

## 플루오렌 혹은 카바졸 기반의 유기태양전지용 고분자 도너의 비교 연구

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### Comparative Study of Fluorene- and Carbazole-based Polymer Donors for Organic Photovoltaic Cells

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**초록:** 본 연구에서는, 트리아졸을 가지는 플루오렌 및 카바졸 기반의 두 공중합체(PFT2Tz와 PCzT2Tz)를 스즈키 짝지음 반응을 이용하여 합성하였고, <sup>1</sup>H NMR로 이들의 구조를 확인하였다. 두 공중합체는 클로로포름이나 클로로벤젠과 같은 일반적인 유기용매에서 용해도가 좋았으며, 300 °C까지 열 안정성을 가진다. GPC, TGA, CV, UV-vis 분광분석기를 이용하여 두 공중합체의 물리적 특성을 조사하였다. PFT2Tz와 PCzT2Tz의 HOMO 준위는 각각 -5.37 eV 과 -5.32 eV로 나타났다. 더 중요하게, PFT2Tz와 비교했을 때, PCzT2Tz 필름은 더 넓고 더 장파장에서 UV-vis 흡수를 나타내었다. 합성한 공중합체를 전자주게로 사용하여 ITO/PEDOT:PSS/공중합체:PC<sub>71</sub>BM/LiF/Al의 구조로 유기태양전지 소자를 제작하여 그 광전 특성을 조사하였다. PCzT2Tz은 2.79 mA/cm<sup>2</sup>의 단락전류( $J_{sc}$ )와 0.68 V의 개방전압( $V_{oc}$ )과 광전변환효율(PCE) 0.67%를 나타내었고, 이는 같은 조건에서 제작된 PFT2Tz 보다 높은 효율이다 (PCE = 0.57%,  $J_{sc}$  = 2.16 mA/cm<sup>2</sup>,  $V_{oc}$  = 0.83 V, FF = 0.32). PFT2Tz의 상대적으로 높은 개방전압은 낮게 위치하는 HOMO 에너지 준위에 의한 것이다. PCzT2Tz의 높은 광전변환효율은 증가된 UV 흡수로 인한 높은 단락전류 때문이다.

**Abstract:** We synthesized two triazole-substituted fluorene- and carbazole-based copolymers PFT2Tz and PCzT2Tz by Suzuki-coupling reaction and characterized them with <sup>1</sup>H NMR. The physical properties of the copolymers were investigated with GPC, TGA, CV, and UV-vis absorption spectroscopy. The HOMO energy levels of PFT2Tz and PCzT2Tz were -5.37 and -5.32 eV, respectively. More importantly, PCzT2Tz film had a broader, red-shifted UV absorption than the PFT2Tz. The organic photovoltaic cells were fabricated with a configuration of ITO/PEDOT:PSS/copolymer:PC<sub>71</sub>BM/LiF/Al using the copolymers as donors. PCzT2Tz showed the higher power conversion efficiency (PCE) of 0.67% ( $J_{sc}$  = 2.79 mA/cm<sup>2</sup>,  $V_{oc}$  = 0.68 V), compared to PFT2Tz (PCE = 0.57%,  $J_{sc}$  = 2.16 mA/cm<sup>2</sup>,  $V_{oc}$  = 0.83 V). The relatively high open-circuit voltage of the PCzT2Tz came from the low-lying HOMO level of the PCzT2Tz donor. The higher PCE of PCzT2Tz can be explained by its relatively improved UV absorption and thus higher short-circuit currents.

