

## Research Article

# Synthesis and Characterization of Carbazole-Benzothiadiazole-Based Conjugated Polymers for Organic Photovoltaic Cells with Triazole in the Main Chain

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We have synthesized a series of carbazole-benzothiadiazole-triazole based copolymers, poly[(*N*-9'-heptadecanyl-2,7-carbazole)-*co*-(5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole))-*co*-((4-(4-butylphenyl)-3,5-diphenyl-4*H*-1,2,4)triazole))] (**PCz3TBz**) by Suzuki coupling polymerization. The optical and electrochemical properties of the copolymers could be tuned by changing the comonomer unit of triazole from 0% to 80%. Organic photovoltaic (OPV) cells were fabricated by blending the synthesized polymers as a donor and PCBM as an acceptor. The material solubility and film morphology were improved by introducing the triazole unit in the main chain. Improved OPV device performance of 1.74% was achieved in the presence of an optimal amount of triazole moieties.

## 1. Introduction

Organic photovoltaic (OPV) cells are promising sources of electrical power that have attracted considerable attention because of their efficiency, low cost, and potential renewable energy applications. The prototypical material system consisting of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub> butyric acid methylester (PCBM) normally gives power conversion efficiencies (PCEs) in a range of about 4-5% [2]. New conjugated polymers with low band gaps that can efficiently harvest solar energy over a broader spectrum are being actively developed. To enhance OPV performance, low-band-gap conjugated materials with appropriate energy levels are required for efficient charge transfer [3]. One successful approach to enhance OPV performance is to arrange electron-donating and electron-accepting units alternately along the conjugated backbone for the use of donor materials in OPVs [1, 4-6]. Many electron-accepting units such as benzothiadiazole (BT) and diketopyrrolopyrrole (DPP) have been synthesized and utilized in OPVs [7, 8].

In organic light-emitting diode (OLED) applications, highly electron-deficient groups such as oxadiazole and

triazole (Tz) units have been introduced into the polymer backbone or as the side group as electron transporting units to adjust the charge-injecting and transporting properties of the copolymers [9-11]. More recently, several reports have described improvements in PCE by incorporating electron deficient moieties into the polymer backbone or as side chains [12-16]. The incorporation of electron deficient groups such as thiadiazole or oxadiazole can improve the performance of OPVs by enhancing electron transfer in comparison to the parent polymer. Previously, we reported on polyfluorenes containing various electron transporting units such as benzothiadiazole (BT), oxadiazole, and triazole (Tz) in the main chain [17, 18]. Interestingly, the photovoltaic properties of the polymers were varied by the introduced electron transporting units and the polymer containing triazole (Tz) showed the improved performance. In this work, we introduce electron-transporting triazole (Tz) units into the well-known carbazole-benzothiadiazole-based copolymer (**PCz3TB**) by Suzuki polymerization to be used as donors for OPVs. The copolymers were designed to have different feed ratios of comonomer units (benzothiadiazole and triazole). The optical properties, film morphology, and

photovoltaic characteristics of the polymers are investigated to establish the relationship between molecular structure and device performance.

## 2. Experimental

**2.1. Materials.** 2,7-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9''-heptadecanyl-carbazole, 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole, and 3,5-bis-(4-bromophenyl)-4-(4-butylphenyl)-4H-[1,2,4]triazole were prepared according to a procedure mentioned in the literature [19]. Aliquat 336, tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>), and sodium carbonate were purchased from Aldrich. All reagents purchased commercially were used without further purification, except for the toluene used as a solvent, which was distilled.

**2.2. Measurements.** Thermal gravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10°C/min using a Perkin Elmer TGA7 thermogravimetric analyzer. UV-Vis spectra were obtained using a Shimadzu UV/vis spectrometer. The polymer films used in the UV-Vis absorption measurements were prepared by spin coating of polymer solution in chlorobenzene. The optical energy band gaps ( $E_g$ ) were estimated from the absorption onset wavelengths ( $E_g = 1240/\lambda_{\text{onset}}$  (eV)) of the polymer films. The electrochemical properties of the polymers were characterized by cyclic voltammetry (CV). The films were prepared by dip coating the polymer solution onto Pt wire, and the measurements were calibrated using the ferrocene value of -4.8 eV as the standard [20]. Film thicknesses were measured using a TENCOR surface profiler.

