Synthesis and Characterization of a Narrow-Bandgap Polymer Containing Alternating Cyclopentadithiophene and Diketo-Pyrrolo-Pyrrole Units for Solar Cell Applications

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ABSTRACT: We have synthesized a narrow-bandgap conjugated polymer (**PCTDPP**) containing alternating cyclopentadithiophene (CT) and diketo-pyrrolo-pyrrole (DPP) units by Suzuki coupling. This **PCTDPP** exhibits a low band gap of 1.31 eV and a broad absorption band from 350 to 1000 nm, which allows it to absorb more available photons from sunlight. A bulk heterojunction polymer solar cell incorporating **PCTDPP** and C_{70} at a blend ratio of 1:3 exhibited a high short-circuit current of 10.87 mA/cm^2 and a power conversion efficiency of 2.27%. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1669–1675, 2010

KEYWORDS: conjugated polymers; copolymerization; diketo-pyrrolo-pyrrole; heteroatom-containing polymers; solar cell

INTRODUCTION The development of conjugated polymers that possess extended delocalized π-electron systems and can be used in organic optoelectronic devices has been an area of intense investigation, with many studies having focused on solar cell devices based on bulk heterojunctions (BHJ) of conjugated polymers.[1–7] Polythiophene derivatives are among the most promising materials for solar cell applications because of their high light absorption and high electronic conductivity. For example, BHJ solar cell devices containing blends of regioregular poly(3-hexylthiophene) (rr-P3HT) as the donor and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as the acceptor can exhibit power conversion efficiencies (PCEs) as high as 4–5%.[8–16] Nevertheless, because the absorption band of rr-P3HT is located at wavelengths of less than 650 nm, it can harvest only 22.4% of the available photons from sunlight.[17] Hence, it remains a challenge to develop polymer materials that feature broader and longer wavelength absorptions to improve the PCEs of such devices.

There are two main approaches toward lowering the bandgaps of polymers. The first involves the introduction of electron donor (D) and acceptor (A) units into the polymer main chain; indeed, alternating such donor and acceptor moieties along a polymer backbone is an effective means of reducing the bandgaps of polymers through intrachain charge transfer. The second involves increasing the coplanarity of the polymeric structure, thereby decreasing the bandgap by increasing the degree of delocalization of the π electrons.[17]

Many D–A conjugated polymers contain thiophene,[18–20] fluorene,[21,22] carbazole,[23–26] and cyclopentadithiophene[27–29] units as donor units, whereas acceptor units are benzothiadiazole,[30,31] quinoxaline,[32,33] and thienopyrazine.[34,35] For example, poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (**PCDTBT**) possesses a band gap of 1.88 eV. BHJ solar cell fabricated with **PCDTBT**/PC$_{71}$BM can achieve a high PCE of 6.1%.[24,36] Another case involves 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**) that has a broad absorption ranging from 380 to 900 nm and a low band gap (1.40 eV). BHJ solar cells based on **PCPDTBT**/PC$_{71}$BM can achieve a PCE of 5.5%.[29,37] One potential strategy for improving the efficiency further is to incorporate planar molecular structures into the polymer backbone. Cyclopentadithiophene (CT)-based polymers generally exhibit low bandgaps and high carrier mobilities because of their highly planar and rigid structures.[37–39] Several narrow-bandgap polymers containing diketopyrrolopyrrole (DPP) units have also been applied in solar cells exhibiting good performance.[40–44] DPP units have planar, highly conjugated, lactam structures, which result in strong π–π interactions and strong electron-withdrawing effects.[45–47]