**Keywords:** organic solar cells (OPV), conjugated polymer, fluorene, carbazole.

## Introduction

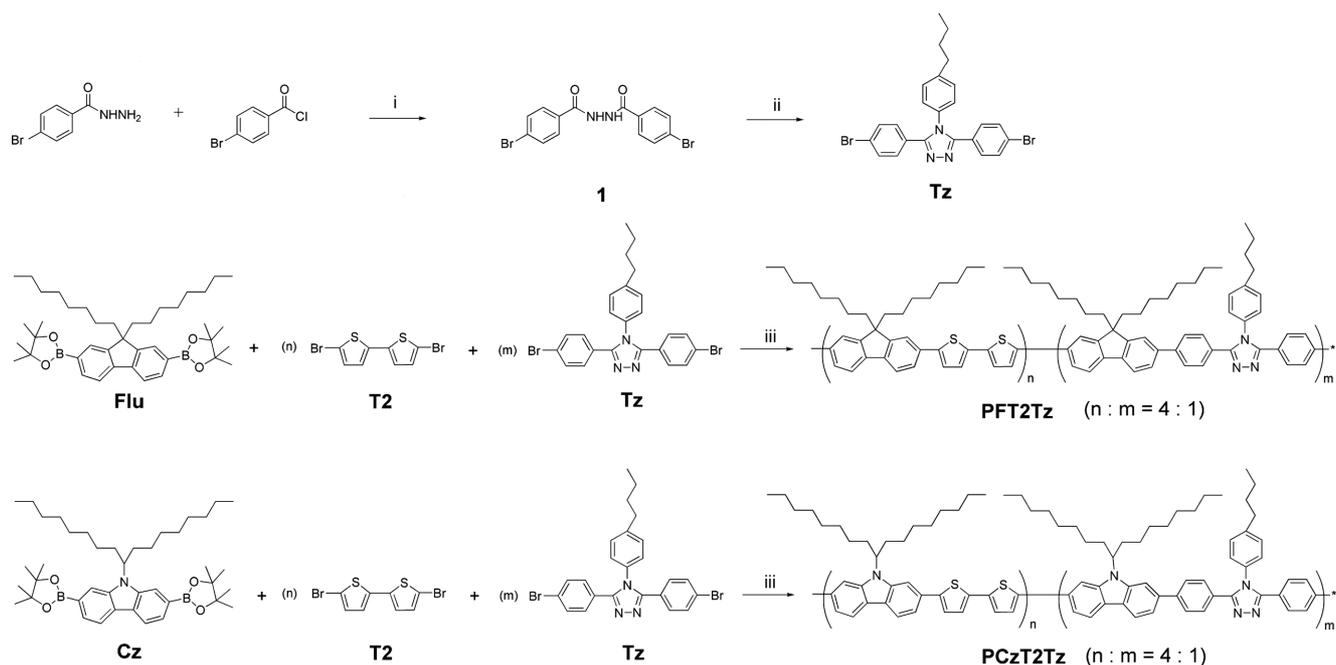
Organic photovoltaic cells (OPVs) have attracted considerable attention as renewable energy sources in the last decade. Their advantages include low cost, flexibility, and easy processability.<sup>1-3</sup> A variety of low band-gap polymer donors have

been developed to achieve a high power conversion efficiency (PCE) upto 10%.<sup>4-6</sup> Various electron-donating (D) and electron-accepting (A) moieties have been combined to achieve D-A-type low band-gap materials for efficient UV absorption.<sup>7</sup> The proper modification of the molecular structure such as an alkyl variation and the introduction of a  $\pi$ -bridge could also effectively control the physical properties of the materials by varying the molecular packing and film morphology.<sup>8-11</sup> For example, K. Kranthiraja *et al.* reported a series of benzodithiophene-based copolymers substituted with alkylselenyl

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**Scheme 1.** Synthetic route to the PCzT2Tz and PFT2Tz. (i) triethylamine, DMF, room temperature, 6 h; (ii) 4-butylaniline,  $\text{PCl}_3$ , 1,2-dichlorobenzene,  $200\text{ }^\circ\text{C}$ , 24 h; (iii)  $\text{Pd}(\text{PPh}_3)_4$ , aq.  $\text{Na}_2\text{CO}_3$ , toluene, Aliquat<sup>®</sup> 336,  $110\text{ }^\circ\text{C}$ , 48 h.

