Effect of Side Chain Conjugation Lengths on Photovoltaic Performance of Two-Dimensional Conjugated Copolymers That Contain Diketopyrrolopyrrole and Thiophene With Side Chains

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ABSTRACT: Two new two-dimensional conjugated copolymers that contain diketopyrrolopyrrole and thiophene with different π conjugation lengths as side chains, called **PDPPMTD** and **PDPPBTD**, were designed and synthesized for use in polymer solar cells (PSCs). The resulting copolymers in the thin film state displayed broad absorption in the visible range with an absorption edge at over 1000 nm, and both had relatively low-lying HOMO levels, at -5.20 and -5.18 eV for **PDPPMTD** and **PDPPBTD**, respectively. The power conversion efficiency (PCE) of the PSC that was based on **PDPPBTD**/PC61BM (w/w = 1:2) reached 4.10 % with a Jsc of 14.5 mA/cm2, a Voc of 0.59 V and

an FF of 48%, while **PDPPMTD**/PC61BM (w/w = 1:2) had a PCE of 2.96% with a Jsc of 12.6 mA/cm2, a Voc of 0.60 V, and an FF of 39%. These results indicate that subtle tuning of the chemical structure can significantly influence Jsc and FF. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *00*, 000–000

KEYWORDS: diketopyrrolopyrrole; donor-acceptor copolymer; polymer solar cell; thiophene with side chains; two-dimensional conjugated copolymer

INTRODUCTION In the last few years, polymer solar cells (PSCs) based on bulk heterojunction (BHJ) concept that consisted of a blend with a donor polymer and a acceptor fullerene derivative, [6,6]-phenyl C_{61} butyric acid methyl ester (PC₆₁BM) or [6,6]-phenyl C₇₁ butyric acid methyl ester ($PC_{71}BM$), have attracted considerable interest because these materials are flexible, lightweight, and potentially low-cost, and so suitable for roll-to-roll production, and the cells in which they are used represent a renewable alternative to fossil energy.¹⁻⁶ Substantial progress has been made in polymer/fullerene hybrid systems that are based on the concept of BHJ, and power conversion efficiencies (PCEs) over 8% have been obtained.⁷⁻⁹ Much attention has been paid to put these BHJ PSCs into large-scale manufacturing (such as rollto-roll production). Notably, only a few of polymers with a high PCE achieve the requirements for roll-to-roll manufacturing.¹⁰⁻¹⁴ Therefore, there is still a plenty of room to develop new polymers with a high PCE for commercialization. The development of materials with a high PCE is challenging for material chemists who must incorporate several required characteristics into a specific molecular design and synthetic sequences. To achieve a high efficiency, a polymer

must have a broad absorption spectrum that matches the solar spectrum as closely as possible, a deep highest occupied molecular orbital (HOMO), excellent carrier mobility, and compatible with the fullerene derivative. For most of the semiconducting polymers that have been developed, in which the push-pull effect is utilized for band gap engineering have become the most useful class of materials for use in donor-acceptor (D-A) type BHJ PSCs because they generally have a narrow band gap and their energy levels [both HOMO and lowest unoccupied molecular orbital (LUMO)] can be easily tuned via appropriate molecular design. However, most polymers that can be used in PSCs have strong absorption ability below 700 nm in the visible region. Few examples exhibit good absorption to the major component of the solar spectrum in the red or near infrared region. Accordingly, a narrow bandgap material that can absorb light in the longer wavelength region is sought to fabricate highly efficient PSCs with less energy loss and enhanced photocurrents.15-18 Of wide range of narrow bandgap materials that have been developed for BHJ PSCs, the diketopyrrolopyrrole (DPP)-based polymers are of particular interest because of their excellent optical and electrical characteristics.^{19–23} The

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electron-deficient character of DPP has been utilized to synthesize large amounts of D-A type materials in which the DPP moiety was directly copolymerized with aromatic electron-rich units. The combination of DPP and unsubstituted thiophene units were particularly advantageous for organic electronic applications. To date, BHJ PSCs that contain DPP moiety have now exceeded the PCEs up to 8% and mobilities of organic thin film transistors have been achieved about 1.5 cm² V⁻¹ s^{-1.24-27} However, most of the above mentioned DPP-based copolymers are linear D-A type materials and only limited number of studies have examined the devices performance on DPP-based copolymers with two-dimensional (2D) configurations.^{16,28,29}

Recently, researchers have developed a new class of 2D conjugated polymers with side chains or conjugated side groups that broaden the absorption region of the polymers; do not reduce the high hole mobility of the polymers, and provide a relatively low-lying HOMO energy level. These polymers are of interest for their high-performance when they use in PSCs.³⁰⁻³⁶ Herein, two 2D conjugated D-A copolymers that contained DPP and thiophene with different π conjugation lengths as side chains, called PDPPMTD and PDPPBTD, were synthesized via Suzuki cross-coupling polymerization, exhibiting favorable light harvesting, charge transporting properties, and photovoltaic properties. The DPP derivative was employed as an electron-withdrawing unit while the thiophene with side chain was used as an electron-donating unit in construction of 2D D-A type copolymers. Therefore, the resulting copolymers exhibit electron D-A architectures, with small bandgaps and wide absorption bands. The D-A strategy has been established as one of the commonly useful strategy for preparing narrow bandgap polymers by taking the advantage of the efficient intramolecular charge transfer (ICT) from the electron-donating to the electron-withdrawing moieties. In this work, the influence of the number of thiophenes on the side chains of the resulted copolymers on their photophysical and electrochemical characteristics are investigated. Additionally, the morphological and photovoltaic properties of the polymer/fullerene blend films are studied in detail. This work demonstrates that subtle tuning of the chemical structure can considerably affect both J_{sc} and FF.

EXPERIMENTAL

Chemicals

All chemicals, unless otherwise noted, were obtained from commercial sources (including Alfa Aesar, Aldrich, and TCI Chemical Co.), and they were utilized as received. Diethyl ether, dichloromethane, ethyl acetate, chlorobenzene, *N*,*N*-dimethylmethanamide (DMF), tetrahydrofuran (THF), *o*-dichlorobenzene (*o*-DCB) and toluene, were freshly distilled and dried before use. 2,5-Bis(2-ethylhexyl)-3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione,³⁷ 2,5-bis(2-eth-ylheyl)-3,6-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl] thiophene-2-yl]-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**DPPB**),³⁸ and 2,2'-bithiophene-5-carbaldehyde³⁹ were prepared according to corresponding literature procedures. The

synthetic routes of (*E*)-4-(5-(2-(2,5-dibromothiophen-3-yl)vinyl)thiophen-2-yl)-*N*,*N*-diphenylaniline (**MTD**), including the intermediates and reactants, *N*,*N*-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**BDA**), 5-bromothiophene-2-carbaldehyde (**BTC**), 5-(4-(diphenylamino)phenyl)thiophene-2carbaldehyde (**DTC**), and diethyl(2,5-dibromothiophene-3-yl) methylphosphonate (**BTP**), were previously established and these compounds were synthesized in our laboratory.^{40,41} [6,6]-Phenyl C₆₁ butyric acid methyl ester (PC₆₁BM), [6,6]-phenyl C₇₁ butyric acid methyl ester (PC₇₁BM) and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) were purchased from UR and H. C. Starck, respectively, and used as received.