In this study, we prepared an extended conjugated molecular structure in which CT moieties were incorporated into a polymeric main chain to increase the effective conjugation length of the system. Scheme 1 displays our synthetic routes
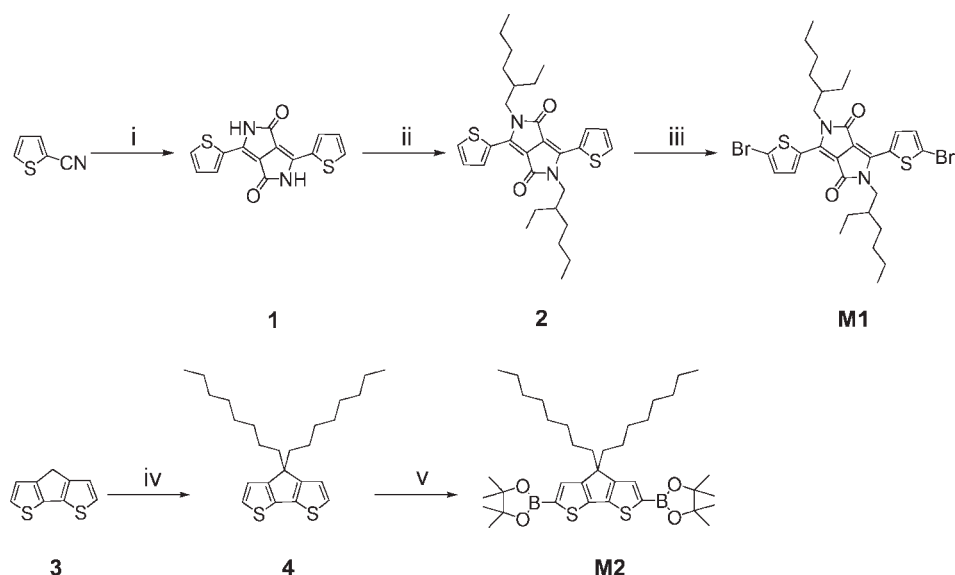
SCHEME 1 Reagents and conditions: (i) dibutyl succinate, Na, *tert*-amyl alcohol, 90 °C, 20 h; (ii) 2-ethylhexyl bromide, DMF, K_2CO_3, 120 °C, 20 h; (iii) NBS, $CHCl_3$, rt, 48 h; (iv) 1-bromooctane, KI, KOH, DMSO, rt, overnight; (v) *n*-BuLi, −78 °C, 1 h; then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, rt, overnight.

toward the planar CT and DPP moieties. We expected the presence of the CT moieties in the polymer backbone to lower the bandgap of the polymer. Scheme 2 displays the copolymerization of the CT and DPP units, performed using a versatile Suzuki cross-coupling reaction.

EXPERIMENTAL

Materials

Thiophene-2-carbonitrile, dibutyl succinate, 2-ethylhexyl bromide, *N*-bromosuccinimide (NBS), 1-bromooctane, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, aliquat 336, tetrakis(triphenylphosphine)palladium(0), bromobenzene, and phenylboronic acid were purchased from Aldrich, Fluka, ACROS, and TCI. Common organic solvents were purchased from Tedia and J. T. Baker. Toluene was dried over calcium hydride; THF was dried over sodium and benzophenone. All other reagents were used as received from their commercial sources.

Measurements and Characterization

^{1}H and ^{13}C NMR spectra were recorded using a Varian Unity-300 NMR spectrometer. The number-average (M_n) and weight-average (M_w) molecular weights of **PCTDPP** were measured through gel permeation chromatography (GPC) using a Waters chromatography unit interfaced with a Waters 2414 differential refractometer. Three 5-μm Waters styragel columns were connected in series in decreasing order of pore size (104, 103, and 102 Å); THF, the eluent and standard polystyrene samples, were used for calibration. Differential scanning calorimetry (DSC) was performed using a Perkin–Elmer Pyris DSC1 instrument operated at a heating rate of 10 °C/min under a N_2 purge. Thermogravimetric analysis (TGA) of **PCTDPP** was performed using a Du Pont TGA 2950 instrument operated at a heating rate of 10 °C/min under a N_2 purge. UV-vis absorption spectra were measured using an HP Agilent-8453 diode array spectrophotometer. Electrochemical cyclic voltammetry (CV) was performed using a BAS 100 electrochemical analyzer and solutions in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the electrolyte; the scan rate was 100 mV/s. A glassy disk carbon electrode coated with a thin film of the polymer was used as the working electrode; a Pt wire was the counter electrode; and Ag/Ag^+ (0.01 M $AgNO_3$) was the reference electrode; ferrocene was the internal standard.

