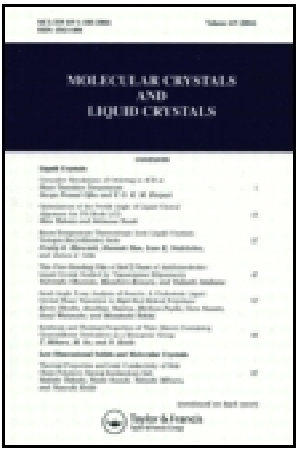

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# Synthesis and Characterization of Carbazole-Thiophene-based Conjugated Polymers for Organic Photovoltaic Cells

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# Synthesis and Characterization of Carbazole-Thiophene-based Conjugated Polymers for Organic Photovoltaic Cells

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*In this paper, we have synthesized a series of carbazole-based copolymers, poly(N-9″-heptadecanyl-2,7-carbazole-*alt*-bithiophene) (**PCzT2**), poly[N-9′-heptadecanyl-2,7-carbazole-*alt*-5,5′-bis(3″-hexyl-2″thienyl)-2,2′-bithiophenyl-5″,5″-diyl] (**PCzT4**), and poly[N-9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (**PCz3TB**), by Suzuki coupling polymerization. The optical and electrochemical properties of copolymers were effectively tuned by changing conjugation lengths of comonomer units from bithiophene to quaterthiophene or by introducing the electron-accepting benzothiadiazole into the polymer main chain. Finally, the organic photovoltaic cells (OPVs) were fabricated by blending of the synthesized polymers as donor and PCBM as acceptor, and the photovoltaic properties of the copolymers such as a power conversion efficiency (PCE), a short-circuit current ($J_{SC}$), an open-circuit voltage ($V_{OC}$), and a fill factor (FF) were evaluated. The relationship between molecular structures and device performances could be explained on the basis of the optical and electrochemical properties of the copolymers.*

**Keywords** Organic photovoltaic cells; solar cells; thiophene; benzothiadiazole; low band gap

## Introduction

Organic photovoltaic cells (OPVs) are promising sources of electrical power that have attracted considerable attention because of their efficiency, low cost, and potential renewable energy applications than ordinary silicon solar cell [1,2]. In recent few years, the OPV field has progressed remarkably both in terms of device performance as well as understanding of the governing physical processes. The prototypical system comprising poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-$C_{61}$ butyric acid methylester (PCBM) is nearing its theoretically optimal device performance [3]. Because the P3HT system can harvest photons with wavelengths below ~650 nm, new conjugated polymers with low band gaps, which can efficiently harvest solar energy over a broader spectrum, are being actively developed [4]. In other words, low band-gap conjugated materials with appropriate energy levels are required for efficient charge transfer in OPVs. One of the successful approaches to reduce band gap is to arrange the electron-donor and electron-acceptor repeating units alternately along the conjugated backbone [5]. Among these, the benzothiadiazole-based copolymers were the most successful, showing PCEs of 1.0–5.5%, due to their high hole

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*Corresponding author. E-mail: ehlim@kitech.re.kr mobilities, structural stability and broad absorption spectra [6]. In addition, as the conjugation length increased, the energy band gap of organic materials decreased.

In this work, we have synthesized a series of carbazole-based copolymers, **PCzT2**, **PCzT4**, and **PCz3TB**, by Suzuki polymerization, which can be used as donor materials for OPV cells. The copolymers were designed to have different conjugation lengths of comonomer units from bithiophene and quaterthiophene or to have the well-known electron-deficient benzothiadiazole unit. The optical, electrochemical, and photovoltaic characteristics of polymers were systematically investigated to establish the relationship between molecular structure and device performance of OPV cells.

## Experimental

### *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 5,5‴-dibromo-3,3‴-dihexyl-[2,2′,5′,2″,5″,2‴]quaterthiophene were prepared according to a literature procedure [7,8]. 5,5′-Dibromo-2,2′-bithiophene, Aliquat®336, tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) and sodium carbonate ($Na_2CO_3$) were purchased from Aldrich. All reagents purchased commercially were used without further purification, except for the toluene used as a solvent, which was distilled.

