



## Synthesis and photovoltaic characterization of *D/A* structure compound based on *N*-substituted phenothiazine and benzothiadiazole

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### ABSTRACT

In this study, poly [(*N*-10'-dodecyl-phenothiazin-3,7-ylene)-alt-(2,2'-bithiophen-5-yl)] (P1) and poly [(*N*-10'-dodecyl-phenothiazin-3,7-ylene)-alt-(5',6'-dioctyloxy-benzothiadiazole-bithiophene)] (P2) were synthesized by Suzuki coupling reaction. Optical and electrochemical characteristics of the synthesized polymers, P1 and P2, were then analyzed, indicating that their wavelength of maximum absorption was 453 nm and 533 nm, respectively, and their band-gap was 1.93 eV and 1.74 eV, respectively. The maximum power conversion efficiency (PCE) of organic photovoltaic cells created by using P1 and P2 were 0.74% (P1:PC<sub>71</sub>BM = 1:4,w/w) and 1.00% (P2:PC<sub>71</sub>BM = 1:3,w/w), respectively, and the short circuit current density ( $J_{SC}$ ), fill factor (FF), and open circuit voltage ( $V_{OC}$ ) of the device were 3.5 mA/cm<sup>2</sup>, 31.8%, and 0.68 V, respectively, for P1 and 3.9 mA/cm<sup>2</sup>, 32.7%, and 0.78 V, respectively, for P2.

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## 1. Introduction

Owing to the advantages of  $\pi$ -conjugated polymers including diverse synthesis methods, ease of molding, and outstanding physical characteristics, they have found application to organic photovoltaic cells (OPVs) [1–5], organic light-emitting diodes (OLEDs) [6–10], organic thin-film transistors (OTFTs) [11–15], and organic transparent conducting electrodes [16,17].

In particular, OPVs are light and can be applied to flexible substrates. They also offer cost advantages as they can be manufactured through a continuous process involving a brush painting method, stamping method, roll to roll, etc. [18,19]. OPVs are structured such that a photo active layer is inserted between indium tin oxide (ITO), a transparent conducting electrode, and a metallic material with a high work function. The photo active layer uses either a bi-layer structure or a bulk-heterojunction (BHJ) structure. Compared to the bi-layer structure on which an electron donor (*D*) and an electron acceptor (*A*) are laminated one over another, the BHJ structure in which *D* and *A* are blended has a larger *D/A* surface area, and thus can effectively separate excited electrons from their holes [20–23]. While the most frequently

used electron donor material currently is poly (3-hexylthiophene) (P3HT), the power conversion efficiency (PCE) of which is reported to be about 5%, there is a limit to enhancing the PCE value because photocurrent and absorption wavelength are low [24–27].

In order to solve this problem, research is being actively carried out to synthesize an electron donor material with a donor/acceptor (*D/A*) structure composed of repeated pairs of a donor moiety with abundant electrons and an acceptor moiety with insufficient electrons, and to apply such materials to OPVs [28–31]. Because the *D/A* polymer can control the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels through charge transfer within molecules, it allows synthesis of low band-gap polymers with wide absorption [32,33].

Among donor materials, phenothiazine has a tricyclic structure including nitrogen and sulfur atoms with abundant electrons; phenothiazine derivatives have HOMO levels of –5.1 to –5.3 eV and an open circuit voltage ( $V_{OC}$ ) of 0.71–0.79 V [34–38]. Moreover, phenothiazine leads to the generation of radical cations as a result of oxidation of electrons, and when oxidation proceeds to the next stage, dications will form. When this process is measured with cyclic voltammetry (CV) per stage,  $E_{1/2}^{0/+1} = 270$  mV and  $E_{1/2}^{+1/+2} = 770$  mV were obtained, respectively, indicating that it progresses via photoreaction with more active transfer of electrons [39,40]. Therefore, it was anticipated that polymers based on phenothiazine can be utilized as excellent electron donors.

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In this study, a polymer with a *D/A* structure based on phenothiazine as an electron donor and on benzothiadiazole as an electron acceptor was synthesized to analyze its characteristics as an OPVs. An alkyl group was substituted at the nitrogen of phenothiazine, and an alkoxy chain was introduced to benzothiadiazole to enhance the solubility of the copolymer. In addition, thiophenes were used as a spacer and characteristics with and without a benzothiadiazole derivative were compared.