Device Fabrication and Characterization of Solar Cells

Devices were in the configuration glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/**PCTDPP**:PCBM/Al. The active layers were prepared by dissolving **PCTDPP** and PCBM (2 wt %) in 1,2-dichlorobenzene at blend ratios varying from 1:1 to 1:4.
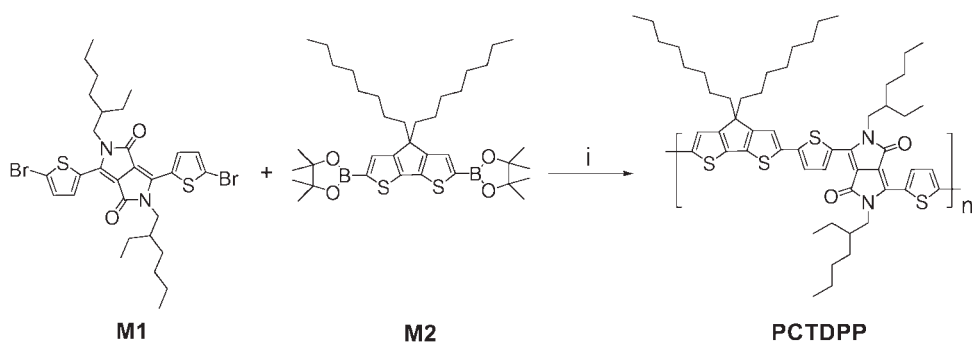
SCHEME 2 Reagents and conditions: (i) Pd(PPh$_3$)$_4$, 2 M K$_2$CO$_{3(aq)}$, toluene, 100 °C, 8 h.

TABLE 1 Molecular Weights and Thermal Properties of PCTDPP

	M_n	M_w	PDI	T_g (°C)	T_d (°C)[a]
PCTDPP	18,000	38,160	2.12	150	385

[a] Temperature at which 5 wt % loss of the initial weight occurred.

After dissolving the components, the resultant solution was spin-coated onto ITO/PEDOT:PSS substrates at 1500 rpm for 60 s. The films were then left to dry at room temperature. No additional thermal treatment was applied to the active layers. The films were subjected to cathode deposition through a shadow mask to result in a device area of 0.12 cm². Aluminum was used as the cathode. The devices were characterized for their photoresponse using an Agilent 4156 semiconductor parameter analyzer, under AM 1.5 radiation (100 mW/cm²). The spectral mismatch factor was calculated by comparison of the solar simulator spectrum and the AM 1.5 spectrum at room temperature.

Synthetic Procedures

4H-Cyclopenta[2,1-b:3,4-b′]dithiophene (**3**) was synthesized according to literature procedures.[48–51] The synthetic procedures for the preparation of the monomers **M1** and **M2** and the copolymer **PCTDDP** are described in Schemes 1 and 2.

3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1)

A mixture of Na (0.490 g, 21.3 mmol) and a catalytic amount of FeCl₃ was dissolved in *tert*-amyl alcohol (10 mL) by heating at 90 °C for 2 h. After cooling to 50 °C, thiophene-2-carbonitrile (0.990 mL, 10.6 mmol) was added and then the mixture was again heated at 90 °C. A solution of dibutyl succinate (1.00 mL, 4.26 mmol) in *tert*-amyl alcohol (5 mL) was added dropwise over 2 h and then the mixture was maintained at 90 °C for 20 h. After cooling to 50 °C, glacial AcOH was added and then the mixture was heated under reflux for 10 min before being filtered. The residue was washed several times with hot MeOH and water, and then the solid was dried under vacuum to yield **1** (0.8 g, 63%). This compound was used directly in the next step without purification.

2,5-Bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (2)

A solution of 2-ethylhexyl bromide (4.89 mL, 27.5 mmol) in DMF (30 mL) was added dropwise to a mixture of Compound **1** (2.50 g, 8.33 mmol), K₂CO₃ (3.83 g, 27.8 mmol), and 18-crown-6 (0.25 g, 0.95 mmol) in DMF (50 mL) at 120 °C and then the mixture was maintained at 120 °C overnight. After cooling to room temperature and filtering, the product was dissolved in CHCl₃ washed with water (3 × 100 mL), and then dried (MgSO₄). The solvent was evaporated under reduced pressure and the crude product was purified through chromatography (SiO₂) to yield **2** (2.05 g, 47%).