side chains, in which the optical, charge carrier, and photovoltaic properties of the  $\pi$ -conjugated polymers varied by the size of the alkyl chains and  $\pi$ -spacer groups as well as the device processing conditions.<sup>9</sup> On the other hands, triazole (Tz) moieties were introduced into the polymer backbone as electron transporting groups to adjust the charge-injecting and transporting properties of the copolymers in organic light emitting diodes (OLEDs). More recently, several reports have described improved device performances in OPVs by incorporating Tz moieties into the side chain<sup>12–14</sup> or molecular backbone.<sup>15–17</sup> In our previous work, we synthesized polyfluorenes containing various electron-deficient groups such as benzothiadiazole, oxadiazole, and Tz in the main chain,<sup>18,19</sup> in which the photovoltaic properties of the copolymers varied by the introduced electron transporting units and the polymer containing Tz showed improved performance.

The alkyl-substituted fluorene and carbazole building blocks, which have similar structures, have been widely used for constructing  $\pi$ -conjugated polymers in OLEDs and organic thin-film transistors due to their high hole mobilities.<sup>20–22</sup> They have also been used as electron-donating units in D–A-type polymer donors for high performance OPVs.<sup>23–27</sup> The physical properties of polyfluorenes and polycarbazoles could be changed due to the introduced electron-accepting comonomers.<sup>28</sup>

In this study, we developed two fluorene- and carbazole-based polymers (PFT2Tz and PCzT2Tz), which were copolymerized with bithiophene and Tz units at the same time. The optical, electrochemical, and photovoltaic properties of the two copolymers were compared to establish the relationship between the molecular structure and device performance.

## Experimental

**Measurement.** The number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-150  $^\circ\text{C}$  instrument calibrated with polystyrene as the standard, with THF used as the eluent. Elemental analyses (EA) were performed with a CHNS-5 EA1108 elemental analyzer from Carlo ERBA Instruments. Thermal gravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  using a Perkin Elmer TGA7 thermogravimetric analyzer. UV-vis spectra were obtained using a Shimadzu UV-vis spectrometer, and photoluminescence (PL) spectra were obtained using a Perkin Elmer spectrofluorometer. The films used in these UV-vis and PL measurements were prepared by spin-coating solutions of the polymers (1 wt% in chloroform). The electrochemical properties of the small molecules were studied by cyclic voltammetry (CV) measurement with a BAS

100B electrochemical analyzer. A three-electrode system was used and consisted of a non-aqueous reference electrode (0.1 M Ag/Ag<sup>+</sup> acetonitrile solution), a platinum working electrode, and a platinum wire as the counter electrode. The oxidation and reduction potentials of the small molecules were measured in acetonitrile with 0.1 M (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N-PF<sub>6</sub>. The films were prepared by dip-coating from a solution of small molecules onto the platinum working electrode, and the measurements were calibrated with the ferrocene value -4.8 eV as the standard. The highest occupied molecular orbital (HOMO) energy levels were calculated with the empirical equation  $I_p(\text{HOMO}) = -(E_{\text{onset}} + 4.39)$  (eV), for which  $E_{\text{onset}}$  is the onset potential of oxidation.<sup>29</sup> Film thicknesses were measured with a TENCOR surface profiler.

**Materials.** 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (F),<sup>20</sup> 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-9-heptadecanilcarbazole (Cz),<sup>30</sup> and 5,5'-dibromo-2,2'-bithiophene (T2) were prepared according to a procedure mentioned in the literature. The air-sensitive Pd(0) complex tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>), Aliquat<sup>®</sup> 336, and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) were purchased from Aldrich. All reagents purchased commercially were used without any further purification, except for the toluene used as a solvent, which was distilled.