5'-Bromo-2,2'-Bithiophene-5-Carbaldehyde (BBC)

To an ice-cooled solution of 2,2'-bithiophene-5-carbaldehyde (0.78 g, 4 mmol) in DMF (10 mL), *N*-bromosuccinimide (0.72 g, 4 mmol) was added portion-wise, and the mixture thus formed was stirred overnight at room temperature. This mixture was poured into iced water, extracted twice using dichloromethane, dried over anhydrous MgSO₄ and evaporated to full dryness. Further purification was conducted on a silica column using hexane:ethyl acetate (20:1) as the eluent to yield **BBC** as a yellowish solid (0.78 g, 71%). ¹H NMR(CD₂Cl₂, 300 MHz, δ /ppm): 9.83 (s, 1H), 7.65 (d, 1H, *J* = 3.9 Hz), 7.20 (d, 1H, 3.9 Hz), 7.12 (d, 1H, *J* = 4.2 Hz), 7.04 (d, 1H, *J* = 3.9 Hz). ¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 182.54, 145.83, 141.99, 137.42, 137.23, 131.20, 126.21, 124.38, 114.17.

5'-(4-(Diphenylamino)phenyl)-2,2'-Bithiophene-5-Carbaldehyde (DBC)

Under an atmosphere of nitrogen, a mixture of BDA (3.71 g, 10 mmol), BBC (2.73 g, 10 mmol), and Pd(PPh₃)₄ (231 mg, 0.2 mmol) was added into a two-neck flask. Next, a mixed solution of 90 mL of degassed toluene and 30 mL of degassed aqueous K_2CO_3 (2 M) were added into the above mixture. The mixture was heated to 120°C and stirred vigorously for 48 h. After the reaction mixture was cooled to room temperature, and then it was extracted using ethyl acetate and water, dried over anhydrous MgSO4 and evaporated to full dryness. Further purification was conducted on a silica column using EA:hexanes (1:10) as the eluent to yield DBC as a yellow solid (3.32 g, 76%). ¹H NMR(CDCl₃, 300 MHz, δ /ppm): 9.85 (s, 1H), 7.67 (d, 1H, I = 3.9 Hz), 7.46 (d, 2H, I = 8.7 Hz), 7.32–7.23 (m, 6H), 7.18–7.04 (m, 9H). ¹³C NMR (CDCl₃, 75 MHz, δ /ppm): 182.48, 148.17, 147.59, 146.40, 141.37, 137.63, 134.18, 129.54, 127.38, 127.20, 126.74, 123.87, 123.59, 123.27.

(*E*)-4-(5'-(2-(2,5-Dibromothiophen-3-yl)vinyl)-2,2'-Bithiophen-5-yl)-*N*,*N*-Diphenylaniline (BTD)

In an atmosphere of nitrogen, CH_3ONa (0.54 g, 10 mmol) was added in portions to a solution of **BTP** (1.96 g, 5 mmol) in 25 mL DMF in an ice bath and stirred for 20 min. Then a solution of **DBC** (1.50 g, 3.42 mmol) in 30 mL DMF was added. The reaction mixture was allowed to warm up slowly to room temperature and then stirred for 5 h. The reacting

system was poured into ice water, extracted with ethyl acetate, washed with brine, dried over magnesium sulfate and distilled under reduced pressure. Further purification was conducted on a silica column (dichloromethane/hexanes, 1:10 as eluent) to afford **BTD** as a yellow solid (1.41 g, 61%). ¹H NMR(CD₂Cl₂, 300 MHz, δ /ppm): 7.57 (d, 2H, *J* = 8.7 Hz), 7.42–7.37 (m, 5H), 7.27–7.14 (m, 11H), 7.11–7.05 (m, 2H), 6.86 (d, 1H, *J* = 15.9 Hz).¹³C NMR (CDcl₃, 75 MHz, δ /ppm): 147.61, 147.51, 143.65, 140.67, 138.89, 137.40, 135.67, 129.48, 127.94, 127.27, 126.51, 125.02, 124.75, 124.29, 123.91, 123.61, 123.36, 123.07, 119.41, 112.11, 109.99. Anal. Calcd for C₃₂H₂₁Br₂NS₃: C,56.90; H, 3.13; N, 2.07; S, 14.24. Found: C, 56.71; H, 2.85; N, 2.33; S, 14.23.

2,5-Bis(2-Ethylheyl)-3,6-bis[5-(4,4,5,5-Tetramethyl-1,3,2-Dioxoborolan-2-yl)thiophene-2-yl]-2,5-

Dihydropyrrolo[3,4-c]pyrrole-1,4-Dione (DPPB)

DPPB was synthesized according to the methods in the literature.³⁸ Under an atmosphere of nitrogen, a solution of diisopropylamine (0.20 mL, 1.41 mmol) in 6 mL of dry THF was put into a two-neck flask. Then, the n-Butyllithium in *n*-hexane (0.50 mL, 1.25 mmol) was added slowly at 0°C to the flask. The freshly prepared LDA solution was added at -25° C within 20 min to 4 mL of a THF solution of 2,5-bis(2ethylhexyl)-3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (264 mg, 0.50 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (280 mg, 1.50 mmol). After stirring at 0°C for 1 h, the reaction was quenched by adding 5 mL of 1 M HCl solution. Following extraction with chloroform, the organic layer was dried over magnesium sulfate and evaporated to full dryness. After that, the residue was dissolved using 5 mL of dichloromethane, and poured into a stirred acetone (300 mL) solution. The obtained precipitate was then filtered off and washed with acetone to form **DPPB** as a pink solid (0.27 g, 70%). ¹H NMR (CDCl₃, 300 MHz, δ /ppm): 8.92 (d, 2H, I = 3.9 Hz), 7.70 (d, 2H, J = 3.9 Hz), 4.03 (m, 4H), 1.82 (m, 2H), 1.36-1.24 (m, 40H), 0.86 (m, 12H). ¹³C NMR (CDCl₃, 75 MHz, δ / ppm): 161.90, 140.65, 137.82, 136.34, 135.78, 108.86, 84.76, 46.05, 39.17, 30.36, 28.83, 24.91, 23.74, 23.18, 14.21, 10.63. Anal. Calcd for C₄₂H₆₂B₂N₂O₆S₂: C,64.95; H, 8.05; N, 3.61; S, 8.26. Found: C, 64.87; H, 8.16; N, 3.56; S, 8.06.

Synthesis of PDPPMTD

In an atmosphere of nitrogen, **MTD** (594 mg, 1.0 mmol) and **DPPB** (777 mg, 1.0 mmol) were added into a two-neck flask. Next, 30 mL of toluene and 4 mL of aqueous K_3PO_4 (1.6 M) were added into the mixture. The reaction mixture was subjected to three freeze-pump-thaw cycles degassing process in order to remove O_2 . Next, $Pd_2(dba)_3$ (22.9 mg, 0.025 mol) and [(t-Bu)_3P]HBF₄ (14.5 mg, 0.05 mol) were added to the reaction mixture was cooled to room temperature, the reaction system was poured into a 400 mL solution of methanol and deionized water (3:1). The precipitate was filtrated with a filter, then dissolved in chloroform, and reprecipitated from water first and then from methanol. Soxhlet extractions were conducted using acetone and ethyl acetate for further purification. Fibrous polymer **PDPPMTD** was obtained as a dark green solid with isolated yields of 40% after drying under a vacuum for 24h. Gel permeation chromatography (GPC) THF: Weight-average molecular weight (M_w) = 59.8 kg/mol and polydispersity index (PDI, M_w/M_n) = 1.75. ¹H NMR (CD₂Cl₂, 300 MHz, δ /ppm): 9.10–8.86 (br, 2H), 7.75–6.65 (m, 21H), 4.20–3.80 (br, 4H), 2.01–0.55 (m, 30H). Anal. Calcd for C₅₈H₅₇N₃O₂S₄: C,72.69; H, 6.21; N, 4.38; S, 13.38. Found: C, 72.00; H, 6.75; N, 4.35; S, 12.78.