¹H NMR (300 MHz, CDCl₃): δ 8.86 (dd, J = 1.2, 3.9 Hz, 2H), 7.60 (dd, J = 1.2, 4.8 Hz, 2H), 7.24 (dd, J = 1.2, 4.8 Hz, 2H), 3.91–3.95 (m, 4H), 1.82–1.84 (m, 2H), 1.21–1.38 (m, 16H), 0.76–1.20 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 161.7, 140.4, 135.2, 130.5, 129.8, 128.4, 107.9, 45.8, 39.1, 30.2, 28.3, 23.5, 23.0, 14.0, 10.5.

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (M1)

NBS (0.36 g, 2.0 mmol) was added to a solution of **2** (0.50 g, 0.95 mmol) in CHCl₃ (30 mL) in a two-neck round-bottom flask covered with Al foil. After stirring at room temperature for 48 h, the reaction mixture was poured into water (100 mL) and extracted with CHCl₃ (3 × 100 mL). The organic layer was dried (MgSO₄) and the solvent was evaporated under reduced pressure. The crude product was purified chromatographically (SiO₂) to yield Compound **M1** (0.34 g, 53%).

¹H NMR (300 MHz, CDCl₃): δ 8.62 (d, J = 4.5 Hz, 2H), 7.19 (d, J = 4.5 Hz, 2H), 3.91–3.95 (m, 4H), 1.79–1.80 (m, 2H), 1.20–1.37 (m, 16H), 0.82–0.88 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 161.4, 139.4, 135.4, 131.4, 131.1, 119.0, 108.0, 46.0, 39.1, 30.1, 28.3, 23.5, 23.0, 14.0, 10.4. Anal. Calcd. for C₃₀H₃₈Br₂N₂O₂S₂: C, 52.79; H, 5.61; N, 4.10. Found: C, 52.50; H, 5.34; N, 3.77%.

4,4-Dioctylcyclopenta[2,1-b:3,4-b′]dithiophene (4)

KOH (3.14 g, 56.2 mmol) was added slowly to a mixture of **3** (2.00 g, 11.2 mmol), 1-bromooctane (8.67 g, 44.9 mmol), and KI (80 mg, 0.48 mmol) in DMSO (55 mL) at 0 °C. After stirring at room temperature overnight, the mixture was poured into water and extracted with hexane (3 × 100 mL). The organic layer was dried (MgSO₄) and the solvent evaporated under reduced pressure. The crude product was purified chromatographically (SiO₂) to yield **4** (3.61 g, 80%).

¹H NMR (300 MHz, CDCl₃): δ 7.12 (d, J = 4.8 Hz, 2H), 6.91 (d, J = 4.8 Hz, 2H), 1.77–1.86 (m, 4H), 1.12–1.55 (m, 20H), 0.80–0.94 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 158.1, 136.4, 124.4, 121.6, 53.2, 37.7, 31.8, 30.0, 29.3, 29.2, 24.5, 22.6, 14.1.
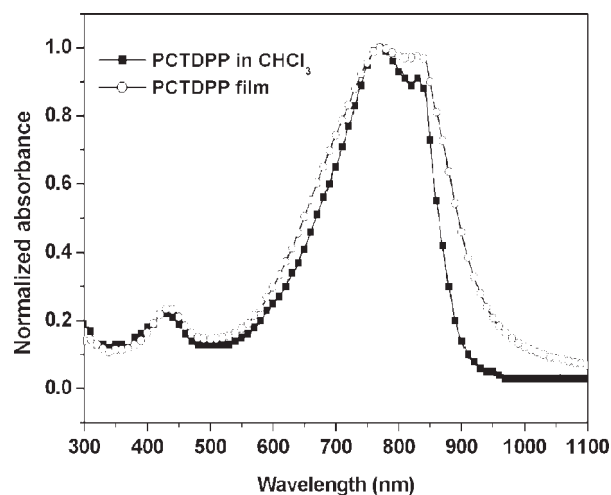

FIGURE 1 Normalized UV-vis absorption spectra of PCTDPP.