**Synthesis.** 3,5-Bis-(4-bromophenyl)-4-(4-butylphenyl)-4H-[1,2,4]triazole (Tz) was prepared according to a procedure mentioned in the literature.<sup>15</sup> The syntheses of the copolymers, poly[(9,9'-dioctylfluorene)-*co*-(bithiophene)-*co*-(3,5-bis-(4-phenyl)-[1,2,4]triazole))] (PFT2Tz) and poly[(*N*-9'-heptadecanil-2,7-carbazole)-*co*-(bithiophene)-*co*-(3,5-bis-(4-phenyl)-[1,2,4]triazole))] (PCzT2Tz) were done with the Suzuki coupling reaction<sup>20,31,32</sup> between the diborolanylaryl compound (F or Cz) and the dibromoaryl compounds, T2 and Tz.

**Synthesis of 4-Bromo-benzoic acid *N*'-(4-bromobenzoyl)-hydrazide (1).** A solution of 4-bromobenzoyl chloride (4.9 g, 22 mmol) in dimethylformamide was added to a solution of 4-bromobenzoic hydrazide (4.8 g, 22 mmol) and triethylamine (2.3 g, 22 mmol) in dimethylformamide. The resulting solution was stirred for 6 h at room temperature. Methanol was added to the reaction mixture. The precipitate was filtered off, washed with methanol and water, and recrystallized from methanol to yield a white solid (6.8 g, 70%).

**Synthesis of 3,5-Bis-(4-bromo-phenyl)-4-(4-butyl-phenyl)-4H-[1,2,4]triazole (Tz).** PCl<sub>3</sub> (2.1 g, 15 mmol) was added to a solution of 4-butylaniline (9.0 g, 60 mmol) in 1,2-dichlorobenzene. After the mixture was stirred at 100 °C for 1 h,

compound 1 (4.0 g, 10 mmol) was added to the reaction mixture. The resulting solution was stirred under reflux overnight and cooled to room temperature. HCl (2 N) was added and the reaction allowed to cool to room temperature. The reaction mixture was filtered through celite and then extracted with dichloromethane and water. The collected organic layer was dried over magnesium sulfate. After removing the solvent under reduced pressure, the crude product was purified by silica gel chromatography with a mixture of ethyl acetate/dichloromethane (1:9) as an eluent to yield the product (3.2 g, 63%).

**Synthesis of PFT2Tz.** Three comonomers, F (0.30 g, 0.47 mmol), T2 (0.12 g, 0.37 mmol), and Tz (0.047 g, 0.092 mmol) were dissolved in distilled toluene with Pd(PPh<sub>3</sub>)<sub>4</sub> (0.0053 g, 0.0046 mmol). Aliquat<sup>®</sup> 336 (0.018 g, 0.045 mmol) and 2M *aq.* Na<sub>2</sub>CO<sub>3</sub> (0.23 g, 2.2 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 methanol and 1 M *aq.* HCl. The polymer were collected by filtration and reprecipitated from methanol. The polymer was purified by a Soxhlet extraction in acetone for 2 days to remove any residual oligomers and catalyst. The reprecipitation procedure in dichloromethane/methanol was then repeated several times. The final product, an orange polymer, was obtained after drying in vacuum at 60 °C. Yield: 240 mg (89%). FTIR (KBr, cm<sup>-1</sup>): 1611 (C=N); 2850, 2925 (alkyl group). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 2.71 (t, 4H, aliphatic H), 2.04 (m, 2H, aliphatic H). Anal. Calcd. for (C<sub>201</sub>H<sub>237</sub>N<sub>3</sub>S<sub>8</sub>)<sub>n</sub>: C: 76.42, H: 6.77, N: 1.20, S: 15.62. Found: C: 76.52, H: 7.86, N: 0.46, S: 12.76.

**Synthesis of PCzT2Tz.** The compound, a dark yellow polymer, was synthesized in the same manner as PFT2Tz using Cz (0.47 g, 0.71 mmol), T2 (0.20 g, 0.62 mmol), Tz (0.050 g, 0.098 mmol), Pd (PPh<sub>3</sub>)<sub>4</sub> (0.008 g, 0.0069 mmol). Aliquat<sup>®</sup> 336 (0.028 g, 0.069 mmol), and 2M *aq.* Na<sub>2</sub>CO<sub>3</sub> (0.34 g, 3.21 mmol). Yield: 180 mg (43%). FTIR (KBr, cm<sup>-1</sup>): 1601 (C=N); 2850, 2925 (alkyl group). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 4.64 (m, 1H, aliphatic H), 2.71 (m, 2H, aliphatic H). Anal. Calcd. For (C<sub>201</sub>H<sub>242</sub>N<sub>8</sub>S<sub>8</sub>)<sub>n</sub>: C: 74.75, H: 6.70, N: 2.93, S: 15.62. Found: C: 78.36, H: 7.58, N: 3.12, S: 10.06.

