

# Synthesis of Three New 1-(2,6-Diisopropylphenyl)-2,5-di(2-thienyl)pyrrole-Based Donor Polymers and Their Bulk Heterojunction Solar Cell Applications

VELLAIAPPILLAI TAMILAVAN,<sup>1</sup> MYUNGKWAN SONG,<sup>2</sup> SUNG-HO JIN,<sup>2</sup> MYUNG HO HYUN<sup>1</sup>

<sup>1</sup>Department of Chemistry, Chemistry Institute for Functional Materials, Pusan National University, Busan 690-735, Republic of Korea

<sup>2</sup>Department of Chemistry Education and Interdisciplinary Program of Advanced Information and Display Materials, Pusan National University, Busan 609-735, Korea

Received 28 June 2010; accepted 28 August 2010

DOI: 10.1002/pola.24360

Published online 13 October 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A series of three new 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole-based polymers such as poly[1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole] (**PTPT**), poly[1,4-(2,5-bis(octyloxy)phenylene)-*alt*-5,5'-(1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole)] (**PPTPT**), and poly[2,5-(3-octylthiophene)-*alt*-5,5'-(1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole)] (**PTTPT**) were synthesized and characterized. The new polymers were readily soluble in common organic solvents and the thermogravimetric analysis showed that the three polymers are thermally stable with the 5% degradation temperature >379 °C. The absorption maxima of the polymers were 478, 483, and 485 nm in thin film and the optical band gaps calculated from the onset wavelength of the optical absorption were 2.15, 2.20, and 2.13 eV, respec-

tively. Each of the polymers was investigated as an electron donor blending with PC<sub>70</sub>BM as an electron acceptor in bulk heterojunction (BHJ) solar cells. BHJ solar cells were fabricated in ITO/PEDOT:PSS/polymer:PC<sub>70</sub>BM/TiO<sub>2</sub>/Al configurations. The BHJ solar cell with **PPTPT**:PC<sub>70</sub>BM (1:5 wt %) showed the power conversion efficiency (PCE) of 1.35% ( $J_{sc} = 7.41 \text{ mA/cm}^2$ ,  $V_{oc} = 0.56 \text{ V}$ , FF = 33%), measured using AM 1.5G solar simulator at 100 mW/cm<sup>2</sup> light illumination. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 5514–5521, 2010

**KEYWORDS:** bulk heterojunction solar cells; conjugated polymers; copolymerization; 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole-based polymers; solar cells; synthesis

**INTRODUCTION** Polymer solar cells (PSCs) have attracted a great deal of attention because of the low-cost, light-weight, and mechanical flexibility.<sup>1–15</sup> The most common PSC structures are the bulk heterojunction (BHJ) solar cells consisting of an interpenetrating network of electron donor (D) and acceptor (A) materials.<sup>1–15</sup> In polymer BHJ solar cells, conjugated polymers are used as electron donor (D) materials and fullerene derivative, [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM), is usually used as electron acceptor (A) material.

Previously, BHJ solar cells made from a blend of poly(3-hexylthiophene) (P3HT) and PCBM were widely investigated and found to show relatively high conversion efficiency of 4.0–5.0%.<sup>16–18</sup> More recently, the power conversion efficiency (PCE) of polymer BHJ solar cells has been improved to around 6.0% to 7.4% by using low band gap conjugated polymers as electron donors and PCBM or [6,6]-phenyl C<sub>70</sub> butyric acid methyl ester (PC<sub>70</sub>BM) as electron acceptor.<sup>19–22</sup> This inspires us to prepare new donor polymers for BHJ solar cells. In BHJ solar cells, the PCE mainly depends on two major factors such as light harvesting and charge separation. In this instance, preparation of new conjugated polymers

having high absorption coefficient with reasonable HOMO-LUMO level is a really challenging work.

In our laboratory, we have been interested in the utilization of 1-aryl-2,5-di(2-thienyl)pyrroles as monomers for the preparation of new alternating  $\pi$ -conjugated polymers which can be used as donor materials in BHJ solar cells. Although 1-dodecyl-2,5-bis(2-thienyl)pyrrole has been used as an electron-rich unit for the preparation of low band gap conjugated polymers consisting of alternating electron-rich and electron-deficient units,<sup>23,24</sup> recently, we prepared 1-aryl-2,5-di(2-thienyl)pyrroles and used them as comonomers for the preparation of indenofluorene-based copolymers.<sup>25</sup> By introducing an *N*-aryl group instead of the *N*-dodecyl group of 1-dodecyl-2,5-di(2-thienyl)pyrrole, the molar absorption was improved because of the increased  $\pi$ -conjugation length of the molecule. Especially, 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole was found to show the highest molar absorption among other 1-dodecyl- or 1-aryl-2,5-di(2-thienyl)pyrroles and the BHJ solar cell fabricated with the blend of indenofluorene-based copolymer incorporating 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole and PC<sub>70</sub>BM (1:5 wt %) was found to show the PCE of 1.12%.<sup>25</sup>

Correspondence to: M. H. Hyun (E-mail: mhhyun@pusan.ac.kr)

*Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 48, 5514–5521 (2010) © 2010 Wiley Periodicals, Inc.

As an effort to utilize 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole further as an electron rich comonomer for the preparation of another alternating  $\pi$ -conjugated polymers which can be used as donor materials in BHJ solar cells, in this study, we copolymerized the electron rich monomer with another successful electron rich monomer such as 2,5-dioctyloxy-1,4-dibromophenylene<sup>26</sup> or 2,5-dibromo-3-octylthiophene.<sup>27</sup> In addition, to elucidate the effect of the electron rich monomer such as 2,5-dioctyloxy-1,4-dibromophenylene or 2,5-dibromo-3-octylthiophene, we also prepared the homo polymer of 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole. In this article, we wish to report the synthesis of a series of three new 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole-based polymers, their optical and electrical properties and their applications in BHJ solar cells.

## EXPERIMENTAL

### Materials and Instruments

All reagents were commercially available from Aldrich or TCI chemicals and used without further purification. Solvents purified by the standard procedure were handled in a moisture-free atmosphere. Flash column chromatography was performed on silica gel (Merck Kieselgel 60, 70-230 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a 300 MHz Varian Mercury Plus spectrometer in deuterated chloroform. The weight average molecular weight ( $M_w$ ) and polydispersity (PDI) of each polymer were determined by gel permeation chromatography (GPC) with the use of a PLgel 5  $\mu$ m MIXED-C column on an Agilent 1100 series liquid chromatography system. Tetrahydrofuran (THF) was used as an eluent and the flow rate was maintained at 1.0 mL/min. The GPC system performance was verified by a polystyrene standard calibration. Thermal analyses were performed under a nitrogen atmosphere at a heating rate of 10 °C/min by using a Mettler Toledo TGA/SDTA 851, DSC 822 analyzer. The optical properties of polymers were investigated at 25 °C in chloroform or as thin films on quartz using a JASCO V-570 spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. Electrochemical properties of polymers were studied by using a CH Instruments Electrochemical Analyzer. Cyclic voltammetry (CV) measurements were performed in chloroform solution containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu<sub>4</sub>NBF<sub>4</sub>) as the supporting electrolyte [Ag/AgCl: reference electrode, platinum wire: counter electrode, ferrocene/ferrocenium (FOC): internal standard]. Atomic force microscopy (AFM) images of blend films were obtained on a Veeco-Multimode AFM operating in the tapping mode.