**2.3. Synthesis.** The syntheses of the copolymers, poly[(N-9'-heptadecanyl-2,7-carbazole)-alt-(5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole))] (**PCz3TB**), and three poly[(N-9'-heptadecanyl-2,7-carbazole)-co-(5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole))-co-(3,5-bis-(4-4-phenyl-[1,2,4]triazole))] (**PCz3TBTz**) were carried out using the Suzuki coupling reaction between the diborolanylaryl compound, 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9''-heptadecanyl-carbazole (**Cz**), and the dibromoaryl compounds, 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (**3TB**) and 3,5-bis-(4-bromophenyl)-4-(4-butylphenyl)-4H-[1,2,4]triazole (**Tz**).

**2.3.1. Synthesis of PCz3TB.** Two comonomers, **Cz** (0.25 g, 0.38 mmol) and **3TB** (0.12 g, 0.38 mmol), were dissolved in distilled toluene (4.5 mL) with the air-sensitive Pd(0) complex, Pd(PPh<sub>3</sub>)<sub>4</sub> (0.004 g, 0.004 mmol). Aliquat336 (0.015 g, 0.037 mmol) and 2 M aq. sodium carbonate (0.18 g, 1.74 mmol) were added to the mixture. After being refluxed for 48 h, the reaction mixture was cooled to about 50°C and added slowly to a vigorously stirred mixture consisting of 230 mL of methanol and 15 mL of 1 M aq. HCl. The polymer fibers were collected by filtration and reprecipitation from methanol. The polymer was purified by a Soxhlet extraction in acetone for 2 days to remove oligomers and catalyst residues. The reprecipitation procedure in dichloromethane/methanol was then repeated several times. The final

product, a yellow polymer, was obtained after drying in vacuum at 60°C, with a yield of 0.42 g (64.4%). Anal. Calcd. for (C<sub>43</sub>H<sub>47</sub>N<sub>3</sub>S<sub>3</sub>)<sub>n</sub>: C: 73.56, H: 6.75, N: 5.99, S: 13.70. Found: C: 65.48, H: 5.97, N: 5.34, S: 11.01.

**2.3.2. Synthesis of PCz3TBTz-1.** **PCz3TBTz-1** was prepared as for **PCz3TB**, using three comonomers, **Cz** (0.55 g, 0.84 mmol), **3TB** (0.30 g, 0.65 mmol), and **Tz** (0.08 g, 0.16 mmol), resulting in purple solid with a yield of 0.20 g (34.0%). Anal. Calcd. for (C<sub>225</sub>H<sub>250</sub>N<sub>16</sub>S<sub>12</sub>)<sub>n</sub>: C: 75.71, H: 7.06, N: 6.28, S: 10.96. Found: C: 74.23, H: 7.41, N: 5.69, S: 10.94.

**2.3.3. Synthesis of PCz3TBTz-2.** **PCz3TBTz-2** was prepared as for **PCz3TBTz-1**, using **Cz** (0.26 g, 0.39 mmol), **3TB** (0.085 g, 0.19 mmol), and **Tz** (0.095 g, 0.19 mmol), resulting in purple solid with a yield of 0.14 g (51.1%). Anal. Calcd. for (C<sub>96</sub>H<sub>109</sub>N<sub>7</sub>S<sub>3</sub>)<sub>n</sub>: C: 78.93, H: 7.52, N: 6.71, S: 6.85. Found: C: 72.50, H: 6.81, N: 5.83, S: 6.99.

**2.3.4. Synthesis of PCz3TBTz-3.** **PCz3TBTz-3** was prepared as for **PCz3TBTz-1** using **Cz** (0.26 g, 0.39 mmol), **3TB** (0.034 g, 0.074 mmol), and **Tz** (0.15 g, 0.30 mmol), resulting in purple solid with a yield of 0.18 g (64.3%). Anal. Calcd. for (C<sub>255</sub>H<sub>295</sub>N<sub>19</sub>S<sub>3</sub>)<sub>n</sub>: C: 82.15, H: 7.97, N: 7.13, S: 2.74. Found: C: 79.19, H: 7.86, N: 6.85, S: 3.03.