Synthesis of PDPPBTD

PDPPBTD (dark green solid) was prepared using the same procedures as described for **PDPPMTD** using **BTD** (676 mg, 1.0 mmol) and **DPPB** (777 mg, 1.0 mmol). Yield: 42%. GPC (THF): $M_w = 57.6$ kg/mol and PDI = 1.55. ¹H NMR (CDCl₃, 300 MHz, δ /ppm): 9.11–8.88 (br, 2H), 7.60–6.62 (m, 23H), 4.20–3.81 (br, 2H), 2.02–0.52 (m, 30H). Anal. Calcd for C₆₂H₅₉N₃O₂S₅: C,71.57; H, 5.91; N, 4.04; S, 15.41. Found: C, 71.82; H, 6.29; N, 4.16; S, 14.43.

Characterization of Copolymers General

A Varian Unity Inova 300WB NMR spectrometer was used to record ¹H and ¹³C NMR spectra. Elemental analyses were conducted using an Elementar Vario EL III elemental analyzer. GPC (Waters GPC-1515 with Refractive Index Detector 2414) was performed with THF as the eluent and polystyrene as the standard to determine the molecular weights of copolymers. Thermogravimetric analysis (TGA) measurements were conducted on a Perkin-Elmer TGA-7 analyzer with a scanning rate of 10 deg/min under an atmosphere of nitrogen to determine the thermal decomposition temperatures (T_d) of copolymers. Hewlett-Packard 8453 and Hitachi F-7000 spectrophotometers were used to obtain the UV-visible absorption and fluorescence spectra of the copolymers, respectively. Cyclic voltammetry (CV) measurements were performed by using an electro-chemical analyzer CHI 612D (with a scanning rate of 50 mV s^{-1}) to determine the Redox potentials of the polymers. The measurements were performed in an anhydrous N₂-saturated solution of 0.1 M Bu₄NClO₄ in MeCN with a platinum (Pt) plate coated with a thin polymer film as the working electrode, a Pt wire as the counter electrode, and an Ag/Ag⁺ (0.10 M AgNO₃ in MeCN) as the reference electrode. The CV curves was calibrated against Ferrecene/Ferrocene⁺. Atomic force microscope (AFM) topographic images of the polymer-fullerene blend films were conducted on a Seiko SII SPA400 in tapping mode. Veeco Dektak 150 surface profiler was used to determine the thickness of the active layer of the device. Transmission electron microscopy (TEM) images of the active layers were performed using a JEOL JEM-1200EX II instrument at an accelerating voltage of 120 kV. Powder X-ray diffraction (XRD) measurements were performed in a Philips X'Pert diffractometer equipped with an X'Celerator detector. The sample was irradiated with a beam of monochromatic Cu K α having a wavelength of 0.154 nm. To determine the hole and electron mobilities of the blend films, hole-only (ITO/PEDOT:PSS/blend film/Au) and electron-only (ITO/



blend film/LiF/Al) devices were fabricated. The carrier mobility was estimated using the well-known Mott-Gurney space-charge-limited-current (SCLC) equation,^{42,43}

$$J = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{L^3}$$

where *J* denotes the current density; ε is the relative permittivity of a blend film; ε_0 is the permittivity of a vacuum; *V* is the applied voltage, and *L* is the thickness of the blend film.

Fabrication and Characterization of PSCs

All PSCs were prepared using the following fabrication procedure.^{44,45} Glass substrates that had been coated with indium tin oxide (ITO) (with patterned lithographically) were cleaned using the following procedures: cleansed with detergent, ultrasonicated in acetone and isopropyl alcohol, dried on a hot plate at 120°C for 5 min, and treated with oxygen plasma for 5 min. Then the hole-transporting material PEDOT:poly(styrenesulfonate) (PEDOT:PSS, Clevios P-VP AI4083) was spin-cast on top of ITO-coated glass at 4000 rpm and dried on a hot plate at 120°C for 10 min. Subsequently, the film-based photo-active layer which blended with fullerene derivatives (both PC61BM and PC71BM) and copolymer at various weight ratios (1:1 to 1:3, w/w) in o-DCB was spincast on the top of the PEDOT:PSS layer at 600 rpm for 60s and then annealed at 140°C for 10 min. Following deposition of the Ca-based (30 nm)/Al (100 nm) cathode, the current density-voltage (I-V) curves of the PSCs (device area was 4 mm^2) were examined under illumination by 100 $mW \ cm^{-2}$ solar light from an AM 1.5G solar simulator (Oriel solar simulator) with current and voltage sources programmable electrometer (Keithley 2400). The calibration of illumination Intensity was using a standard Si-photodiode detector that was contained a KG-5 filter. To measure the incident photonto-electron conversion efficiency (IPCE), a xenon lamp connecting to a monochromator was used as the light source and its output was monitored using a photodiode with a lock-in amplifier. All electrical measurements were made in air.

RESULTS AND DISCUSSION

Characterization of Copolymers

Scheme 1 describes the synthesis of monomers that are used herein and the designed copolymers. The synthetic routes of MTD, including the intermediates and reactants were synthesized as in our previous report.^{40,41} Another monomer, **BTD**, was obtained from a Wittig-Horner-Emmons reaction of BTP with DBC, which had been easily prepared by reacting BDA with **BBC** in the presence of $Pd(PPh_3)_4$ as a catalyst in a Suzuki cross-coupling reaction. PDPPMTD was also synthesized by the Suzuki cross-coupling polymerization of MTD and **DPPB**, but the catalyst was $Pd_2(dba)_3$ to increase the degree of polymerization. PDPPBTD was synthesized using the same method, by coupling BTD and DPPB. The copolymers thus obtained were purified by repeated precipitation and Soxhlet extractions. The resulting copolymers were soluble in some organic solvents such as THF, chloroform, toluene, chlorobenzene and o-DCB (See Supporting Information Table S1 and Fig. S1 for the solubility tests). This high solubility may arise from the slightly twisted conformation that is caused by the introduction of bulky aromatic side chains, which increase the steric hindrance of the polymer main chains. Table 1 presents the number-average (M_n) and weight-average (M_w) molecular weights of these polymers, as determined by GPC with THF as the eluent and polystyrene as the standard. The number-average molecular weights (M_n) of **PDPPMTD** and **PDPPBTD** were found to be 59.8 and 57.6 kg mol⁻¹ respectively, and the respective polydispersity indices were 1.75 and 1.55.

The operational stability of an optoelectronic device is directly related to the thermal stability of the conjugated polymers within it. Therefore, a high T_{d} is preferred for the application of a conjugated polymer to PSCs.⁴⁰ As indicated in Table 1, **PDPPMTD** and **PDPPBTD** had T_d values (at which a 5% weight loss occurred) of 375 and 394°C, respectively, under an atmosphere of nitrogen. These copolymers clearly exhibited favorable thermal stability, which sufficed for their application to use in PSCs. Powder XRD measurements were carried out to evaluate the crystallinity of these copolymers (See Fig. S2 in Supporting Information). The XRD patterns of PDPPMTD and PDPPBTD are similar, which implies that these two copolymers are amorphous. However, a broad reflection with high intensity at $2\theta = 24.7^{\circ}$ (corresponding to a π - π stack d spacing of 3.6 Å) were observed in both XRD profiles, this results suggest that π - π stacking interaction can be obtained in both copolymers even though they are structurally disordered.²⁹ Their ability to form the aggregates is beneficial for allowing locally efficient ICT.