### Device Preparation

The polymer BHJ solar cells were constructed as follows. A transparent ITO electrode was coated on glass substrates (80 nm thick, 20  $\Omega$ /sq sheet resistance) and the ITO-coated glass substrates were cleaned with detergent, deionized water, acetone, and isopropyl alcohol sequentially in an ultrasonic bath. After drying the substrates, a 40 nm thick layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (H.C.Stack, PH500) was spin-coated onto

the pre-cleaned and UV-ozone treated ITO substrates and baked in air at 150 °C for 30 min. Subsequently, the active layer (thickness: 80 nm) was prepared by spin-coating a blend solution of each of the polymers and PC<sub>70</sub>BM in a weight ratio of 1:3, 1:4, or 1:5 wt % in 1,2-dichlorobenzene and chloroform (1:1 wt %) onto the ITO/PEDOT:PSS substrates. After drying, the TiO<sub>x</sub> precursor solution (1 wt %) was spin-casted (4000 rpm) onto the active layer with a thickness of around 10 nm and then heated at 80 °C for 10 min in air. After being subjected to a vacuum ( $5 \times 10^{-6}$  Torr), an Al electrode with thickness of around 100 nm were deposited onto the TiO<sub>x</sub> layer. Finally, the polymer BHJ solar cell devices were subjected to annealing at 100 °C for 30 min in a glove box. The top metal electrode area, comprising the active area of the solar cells, was found to be 4 mm<sup>2</sup>. The BHJ solar cell performance was measured using a AM 1.5G solar simulator (Oriel 300 W) at 100 mW/cm<sup>2</sup> light illumination after adjusting the light intensity using Oriel power meter (model No. 70260 which was calibrated using laboratory standards that are traceable to the National Institute of Standards and Technologies). Current–voltage ( $I$ - $V$ ) characteristics of the polymer BHJ solar cell devices were measured using a standard source measurement unit (Keithley 236). All fabrication steps and characterization measurements were performed in an ambient environment without a protective atmosphere. The thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of  $\pm 1$  nm.

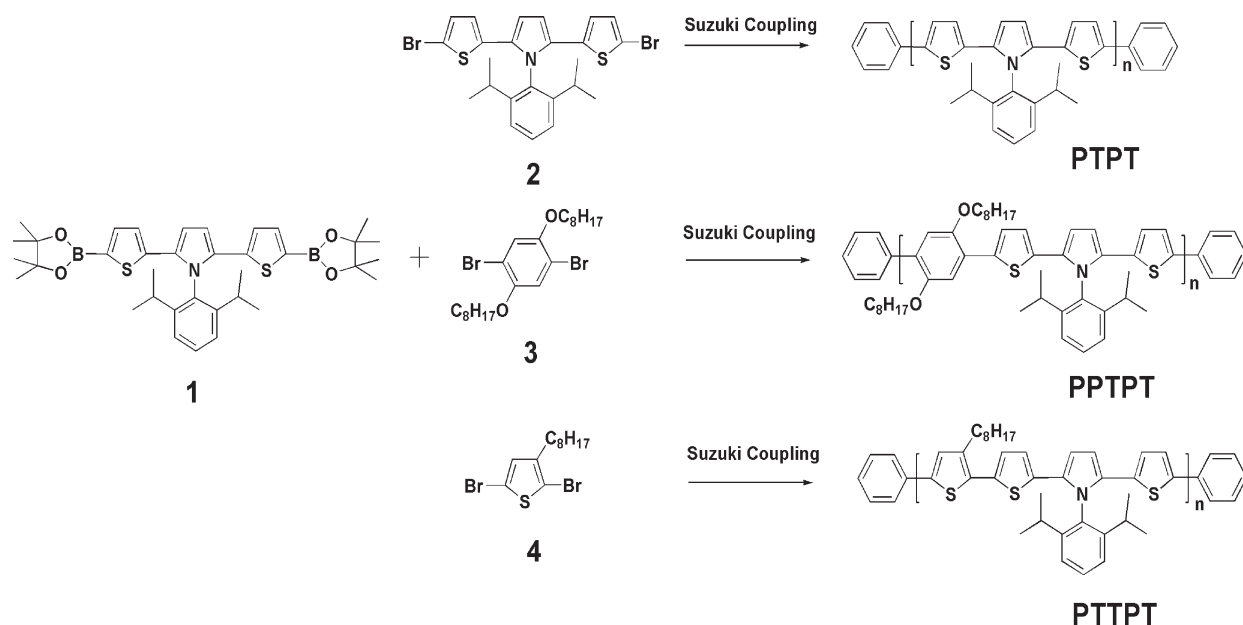
### Synthesis

The polymers were synthesized as shown in Scheme 1. The detailed synthetic procedures are as following.

#### 1-(2,6-Diisopropylphenyl)-2,5-di(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl)pyrrole (1)

1-(2,6-Diisopropylphenyl)-2,5-di(5-bromo-2-thienyl)pyrrole (2) (1.6 g, 2.9 mmol), which was prepared via the procedure reported,<sup>25</sup> was dissolved in dry THF (60 mL) and the solution was cooled to  $-78$  °C in a bath containing dry ice-acetone for 20 min. To the cooled solution was added *n*-BuLi (1.6 M in hexane, 3.8 mL, 6.0 mmol) drop by drop with stirring. The solution was allowed to stir at  $-78$  °C in the same bath, and then at room temperature for 3 h, and then again at  $-78$  °C for 20 min. To the cooled solution was added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.2 mL, 6.0 mmol) drop by drop, and then the whole mixture was slowly warmed to room temperature with stirring. After stirring for 24 h, the reaction mixture was poured into water, and the aqueous solution was extracted with ethyl acetate (50 mL) three times. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the residue was purified by silica gel column chromatography (hexane:ethyl acetate, 9:1, v/v) to afford **1**. (1.5 g, 80%). mp 196–197 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.52–7.57 (t, 1H), 7.27–7.30 (d, 2 H), 7.19–7.20 (d, 2 H), 6.72 (s, 2 H), 6.02–6.03 (d, 2 H), 2.40–2.56 (m, 2 H), 1.30 (s, 24 H), 0.86–0.89 (d, 12 H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 147.64, 142.40, 137.88,



**SCHEME 1** Synthetic routes for the synthesis of polymers **PTPT**, **PPTPT**, and **PTTPT**. After Suzuki coupling, each polymer was end-capped with phenylboronic acid and then bromobenzene.