### *Synthesis*

The syntheses of the copolymers, poly(N-9″-heptadecanyl-2,7-carbazole-*alt*-bithiophene) (**PCzT2**), poly[N-9′-heptadecanyl-2,7-carbazole-*alt*-5,5′-bis(3″-hexyl-2″thienyl)-2,2′-bithiophenyl-5″,5″-diyl] (**PCzT4**), and poly[N-9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (**PCz3TB**), 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, and the corresponding dibromoaryl compounds, 5,5′-dibromo-2,2′-bithiophene, 5,5‴-dibromo-3,3‴-dihexyl-[2,2′,5′,2″,5″,2‴]quaterthiophene, and 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5] thiadiazole, respectively [9].

Synthesis of **PCzT2**: 5,5′-Dibromo-2,2′-bithiophene(0.12 g, 0.38 mmol), 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-N-9″-heptadecanyl-carbazole (0.26 g, 0.39 mmol), and the air-sensitive Pd(0) complex, $Pd(PPh_3)_4$ (0.004 g, 0.004 mmol) were dissolved in distilled toluene (4.5 mL). Aliquat®336 (0.015 g, 0.038 mmol) and 2 M aqueous sodium carbonate (0.89 ml, 0.19 g, 1.79 mmol) were added to the mixture. After stirring and heating 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 aqueous 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 0.17 g (76.6%). Anal. Calcd. for $(C_{37}H_{45}NS_2)_n$: C: 78.25, H: 7.99, N: 2.47, S: 11.29. Found: C: 78.03, H: 7.54, N: 2.46, S: 11.37.

Synthesis of **PCzT4**: **PCzT4** was prepared as for **PCzT2**, using 5,5‴-dibromo-3,3‴-dihexyl-[2,2′,5′,2″,5″,2‴]quaterthiophene (0.25 g, 0.38 mmol), resulting in a red solid.

Yield: 0.16 g (45.9%) Anal. Calcd. for $(C_{57}H_{73}NS_4)_n$: C: 76.03, H: 8.17, N: 1.56, S: 14.24. Found: C: 76.29, H: 8.22, N: 1.74, S: 12.61.

Synthesis of **PCz3TB**: **PCz3TB** was prepared as for **PCzT2**, using 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (0.35 g, 0.76 mmol), 2,7-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-N-9″-heptadecanyl-carbazole (0.52 g, 0.78 mmol), $Pd(PPh_3)_4$ (0.008 g, 0.0076 mmol), Aliquat®336 (0.03 g, 0.08 mmol), and 2M aqueous sodium carbonate (1.79 ml, 0.38 g, 3.59 mmol) in toluene (4.5 mL), resulting in a violet color solid. Yield: 0.42 g (76.8%). Anal. Calcd. for $(C_{43}H_{47}N_3S_3)_n$. C: 73.56, H: 6.75, N: 5.99, S: 13.70. Found: C: 67.26, H: 6.32, N: 4.49, S: 10.47.

### *Fabrication of OPV Device*

The organic photovoltaic devices were fabricated with the configuration ITO/PEDOT:PSS (40 nm)/polymer:$PC_{71}BM$ (60 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 (4500 rpm, 30 s) and annealed at 120°C for 20 min. The active layer consisting of copolymers and [6,6]-phenyl-$C_{71}$-butyric acid methyl ester ($PC_{71}BM$) was spin-coated from a chlorobenzene solution. Prior to use, a chlorobenzene solution of polymer and $PC_{71}BM$ with the total concentration of 20 mg/mL was stirred at room temperature overnight to ensure complete dissolution. The solutions were filtered through a 0.45 $\mu$m polytetrafluoroethylene (PTFE) membrane syringe before applied dropwise onto the substrates. Next, the Al metal layer was deposited as the cathode electrode. The area of the device was 4 $mm^2$. 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 $mW/cm^2$).