TABLE 2 Optical and Electrochemical Properties of PCTDPP

	λ_{max} (nm) sol	λ_{max} (nm) film	E_g^{opt} (eV)[a]	E_{onset}^{ox} (V)	E_{onset}^{red} (V)	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)[b]
PCTDPP	764	772	1.31	0.15	−1.49	−4.95	−3.31	1.64

[a] The value of E_g^{opt} was calculated from the edge of the absorption spectrum of the film.

[b] E_g^{ec} = HOMO−LUMO.

2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,4-dioctylcyclopenta[2,1-b:3,4-b']dithiophene (M2)

n-Butyllithium (1.2 M, 8.72 mL, 10.5 mmol) was added dropwise to a solution of **4** (2.00 g, 4.98 mmol) in dry THF in a three-neck round-bottom flask cooled at −78 °C. After stirring at −78 °C for 1 h, the mixture was warmed to room temperature over a period of 3 h. The reaction mixture was cooled to −78 °C again and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.10 mL, 19.9 mmol) was added in one portion. The solution was warmed to room temperature and stirred overnight before being poured into water and extracted with EtOAc (3 × 100 mL). The organic layer was dried (MgSO₄) and the solvent evaporated under reduced pressure. The crude product was recrystallized (MeOH) to yield **M2** (1.63 g, 50%).

^{1}H NMR (300 MHz, CDCl₃): δ 7.40 (s, 2H), 1.78 (m, 4H), 1.33 (s, 24H), 1.09–1.27 (br, 20H), 0.80–0.90 (m, 10H). ^{13}C NMR (75 MHz, CDCl₃): δ 161.5, 143.9, 131.1, 84.0, 52.7, 37.8, 31.7, 30.0, 29.3, 29.2, 24.7, 24.4, 22.6, 14.0. Anal. Calcd. for C₃₇H₆₀B₂O₄S₂: C, 67.89; H, 9.24. Found: C, 67.70; H, 9.42%.

PCTDPP

A mixture of **M1** (100 mg, 0.150 mmol), **M2** (96.1 mg, 0.150 mmol), aliquat 336 (ca. 20 mg), K₂CO₃(aq) (2 M, 1.41 mL), and toluene (2.82 mL) was degassed at 60 °C for 10 min. Pd(PPh₃)₄ was added to the mixture, which was then heated at 110 °C for 8 h. Phenylboronic acid (49.9 mg, 0.301 mmol) was added and then the mixture was stirred 12 h. Subsequently, bromobenzene (0.03 mL, 0.301 mmol) was also added to the mixture, and the whole mixture was stirred for another 12 h. The reaction mixture was poured into MeOH (50 mL) and filtered. The precipitated material was purified by washing with MeOH, acetone, and hexane in a Soxhlet system. The solid residue was then dissolved in CHCl₃ and filtered. The solution was added into MeOH and the pure polymer was collected by filtration (80 mg, 57%).

^{1}H NMR (300 MHz, CDCl₃): δ 8.86 (br, 2H), 7.15 (br, 2H), 6.89–6.93 (m, br, 2H), 4.06 (br, 4H), 1.87 (br, 6H), 1.23 (br, 40H), 0.87 (br, 18H). ^{13}C NMR (75 MHz, CDCl₃): δ 160.9, 159.6, 143.3, 138.2, 137.3, 127.6, 123.4, 118.3, 107.8, 54.5, 45.9, 39.2, 37.9, 31.8, 30.1, 29.6, 29.4, 29.3, 28.6, 24.5, 23.7, 23.1, 22.6. 14.0, 10.6, 0.9. Anal. Calcd. for C₅₅H₇₄N₂O₂S₄: C, 71.53; H, 8.08; N, 3.03. Found: C, 72.08; H, 7.89; N, 3.03%.

