acetate/hexane

or methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F pre-coated aluminum plates with fluorescent indicator UV254. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under electron impact (EI) conditions in the Korea Basic Science Institute (Daegu). The UV-vis absorption spectra were recorded by a Varian 5E UV/VIS/NIR spectrophotometer, while the Oriel InstaSpec IV CCD detection system with xenon lamp was used for the photoluminescence and electroluminescence spectra measurements. The AFM instrumentation consisted of a Veeco NanoScope AFM and standard silicon cantilever (Veeco; tip radius, 8 nm; normal spring constant, 21-78 N/m; scan rate, 2.0 Hz) at ambient conditions (in air, 20°C).

Solar cells were fabricated on an indium tin oxide (ITO)-coated glass substrate with the following structure; ITO-coated glass substrate/poly(3,4-ethylenedioxythiophene) (PEDOT:PSS)/polymer: PCBM/Al. The ITO-coated glass substrate was first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. PEDOT:PSS (Baytron PH) was spin-cast from aqueous solution to form a film of 40nm thickness. The substrate was dried for 10 min at 140°C in air and then transferred into a glove box to spin-cast the active layer. A solution containing a mixture of polymer:PCBM in chlorobenzene solvent with concentration of 7 wt/ml % was then spin-cast on top of the PEDOT/PSS layer. The film was dried for 60 min at 70°C in the glove box. The sample was heated at 80°C for 10 min in air. Then, an aluminum (Al, 100 nm) electrode was deposited by thermal evaporation in a vacuum of about 5×10^{-7} Torr. Current density-voltage (J-V) characteristics of the devices were measured using a Keithley 236 Source Measure Unit. Solar cell performance utilized an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 1000 Wm^{-2}. An aperture ($12.7mm^2$) was used on top of the cell to eliminate extrinsic effects such as cross-talk, waveguiding, shadow effects, etc. The spectral mismatch factor was calculated by comparison of solar simulator spectrum with AM 1.5 spectrum at room temperature. The IPCE is a measure of the photon to electron conversion efficiency at a particular irradiation wavelength (equation 1).

$$\mathrm{IPCE} = (1240 \times J_{SC})/(\lambda_i \times P_{in}) \quad (1)$$

*Synthesis of ethyl 2-(5-bromo-2-thienyl)acetate (**2**).* Ethyl 2-thiopheneacetate (**1**) (10 g, 66.66 mmol) was brominated with *N*-bromosuccinimide (NBS) (13 g, 73.26 mmol) in THF (20 mL) at room temperature. After stirring for 24 h, water (200 mL) and ethyl acetate (400 mL) were added. The organic layer was washed with 3 × 200 mL of water and concentrated under reduced pressure. The residue was purified by flash column chromatography to give compound **2** as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, 3H, $J = 7.1$ Hz), δ 3.76 (s, 2H), δ 4.19 (q, 2H, $J = 7.1$ Hz), δ 6.69 (d, 1H, $J = 3.8$ Hz), δ 6.90 (d, 1H, $J = 3.8$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.35, 36.07, 61.59, 111.55, 127.31, 129.66, 137.09, 170.05; HRMS(EI^+, m/z) calcd for $C_8H_9BrO_2S$ 247.9507, measured 247.9509.

Synthesis of N,N′*-bis(4-decylphenyl)ethanediimidoyl dichloride (**5**).* A solution of 4-decyl benzenamine (**3**) (5 g, 21.42 mmol) and oxalyl chloride (**4**) (5 mL, 44.98 mmol) in toluene (50 mL) was treated with PCl_5 (5 g, 23.56 mmol) at room temperature. After stirring for 30 min, the reaction mixture was heated at 100°C until no further hydrogen chloride was formed. The reaction mixture was concentrated under reduced pressure and crude product was recrystallized from hexane/ CH_2Cl_2 to afford compound **5** as a yellow crystal. mp 177°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, 6H, $J = 6.9$ Hz), 1.28 (m, 28H,), 1.59 (m, 4H), 2.60 (t, 4H, $J = 7.4$ Hz), 7.21 (d, 4H, $J = 8.5$ Hz), 7.58 (d, 4H, $J = 7.5$ Hz); ^{13}C