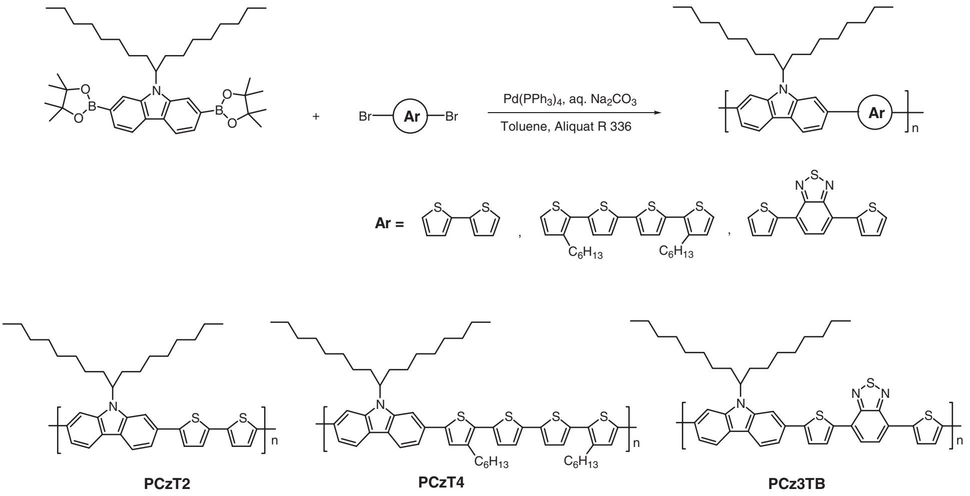
### *Measurements*

NMR spectra were recorded on an Avance 600 (Bruker) spectrometer. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a GPCV 2000 instrument (Waters) calibrated using THF as eluent and polystyrene as standard. 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 and PL spectra were obtained using LS55 (PerkinElmer) spectrofluorometer. The polymer films used in the UV-vis and PL measurements were prepared by spin-coating of polymer solution in chlorobenzene in the same way as the OPV fabrication. The optical energy band gaps ($E_g$) were estimated from the absorption onset wavelengths ($E_g = 1240/\lambda_{onset}$ (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. Film thicknesses were measured using a TENCOR surface profiler.

## Results and Discussion

### *Synthesis and Thermal Property*

We have synthesized three carbazole-thiophene-based copolymers, **PCzT2**, **PCzT4**, and **PCz3TB**, through Suzuki coupling reaction. (Scheme 1) The **PCzT2** and **PCzT4**



**Scheme 1.** Synthetic route to the **PCzT2**, **PCzT4**, and **PCz3TB**.

copolymers were designed to have different conjugation lengths by controlling the number of thiophenes. In **PCz3TB**, the electron-accepting benzothiadiazole group was introduced into the polymer backbone. The weight-average molecular weights ($M_w$) of **PCzT2**, **PCzT4**, and **PCz3TB** were 57831, 17276, and 76188, respectively, which were determined by GPC. The relatively low molecular weight of **PCzT4** is probably due to the limited solubility.

The thermal behaviors of the polymers were obtained by TGA analysis (Fig. 1). All the polymers exhibited excellent thermal stability, with 5% weight loss at 410, 416, and 362°C for **PCzT2**, **PCzT4**, and **PCz3TB**, respectively, which is comparable to that of P3HT (424°C [10]) indicating high thermal stability of the copolymers.