**Fabrication of the OPV Devices.** 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 120 °C for 30 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. The blending ratio of polymer and PC<sub>71</sub>BM was 1:3. 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 polytetrafluoroethylene membrane syringe (0.45 μm). 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 80 °C or 120 °C, 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 1.5G (100 mW/cm<sup>2</sup>).

## Results and Discussion

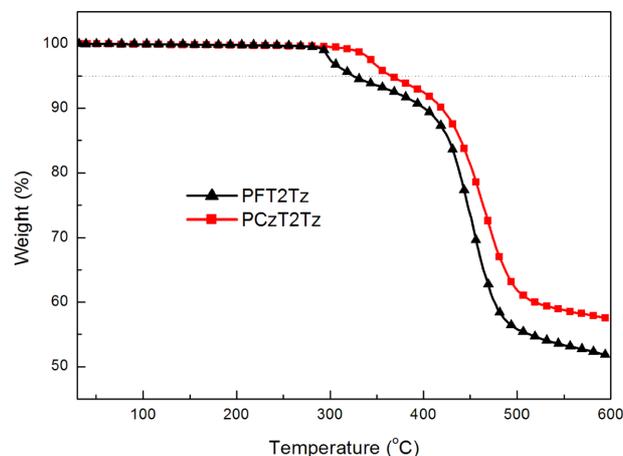
**Synthesis and Thermal Properties.** The fluorene (or carbazole)-bithiophene-triazole-based copolymers (PFT2Tz and PCzT2Tz) were synthesized with the Suzuki coupling reaction between the diborolanylaryl compounds of fluorene and carbazole (F or Cz) and the dibromoaryl compounds of bithiophene and triazole (T2 and Tz). The feed ratio of the two dibromides (T2 and Tz) was adjusted to 4:1, which was optimized in our previous work based on polycarbazole.<sup>17</sup> EA and <sup>1</sup>H NMR were used to calculate the actual ratio in the copolymers. PFT2Tz and PCzT2Tz contained a triazole unit content of 5% and 18%, respectively. The synthetic routes towards copolymers are outlined in Scheme 1. The molecular weights, feed, and actual ratios of the repeat units in the copolymers are listed in Table 1. The *M<sub>n</sub>* of PFT2Tz and PCzT2Tz, determined using GPC with a polystyrene standard, were 4280 and 24500, respectively, with polydispersity indices of 1.71 and 2.04, respectively. 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<sub>5d</sub>*) upon heating to 300 °C under a nitrogen atmosphere.

**Optical and Electrochemical Properties.** Figure 2(a) shows the UV-vis absorption spectra of the polymers in dilute chlorobenzene solution and the films. In solution, the two copolymers showed similar UV-vis absorption with the maxima at around 455 nm. In films, both copolymers showed a relatively broad UV-vis absorption from the increased molecular