**2.4. Fabrication of OPV Device.** The organic photovoltaic devices were fabricated with the configuration ITO/PEDOT:PSS (40 nm)/polymer:PC<sub>71</sub>BM (60 nm)/LiF (1 nm)/Al (100 nm). The ITO-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, isopropyl alcohol, and methanol. The poly(ethylene dioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) layer was spin-coated on the substrate and annealed at 140°C for 10 min. The active layer consisting of copolymers and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) was spin-coated from a chlorobenzene solution. Prior to use, a chlorobenzene solution of polymer and PC<sub>71</sub>BM with the total concentration of 20 mg/mL was stirred at room temperature overnight to ensure complete dissolution. The polymer solutions were spin-coated onto the substrate after being filtered through a 0.45 μm polytetrafluoroethylene (PTFE) membrane syringe. Next, the LiF and Al layers were deposited as the cathode electrode. The area of the device was 4 mm<sup>2</sup>. After annealing at 100°C for 10 min, the current-voltage (*J-V*) characteristics of the polymer:PCBM films were measured with a Keithley 2400 source-measure unit in air under white light illumination of AM 1.5 (100 mW/cm<sup>2</sup>).

## 3. Results and Discussion

**3.1. Synthesis and Thermal Property.** The syntheses of the carbazole-benzothiadiazole-triazole-based copolymers (**PCz3TBTz-1**, **PCz3TBTz-2**, and **PCz3TBTz-3**) were carried out using Suzuki coupling reaction between the diborolanylaryl compound, 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9''-heptadecanyl-carbazole and the dibromoaryl compounds, 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (**3BT**) and 3,5-bis-(4-bromophenyl)-4-(4-butylphenyl)-4H-[1,2,4]triazole (**Tz**). The feed

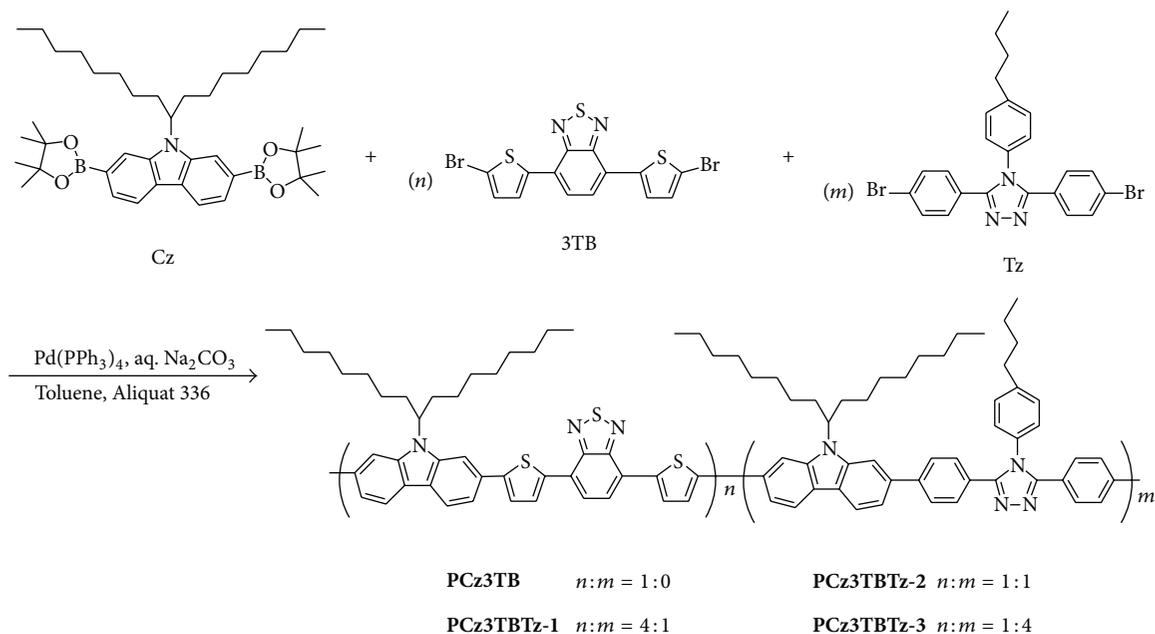
SCHEME 1: Synthetic route to the **PCz3TB** and three **PCz3TBTz**s.