Optical Properties of the Conjugated Copolymers

Figure 1 displays the absorption spectra of PDPPMTD and PDPPBTD in toluene solutions and solid films. Table 2 summarizes the corresponding absorption data of these copolymers. In solution, both copolymers exhibited broad absorption with two obvious absorption peaks and an absorption edge at over 1000 nm. The first absorption band in the range 300–500 nm originated from the n- π^* transition of the conjugated side chain and the π - π * transition of the copolymer main chain. The second absorption band in the range 500-1000 nm is attributed to the ICT interactions between the donors (thiophene derivatives units) and acceptors (DPP units) along the main chain.^{46,47} The absorption peaks of these copolymers in thin film state are redshifted from those of the same copolymers in solution and the absorption band is remarkably broadened, as revealed by the full width at half-maximum. This phenomenon arises from the π - π stacking interaction between the polymer chains. PDPPBTD exhibits a broad absorption and slight red-shift in the first absorption band at short wavelengths both in solution and in the thin film state, as compared to PDPPMTD—an effect that is attributed to the longer effective conjugation in the side chain and the reduction of the twist angle between the conjugated side chain and the polymer backbone. This finding implies the presence of an additional thiophene moiety in the side chain that increases the



SCHEME 1 Synthetic routes for monomers and copolymers PDPPMTD and PDPPBTD.

conjugation length as well as the absorption range. If this interpretation is correct, it suggests that increasing the conjugated length in the side chain results in the capture of sunlight at shorter wavelengths and contributes to the performance of the resultant PSC devices. Generally, conjugated polymers with relatively broad absorption are favorable for harvesting solar light. This broad absorption characteristic is expected to improve the absorption efficiency of the active layer and, thereby, increase the induced photocurrent in PSCs.⁴⁰

Electrochemical Properties of Conjugated Copolymers

The electrochemical properties of all of the copolymers herein were elucidated by CV and the HOMO and LUMO energy levels of these conjugated copolymers were estimated. Figure 2 shows the oxidation and reduction behaviors that are evident from the CV curves of the copolymers. The potentials were performed in a 0.1 M electrolyte of tetrabutylammonium hexafluorophosphate in acetonitrile using a scan rate of 100 mV

TABLE 1 Molecular Weights and Thermal Properties of Copolymers

Copolymers	<i>M</i> n ^a (kg/mol)	<i>M</i> w ^a (kg/mol)	PDI (<i>M_w/M_n</i>)	τ _d ^b (°C)
PDPPMTD	59.8	104.8	1.75	394
PDPPBTD	57.6	107.1	1.55	375

 $^{\rm a}$ ${\it M}_{\rm n},$ ${\it M}_{\rm w}$ and PDI of the polymers were determined by GPC using polystyrene standards in THF.

^b Temperature of 5% weight loss.



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FIGURE 1 UV-vis absorption spectra of copolymers in dilute toluene solutions and as thin films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

 S^{-1} , with an Ag/Ag⁺ reference electrode, a Pt plate coated polymer as working electrode, and a Pt wire as counter electrode. The HOMO values of **PDPPMTD** and **PDPPBTD** were calculated from the potentials at the onset of oxidation, taking the ferrocene as the reference level (4.8 eV) below the vacuum level, according to the following equation.

HOMO =
$$-e(E_{on}^{ox}-E_{on}^{ferrocene}+4.8)(eV)$$

Therefore, the HOMO levels of **PDPPMTD** and **PDPPBTD** were -5.20 and -5.18 eV, respectively. Since the reduction potentials of **PDPPMTD** and **PDPPBTD** were indeterminate, the LUMO levels were estimated from the obtained HOMO levels and the optical bandgap (E_g^{opt}) values were obtained from the absorption edges of UV-visible spectra using the following equation,

$$LUMO = E_a^{opt} + HOMO(eV)$$

The E_g^{opt} values of these copolymers that were calculated from the absorption edges of UV-visible spectra in the thin film state were approximately 1.29 eV. Accordingly, the LUMO levels of **PDPPMTD** and **PDPPBTD** were -3.91 and -3.89 eV, respectively. Although the optical bandgaps of these copolymers were almost identical, the HOMO level of

TABLE 2 Photophysical and Electrochemical Properties of Copolymers

Copolymers	In solution ^a (nm) λ_{\max}^{abs}	In Film ^b (nm) λ ^{abs} _{max}	HOMO/ LUMO ^c (eV)	${}^{\mathrm{d}}E_{g}^{opt}(V)$
PDPPMTD	397, 761	401, 764	-5.20/-3.91	1.29
PDPPBTD	415, 756	420, 778	-5.18/-3.89	1.29

^a Measured in toluene solution.

^b Casted from *o*-DCB solution.

^c The energy levels were calculated according to: HOMO = $-e(E_{on}^{ox}-E_{on}^{ferrocene} + 4.8)$ (eV), LUMO = E_{q}^{opt} + HOMO (eV).

^d Optical band gap was estimated from the wavelength of the optical edge of the copolymer film.



FIGURE 2 Cyclic voltammograms of copolymer films on platinum plates in acetonitrile solution of 0.1 mol L^{-1} Bu₄NCIO₄. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PDPPBTD was slightly raised by the addition of an electrondonating thiophene moiety into the conjugated side chain that was not present **PDPPMTD**. Table 2 presents the electrochemical properties of the copolymers. All of the copolymers exhibited favorable stability in air with a HOMO energy level below the oxidation-in-air threshold around -5.2 eV, and this relatively low HOMO level of the copolymers supports a high open-circuit voltage (V_{oc}) for a PSC device in which they are used.⁴⁸⁻⁵⁰

The charge carrier mobility of the active layer in a PSC is one of the essential factors that govern the performance of the device, because it is directly related to exciton dissociation, charge transport, and recombination.¹⁶ To probe the effects of the conjugated side chains on the charge transport of the copolymers, the SCLC method was performed to measure the mobility of the copolymers by using hole-only devices with an ITO/PEDOT:PSS/blend film/Au structure and electron-only devices with an ITO/blend film/LiF/Al structure, at an optimized copolymer:PC61BM blend ratio under the conditions used to fabricate the solar cell devices (See PV Properties of PSCs for a detailed discussion). As displayed in Figure 3, the hole mobilities ($\mu_{SCLC,h}$) of **PDPPMTD** and **PDPPBTD** are 1.56 imes 10⁻⁵ and 2.11 imes 10⁻⁵ cm² V⁻¹ S^{-1} , respectively, while the electron mobilities ($\mu_{SCLC,e}$) of PDPPMTD and PDPPBTD are 2.08 \times 10^{-5} and 2.20 \times 10^{-5} cm² V⁻¹ S⁻¹, respectively. The **PDPPBTD** blend film exhibits higher carrier mobilities and a better charge balance than does the PDPPMTD blend film. These results suggest that the conjugated lengths of the side chains have an important role in charge transport. This effect is attributed to the increased orbital overlap and reduced torsion angles of PDPPBTD relative to those of PDPPMTD. Thus the **PDPPBTD**-based solar cell is expected to have high *J*_{sc} and FF values owing to the balanced charge carrier transport in the active layer.¹⁶ The effects of treatment with 1,8-diiodooctane (DIO) on the charge-transport properties of the



FIGURE 3 Current and voltage (*I-V*) curves of (a) hole- and (b) electron-only devices that contain copolymer and $PC_{61}BM$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PDPPBTD blend film were also examined. The hole and electron mobilities of the DIO-treated **PDPPBTD** blend film are 1.85×10^{-5} and 2.41×10^{-5} cm² V⁻¹ S⁻¹, respectively. The DIO-treated **PDPPBTD** blend film has much higher electron mobility than the untreated blend film, indicating that DIO treatment improved the morphology of the blend film (See active layer morphology investigation for a detailed discussion). Table 3 summarizes the carrier mobilities of these blend films.