**Table 1. Physical Properties of Copolymers**

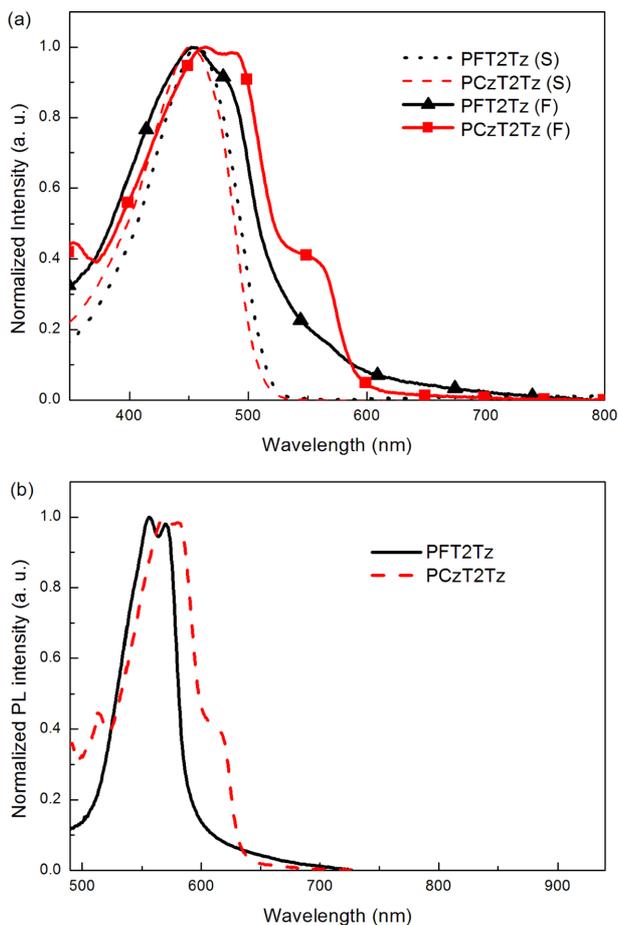
	PFT2Tz	PCzT2Tz
Ratio	(F:T2:Tz)	(Cz:T2:Tz)
Feed ratio	50:40:10	50:40:10
Actual ratio <sup>a</sup>	62:33:5	56:26:18
<i>M<sub>n</sub></i> <sup>b</sup>	4280	24500
<i>M<sub>w</sub></i> <sup>b</sup>	7300	49930
PDI ( <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> )	1.71	2.04
<i>T<sub>5d</sub></i> (°C)	323	364
Solution ( $\lambda_{\max}$ , nm) Abs.	458	451
Film ( $\lambda_{\max}$ , nm) Abs.	454	464, 490
<i>E<sub>onset</sub></i> (V versus SCE) <sup>c</sup>	0.98	0.93
HOMO (eV) <sup>d</sup>	-5.37	-5.32
LUMO (eV)	-3.04	-3.22
<i>E<sub>g</sub></i> (eV) <sup>e</sup>	2.33	2.10

<sup>a</sup>Actual ratio in polymers determined by EA and <sup>1</sup>H NMR. <sup>b</sup>*M<sub>n</sub>* and *M<sub>w</sub>* stand for the number-average and weight-average molecular weights, respectively, determined by GPC. <sup>c</sup>*E<sub>onset</sub>* stands for onset potential of oxidation. <sup>d</sup>Calculated using the empirical equation: *I<sub>p</sub>*(HOMO) = -(*E<sub>onset</sub>* + 4.39) (eV). <sup>e</sup>Optical band gaps (*E<sub>g</sub>*) taken as the absorption onsets in the UV-vis spectra of the polymer films (*E<sub>g</sub>* = 1240/ $\lambda_{\text{onset}}$  eV).