TABLE 1: Physical properties of polymers.

	<b>PCz3TB</b>	<b>PCz3TBTz-1</b>	<b>PCz3TBTz-2</b>	<b>PCz3TBTz-3</b>
Ratio (Cz : 3TB : Tz)				
Feed ratio	50 : 50 : 0	50 : 40 : 10	50 : 25 : 25	50 : 10 : 40
Actual ratio <sup>a</sup>	61 : 39 : 0	62 : 35 : 3	60 : 24 : 16	56 : 10 : 34
$M_n^b$	94800	95300	77400	8300
$M_w^b$	121700	135100	110200	11700
PDI ( $M_w/M_n$ )	1.28	1.42	1.42	1.41
$T_{5d}$ (°C)	361	359	354	369
Solution ( $\lambda_{max}$ , nm) Abs.	380, 530	380, 536	380, 536	365, 528
Film ( $\lambda_{max}$ , nm) Abs.	390, 560	392, 566	383, 550	356, 539
$E_{onset}$ (V versus SCE) <sup>c</sup>	0.98	0.96	0.99	0.92
HOMO (eV) <sup>d</sup>	-5.37	-5.35	-5.38	-5.31
LUMO (eV)	-3.51	-3.49	-3.48	-3.36
$E_g$ (eV) <sup>e</sup>	1.86	1.86	1.90	1.95

<sup>a</sup>Actual ratio in polymers determined by elemental analysis.

<sup>b</sup> $M_n$  and  $M_w$  stand for the number-average and weight-average molecular weights, respectively, determined by GPC.

<sup>c</sup> $E_{onset}$  stands for onset potential of oxidation.

<sup>d</sup>Calculated using the empirical equation:  $I_p(\text{HOMO}) = -(E_{onset} + 4.39)$ .

<sup>e</sup>Optical band gaps ( $E_g$ ) taken as the absorption onsets in the UV-vis spectra of the polymer films ( $E_g = 1240/\lambda_{onset}$  eV).

ratios of two dibromides (**3BT** and **Tz**) were varied from 4:1, 2:2, to 1:4 to assess the effect of triazole units on the OPV performance. For comparison, the well-known OPV donor polymer, **PCz3TB**, was also synthesized at the same time. Three **PCz3TBTz** copolymers have the same polymer backbone as **PCz3TB**. In the carbazole and 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (**3BT**) backbone, we incorporated an electron-transporting moiety, 4-(4-butylphenyl)-4H-[1,2,4]triazole (**Tz**), as the third comonomer. The synthetic routes toward copolymers are outlined in Scheme 1. Three **PCz3TBTz** copolymers were designed

to have 10, 25, and 40% triazole unit content instead of **3TB** unit content; however, the actual ratios of the repeat units in the real copolymers could be different from the feed ratios due to the difference of reactivity between comonomers. An elemental analysis (EA) was used to calculate the actual ratio in the copolymers. **PCz3TBTz-1**, **PCz3TBTz-2**, and **PCz3TBTz-3** contained 3, 16, and 34% triazole unit content. The molecular weights, feed, and actual ratios of the repeat units in the copolymers are listed in Table 1. The number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights of the synthesized polymers were determined with

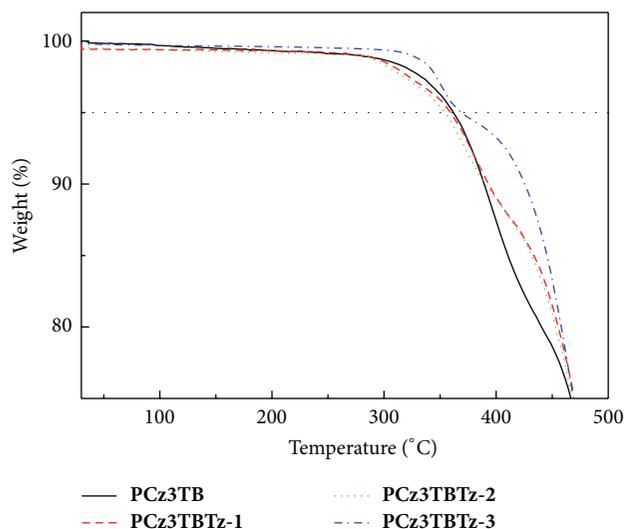


FIGURE 1: TGA thermograms of the copolymers.