PV Properties of PSCs

PSCs were fabricated from copolymer as the donor and $PC_{61}BM$ or $PC_{71}BM$ as the acceptor; they had a traditional device structure of ITO/PEDOT:PSS/copolymer:PC₆₁BM or $PC_{71}BM/Ca/Al$ and were utilized to investigate the photovoltaic properties of these two copolymers. At first, the active layer was spin-cast using *o*-DCB as the solvent, and the concentration was 24 mg/mL. Copolymer/PC₆₁BM weight ratios of 1:1, 1:2, and 1:3, were used. The optimal copolymer/PC₆₁BM weight ratio for both **PDPPMTD**- and **PDPPBTD**-based devices was found to be 1:2. Figure 4 plots typical photocurrent density-voltage (*I-V*) characteristics of the PSCs

Copolymer/PC ₆₁ BM $(w/w = 1:2)$	$\mu_{SCLC,h}$ (cm ² V ⁻¹ S ⁻¹)	$^{\mu_{ t SCLC,e}}$ (cm $^{ ext{2}} ext{V}^{-1} ext{S}^{-1}$)
PDPPMTD	$1.56 imes10^{-5}$	$2.11 imes10^{-5}$
PDPPBTD	$2.08 imes10^{-5}$	$2.20 imes10^{-5}$
PDPPBTD ^a	$1.85 imes10^{-5}$	$2.41 imes10^{-5}$

^a Processed with DIO (3 vol %).

that were based on the blends of copolymer/fullerenes (PC₆₁BM and PC₇₁BM), measured under simulated AM 1.5 G illumination (100 mW/cm²). Table 4 presents the detailed photovoltaic characteristics of these devices, including V_{oc} , the short-circuit current density (J_{sc}), the fill factor (FF), and PCE. The **PDPPMTD**-based devices exhibited a V_{oc} in the range of 0.56–0.60 V with various PC₆₁BM contents in the blends (devices i-iii), and the device with the weight ratio of 1:2 showed the highest J_{sc} as shown in Figure 4 and Table 4. The variation in PCE among the three devices is ascribed to the morphologies of the blend films, which are responsible for the variation in the V_{oc} and J_{sc} values of the corresponding devices (See active layer morphology investigation for a detailed discussion).

Larger V_{oc} and higher J_{sc} values resulted in a higher PCE value among three PSCs, so the **PDPPMTD**/PC₆₁BM-based (w/w = 1:2) PSC had the highest PCE of 2.96%, with a J_{sc} of 12.6 mA/cm², a V_{oc} of 0.60 V, and an FF of 39%. Solar cell efficiency was further optimized by using a 1:2 blending ratio for **PDPPMTD** with PC₇₁BM as the acceptor. Replacing PC₆₁BM with PC₇₁BM as an acceptor in the active layer normally increases the photocurrent, as the latter has higher absorption in the visible region.^{45,51} When PC₇₁BM was used instead of PC₆₁BM as the electron acceptor in the devices, however, the **PDPPMTD**/PC₇₁BM-based (w/w = 1:2) devices (device iv) exhibited a slightly lower J_{sc} value and a PCE of 2.16% was achieved. We suspect that the variation in J_{sc}



FIGURE 4 Current density-potential characteristics of illuminated (AM 1.5 G, 100 mW/cm²) BHJ solar cells. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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No.	Active Layer(w/w ratio)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
i	PDPPMTD: PC ₆₁ BM (1:1)	0.56	7.5	39	1.64 [1.61] ^c
ii	PDPPMTD: PC ₆₁ BM (1:2)	0.60	12.6	39	2.96 [2.85]
iii	PDPPMTD: PC ₆₁ BM (1:3)	0.58	9.4	38	2.07 [1.95]
iv	PDPPMTD: PC ₇₁ BM (1:2)	0.60	10.9	33	2.16 [2.05]
v	PDPPBTD: PC ₆₁ BM (1:2)	0.59	14.5	48	4.10 [3.97]
vi	PDPPBTD: PC71BM (1:2)	0.58	9.5	47	2.59 [2.38]
vii	PDPPBTD: PC ₆₁ BM (1:2) ^a	0.59	10.7	48	3.03 [2.91]
viii	PDPPBTD: PC ₆₁ BM (1:2) ^b	0.60	9.6	44	2.53 [2.30]

TABLE 4 Photovoltaic Performance of BHJ Solar Cells

^a Processed with DIO (3 vol %).

^b Spin-cast from dichlorobenzene:chloroform (4:1 by volume).

values at the same blend ratio with different acceptors arose mainly from the variation in the morphologies of the active layers. The PDPPBTD:PC61BM blend ratio was optimized and the best PCE of 4.10% was achieved with a I_{sc} of 14.5 mA/cm², a $V_{\rm oc}$ of 0.59 V, and an FF of 48%, with the optimal blend weight ratio of 1:2 (device v). We attribute the fact that PDPPBTD had the highest value of PCE to its extended π -conjugated area in the side chain and the fact that its absorption region between 300-500 nm was slightly higher than that of PDPPMTD. In addition, the PCE declined from 4.10% to 2.59% when the acceptor was replaced by $PC_{71}BM$ (device vi). A similar effect has been observed in the PDPPMTD/PC71BM-based device, for which a slightly lower J_{sc} was ascribed to the morphologies of the blended active layers. Numerous groups have recently demonstrated that device performance can be substantially enhanced by treatment with some additive, such as DIO, which has been proven to change efficiently the interpenetrating nanoscale morphology of a BHJ cell. 16,52,53 To exploit this effect, 3 vol % DIO (3 vol % relative to DCB) was added to improve the morphology of the polymer blend herein, especially that used for the best **PDPPBTD**/PC₆₁BM-based (w/w = 1:2) device without DIO treatment. The DIO-treated PDPPBTDbased device (device vii) exhibited a PCE of 3.03%, with a I_{sc} of 10.7 mA/cm², a $V_{\rm oc}$ of 0.59 V, and an FF of 48%. These $V_{\rm oc}$ and FF values are almost the same as those of the untreated device, but the J_{sc} value is lower. The charge imbalance that is caused by the hole and electron mobilities of the blend film after the DIO treatment is likely to affect device performance. Furthermore, the co-solvent system has been proved to improve the film morphology in a BHJ cell, retarding the aggregation of the conjugated polymer and PCBM, to prevent the formation of oversized polymer or PCBM aggregates. The most commonly used co-solvents are chloroform (CF) and o-DCB. When the low boiling point of pure CF is applied to process the blend films, the morphology of blend films that are formed is always poor for the rapid drying caused by pure CF.^{16,54} However, most polymers exhibit high solubility in pure CF solvent. Consequently, incorporating some solvent with a low boiling point, such as CF, as a co-solvent can improve the film morphology. To

^c The values in square brackets indicate the average values of PCEs.