RESULTS AND DISCUSSION

Synthesis and Characterization

Schemes 1 and 2 illustrate the synthetic routes that we used to prepare the monomers **M1** and **M2** and the copolymer **PCTDPP**. 3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrolo-1,4(2*H*,5*H*)-dione (**1**) was synthesized through the condensation of thiophene-2-carbonitrile and dibutyl succinate; without further purification, it was alkylated to provide Compound **2**. **M1** was obtained through subsequent bromination. 4*H*-Cyclopenta[2,1-b:3,4-b']dithiophene (**3**) was alkylated to provide Compound **4**, which was successively treated with *n*-BuLi and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to yield **M2**. Copolymerization of **M1** and **M2** through Suzuki cross-coupling provided the copolymer **PCTDPP**. The structures of the monomers and polymer were confirmed using ^{1}H and ^{13}C NMR spectroscopy and ELEM. ANAL. Table 1 lists the molecular weights, thermal decomposition temperature, and glass transition temperature of the polymer. The number-average weight (M_n) and polydispersity index (PDI) of polymer were 18,000 g/mol and 2.12, respectively. The polymer exhibited good thermal stability, with its 5% weight-loss temperature (T_d) at 385 °C and a high glass transition temperature (T_g) of 150 °C. It was soluble in several chlorinated organic solvents, including CHCl₃, chlorobenzene, and 1,2-dichlorobenzene.

Optical Properties

Figure 1 presents the absorption spectra of the polymers in dilute solution and as thin films; Table 2 summarizes the corresponding optical data. In dilute CHCl₃, **PCTDPP** exhibited a small absorption band at 350–480 nm, which originated from the presence of CT moieties, and a large and broad absorption band between 500 and 900 nm, which arose from intramolecular charge transfer (ICT) between the CT and DPP units. The absorption maximum of **PCTDPP** in CHCl₃ was located at 764 nm—a longer wavelength than that of a DPP-derivative polymer featuring a quaterthiophene
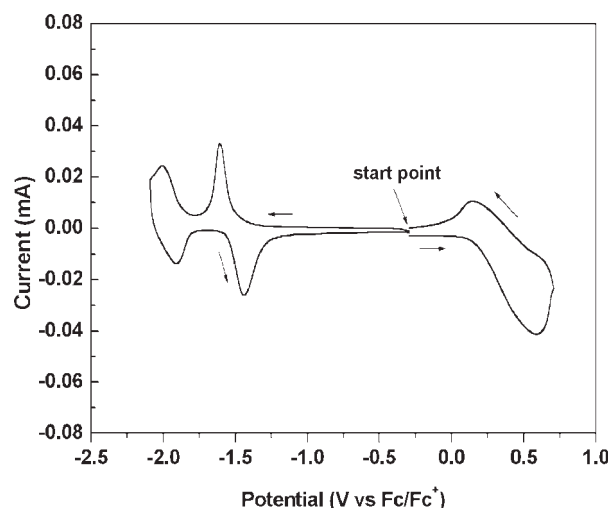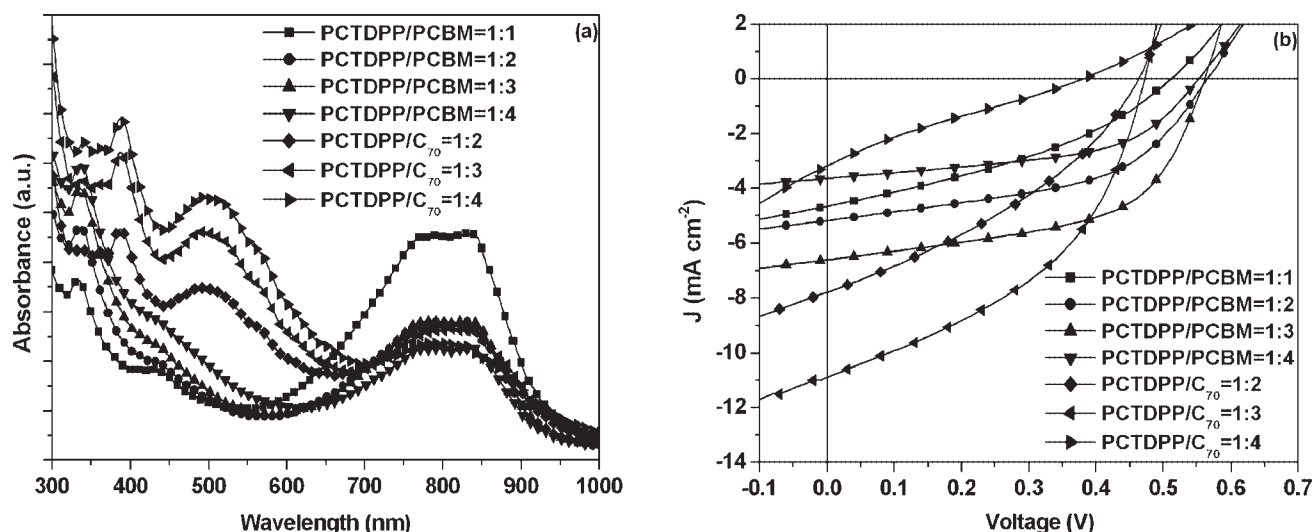