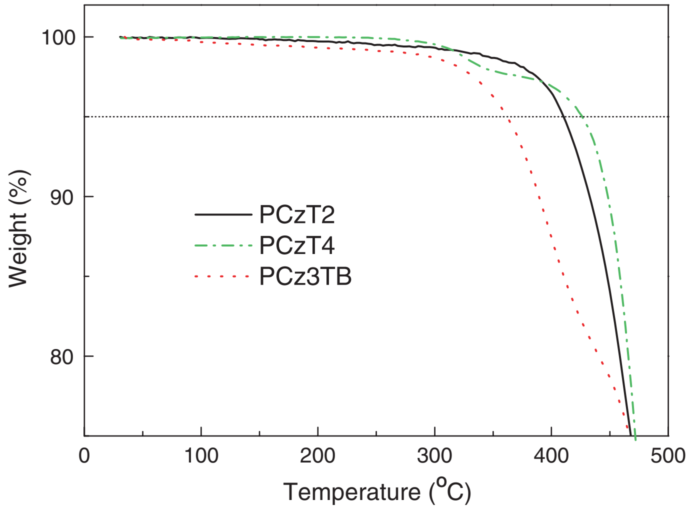


**Figure 1.** Thermal gravimetric analysis (TGA) thermograms of the copolymers.

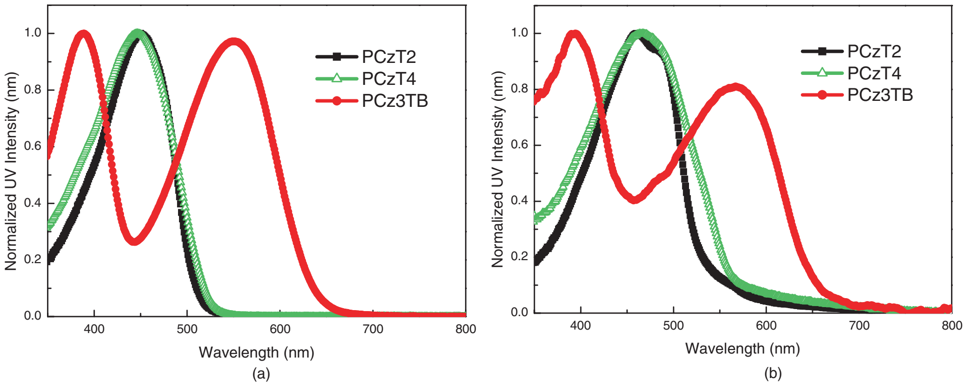


**Figure 2.** UV-visible absorption spectra in (a) solution and (b) film.

### Optical and Electrochemical Properties

Figure 2 shows the UV-vis absorption spectra of the polymers in dilute chlorobenzene and as film. In solution, **PCzT2** showed UV absorption maximum at 457 nm. In spite of its longer conjugation length of quaterthiophene, **PCzT4** exhibited relatively blue-shifted absorption maximum at 447 nm, probably due to low molecular weight. Meanwhile, **PCz3TB** showed two absorption bands at around 390 and 555 nm and the low energy band is due to intramolecular charge transfer (ICT) interaction between the donor (thiophene) and the acceptor (benzothiadiazole) [11]. As film, the UV-vis absorption spectra of the copolymers were clearly red-shifted compared to solution state. The **PCzT2**