exploit this merit, the co-solvent system (o-DCB:CF = 4:1 by volume) was utilized to improve the PCE of the best PDPPBTD-based device herein. Also, as displayed in Figure 4 and Table 4, the device (device viii) that was cast from the co-solvent system exhibited a PCE of 2.53%, with a J_{sc} of 9.6 mA/cm², a V_{oc} of 0.60 V, and an FF of 44%. These J_{sc} and FF values were lower than those of the device that was cast from pure o-DCB, as a result of the morphological changes that were induced by processing with the co-solvent. The fact that **PDPPBTD**/PC₆₁BM-based devices have higher *J*_{sc} and FF than **PDPPMTD**/PC₆₁BM-based devices under the same optimized conditions (device v and device ii), apparently arises from the greater light-harvesting ability and charge mobility of PDPPBTD. Notably, all of the PDPPBTDbased PSCs have higher FF values than the PDPPMTD-based PSCs. To confirm the improvement in J_{sc} , external quantum efficiency (EQE) curves of the PSCs that were fabricated under the same optimal conditions were measured and are plotted in Figure 5. Two PSCs exhibited a broad response range, from 300 to 1000 nm, revealing that these PSC devices respond favorably to sunlight. Clearly, the PDPPBTD/PC₆₁BM-based PSC has a broader absorption region and higher EQE value in sunlight throughout this



FIGURE 5 EQE curves of photovoltaic cells with (copolymer: $PC_{61}BM = 1:2$) as active layer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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FIGURE 6 AFM topographic images of (a) PDPPMTD/PC₆₁BM (w/w = 1:1), (b) PDPPMTD/PC₆₁BM (w/w = 1:2), (c) PDPPMTD/PC₆₁BM (w/w = 1:3), (d) PDPPMTD/PC₇₁BM (w/w = 1:2), (e) PDPPBTD/PC₆₁BM (w/w = 1:2), (f) PDPPBTD/PC₇₁BM (w/w = 1:2), (g) DIO-treated PDPPBTD/PC₆₁BM (w/w = 1:2), and (h) PDPPBTD/PC₆₁BM (w/w = 1:2) cast using co-solvent, in tapping mode. Area of all images is 300 nm \times 300 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

range than does the **PDPPMTD**/PC₆₁BM-based PSC. These results demonstrate that increasing the conjugated length of the side chain considerably improved the photovoltaic properties of the polymer herein. Furthermore, the J_{sc} values that were calculated from the EQE curves under standard AM 1.5G conditions match closely those obtained from the *I-V* measurements. Notably, the **PDPPBTD** blend with PC₆₁BM displayed a slightly higher intensity of EQE than did the **PDPPMTD**/PC₆₁BM blends, which finding is consistent with the UV-Vis spectra of the polymer films. The enhanced light absorption is also consistent with the increased EQE, indicating its contribution to the increase in J_{sc} .¹⁶

Active Layer Morphology Investigation

Optimal phase segregation and the formation of a bicontinuous interpenetrating network between the polymer donor and the PC₆₁BM or PC₇₁BM acceptor are essential to achieving high device performance, and strongly affect the charge separation and exciton dissociation.^{16,55} Tapping-mode atomic force microscopy (AFM) was utilized to gain further insight into the morphology of the active layer. Figure 6 shows AFM images of blend films that are identical to those that were used to fabricate the active layers in the devices that are listed in Table 4. Thin films of PDPPMTD/PC₆₁BM blends with various weight ratios (w/w = 1:1-1:3) were observed to have rather smooth surfaces [root-mean-square (RMS) roughness = 0.24-0.73 nm], implying that all blend films exhibited satisfactory miscibility. Additionally, as displayed in Figure 6(a-c), the PDPPMTD/PC₆₁BM blend film with a weight ratio of 1:2 exhibited a bicontinuous interpenetrating network unlike the other blend films, although the **PDPPMTD**/PC₆₁BM blend film with a weight ratio of 1:3

ing that the ideal morphology consists of a nanoscale interpenetrating network between donor and acceptor that provides a large interface area for exciton dissociation and continuous percolating paths for the transport of holes and electrons to the corresponding electrodes.⁵⁶ Clearly, the suitable morphology of the blend films is essential to obtain better device performance of the PSCs. When the acceptor PC₆₁BM was replaced with PC₇₁BM, as presented in Figure 6(d), the **PDPPMTD**/PC₇₁BM (w/w = 1:2) blend film showed clearer grain aggregation and homogeneous dispersion (RMS roughness = 0.65 nm) than did the **PDPPMTD**/ PC61BM blend film. Obviously, suitable domain sizes and phase separation can optimize photovoltaic performance. The **PDPPBTD**/PC₆₁BM (w/w = 1:2) blend film [Fig. 6(e)] was observed to have a similar bicontinuous interpenetrating network. The **PDPPBTD**/PC₆₁BM (w/w = 1:2) blend film displayed lower RMS roughness than the PDPPMTD/ $PC_{61}BM$ (w/w = 1:2) blend film (0.47 and 0.68 nm for PDPPBTD and PDPPMTD, respectively.), suggesting that the introduction of an additional thiophene unit into each side chain improved compatibility with $PC_{61}BM$. Notably, the I_{sc} and FF values of PDPPBTD-based devices are higher not only because of the film morphology but also because of the charge mobility, as evidenced by SCLC measurements. Hence, the introduction of more thiophene rings into the side chains enhanced the compatibility with PC61BM as well as its light harvesting ability and charge mobility. This fact may explain why PDPPBTD outperformed PDPPMTD. However, clearer grain aggregates were observed in the PDPPBTD-based blend film when the acceptor PC61BM was replaced with PC71BM, with an RMS roughness of 0.49 nm, as shown in

had the lowest surface roughness of the blend films, indicat-





FIGURE 7 TEM images of (a) PDPPMTD/PC₆₁BM (w/w = 1:1), (b) PDPPMTD/PC₆₁BM (w/w = 1:2), (c) PDPPMTD/PC₆₁BM (w/w = 1:3), (d) PDPPMTD/PC₇₁BM (w/w = 1:2), (e) PDPPBTD/PC₆₁BM (w/w = 1:2), (f) PDPPBTD/PC₇₁BM (w/w = 1:2), (g) DIO-treated PDPPBTD/PC₆₁BM (w/w = 1:2), and (h) PDPPBTD/PC₆₁BM (w/w = 1:2) cast using co-solvent.

Figure 6(f); therefore the PDPPBTD/PC71BM-based device had the lower J_{sc} . The lower J_{sc} of the **PDPPBTD**/PC₇₁BMbased device can be explained by the large number of carrier recombinations on account of the clear grain-aggregation in the blend film. To elucidate the effect of DIO treatment, the morphology of the film was also examined, as presented in Figure 6(g). When a small amount of DIO (3 vol % relative to DCB) was added in the processing of the PDPPBTD/ $PC_{61}BM$ (w/w = 1:2) blends, the surface of the active layer became very smooth, with an RMS roughness of 0.28 nm, revealing improved aggregation of the polymer and PC₆₁BM in the active layer. However, treatment with DIO reduced J_{sc} . We suspect that this reduction arose mainly from the fact that DIO treatment increased the imbalance in charge carrier transport in the active layer (Table 3), reducing the $J_{\rm sc}$ value. The morphology of the PDPPBTD/PC61BM blend film that was cast from CF and o-DCB solution (co-solvents) was also studied using AFM, as shown in Figure 6(h). Extensive phase separation and relatively high levels of surface roughness (RMS roughness = 2.41 nm) were observed following casting from the co-solvents, and these observations may explain why the device that was cast from o-DCB solution outperformed that cast from the co-solvent. As reported above, the fabrication of a PSC device can be further improved by using DIO as an additive or by using a co-solvent during the processing of the active layer. In our work, we use these two methods to optimize the device performance of PDPPBTD. No further improvement was observed when these two methods were used and the use of a single solvent without an additive is favored to simplify the device fabrication process.