gel permeation chromatography (GPC). The  $M_w$  values of **PCz3TB**, **PCz3TBTz-1**, **PCz3TBTz-2**, and **PCz3TBTz-3** were 121800, 135100, 110200, and 11700, respectively, and their polydispersity indices (PDIs) ranged from 1.28 to 1.42. The thermal stability of the copolymers was evaluated in a nitrogen atmosphere by TGA. As shown in Figure 1, the copolymers exhibited good thermal stability and the weight loss was less than 5% ( $T_{5d}$ ) upon heating to 350°C.

**3.2. Optical and Electrochemical Properties.** The UV-Vis absorption spectra of four copolymers in chlorobenzene solutions with the dilute concentration are shown in Figure 2(a), and the main optical properties are listed in Table 1. All the UV-Vis absorption spectra have two absorption peaks, which could be assigned to the  $\pi-\pi^*$  transition of the conjugated backbone and intramolecular charge transfer (ICT) interactions between the thiophene donor and the benzothiadiazole/triazole acceptor units [21]. The absorption spectra of the film state are red-shifted relative to those of the solution state (see Figure 2(b)), likely due to increased intermolecular interactions between neighboring molecules in the film state. By increasing the ratio of triazole in the copolymer from **PCz3TB**, **PCz3TBTz-1**, **PCz3TBTz-2** to **PCz3TBTz-3**, the absorption intensity in the long wavelength region was gradually decreased. In other words, replacement of the benzothiadiazole moiety with the triazole moiety in the main chain exceeding 10% appeared to decrease inter- and intramolecular interactions between donor and acceptor moieties. The optical band gaps,  $E_g$ , of the copolymers are estimated from the absorption onset wavelengths of the UV-Vis spectrum of the polymer film (Table 1). The UV absorption and optical band gap of **PCz3TBTz-1** are similar to those of **PCz3TB**, and greater addition of the triazole unit into the main chain in **PCz3TBTz-2** and **PCz3TBTz-3** resulted in an increase of the band gap of copolymers as compared to that of **PCz3TB**. The electrochemical properties of the polymers were also measured to determine their highest