134.84, 130.57, 130.52, 124.95, 123.24, 110.78, 84.16, 28.49, 24.97, 23.95, 23.86; HRMS (EI+, m/z) [M+] Calcd for  $\text{C}_{36}\text{H}_{47}\text{B}_2\text{NO}_4\text{S}_2$  643.3133, found 643.3135.

#### General Procedure for Polymerization

A solution of **1** (0.26 g, 0.4 mmol) and **2** (0.22 g, 0.4 mmol) for polymer **PTPT**, **1** (0.26 g, 0.4 mmol) and **3** (0.20 g, 0.4 mmol) for polymer **PPTPT**, or **1** (0.26 g, 0.4 mmol) and **4** (0.14 g, 0.4 mmol) for polymer **PTTPT** in THF (60 mL) was purged well with nitrogen for 45 min and then Pd ( $\text{PPh}_3$ )<sub>4</sub> (0.02 g, 5 mol %) and aqueous 2 M  $\text{K}_2\text{CO}_3$  (7 mL) were added. The whole mixture was refluxed with vigorous stirring under nitrogen atmosphere. After refluxing for 48 h, 50 mg of phenylboronic acid was added. The whole mixture was refluxed for 6 h and then 0.1 mL of bromobenzene was added and refluxed again for 6 h. The reaction mixture was cooled and then poured into the mixed solvent of methanol and water (200 mL:100 mL) with vigorous stirring. The precipitate was recovered by filtration, washed well with 2 N HCl solution, and then extracted with methanol for 24 h and acetone for 24 h in a Soxhlet apparatus. After drying, each of three polymers was obtained as dark brown solids.

**PTPT**: Yield (0.23 g, 74%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.54 (t, 1H), 7.25–7.28 (d, 2H), 6.62–6.64 (d, 4H), 6.08–6.09 (d, 2H), 2.46 (m, 2H), 0.90–0.92 (d, 12H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 148.05, 134.68, 134.32, 133.67, 130.79, 130.15, 124.98, 123.34, 123.12, 109.62, 28.53, 23.97; Anal. Calcd for  $\text{C}_{24}\text{H}_{25}\text{NS}_2$ : C, 73.61; H, 6.43; N, 3.58; S, 16.38. Found: C, 72.04; H, 5.23; N, 4.79; S, 15.50.

**PPTPT**: Yield (0.22 g, 67%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.54 (t, 1H), 7.28–7.30 (d, 2H), 7.16–7.18 (d, 2H), 7.05 (s, 2H), 6.70 (s, 2H), 6.14 (s, 2H), 3.96 (m, 4H), 2.55 (m, 2H), 1.83 (m, 4H), 1.31 (m, 20H), 0.95 (m, 18H);  $^{13}\text{C}$  NMR (75

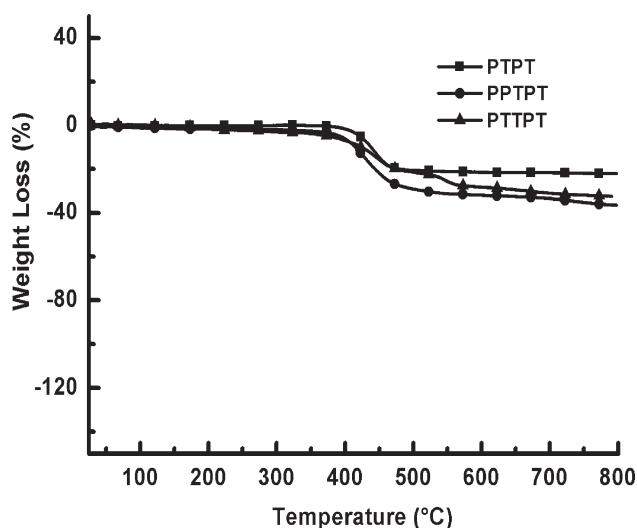
MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 149.19, 148.10, 136.62, 135.35, 134.98, 130.33, 125.44, 124.82, 122.72, 122.38, 112.04, 109.40, 32.12, 29.96, 29.68, 29.58, 28.58, 26.46, 24.00, 22.95, 14.41; Anal. Calcd for  $\text{C}_{46}\text{H}_{61}\text{NO}_2\text{S}_2$ : C, 76.30; H, 8.49; N, 1.93; S, 8.86. Found: C, 75.56; H, 7.75; N, 1.69; S, 7.75.

**PTTPT**: Yield (0.19 g, 72%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.54 (t, 1H), 7.27–7.34 (d, 2H), 6.74–6.77 (m, 2H), 6.65–6.67 (m, 2H), 6.41 (s, 1H), 6.05 (s, 2H), 2.52 (m, 4H), 1.49 (m, 2H), 1.28 (m, 10H), 0.95 (m, 15H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 148.15, 140.06, 134.72, 130.68, 130.14, 129.61, 126.31, 125.71, 125.01, 123.29, 109.47, 32.18, 30.72, 29.96, 29.81, 29.73, 29.55, 28.57, 23.97, 22.95, 14.41; Anal. Calcd for  $\text{C}_{36}\text{H}_{43}\text{NS}_3$ : C, 73.79; H, 7.40; N, 2.39; S, 16.42. Found: C, 72.21; H, 7.28; N, 3.35; S, 16.46.

## RESULTS AND DISCUSSIONS

### Synthesis and Characterization

Polymers **PTPT**, **PPTPT**, and **PTTPT** were prepared by Suzuki polycondensation reaction between monomer **1** and monomer **2**, between monomer **1** and monomer **3**, or between monomer **1** and monomer **4**, respectively, and then by end capping with phenylboronic acid and bromobenzene as outlined in Scheme 1. Monomer **1** was prepared by treating monomer **2**, which was prepared via the procedure we reported previously,<sup>25</sup> with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Comonomers, 2,5-dioctyloxy-1,4-dibromophenylene **3**<sup>26</sup> and 2,5-dibromo-3-octylthiophene **4**,<sup>27</sup> were synthesized via the known procedures. Each of polymers **PTPT**, **PPTPT**, and **PTTPT** was purified by Soxhlet extraction to afford dark brown color solid material with a reasonable yield of around 70%. All three polymers exhibited excellent solubility in common organic solvents such as chloroform, tetrahydrofuran, toluene, chlorobenzene, and



**FIGURE 1** TGA curves for polymers **PTPT**, **PPTPT**, and **PTTPT**.

dichlorobenzene. The weight average molecular weights ( $M_w$ ) of polymers **PTPT**, **PPTPT**, and **PTTPT** were 7140, 19,600, and 14,600 and their polydispersities were 1.20, 1.72, and 1.44, respectively. Polymers **PTPT**, **PPTPT**, and **PTTPT** were found to be thermally stable with the 5% decomposition temperatures of 422 °C, 393 °C, and 379 °C, respectively, as shown by the thermogravimetric analysis (TGA) curves in Figure 1. The polymerization results and the thermal properties of polymers **PTPT**, **PPTPT**, and **PTTPT** are summarized in Table 1.

