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

GUAN-YU CHEN,1 CHIEN-MING CHIANG,1 DHANANJAY KEKUDA,2 SHANG-CHE LAN,1 CHIH-WEI CHU,2,3 KUNG-HWA WEI*1

1Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan
2Research Center for Applied Sciences, Academia Sinica, Taipei 115, Taiwan
3Department of Photonics, National Chiao Tung University, Hsinchu 300, Taiwan

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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 C70 at a blend ratio of 1:3 exhibited a high short-circuit current of 10.87 mA/cm² 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-C61-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. A bulk heterojunction polymer solar cell incorporating rr-P3HT and C70 at a blend ratio of 1:3 exhibited a high short-circuit current of 10.87 mA/cm² and a power conversion efficiency of 2.27%. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1669–1675, 2010

Many D–A conjugated polymers contain thiophene,18–20 fluorene,21,22 carbazole,23–26 and cyclopentadithiophene27–29 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/PC71BM can achieve a high PCE of 6.1%.24,36 Another case involves poly[2,6-(4,4-bis[2-ethylhexyl]-4H-cyclopent[a][1,2-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/PC71BM 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...
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-$\mu$m 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.
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.¹⁰⁻¹¹³ 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-Bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)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%).

#### 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%).

#### 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%).

### Table 1: Molecular Weights and Thermal Properties of PCTDPP

<table>
<thead>
<tr>
<th></th>
<th>Mᵣ</th>
<th>Mₘ</th>
<th>PDI</th>
<th>Tₙ (°C)</th>
<th>Tₛ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCTDPP</td>
<td>18,000</td>
<td>38,160</td>
<td>2.12</td>
<td>150</td>
<td>385</td>
</tr>
</tbody>
</table>

* Temperature at which 5 wt % loss of the initial weight occurred.

#### FIGURE 1

Normalized UV-vis absorption spectra of PCTDPP.
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%).

3H 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). 13C 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%.

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]pyrrole-1,4(2H,5H)-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. 4H-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 1H and 13C 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 (Mn) 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 (T5) at 385 °C and a high glass transition temperature (Tg) 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

<table>
<thead>
<tr>
<th>λ∞ (nm) sol</th>
<th>λ∞ (nm) film</th>
<th>E°g (eV)</th>
<th>E°onsmin (V)</th>
<th>E°onsmax (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>E°c (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCTDPP</td>
<td>764</td>
<td>772</td>
<td>1.31</td>
<td>0.15</td>
<td>−1.49</td>
<td>−4.95</td>
<td>−3.31</td>
</tr>
<tr>
<td>M1</td>
<td>787</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td>782</td>
<td></td>
<td></td>
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</tbody>
</table>

* a The value of E°ons was calculated from the edge of the absorption spectrum of the film.

*b E°c = HOMO–LUMO.
segments as the donor (650 nm)\textsuperscript{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 ($E_{\text{opt}}$), 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\textsuperscript{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.\textsuperscript{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.\textsuperscript{55} The low onset oxidation 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.\textsuperscript{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).\textsuperscript{16,29} The fact that the electrochemical band gap ($E_{\text{EC}}$) is higher than the optical band gap ($E_{\text{opt}}$), may be due to the interface energy barrier presented between the polymer film and the electrode surface.\textsuperscript{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.

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

*Polymer solar cell device structure: ITO/PEDOT:PSS/polymer:PCBM/Al.*
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. 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. 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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REFERENCES AND NOTES