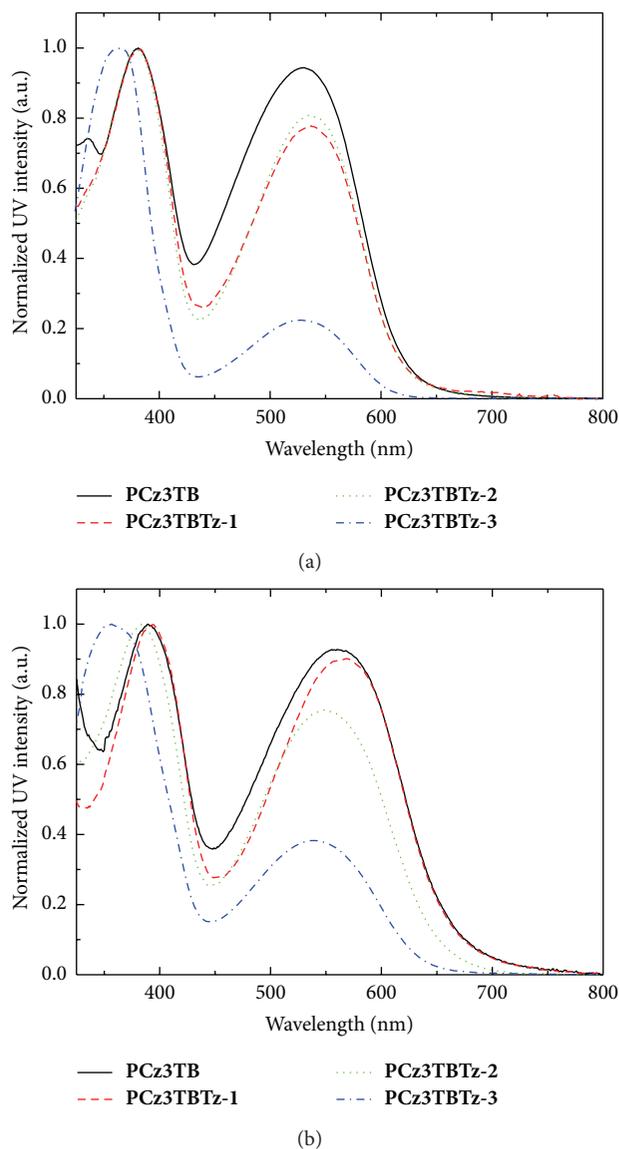


FIGURE 2: UV-Visible absorption spectra in (a) solution and (b) film.

occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels. Figure 3 shows the anodic scan of the CV of the copolymers. The onset of oxidation for copolymers occurred in a range of 0.92 to 0.98 V (vs SCE), which corresponds to their HOMO levels in a range of  $-5.31$  to  $-5.38$  eV (Table 1), according to the empirical relationship proposed by Leeuw et al.  $I_p(\text{HOMO}) = -(E_{\text{onset}} + 4.39)$ , where  $E_{\text{onset}}$  is the onset potential of oxidation [22]. The effects of the HOMO levels and band gaps on the photovoltaic properties are discussed below.

**3.3. Organic Photovoltaic Properties.** To investigate the current-voltage characteristics of the copolymers, devices with the configuration of ITO/PEDOT:PSS (40 nm)/polymer:PC<sub>71</sub>BM (60 nm)/LiF (1 nm)/Al (100 nm) were fabricated. The blending ratio of polymer and PCBM was adjusted

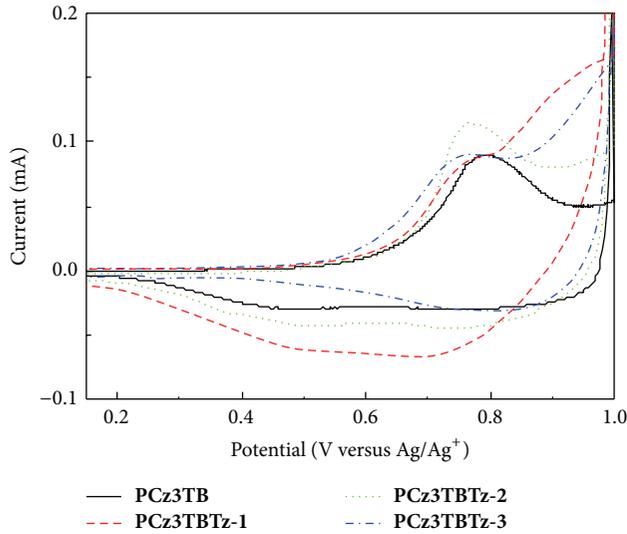
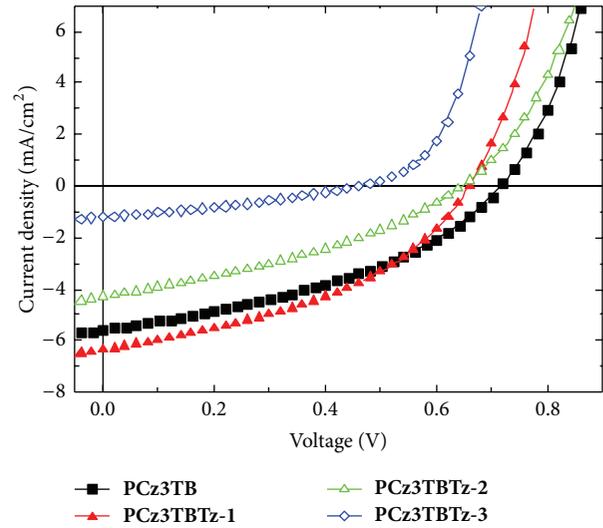


FIGURE 3: CV of the polymer films.