### Optical and Electrochemical Properties

Figure 2 shows the solution and thin film state absorption spectra of polymers **PTPT**, **PPTPT**, and **PTTPT**. All three polymers display absorption maxima in the visible region, and show absorption bands covering from 300 to 600 nm. These absorptions are expected to be accompanied by the  $\pi$ - $\pi^*$  transition of polymers. The absorption maximum wavelength of **PPTPT** is shorter than that of **PTPT** by 23 nm in chloroform. In turn, the absorption maximum wavelength of **PTTPT** is shorter than that of **PTPT** by 9 nm in chloroform. The presence of the octyloxy or octyl group in copolymer backbone of **PPTPT** or **PTTPT** might lead to slightly increased conformational disorder. In this instance, the absorption maximum of **PPTPT** or **PTTPT** is expected to be blue-shifted compared to that of **PTPT**. In addition, the conformational disorder of **PPTPT** having two octyloxy groups is expected to be greater than that of **PTTPT** having one octyl group. Consequently, **PPTPT** shows the more blue-shifted absorption than **PTTPT**. In film state, all three polymers showed very similar absorption maxima. The film state absorption bands are red-shifted by 15 nm for **PPTPT**, 3 nm for **PTTPT**, and blue-shifted by 13 nm for **PTPT** compared to those in solution. The absorption study clearly indicated the copolymers **PPTPT** and **PTTPT** are well conjugated in film, but homopolymer **PTPT** is better conjugated in solution. The absorption maximum of the indenofluorene-based copolymer incorporating 1-(2,6-diisopropylphenyl)-2,5-bis

**TABLE 1** Polymerization Results, Thermal, Optical, and Electrochemical Properties of **PTPT**, **PPTPT**, and **PTTPT**

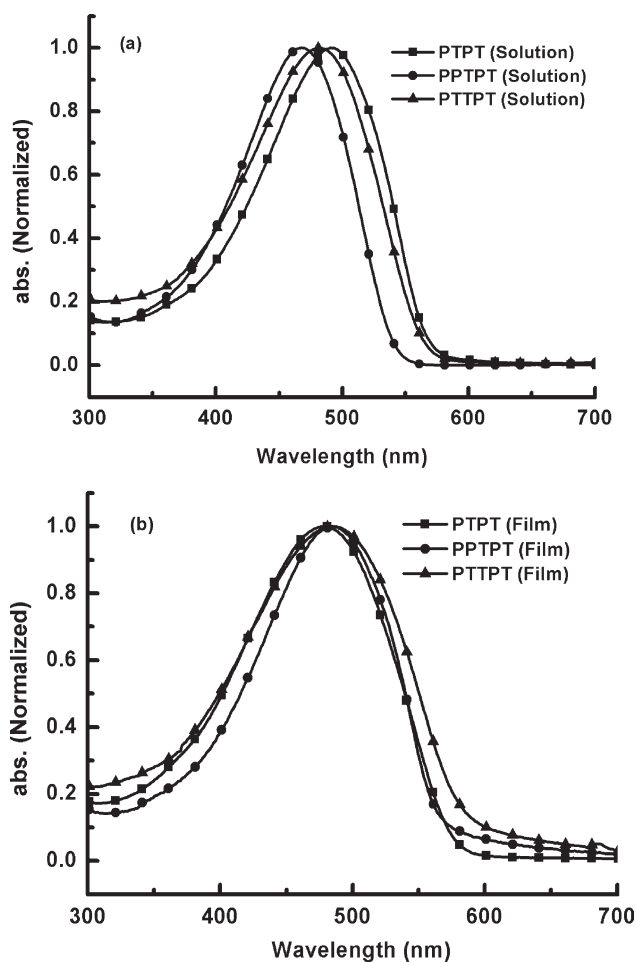
		<b>PTPT</b>	<b>PPTPT</b>	<b>PTTPT</b>
$M_w^a$		$7.14 \times 10^3$	$1.96 \times 10^4$	$1.46 \times 10^4$
PDI <sup>a</sup>		1.20	1.72	1.44
TGA <sup>b</sup>		422	393	379
Abs (nm)	Solution	491	468	482
	Film <sup>c</sup>	478	483	485
PL (nm)	Solution	574	566	542
	Film <sup>c</sup>	580	557	567
HOMO (eV)		-5.15	-5.14	-5.13
LUMO (eV)		-3.00	-2.94	-3.00
$E_g$ (eV) <sup>d</sup>		2.15	2.20	2.13

<sup>a</sup> Weight average molecular weight ( $M_w$ ) and polydispersity (PDI) of the polymers were determined by GPC using polystyrene standards.

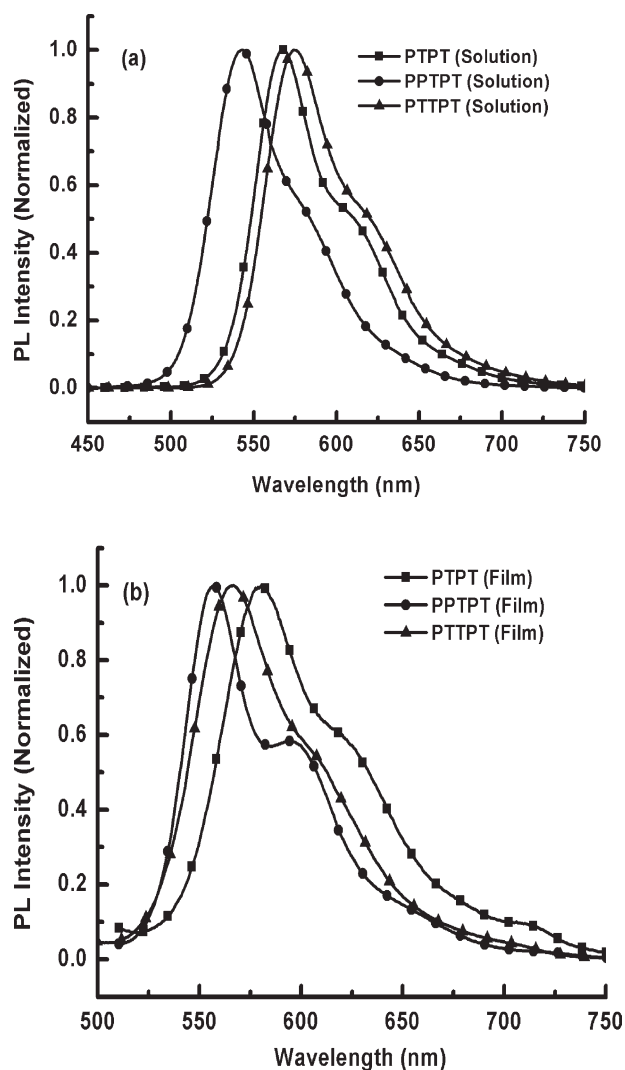
<sup>b</sup> Onset decomposition temperature (5% weight loss) measured by TGA under  $N_2$ .