**Figure 1.** TGA curves of PCzT2Tz and PFT2Tz with a heating rate of 10 °C/min under a nitrogen atmosphere.

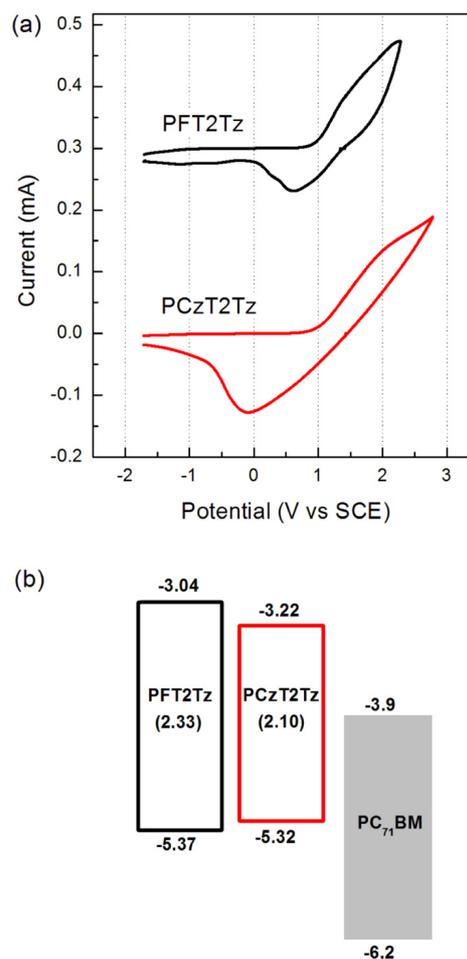
aggregation.<sup>31</sup> While the UV-vis absorption of the PFT2Tz film ( $\lambda_{\max}$  = 453 nm) was slightly broader than that of the solution, the PCzT2Tz film showed a much more red-shifted broader absorption with the maximum at 463 and 490 nm. This clear red-shift of PCzT2Tz from solution to film indicates the relatively good film aggregation of PCzT2Tz, which is favorable for the sunlight harvesting ability. The optical band gaps (*E<sub>g</sub>*) of the PFT2Tz and PCzT2Tz, estimated from the absorption



**Figure 2.** (a) UV-vis absorption spectra of solution (S) and film (F); (b) PL emission spectra of the films.

onset wavelength of the oligomer films ( $E_g = 1240/\lambda_{\text{onset}}$  (eV)) were 2.33 and 2.10 eV, respectively. The relatively more narrow band gap and clear red-shift from solution to film of PCzT2Tz may result in a higher short-circuit current ( $J_{\text{SC}}$ ) in the OPV cells.<sup>33</sup> Figure 2(b) shows the PL emission spectra of the polymer films which were excited at the absorption maxima of the corresponding UV-vis spectra. The PL emission maxima of the PFT2Tz and PCzT2Tz films appeared at 555 and 568 nm, respectively.

The electrochemical properties of the polymers were characterized with the CV measurements and the highest occupied molecular orbital (HOMO) levels of PFT2Tz and PCzT2Tz were found to be -5.37 and -5.32 eV, respectively. It is worth noting that PFT2Tz had a relatively low-lying HOMO energy level than that of PCzT2Tz. A similar phenomenon was observed in our previous work, in which the fluorene-based small molecules exhibited low-lying HOMO energy levels compared to their carbazole-based analogs.<sup>34,35</sup> From the opti-

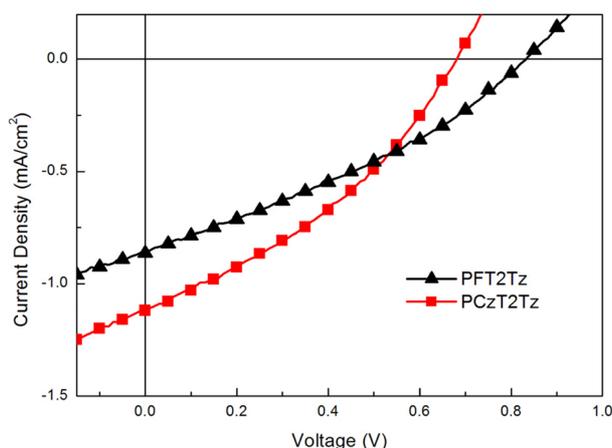


**Figure 3.** (a) Cyclic voltammetry graph; (b) energy diagrams of PFT2Tz and PCzT2Tz with PC<sub>71</sub>BM.

cal  $E_g$  and HOMO energy levels, the lowest unoccupied molecular orbital (LUMO) levels of PFT2Tz and PCzT2Tz were calculated as -3.04 and -3.22 eV, respectively. The energy diagram of the polymers is shown in Figure 3 together with PC<sub>71</sub>BM for comparison. All the optical and electrochemical properties of the copolymers are summarized in Table 1.