to be 1:3. Figure 4 shows the current density versus voltage ( $J$ - $V$ ) curves for copolymer: PCBM devices and the photovoltaic properties of the blend films are summarized in Table 2. As shown in Figure 4, **PCz3TBTz-1** showed the highest device performance, with a power conversion efficiency (PCE) of 1.74%, compared to **PCz3TB** (1.55%), **PCz3TBTz-2** (0.98%), and **PCz3TBTz-3** (0.18%). The device performances were attributed to increases of the short-circuit current ( $J_{SC}$ ) and open-circuit voltage ( $V_{OC}$ ) values. Despite a slight decrease of the  $V_{OC}$  value from 0.72 V (**PCz3TB**) to 0.66 V (**PCz3TBTz-1**), **PCz3TBTz-1** showed a higher  $J_{SC}$  value of 6.36 mA/cm<sup>2</sup> than **PCz3TB** (5.56 mA/cm<sup>2</sup>), and the  $J_{SC}$  and  $V_{OC}$  values gradually decreased by increasing the feed ratios of the triazole unit in **PCz3TBTz-2** (4.29 mA/cm<sup>2</sup>, 0.65 V) and **PCz3TBTz-3** (1.21 mA/cm<sup>2</sup>, 0.46 V). As described above, although the UV absorption and optical band gap of **PCz3TBTz-1** are similar with those of **PCz3TB**, **PCz3TBTz-2** and **PCz3TBTz-3** with more triazole units in the main chain showed lower UV absorption intensity in the long wavelength region and an increased optical band gap, compared with **PCz3TB** and **PCz3TBTz-1**. Low-band-gap conjugated materials with appropriate energy levels are required for efficient charge transfer in OPVs [23]. The gradually decreased efficiencies of **PCz3TBTz-2** and **PCz3TBTz-3** relative to **PCz3TB** can be explained by the gradually decreased UV absorption intensity in the long wavelength region and the gradually increased band gaps. In addition, the significantly low efficiency of **PCz3TBTz-3** might stem from its low molecular weight compared to the other copolymers.

In other words, the feed ratio of comonomer units of **3TB** and **Tz** was optimized and the highest PCE of 1.74% was achieved in **PCz3TBTz-1**. This increased performance of **PCz3TBTz-1** can be explained by its improved solubility and surface morphology. Figure 5 compares the surface morphologies of the **PCz3TBTz-1**:PCBM blend film with **PCz3TB**:PCBM blend film, determined from AFM measurements. The root-mean-square (RMS) roughness of the

FIGURE 4:  $J$ - $V$  curves of photovoltaic cells of copolymers.TABLE 2: OPV performances of the polymer: PC<sub>71</sub>BM OPV cells<sup>a,b</sup>.

Active layer	$J_{SC}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	FF (%)	PCE (%)
<b>PCz3TB</b>	5.56	0.72	0.39	1.55 (1.54)
<b>PCz3TBTz-1</b>	6.36	0.66	0.41	1.74 (1.69)
<b>PCz3TBTz-2</b>	4.29	0.65	0.35	0.98 (0.94)
<b>PCz3TBTz-3</b>	1.21	0.46	0.32	0.18 (0.17)

<sup>a</sup>Thickness of the active layer was adjusted to 60 nm (blend ratio: polymer: PCBM = 1:3).

<sup>b</sup>The values shown here are for the best device, and the average performances among three samples are also shown in parenthesis.

**PCz3TBTz-1**:PCBM film was 1.78 nm, which was nearly ten times that of the **PCz3TB**:PCBM film. Similar phenomenon was observed in our previous work with **PF3TB** and **PF3TBTz** [18]. The larger RMS value of **PCz3TBTz-1** suggests that it has rougher surface morphology, indicative of increased polymer aggregation [24]. The suitable phase separation by polymer aggregation facilitated improved charge transport and carrier collection efficiency, resulting in reduced charge recombination and an increased  $J_{SC}$  value in the device [15]. The better morphology of **PCz3TBTz-1** is ascribed to improved solubility by introduction of the alkyl-substituted triazole unit into the main chain. Further research on modification of the polymer structure is currently underway.