<sup>c</sup> Measurements in thin film were performed onto the quartz substrate.

<sup>d</sup> Band gap estimated from the onset wavelength of the optical absorption in thin film.



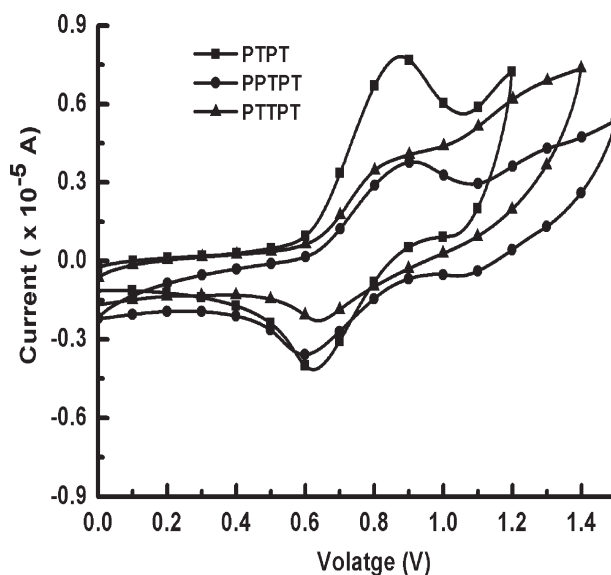
**FIGURE 2** UV-visible absorption spectra of polymers **PTPT**, **PPTPT**, and **PTTPT** in chloroform (a) and thin film (b).



**FIGURE 3** Photoluminescence spectra of polymers **PTPT**, **PPTPT**, and **PTTPT** in chloroform (a) and thin film (b).

(2-thienyl)pyrrole was reported to show the absorption maximum at 465 nm.<sup>25</sup> However, the new polymers prepared in this study show a considerable red shift of around 20 nm, which reveals the more effective  $\pi$ -conjugation of the new polymers. The optical band gaps of polymers **PTPT**, **PPTPT**, and **PTTPT** were calculated from the onset wavelength of the optical absorption in thin film to be 2.15 eV, 2.20 eV, and 2.13 eV, respectively.

Figure 3 shows the photoluminescence (PL) spectra of polymers **PTPT**, **PPTPT**, and **PTTPT** in solution and in thin film. The PL measurements were carried out in chloroform and in the thin film upon photo excitation at absorption maxima of the polymers. Polymers **PTPT**, **PPTPT**, and **PTTPT** exhibited greenish yellow emission peaks at 574 nm, 566 nm, and 542 nm, respectively, in solution and 580 nm, 557 nm, and 567 nm, respectively, in thin film. The shoulder peaks observed in all PL spectra might be due to the extended intermolecular interaction of the  $\pi$ -conjugated branches as previously reported for thiophene derivative pendant systems.<sup>28</sup> The

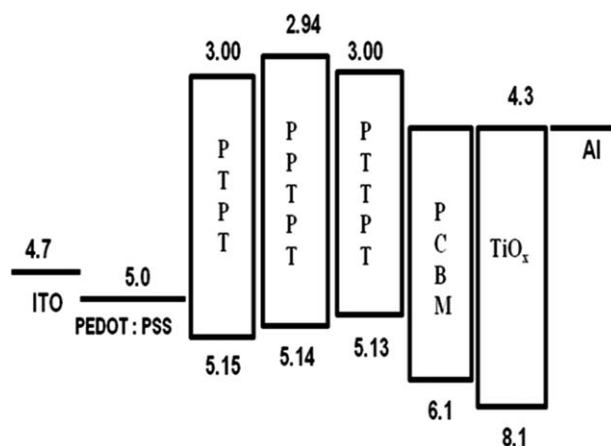


**FIGURE 4** CV curve of polymers **PTPT**, **PPTPT**, and **PTTPT** in film.

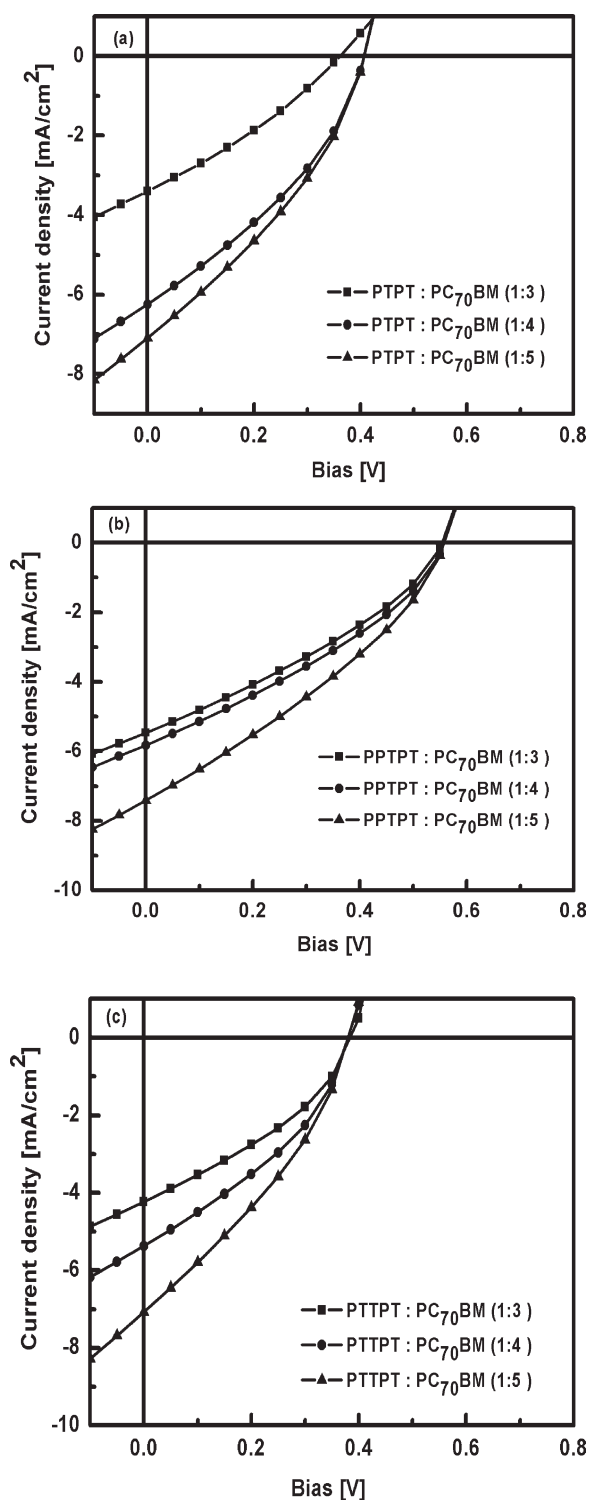
summary for the optical properties of polymers **PTPT**, **PPTPT**, and **PTTPT** are also included in Table 1.