**Photovoltaic Properties of the Blended Films.** To investigate the current density-voltage ( $J$ - $V$ ) characteristics of the copolymers, devices with the configuration of ITO/PEDOT:PSS (40 nm)/polymer:PC<sub>71</sub>BM (1:3, 60 nm)/LiF (1 nm)/Al (100 nm) were fabricated. Figure 4 shows the  $J$ - $V$  curves for the copolymer:PC<sub>71</sub>BM devices, and the photovoltaic properties of the blended films are summarized in Table 2. The blended film of PCzT2Tz and PC<sub>71</sub>BM had higher device performance with a PCE of 0.67%, compared to the PFT2Tz:PC<sub>71</sub>BM film (0.57%).

The photovoltaic parameters of the open-circuit voltage



**Figure 4.**  $J$ - $V$  curves of P3HT:polymer devices.

**Table 2. Photovoltaic Performances of the Polymer:PC<sub>71</sub>BM Films**

Polymer	$T_a^a$ (°C)	$V_{OC}$ (V)	$J_{SC}$ (mA/cm <sup>2</sup> )	FF	PCE (%)
PFT2Tz	80	0.83	2.16	0.32	0.57
PCzT2Tz	120	0.68	2.79	0.35	0.67

<sup>a</sup> $T_a$ : annealing temperature.

( $V_{OC}$ ) and  $J_{SC}$  were changed by the fluorene and carbazole cores. PFT2Tz had a higher  $V_{OC}$  value of 0.83 V than that of PCzT2Tz (0.68 V) which could be explained by the HOMO energy levels of the copolymers. In general, the  $V_{OC}$  values are strongly dependent on the energy difference between the HOMO of the donor and the LUMO of the acceptor.<sup>36</sup> Compared to PCzT2Tz (-5.32 eV), the relatively low-lying HOMO energy level of PFT2Tz (-5.37 eV) resulted in a higher  $V_{OC}$  value in the OPVs. In addition, the  $V_{OC}$  of PCzT2Tz is lower than that of PFT2Tz despite the small difference in their HOMO energy levels. Such phenomenon was also observed in our previous work,<sup>37</sup> in which the strong aggregation resulted in the destabilized high-lying HOMO and stabilized low-lying LUMO levels via the enhanced molecular orbital interactions.

Despite the lower  $V_{OC}$  value, PCzT2Tz had a higher PCE than that of PFT2Tz which was mainly attributed to the increases of  $J_{SC}$  and the fill factor (FF) values. PCzT2Tz exhibited a higher  $J_{SC}$  value of 2.79 mA/cm<sup>2</sup> compared to PFT2Tz (2.16 mA/cm<sup>2</sup>). The higher  $J_{SC}$  value of PCzT2Tz is due to the UV-vis absorption in the longer wavelength region and the relatively more narrow optical band gap which is favorable for a light harvesting ability. The clear red-shift from solution to film and thus a better molecular aggregation also support better

charge transport in the PCzT2Tz film.<sup>33</sup> Further improvements in the photovoltaic characteristics could potentially be achieved by incorporating other unit into the polymer backbone and increasing molecular weights of polymers.

## Conclusions

We synthesized carbazole- and fluorene-based copolymers containing bithiophene and triazole moieties in the main chains through palladium-catalyzed Suzuki polymerization. The copolymers have good solubility and thermally stable upto 300 °C. The optical, electrochemical, and photovoltaic performances varied based on the fluorene and carbazole cores. From the CV measurement, PCzT2Tz (-5.32 eV) had a relatively high-lying HOMO energy level than that of PFT2Tz (-5.37 eV). More importantly, PCzT2Tz showed a relatively red-shifted UV absorption and more narrower band-gap, and good molecular aggregation compared to PFT2Tz. PCzT2Tz had a higher PCE of 0.67%, mainly due to the more red-shifted UV-vis absorption and narrow band-gap and subsequently, better  $J_{SC}$ .

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