TEM was carried out to investigate the space image of the separated morphology of the copolymer–fullerene blends. Figure 7(a–h) display TEM images of the copolymer–fullerene blend films that are identical to those that were used to fabricate the active layers in the devices. The polymer and fullerene domains appear as bright and dark regions, respectively, owing to their different degrees of electron scatting.⁴²

Thin film of **PDPPMTD**/PC₆₁BM with a weight ratio of 1:1 displayed a fine and homogeneous morphology, as shown in Figure 7(a), which indicated good miscibility between **PDPPMTD** and PC₆₁BM. In addition, the **PDPPMTD**/PC₆₁BM (w/w = 1:2) blend film exhibited an interconnected network structure, as presented in Figure 7(b), suggesting that a well-organized bicontinuous network was obtained in this blend film. In contrast, the PDPPMTD/PC61BM blend film with a weight ratio of 1:3 [Fig. 7(c)] showed much larger pn junction domains which are not favorable for efficient exciton dissociation, leading to relatively low in J_{sc} .⁵⁷ When the acceptor PC₆₁BM was replaced with PC₇₁BM, as shown in Figure 7(d), the **PDPPMTD**/PC₇₁BM (w/w = 1:2) blend film displayed a few vividly aggregated PC71BM domains. The morphology of **PDPPBTD**/PC₆₁BM (w/w = 1:2) blend film [Fig. 7(e)] showed similar features to that of PDPPMTD/ $PC_{61}BM$ (w/w = 1:2) blend film, thus we suggest that the difference in devices performance apparently arose mainly from the light harvesting ability and carrier mobility. Furthermore, a few ambiguously PC71BM aggregates were observed in the PDPPBTD-based blend film when the acceptor PC₆₁BM was replaced with PC₇₁BM [Fig. 7(f)]. Upon addition of 3 vol % DIO in the processing of the PDPPBTD/ $PC_{61}BM$ (w/w = 1:2) blend film, moderately homogeneous morphology was obtained, as presented in Figure 7(g). For the **PDPPBTD**/PC₆₁BM (w/w = 1:2) thin film cast from the co-solvents [Fig. 7(h)], large diffused PC61BM domains with spots were observed. Although the distinct fibrillar structure for each of the blends was not observed in the TEM images,^{58,59} the obtained TEM results that were correlated well with the AFM images.

CONCLUSION

In summary, two new two-dimensional copolymers that contain DPP and thiophene with different π conjugation lengths as side chains, called **PDPPMTD** and **PDPPBTD**, were successfully designed and synthesized by Suzuki cross-coupling polymerization reactions. The synthesized copolymers exhibited broad absorptions, favorable thermal properties, and molecular energy levels that make them promising materials for use in PSCs. For PSC devices that are based on PDPPMTD and PDPPBTD, PCEs in the range 1.64-4.10% in BHJ with PC₆₁BM or PC₇₁BM were achieved. More importantly, incorporating additional thiophene rings into the side chains of PDPPBTD broadened the absorption spectrum and increased the charge mobility over those for PDPPMTD. The subtle tuning of the chemical structure of the side chains appeared significantly to influence the J_{sc} and FF. The device that was based on the **PDPPBTD**/PC₆₁BM (w/w = 1:2) blend film had the best PCE of 4.10% with a J_{sc} of 14.5 mA/ $\rm cm^2$, a $V_{\rm oc}$ of 0.59 V, and an FF of 48%. The highest PCE of the device that was based on the PDPPMTD/PC₆₁BM (w/w = 1:2) blend film was 2.96%, with a J_{sc} of 12.6 mA/cm², a $V_{\rm oc}$ of 0.60 V, and an FF of 39%. The increased $J_{\rm sc}$ and FF of the PDPPBTD-based PSC apparently arose from the enhanced light harvesting ability, carrier mobility and morphology, as evidenced by EQE, SCLC, AFM and TEM measurements. The findings herein provide significant insight into, and a feasible method for the development of, a new generation of low-bandgap materials. The photovoltaic properties of these 2D conjugated copolymers can be tuned by varying their conjugated side chains.

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REFERENCES AND NOTES

1 S. P. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, A. J. Heeger, *Nat. Photon.* **2009**, *3*, 297–302.

- **2** L. Huo, J. Hou, S. Zhang, H. Y. Chen, Y. Yang, *Angew. Chem. Int. Ed.* **2010**, *49*, 1500–1503.
- **3** Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, *Adv. Mater.* **2010**, *22*, E135–E138.
- **4** S. Gunes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* **2007**, *107*, 1324–1338.
- **5** Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray, L. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 7792–7799.
- **6** T. Umeyama, H. Imahori, *J. Mater. Chem. A* **2014**, *2*, 11545–11560.
- **7** J. Li, Y. Zhao, H.S. Tan, Y. Guo, C.-A. Di, G. Yu, Y. Liu, M. Lin, S. H. Lim, Y. Zhou, H. Su, B. S. Ong, *Sci. Rep.* **2012**, *2*, 754.
- **8** H. Chen, Y. Guo, G. Yu, Y. Zhao, J. Zhang, D. Gao, H. Liu, Y. Liu, *Adv. Mater.* **2012**, *24*, 4618–4622.
- **9** Z. He, C. Zhong, S. Su, M. Xu, H. Wu, Y. Cao, *Nat. Photon.* **2012**, *6*, 591–595.
- 10 F. C. Krebs, Sol. Energy Mater. Sol. Cells 2009, 93, 394-412.
- **11** E. Bundgaard, O. Hagemann, M. Manceau, M. Jørgensen, F.C. Krebs, *Macromolecules* **2010**, *43*, 8115–8120.

12 F. C. Krebs, M. Jorgensen, Adv. Opt. Mater. 2014, 2, 465–477.

13 M. Manceau, E. Bundgaard, J. E. Carlé, O. Hagemann, M. Helgesen, R. Søndergaard, M. Jørgensen, F. C. Krebs, *J. Mater. Chem.* **2011**, *21*, 4132–4141.

14 M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, F. C. Krebs, *Adv. Mater.* 2012, *24*, 580–612.

15 Y. Li, J. Zou, H.-L. Yip, C.-Z. Li, Y. Zhang, C.-C. Chueh, J. Intemann, Y. Xu, P.-W. Liang, Y. Chen, A. K.-Y. Jen, *Macromolecules* **2013**, *46*, 5497–5503.

16 Y. Li, C.-Y. Chang, Y. Chen, Y. Song, C.-Z. Li, H.-L. Yip, A. K.-Y. Jen, C. Li, *J. Mater. Chem. C* **2013**, *1*, 7526–7533.

17 L. Dou, W.-H. Chang, J. Gao, C.-C. Chen, J. You, Y. Yang, *Adv. Mater.* 2013, *25*, 825–831.

18 H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. S. Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. J. Janssen, T. Anthopoulos, H. Sirringhaus, M. Heeney, I. McCulloch, *J. Am. Chem. Soc.* **2011**, *133*, 3272–3275.

19 E. Zhou, Q. Wei, S. Yamakawa, Y. Zhang, K. Tajima, C. Yang, K. Hashimoto, *Macromolecules* **2010**, *43*, 821–826.

20 R. S. Ashraf, Z. Chen, D. S. Leem, H. Bronstein, W. Zhang, B. Schroeder, Y. Geerts, J. Smith, S. Watkins, T. D. Anthopoulos, H. Sirringhaus, J. C. de Mello, M. Heeney, I. McCulloch, *Chem. Mater.* **2011**, *23*, 768–770.