The electrochemical properties of polymers **PTPT**, **PPTPT**, and **PTTPT** were investigated by CV (Fig. 4). From the CV measurements on drop-cast polymer films, the highest occupied molecular orbital (HOMO) energy levels of polymers **PTPT**, **PPTPT**, and **PTTPT** were calculated to be -5.15 eV, -5.14 eV, and -5.13 eV, respectively. In addition, the lowest unoccupied molecular orbital (LUMO) energy levels of polymers **PTPT**, **PPTPT**, and **PTTPT** were calculated from the values of band gaps and the HOMO energies to be -3.00 eV, -2.94 eV, and -3.00 eV, respectively. These results indicate that the alternating repeat units such as 2,5-dioctyloxyphenylene or 3-octylthiophene of the polymers have only a slight influence on their HOMO or LUMO levels.

Since the open circuit voltage ( $V_{oc}$ ) of PSCs is correlated with the difference between the HOMO level of the electron



**FIGURE 5** The energy level diagram of polymers **PTPT**, **PPTPT**, **PTTPT**, and **PC<sub>70</sub>BM** with all other materials used in BHJ solar cell.



**FIGURE 6**  $J$ - $V$  characteristics of BJJ solar cells prepared from ITO/PEDOT:PSS/PTPT:PC<sub>70</sub>BM/TiO<sub>x</sub>/Al (a), ITO/PEDOT:PSS/PPTPT:PC<sub>70</sub>BM/TiO<sub>x</sub>/Al (b), and ITO/PEDOT:PSS/PTTPT:PC<sub>70</sub>BM/TiO<sub>x</sub>/Al (c) under AM 1.5 irradiation (100 mW/cm<sup>2</sup>).

donor and the LUMO level of the electron acceptor,<sup>29</sup> the lower HOMO levels of the three new polymers can result in higher  $V_{oc}$  in the resulting PSCs. The LUMO levels of the three polymers are higher than that of PC<sub>70</sub>BM (−4.3 eV),<sup>30</sup>

and, consequently, the photoinduced electron transfer from the polymers (as donor) to PC<sub>70</sub>BM (as acceptor) can be allowed.<sup>29</sup> Judging from the CV results, the new polymers are expected to show promising electrochemical properties as polymer donor materials. Figure 5 illustrates the energy levels of the three polymers and PC<sub>70</sub>BM with some of other materials used in BJJ solar cells.

### BJJ Solar Cell Properties

BJJ solar cells were fabricated with an active layer made from a blend of PTPT, PPTPT, or PTTPT as the electron donor and PC<sub>70</sub>BM as the electron acceptor. The overall structure of BJJ solar cells was as follows: ITO/PEDOT:PSS/PTPT or PPTPT or PTTPT:PC<sub>70</sub>BM/TiO<sub>x</sub> (5 nm)/Al (100 nm). The active layer was sandwiched between the hole transporting (PEDOT:PSS) layer and the hole blocking (TiO<sub>x</sub>) layer. The solution processible hole blocking as well as electron transporting TiO<sub>x</sub> layer was made between the active layer and the metal electrode. To achieve high PCE, finding the optimum ratio of polymer:PC<sub>70</sub>BM is most important because the charge carrier mobility is higher at one particular ratio than the other ratio.<sup>31</sup> In our study, we made three devices for each polymer with 1:3 wt %, 1:4 wt %, and 1:5 wt % ratio of the polymer and PC<sub>70</sub>BM in the active layer.

The current density-voltage ( $J$ - $V$ ) characteristics of the devices prepared from PTPT, PPTPT, and PTTPT measured under the illumination of AM 1.5 G (100 mW/cm<sup>2</sup>) from a solar simulator are shown in Figure 6 and summarized in Table 2. From the initial OPV studies, the maximum PCE was found to be 1.35% for the device made from PPTPT:PC<sub>70</sub>BM (1:5 wt %) as an active layer with a  $V_{oc}$  of 0.56 V, a short-circuit current density ( $J_{sc}$ ) of 7.41 mA/cm<sup>2</sup>, and a fill factor (FF) of 33% as shown in Table 2. In every case, the PCE of the device made from polymer:PC<sub>70</sub>BM (1:5 wt %) is higher than that of the device made from polymer:PC<sub>70</sub>BM (1:3 wt %) or polymer:PC<sub>70</sub>BM (1:4 wt %) measured under

**TABLE 2** Solar Cell Performance of PTPT, PPTPT, and PTTPT as Electron Donors with PC<sub>70</sub>BM as an Electron Acceptor in ITO/PEDOT:PSS/PTPT (or) PPTPT (or) PTTPT:PC<sub>70</sub>BM/TiO<sub>x</sub>/Al Device