FIGURE 2 CV trace of PCTDPP.

FIGURE 3 (a) Absorption spectra and (b) plots of illuminated current density (J) with respect to applied voltage (V) at various PCTDPP:PCBM and PCTDPP:C_{70} blend ratios.

segments as the donor (650 nm)[41]—because the presence of planar CT units in the polymer backbone increased the degree of coplanarity and provided a longer effective conjugation length. Relative to the solution absorption, the absorption spectrum of the polymer solid film was slightly broadened and exhibited a slight red shift, indicating that good intermolecular interactions and aggregation occurred in the solid-state again, as a result of the more-planar structure and strong polarity of the lactam moieties of the DPP units. The optical band gap (E_g^{opt}), calculated from the absorption edge (948 nm) of the solid state film, was 1.31 eV. Because this polymer exhibited a broad absorption range (350–1000 nm) and a low bandgap, we suspected that its good overlap with the solar spectrum would improve the degree of light harvesting and enhance the photocurrent of the devices.

Electrochemical Properties

CV is used widely to calculate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of polymers. We performed CV of a polymer film in acetonitrile containing 0.1 M TBAPF$_6$ at a potential scan rate of 100 mV/s. Figure 2 reveals that **PCTDPP** exhibited reversible reduction and oxidation processes, implying excellent electrochemical stability and high structural stability in charged states[29,52,53]; Table 2 summarizes the CV data. The onset oxidation and reduction potentials of **PCTDPP** were located at 0.15 and −1.49 V, respectively. The HOMO and LUMO energy levels of **PCTDPP** were −4.95 and −3.31 eV, respectively, relative to ferrocene (4.80 eV below the vacuum) as the reference.[26,44,54] We assign the oxidation potential to oxidation of the CT units, because CT has a HOMO energy level of about −5.1 eV.[55] The low onset oxidation potential of **PCTDPP** confirms that the electron-donor ability of CT is strong, leading to a decreased bandgap relative to that of the DPP-derivative polymer incorporating quaterthiophene moieties as donor units. We attributed the reduction potential to the reduction of the DPP units.[41] Low

onset reduction potential of **PCTDPP** indicates that DPP possesses a strong electron-withdrawing ability due to the lactam structures. To overcome the exciton binding energy of the polymer and, thereby, transport electrons from the polymer to PCBM, the LUMO energy level of the polymer must be positioned above the LUMO energy level of PCBM by at least 0.3 eV.[56,57] Gratifyingly, the LUMO energy level of **PCTDPP** suggests that electrons could be transported efficiently to PCBM; that is, the LUMO offset was 0.85 eV relative to the LUMO energy level of PCBM (−4.1 eV).[16,29] The fact that the electrochemical band gap (E_g^{ec}) is higher than the optical band gap (E_g^{opt}), may be due to the interface energy barrier presented between the polymer film and the electrode surface.[31,58]

Photovoltaic Properties

Figure 3 displays the absorption spectra of **PCTDPP**/PCBM blends and the photocurrents of devices having the structure ITO/PEDOT:PSS/**PCTDPP**:PCBM/Al under illumination at AM 1.5 G and 100 mW/cm^2. The absorption spectra of the active layer exhibits absorptions at wavelengths in the range from 600 to 950 nm, contributed by **PCTDPP**, and a small peak at about 350 nm resulting from the presence of PCBM. The

TABLE 3 Photovoltaic Properties of Polymer Solar Cells[a]