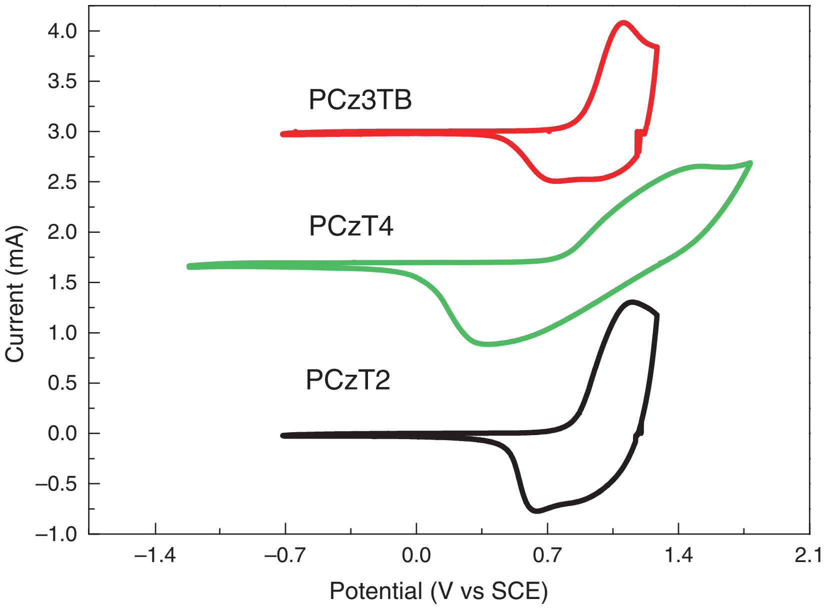


**Figure 3.** Cyclic voltammogram of the polymer films

and **PCzT4** films showed absorption maxima at 460 and 464 nm, respectively. Similar with solution, **PCz3TB** film showed much more red-shifted absorption spectra with maxima at 393 and 570 nm. This clearly red-shifted UV-vis absorption indicates good film aggregation.

The electrochemical properties of the polymers were investigated in order to gauge their electronic properties (Fig. 3). The films were prepared by dip-coating the polymer solution on to a Pt wire and the measurements were calibrated using the ferrocene value of –4.8 eV as the standard. The highest occupied molecular orbital (HOMO) levels were calculated using the equation $I_p(\text{HOMO}) = -(E_{\text{onset}} + 4.39)$, where $E_{\text{onset}}$ is the onset potential of oxidation [12]. In the anodic scan, the onsets of oxidation of **PCzT2**, **PCzT4**, and **PCz3TB** were found to occur at 0.83, 0.74, and 0.85 V (vs SCE), respectively, corresponding to the ionization potential values ($I_p$) of –5.22, –5.13, and –5.24 eV, respectively. As the thiophene number increased from bithiophene to quaterthiphene, the band gaps were reduced from 2.34 to 2.19 eV. Interestingly, owing to the introduction of benzothiadiazole unit, **PCz3TB** has clearly reduced optical band gap of 1.90 eV. The increased absorption ability of **PCz3TB** with its lowered energy band gap is caused by the arrangement of the electron-donor and electron-acceptor repeating units alternatively along the conjugated backbone. The HOMO and the lowest unoccupied molecular orbital (LUMO) energy levels and band gaps of the copolymers are listed in Table 1, and their energy diagram is shown in Fig. 4 together with that of PCBM.

**Table 1.** Physical properties of polymers.

| | **PCzT2** | **PCzT4** | **PCz3TB** |
|---|---|---|---|
| $M_n$[a] | 46595 | 9890 | 70278 |
| $M_w$[a] | 57831 | 17276 | 76188 |
| PDI ($M_w/M_n$) | 1.2 | 1.7 | 1.1 |
| $T_{5d}$ (°C) | 410 | 416 | 362 |
| UV $\lambda_{max}$ (nm) | | | |
| Soln | 457 | 447 | 390,555 |
| Film | 460 | 464 | 393,570 |
| $E_{pc}$ (V vs SCE)[b] | 1.15 | 1.78 | 1.10 |
| $E_{pa}$ (V vs SCE)[b] | 0.65 | 0.34 | 0.70 |
| $E_{1/2}$ (V vs SCE)[b] | 0.90 | 1.06 | 0.90 |
| $E_{onset}$ (V vs SCE)[b] | 0.83 | 0.74 | 0.85 |
| HOMO (eV)[c] | −5.22 | −5.13 | −5.24 |
| LUMO (eV) | −2.88 | −2.94 | −3.34 |
| $E_g$ (eV)[d] | 2.34 | 2.19 | 1.9 |

[a] $M_n$ and $M_w$ stand for the number-average and weight-average molecular weights, respectively, determined by GPC.

[b] $E_{pa}$, $E_{pc}$, $E_{1/2}$, and $E_{onset}$ stand for anodic peak potential, cathodic peak potential, the average of the anodic and cathodic peak potentials, and onset potential of oxidation, respectively.