21 S. Qu, H. Tian, Chem. Commun. 2012, 48, 3039-3051.

22 Y. Lin, L. Ma, Y. Li, Y. Liu, D. Zhu, X. Zhan, *Adv. Energy Mater.* 2013, *3*, 1166–1170.

23 Y. Lin, Y. Li, X. Zhan, Adv. Energy Mater. 2013, 3, 724–728.

24 J. C. Bijleveld, A. P. Zoombelt, S. G. J. Mathijssen, M. M. Wienk, M. Turbiez, D. M. de Leeuw, R. A. J. Janssen, *J. Am. Chem. Soc.* 2009, *131*, 16616–16617.

25 J. S. Lee, S. K. Son, S. Song, H. Kim, D. R. Lee, K. Kim, M. J. Ko, D. H. Choi, B. Kim, J. H. Cho, *Chem. Mater.* **2012**, *24*, 1316–1323.

26 K. H. Hendrik, G. H. L. Heintges, V. S. Gevaerts, M. M. Wienk, R. A. J. Janssen, *Angew. Chem. Int. Ed.* **2013**, *52*, 8341–8344.

27 J. S. Ha, K. H. Kim, D. H. Choi, *J. Am. Chem. Soc.* **2011**, *133*, 10364–10367.

28 J. Yuan, X. Huang, F. Zhang, J. Lu, Z. Zhai, C. Di, Z. Jiang, W. Ma, *J. Mater. Chem.* 2012, *22*, 22734–22742.

29 S. Zhang, L. Ye, Q. Wang, Z. Li, X. Guo, L. Huo, H. Fan, J. Hou, *J. Phys. Chem. C* **2013**, *117*, 9550–9557.

30 Y. Li, Y. Zou, Adv. Mater. 2008, 20, 2952-2958.

31 L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li, J. Hou, *Angew. Chem. Int. Ed.* **2011**, *50*, 9697–9702.

32 M. Wang, X. Hu, P. Liu, W. Li, X. Gong, F. Huang, Y. Cao, *J. Am. Chem. Soc.* **2011**, *133*, 9638–9641.

33 H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu, W. You, *Angew. Chem. Int. Ed.* **2011**, *50*, 2995–2998.

34 F. Huang, K. S. Chen, H. L. Yip, S. K. Hau, O. Acton, Y. Zhang, J. D. Luo, A. K.-Y. Jen, *J. Am. Chem. Soc.* **2009**, *131*, 13886–13887.

35 Z. Gu, P. Tang, B. Zhao, H. Luo, X. Guo, H. Chen, G. Yu, X. Liu, P. Shen, S. Tan, *Macromolecules* **2012**, *45*, 2359–2366.

36 X. Guo, M. J. Zhang, J. H. Tan, S. Q. Zhang, L. J. Huo, W. P. Hu, Y. F. Li, J. H. Hou, *Adv. Mater.* **2012**, *24*, 6536–6541.

37 L. Huo, J. Hou, H.-Y. Chen, S. Zhang, Y. Jiang, T. L. Chen, Y. Yang, *Macromolecules* **2009**, *42*, 6564–6571.

38 H. Bürckstümmer, A. Weissenstein, W. Bialas, F. Würthner, *J. Org. Chem.* **2011**, *76*, 2426–2432. **39** Z. Lu, C. Li, T. Fang, G. Li, Z. Bo, *J. Mater. Chem. A* **2013**, *1*, 7657–7665.

40 H.-J. Wang, L.-H. Chan, C.-P. Chen, S.-L. Lin, R.-H. Lee, R.-J. Jeng, *Polymer* **2011**, *52*, 326–338.

41 H.-J. Wang, L.-H. Chan, C.-P. Chen, R-H. Lee, W.-C. Su, R.-J. Jeng, *Thin Solid Films* **2011**, *519*, 264–5269.

42 J.-M. Jiang, H.-K. Lin, Y.-C. Lin, H.-C. Chen, S.-C. Lan, C.-K. Chang, K.-H. Wei, *Macromolecules* **2014**, *47*, 70–78.

43 E. Voroshazi, K. Vasseur, T. Aernouts, P. Heremans, A. Baumann, C. Deibel, X. Xue, A. J. Herring, T. A. Lada, H. Richter, B. P. Rand, *J. Mater. Chem.* **2011**, *21*, 17345–17352.

44 L.-H. Chan, S.-Y. Juang, M.-C. Chen, Y.-J. Lin, *Polymer* 2012, *53*, 2334–2346.

45 L.-H. Chan, L.-C. Lin, C.-H. Yao, Y.-R. Liu, Z.-J. Jiang, T.-Y. Cho, *Thin Solid Films* **2013**, *544*, 386–391.

46 J. H. Tsai, C. C. Chueh, W. C. Chen, C. Y. Yu, G. W. Hwang, C. Ting, E. C. Chen, H. F. Meng, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 2351–2360.

47 D. Chen, Y. Yang, C. Zhong, Z. Yi, F. Wu, L. Qu, Y. Li, Y. Li, J. Qin, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 3852–3862.

48 D. M. de Leeuw, M. M. J. Simenon, A. R. Brown, R. E. F. Einerhand, *Synth. Met.* **1997**, *87*, 53–59.

49 N. Leclerc, A. Michaud, K. Sirois, J. F. Morin, M. Leclerc, *Adv. Funct. Mater.* **2006**, *16*, 1694–1704.

50 Y. Li, Z. Li, C. Wang, H. Li, H. Lu, B. Xu, W. Tian, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 2765–2776.

51 Y. Liang, Y. Wu, D. Feng, S. T. Tsai, H. J. Son, G. Li, L. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 56–57.

52 J. K. Lee, W. L. Ma, C. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan, A. J. Heeger, *J. Am. Chem Soc.* **2008**, *130*, 3619–3623.

53 P. Shen, H. Bin, L. Xiao, Y. Li, *Macromolecules* 2013, *46*, 9575–9586.

54 Y. Zhang, J. Zou, H.-L. Yip, Y. Sun, J. A. Davies, K.-S. Chen, O. Acton, A. K.-Y. Jen, *J. Mater. Chem.* **2011**, *21*, 3895–3902.

55 Y. Sun, S.-C. Chien, H.-L. Yip, Y. Zhang, K.-S. Chen, D. F. Zeigler, F.-C. Chen, B. Lin, A. K.-Y. Jen, *J. Mater. Chem.* 2011, *21*, 13247–13255.

56 Y. W. Li, Q. Guo, Z. F. Li, J. N. Pei, W. J. Tian, *Energy Environ. Sci.* 2010, *3*, 1427–1436.

57 J.-H. Kim, S. A. Shin, J. B. Park, C. E. Song, W. S. Shin, H. Yang, Y. Li, D.-H. Hwang, *Macromolecules* **2014**, *47*, 1613–1622.

58 W. Li, K. H. Hendriks, A. Furlan, W. S. C. Roelofs, M. M. Wienk, R. A. J. Janssen, *J. Am. Chem Soc.* **2013**, *135*, 18942–18948.

59 W. Li, K. H. Hendriks, A. Furlan, W. S. C. Roelofs, S. C. J. Meskers, M. M. Wienk, R. A. J. Janssen, *Adv. Mater.* **2014**, *26*, 1565–1570.