Weight Ratio of Polymer to PCBM	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
PCTDPP:PCBM = 1:1	0.51	4.66	0.35	0.84
PCTDPP:PCBM = 1:2	0.56	5.18	0.49	1.44
PCTDPP:PCBM = 1:3	0.56	6.60	0.55	2.05
PCTDPP:PCBM = 1:4	0.55	3.63	0.51	1.02
PCTDPP:C$_{70}$ = 1:2	0.46	7.84	0.34	1.21
PCTDPP:C$_{70}$ = 1:3	0.47	10.87	0.45	2.27
PCTDPP:C$_{70}$ = 1:4	0.37	3.17	0.21	0.24

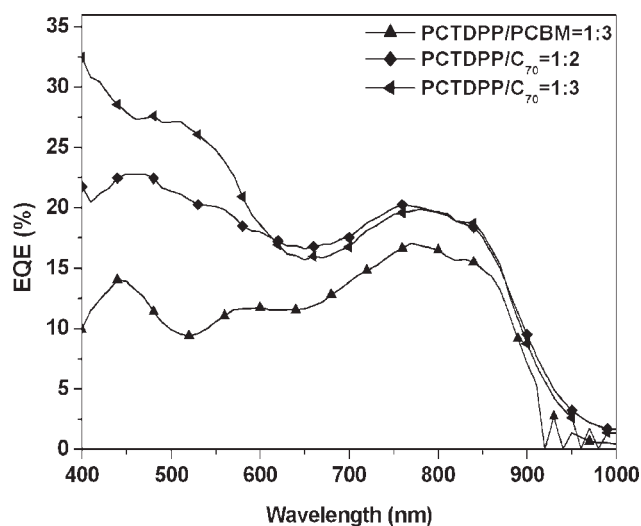[a] Polymer solar cell device structure: ITO/PEDOT:PSS/polymer:PCBM/Al.

FIGURE 4 EQE spectra of the active layers (PCTDPP/C_{70}) at blend ratios of 1:2, 1:3, and PCTDPP/PCBM at blend ratios of 1:3.

broad absorption band indicates that all available photons from sunlight have the potential to be absorbed by the active layer. Table 3 summarizes the performance of the devices. The short circuit current density (J_{sc}) increased significantly when we increased the amount of PCBM from a blend ratio of 1:1–1:3. Increasing the loading weight ratio of PCBM to 1:4, however, decreased the short circuit current, presumably because of increased aggregation of PCBM.[59] For a blend ratio of 1:3, we obtained values of J_{sc} and PCE of 6.60 mA/cm^2 and 2.05%, respectively. Next, we prepared solar cell devices incorporating C_{70} as a replacement for PCBM as the electron acceptor. Figure 3(a) reveals the presence of an absorption in the short wavelength range (ca. 500 nm) that arose from C_{70}, thereby leading an increased absorption intensity in the short wavelength range.[60] Figure 4 displays the external quantum efficiency (EQE) curve of the device; its shape resembles that of the absorption spectra of the active layer, implying that all of the absorbed photons contributed to induce the photocurrent. The device exhibited a very broad response range, from 400 to 950 nm, which allowed the active layer to absorb more available photons and enhance the photocurrent of the devices. A higher quantum efficiency at a wavelength of about 500 nm was obtained for the device incorporating a blend ratio of 1:3; that is, it was enhanced upon increasing the loading weight of C_{70}. The short-circuit current also decreased when the weight ratio of **PCTDPP** to C_{70} is 1:4, which exhibiting a similar trend with that of **PCTDPP**/PCBM. Accordingly, the device based on **PCTDPP**:C_{70} (1:3) exhibited the highest values of J_{sc} and PCE-10.87 mA/cm^2 and 2.27%, respectively.

CONCLUSIONS

We have used Suzuki coupling to synthesize a new polymer, **PCTDPP**, that features alternating CT and DPP units in its main chain. This polymer possesses a high glass transition temperature, good solubility, and high thermal stability.

Incorporating planar CT units in the polymer backbone lowered the bandgap of the copolymer to 1.31 eV and broadened the absorption band to the range from 350 to 1000 nm. The maximum values of J_{sc} and PCE (10.87 mA/cm^2 and 2.27%, respectively) were obtained from the device incorporating **PCTDPP** and C_{70} at a blend ratio of 1:3.

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