[c] Calculated using the empirical equation: $I_p(\text{HOMO}) = -(E_{\text{onset}} + 4.39)$.

[d] Optical band gaps ($E_g$) taken as the absorption onsets in the UV-vis spectra of the polymer films ($E_g = 1240/\lambda_{\text{onset}}$ eV).

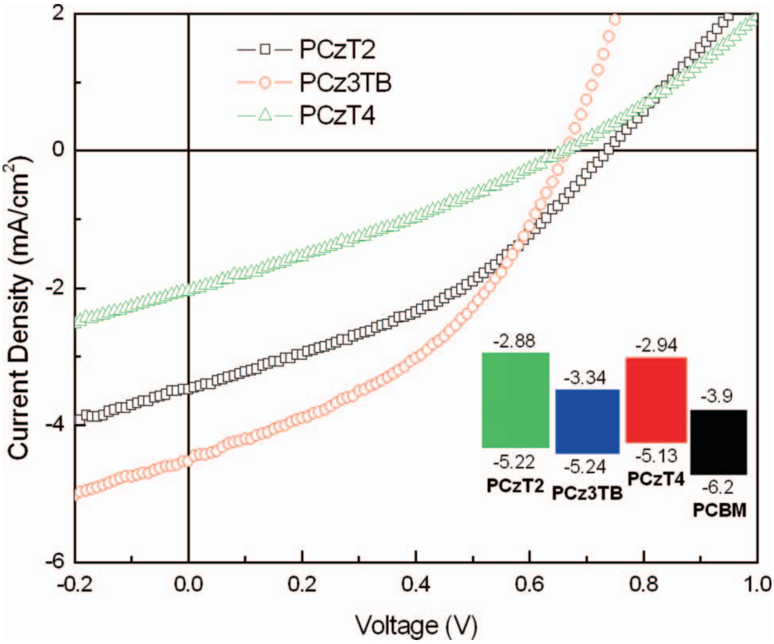


**Figure 4.** The energy band gap diagram and J-*V* curves of photovoltaic cells of copolymers.

### *Organic Photovoltaic Properties*

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. In this work, the blending ratio of polymer and PCBM was adjusted to be 1:3. As shown in Table 2, **PCz3TB** showed the highest device performance, with a PCE of 1.22% compared to **PCzT4** (0.40%) and **PCzT2** (0.97%). The device performances were mainly attributed from the increase of a short circuit current ($J_{SC}$) values rather than an open circuit voltage ($V_{OC}$) and a fill factor (FF). The $J_{SC}$ values were gradually increased on going from **PCzT4** (2.04 mA/cm$^2$) and **PCzT2** (3.47 mA/cm$^2$) to **PCz3TB** (4.52 mA/cm$^2$) and a $J_{SC}$ value of **PCz3TB** was nearly doubled with that of **PCzT4**. Such a good performance of **PCz3TB** can be explained by its broad UV absorption as well as low energy band gap. In addition, the relatively low efficiency of **PCzT4** might be from the low molecular weight and the high HOMO energy level. Further research on the modification of the polymer structure are currently underway [7].

**Table 2.** OPV performances of the polymer: $PC_{71}BM$ OPV cells.

| Active layer[a] | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | PCE (%) |
|---|---|---|---|---|
| **PCzT2** | 3.47 | 0.74 | 0.38 | 0.97 |
| **PCzT4** | 2.04 | 0.66 | 0.40 | 0.40 |
| **PCz3TB** | 4.52 | 0.66 | 0.41 | 1.22 |

[a] Thickness of the active layer was adjusted to 60 nm.

## Conclusions

We have synthesized three carbazole-based copolymers containing thiophene and benzothiadiazole units into the main chains through palladium-catalyzed Suzuki polymerization. The absorption and emission maxima of the polycarbazoles were varied according to the nature of comonomer units. Because of its broad and red-shifted UV absorption, **PCz3TB** showed the best PCE efficiency of 1.22%.

## Acknowledgment

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