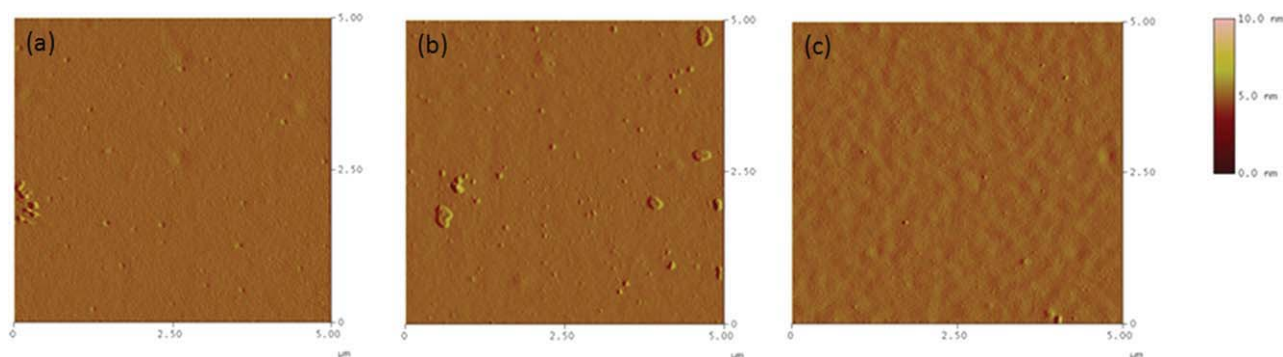
Ratio of Polymers and PC <sub>70</sub> BM (wt %)	$V_{oc}$ (V) <sup>a</sup>	$J_{sc}$ (mA/cm <sup>2</sup> ) <sup>b</sup>	FF (%) <sup>c</sup>	PCE (%) <sup>d</sup>
PTPT (1):PC <sub>70</sub> BM (3)	0.36	3.39	30	0.37
PTPT (1):PC <sub>70</sub> BM (4)	0.41	6.24	35	0.89
<b>PTPT (1):PC<sub>70</sub>BM (5)</b>	<b>0.41</b>	<b>7.09</b>	<b>34</b>	<b>0.98</b>
PPTPT (1):PC <sub>70</sub> BM (3)	0.55	5.47	33	0.99
PPTPT (1):PC <sub>70</sub> BM (4)	0.56	5.83	33	1.09
<b>PPTPT (1):PC<sub>70</sub>BM (5)</b>	<b>0.56</b>	<b>7.41</b>	<b>33</b>	<b>1.35</b>
PTTPT (1):PC <sub>70</sub> BM (3)	0.38	4.24	36	0.58
PTTPT (1):PC <sub>70</sub> BM (4)	0.37	5.37	37	0.74
<b>PTTPT (1):PC<sub>70</sub>BM (5)</b>	<b>0.37</b>	<b>7.08</b>	<b>34</b>	<b>0.90</b>

<sup>a</sup> Open-circuit voltage.

<sup>b</sup> Short-circuit current density.

<sup>c</sup> Fill factor.

<sup>d</sup> Power conversion efficiency.



**FIGURE 7** AFM image obtained by tapping-mode on the surface for **PTPT:PC<sub>70</sub>BM** (1:5 wt %) (a), **PPTPT:PC<sub>70</sub>BM** (1:5 wt %) (b), and **PTTPT:PC<sub>70</sub>BM** (1:5 wt %) (c) spin coated thin film.

the identical condition. From these results, the higher content of PC<sub>70</sub>BM is expected to be more favorable for the efficient light harvesting and electron-hole separation. With increasing the PC<sub>70</sub>BM content, the  $J_{sc}$  increases for all three polymer devices. By increasing the the PC<sub>70</sub>BM content, the charge carrier mobility is expected to increase.

The device made from **PTPT:PC<sub>70</sub>BM** (1:5 wt %) and **PTTPT:PC<sub>70</sub>BM** (1:5 wt %) showed the PCE of 0.98% and 0.90%, respectively. These PCEs are even lower than those of the devices made from **PPTPT:PC<sub>70</sub>BM** (1:4 wt %) or **PPTPT:PC<sub>70</sub>BM** (1:3 wt %). The devices made from **PTPT:PC<sub>70</sub>BM** (1:5 wt %) or **PTTPT:PC<sub>70</sub>BM** (1:5 wt %) exhibit the higher  $J_{sc}$  (7.09 and 7.08 mA/cm<sup>2</sup>, respectively) and the lower  $V_{oc}$  (0.41 and 0.37 V, respectively) than the devices made from **PPTPT:PC<sub>70</sub>BM** (1:4 wt %) or **PPTPT:PC<sub>70</sub>BM** (1:3 wt %) while all devices exhibit quite similar FFs. These results indicate that the relatively high PCE of the devices made from **PPTPT:PC<sub>70</sub>BM** is relied on the relatively high  $V_{oc}$ . According to the BHJ solar cell model, the  $V_{oc}$  is determined by the energy difference between the HOMO level of the donor and the LUMO level of the acceptor<sup>28</sup> and, in addition, the  $V_{oc}$  is influenced by the quality of the heterojunction, which was highly influenced by the film preparation conditions.<sup>26</sup> The energy differences between the HOMO levels of the three polymers and the LUMO level of PC<sub>70</sub>BM should be quite similar because the HOMO levels of the three polymers are similar. Consequently, the relatively high  $V_{oc}$  of the device made from **PPTPT:PC<sub>70</sub>BM** seems to be originated from the quality of the heterojunction. The presence of octyloxy groups in **PPTPT** back bone is expected to improve the quality of the heterojunction and, consequently, to improve the PCE. The theoretical  $V_{oc}$  values calculated from the HOMO levels of the three polymers and the LUMO level of PC<sub>70</sub>BM should be over 0.83 V, but the experimental  $V_{oc}$  values are 0.56 V or less as shown in Table 2. In this instance, we hope that the device performance would be improved considerably by the device optimization.

In BHJ solar cells, the surface morphology of the active layer is quite important to their photovoltaic performance.<sup>32</sup> Indeed, the proper organization of polymers and PC<sub>70</sub>BM will help to achieve the optimum performance. Figure 7

shows the AFM images of the active layers of **PTPT:PC<sub>70</sub>BM** (1:5 wt %), **PPTPT:PC<sub>70</sub>BM** (1:5 wt %) and **PTTPT:PC<sub>70</sub>BM** (1:5 wt %). Their surfaces are quite smooth. The root-mean-square (rms) roughness of the three active layers is 1.73, 1.35, and 1.30 nm, respectively. The main morphological feature of the composite film shows a homogeneous distribution of the two components within the nanoscale.

## CONCLUSIONS

In this study, we successfully synthesized a series of three new donor polymers such as **PTPT**, **PPTPT**, and **PTTPT** containing 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole via the Suzuki polycondensation reaction with reasonable yields. All three polymers showed similar optical and electrochemical properties. However, BHJ solar cell properties of the three polymers as electron donor materials with PC<sub>70</sub>BM as electron acceptor in the active layer were quite different. Among others, the BHJ solar cells fabricated in ITO/PEDOT:PSS/**PPTPT:PC<sub>70</sub>BM**/TiO<sub>x</sub>/Al configurations were found to show the highest solar cell performance, the PCE being 1.35% ( $J_{sc}$  = 7.41 mA/cm<sup>2</sup>,  $V_{oc}$  = 0.56 V, FF = 33%) when the blend ratio of **PPTPT** and PC<sub>70</sub>BM in the active layer was 1:5 wt %. We assume that the relatively high solar cell performance of the device made from **PPTPT:PC<sub>70</sub>BM** is attributed to the octyloxy groups in **PPTPT** back bone. The octyloxy groups in **PPTPT** back bone is expected to improve the quality of the heterojunction between the polymer and PC<sub>70</sub>BM and, consequently, to improve the PCE.