## 4. Conclusions

We synthesized three carbazole-benzothiadiazole-based copolymers containing different amounts of triazole into the main chains through palladium-catalyzed Suzuki polymerization. The absorption intensity of the copolymers varied according to the amount of triazole. The feed ratio of comonomer units was optimized and the highest PCE of 1.74%

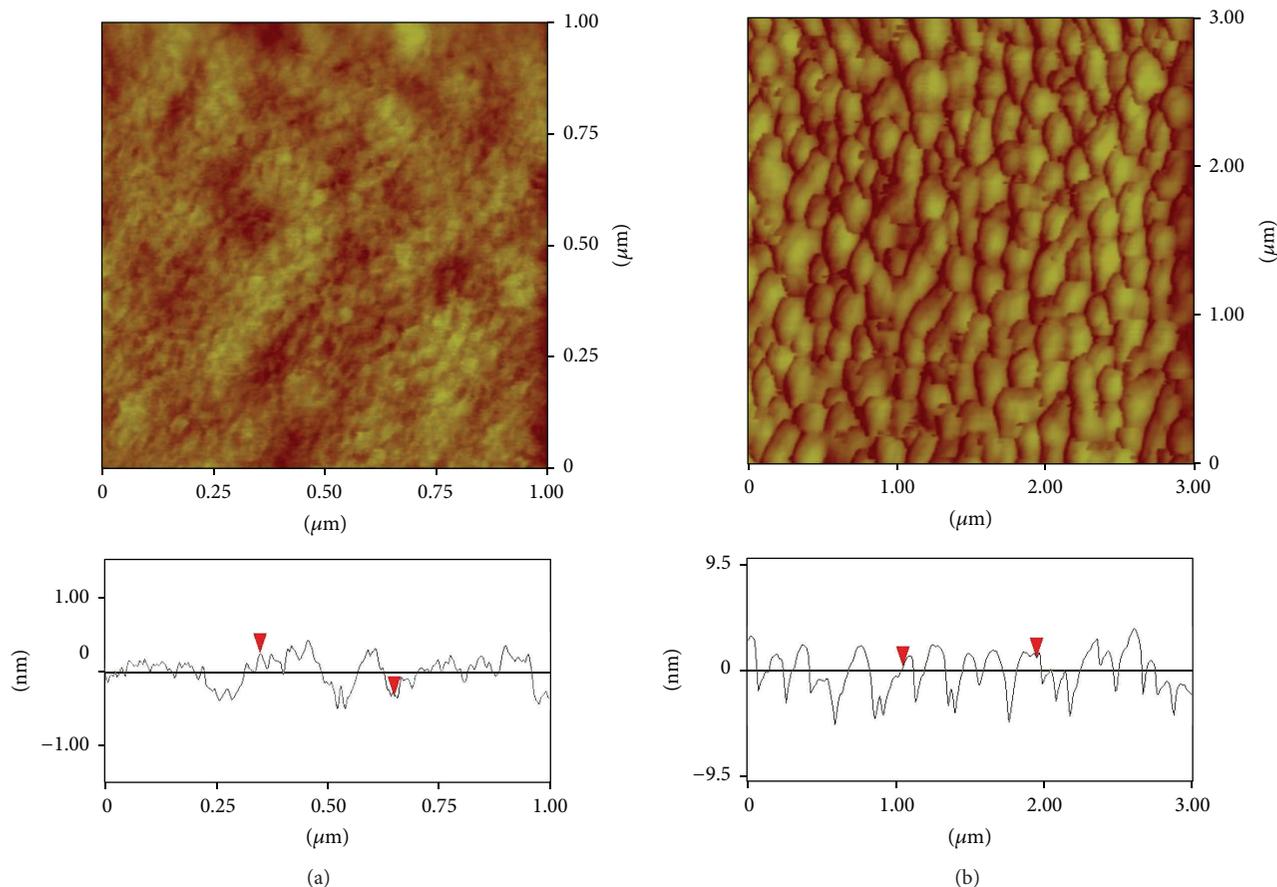


FIGURE 5: Topographic AFM images of (a) **PCz3TB:PCBM** and (b) **PCz3TBTz-I:PCBM** films.

was achieved in **PCz3TBTz-I**. This is attributed to its better morphology and solubility.

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