NMR (75 MHz, $CDCl_3$) δ 14.32, 22.90, 29.46, 29.54, 29.71, 29.81, 31.12, 31.65, 32.12, 35.67, 119.99, 121.16, 129.08, 129.37, 134.11, 140.68, 157.67; HRMS(EI^+, m/z) calcd for $C_{34}H_{50}Cl_2N_2$ 556.3351, measured 555.3276.

*Synthesis of 1,4-bis(4-decylbutylphenyl)-3,6-(bis-(5-bromo-2-thienyl)-pyrrolo[3,2-*b*]pyrrole-2,5(1*H*,4*H*)-dione (**6**).* Ester **2** (2.57 g, 10.3 mmol) and 1 M $NaN(SiMe_3)_2$ (9 ml, 44.8 mmol) were dissolved in THF (50 mL) at room temperature under argon. After stirring for 1 h, the reaction mixture was cooled to -78°C and a THF solution (30 mL) of the compound 5 (2.5g, 4.48 mmol) was slowly added. After stirring for 48 h at room temperature, aqueous solution of NH_4Cl (200 mL) and ethyl acetate (400 mL) was added. The mixture was washed with 3 × 200 mL of water. The organic phase was concentrated under reduced pressure and the residue was purified by flash column chromatography (hexane:CH_2Cl_2 = 15:1) to give compound **6** as an orange solid. mp 187°C; ^{1}H NMR (300 MHz, $CDCl_3$) 0.89 (t, 6H, J = 7.1 Hz), 1.28∼1.34 (m, 28H), 1.63 (m, 4H), 2.67 (t, 4H, J = 7.4 Hz), 5.97 (d, 2H, J = 4.1 Hz), 6.67 (d, 2H, J = 4.1 Hz), 7.19 (d, 4H, J = 8.5 Hz), 7.26 (d, 4H, J = 7.2 Hz); ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.34, 22.91, 29.37, 29.57, 29.73, 29.86, 29.89, 31.71, 32.13, 35.82, 100.35, 116.51, 127.36, 129.46, 129.60, 130.03, 131.14, 131.46, 142.52, 144.17, 170.23; HRMS(EI^+, m/z) calcd for $C_{46}H_{55}O_2N_2Br_2S_2$ 889.2072, measured 887.1906.

*Synthesis of the poly[*N-*9′-heptadecanyl-2,7-carbazole-*alt-*5,5-(1,4-bis(4-decylphenyl)-3,6-(bis-(2-thienyl)-pyrrolo[3,2-*b*]pyrrole-2,5(1*H*,4*H*)-dione)] (**P1**).* Carefully purified 1,4-bis(4-decylbutylphenyl)-3,6-(bis-(5-bromo-2-thienyl)-pyrrolo[3,2-*b*]pyrrole-2,5(1*H*,4*H*)-dione (**6**) (200 mg, 0.22 mmol), 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-*N*-9″-heptadecanylcarbazole (**7**) (148 mg, 0.22 mmol), and $(PPh_3)_4Pd(0)$ (50 mg) were dissolved in a mixture of toluene (6 mL) and aqueous 2M K_2CO_3 (2 mL).. The mixture was refluxed with vigorous stirring for 3 days under argon atmosphere. After 72 h, phenylboronic acid (50 mg) was added to the reaction mixture then 12 h later, bromobenzene (1 mL) was added and the reaction mixture was refluxed overnight to complete the end-capping reaction. After cooling to room temperature, the mixture was poured into methanol. The precipitated material was recovered by filtration. The resulting solid material was reprecipitated using 100 mL of THF/1.0 L of methanol several times to remove residual amount of catalyst. The resulting polymer was soluble in THF, $CHCl_3$, ODCB and toluene.

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