M. H. Hyun acknowledges the financial support from the National Core Research Center Program through the National Research Foundation of Korea (No. 2010-0008-269). S. H. Jin greatly acknowledges the financial support by KOSEF grant funded by the Korea government (MEST) (No. M10600000157-06J0000-15710).

## REFERENCES AND NOTES

- Shin, W. S.; Kim, S. C.; Lee, S. J.; Jeon, H. S.; Kim, M. K.; Naidu, B. V. K.; Jin, S. H.; Lee, J. K.; Lee, J. W.; Gal, Y. S. *J Polym Sci Part A: Polym Chem* 2007, 45, 1394–1402.

- 2 Huo, L.; He, C.; Han, M.; Zhou, E.; Li, Y. *J Polym Sci Part A: Polym Chem* 2007, 45, 3861–3871.
- 3 Lee, J. K.; Ma, W. L.; Brabec, C. J.; Yuen, J.; Moon, J. S.; Kim, J. Y.; Lee, K.; Bazan, G. C.; Heeger, A. J. *J Am Chem Soc* 2008, 130, 3619–3623.
- 4 Chen, C. P.; Chan, S. H.; Chao, T. C.; Ting, C.; Ko, B. T. *J Am Chem Soc* 2008, 130, 12828–12833.
- 5 Chen, M. H.; Hou, J.; Hong, Z.; Yang, G.; Sista, S.; Chen, L. M.; Yang, Y. *Adv Mater* 2009, 21, 1–5.
- 6 Gadisa, A.; Oosterbaan, W. D.; Vandewal, K.; Bolsee, J. C.; Bertho, S.; Haen, J. D.; Lutsen, L.; Vanderzande, D.; Manca, J. V. *Adv Funct Mater* 2009, 19, 1–7.
- 7 Wang, E.; Wang, M.; Wang, L.; Duan, C.; Zhang, J.; Cai, W.; He, C.; Wu, H.; Cao, Y. *Macromolecules* 2009, 42, 4410–4415.
- 8 Liang, F.; Lu, J.; Ding, J.; Movileanu, R.; Tao, Y. *Macromolecules* 2009, 42, 6107–6114.
- 9 Li, K. C.; Hsu, Y. C.; Lin, J. T.; Yang, C. C.; Wei, K. H.; Lin, H. C. *J Polym Sci Part A: Polym Chem* 2009, 47, 2073–2092.
- 10 Hsu, S. L. C.; Lin, Y. C.; Lee, R. F.; Sivakumar, C.; Chen, J. S.; Chou, W. Y. *J Polym Sci Part A: Polym Chem* 2009, 47, 5336–5343.
- 11 Peet, J.; Heeger, A. J.; Bazan, G. C. *Acc Chem Res* 2009, 42, 1700–1708.
- 12 Wu, P. T.; Ren, G.; Kim, F. S.; Li, C.; Mezzenga, R.; Jenekhe, S. A. *J Polym Sci Part A: Polym Chem* 2010, 48, 614–626.
- 13 Yang, Y. L.; Lee, Y. H.; Chang, C. J.; Lu, A. J.; Hsu, W. C.; Wang, L.; Leung, M. K.; Dai, C. A. *J Polym Sci Part A: Polym Chem* 2010, 48, 1607–1616.
- 14 Chen, G. Y.; Chiang, C. M.; Kekuda, D.; Lan, S. C.; Chu, C. W.; Wei, K. H. *J Polym Sci Part A: Polym Chem* 2010, 48, 1669–1675.
- 15 Song, J.; Zhang, C.; Li, C.; Qin, R.; Li, B.; Liu, Z.; Bo, Z. *J Polym Sci Part A: Polym Chem* 2010, 48, 2571–2578.
- 16 Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv Funct Mater* 2005, 15, 1617–1622.
- 17 Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat Mater* 2005, 4, 864–868.
- 18 Reyes-Reyes, M.; Kim, K.; Carrolla, D. L. *Appl Phys Lett* 2005, 87, 083506.
- 19 Liang, Y.; Feng, D.; Wu, Y.; Tsai, S. T.; Li, G.; Ray, C.; Yu, L. *J Am Chem Soc* 2009, 131, 7792–7799.
- 20 Liang, Y.; Xu, Z.; Xia, J.; Tsai, S. T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. *Adv Mater* 2010, 22, 1–4.
- 21 Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat Photonics* 2009, 3, 297–303.
- 22 Hou, J.; Chen, H. Y.; Zhang, S.; Chen, R. I.; Yang, Y.; Wu, Y.; Li, G. *J Am Chem Soc* 2009, 131, 15586–15587.
- 23 Dhanabalan, A.; van Duren, J. K. J.; van Hal, P. A.; van Dongen, J. L. J.; Janssen, R. A. J. *Adv Funct Mater* 2001, 11, 255–262.
- 24 Liu, Y.; Summers, M. A.; Edler, C.; Fréchet, J. M. J.; McGehee, M. D. *Adv Mater* 2005, 17, 2960–2964.
- 25 Tamilavan, V.; Sakthivel, P.; Li, Y.; Song, M.; Kim, C. H.; Jin, S. H.; Hyun, M. H. *J Polym Sci Part A: Polym Chem* 2010, 48, 3169–3177.
- 26 Wen, S.; Pei, J.; Zhou, Y.; Li, P.; Xue, L.; Li, Y.; Bin Xu, B.; Tian, W. *Macromolecules* 2009, 42, 4977–4984.
- 27 Chang, Y. T.; Hsu, S. L.; Su, M. H.; Wei, K. H. *Adv Funct Mater* 2007, 17, 3326–3331.
- 28 Jeon, H. S.; Lee, S. K.; Lee, E. J.; Park, S. M.; Kim, S. C.; Jin, S. H.; Gal, Y. S.; Lee, J. W.; Im, C. *Macromolecules* 2007, 40, 4794–4801.
- 29 Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv Mater* 2009, 21, 1323–1338.
- 30 Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T. Q.; Dante, M.; Heeger, A. J. *Science* 2007, 317, 222–225.
- 31 Barrau, S.; Andersson, V.; Zhang, F.; Masich, S.; Bijleveld, J.; Andersson, M. R.; Inganäs, O. *Macromolecules* 2009, 42, 4646–4650.
- 32 Zhou, Y. H.; Wang, Y. N.; Wu, W. C.; Wang, H.; Han, L.; Tian, W. J.; Bassler, H. *Sol Energy Mater Sol Cells* 2007, 91, 1842–1848.