## 2. Experimental

### 2.1. Materials

Phenothiazine, *n*-butyllithium, aliquat 336, tin chloride, 2-iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, tetrahydrofuran (THF), palladium-tetrakis(triphenylphosphine), bis(triphenylphosphine)-palladium(II) dichloride, tributyl(thiophen-2-yl)stannane, and bromine were purchased from Aldrich, whereas catechol, 1-bromododecane, triethylamine (TEA), *N*-bromosuccinimide (NBS), and 1-bromooctane were bought from Alfa Aesar, and were used without additional purification. Meanwhile, hexane, sodium hydroxide, toluene, acetic acid, nitric acid, magnesium sulfate, dimethylsulfoxide (DMSO), diethyl ether, acetone, potassium carbonate, thionyl chloride, methylene chloride (MC), ethanol, hydrochloric acid, chloroform, and *N,N*-dimethylformamide (DMF) were purchased from Daejung Chemicals and Metals. 1,2-Bis(octyloxy)benzene (6) [41], 1,2-dinitro-4,5-bis(octyloxy)benzene (7) [41], 4,5-bis(octyloxy)benzene-1,2-diaminium chloride (8) [41], 5,6-bis(octyloxy)benzo[*c*][1,2,5]thiadiazole (9) [41], 4,7-dibromo-5,6-bis(octyloxy)benzo[*c*][1,2,5]thiadiazole (10) [41], 5,6-bis(octyloxy)-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (11) [41], 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]thiadiazole (12) [41], and 5,5'-dibromo-2,2'-bithiophene (13) [42] were synthesized in accordance with the pertinent references.

### 2.2. Instruments and equipments

The molecular structure of the synthesized compound was confirmed by using <sup>1</sup>H NMR and <sup>13</sup>C NMR (Bruker AVANCE 250 spectrometer), and the weight of the synthesized polymer was measured with gel permeation chromatography (GPC). For measurement of UV-vis spectra (Beckman Coulter DU 730), polymer was melted in chloroform, drop-cast, and made into a film to measure its absorbance, and its luminescence properties were measured by using photoluminescence (PL, Hitachi F-4500 spectrophotometer). Cyclic voltammetry (CV, Zahner IM6eX) was used to measure the redox potential of the synthesized polymer at a scan rate of 50 mV/s, and Ag/AgCl was used as a reference electrode. The measured values were used to calculate the energy level with ferrocene as the correction value.

### 2.3. Photovoltaic cell device fabrication

A photovoltaic cell device was fabricated with a structure of glass/ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM (weight ratio = 1:1/1:3/1:4)/BaF<sub>2</sub>/Ba/Al. PEDOT:PSS solution on the ITO substrate was spin-coated and heat-treated for 5 min at 140 °C. The synthesized polymer and PC<sub>71</sub>BM were dissolved in *ortho*-dichlorobenzene (ODCB) and spin-coated on top of the PEDOT:PSS layer, and then fabricated by depositing (10<sup>-6</sup> Torr or less) BaF<sub>2</sub> (2 nm), Ba (2 nm) and Al (100 nm) sequentially at a thermal evaporator. The devices were evaluated at 298 K in air using a Class A Oriel solar simulator (Oriel 96000 150 W solar simulator) having a xenon lamp that simulates AM 1.5 G irradiation (100 mW/cm<sup>2</sup>) from 400 to 1100 nm. The instrument was calibrated with a monocrystalline Si diode fitted with a KG5 filter to bring the spectral mismatch to

unity. The calibration standard was calibrated by the National Renewable Energy Laboratory (NREL).

### 2.4. Synthesis

#### 2.4.1. Synthesis of monomer 2

1.0 equiv. phenothiazine and 6.25 equiv. sodium hydroxide were put inside a 2-neck flask, and DMSO was used as the solvent. When the reactants were dissolved sufficiently, 1.20 equiv. of 1-bromododecane was applied slowly. The reaction was carried out in a nitrogen atmosphere. The progress of reaction and end point were determined by TLC monitoring. The mixture with the completed reaction was extracted by using ethyl acetate and the organic layer was washed three times with water, and then washed again with brine. MgSO<sub>4</sub> was added to the collected organic layer and it was kept overnight. The solvent was removed through vacuum evaporation and then purified by using column chromatography (hexane/ethyl acetate = 20/1) [43,44] (yield: 97.6%).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ (ppm) 0.90 (t, 3H), 1.26–1.46 (m, 18H), 1.84 (m, 2H), 3.84 (t, 2H), 6.84–6.94 (m, 4H), 7.12–7.18 (m, 4H). <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>): δ (ppm) 13.7, 22.4, 26.9, 27.2, 28.1, 28.6, 29.1, 29.4, 29.5, 31.8, 32.9, 47.7, 115.4, 122.2, 125.5, 126.9, 127.3, 145.5

#### 2.4.2. Synthesis of monomer 3

1.0 equiv. monomer 2 was dissolved in DMF at the nitrogen purge state in a 2-neck flask. When it was completely dissolved, NBS was dissolved in DMF and dropped slowly. The reaction at this time was carried out in an ice bath. When dropping was completed, the reaction was performed at room temperature, and the reaction end point was determined through TLC monitoring. The mixture with the completed reaction was extracted with ethyl acetate, and the organic layer was washed three times with water and then washed again with brine. MgSO<sub>4</sub> was added to the collected organic layer and it was kept overnight. The solvent was removed through vacuum evaporation and then refined by using column chromatography (hexane/MC = 7/3) [45,46] (yield: 70.0%).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ (ppm) 0.89 (t, 3H), 1.25–1.42 (m, 18H), 1.74 (m, 2H), 3.75 (t, 2H), 6.67 (d, 2H), 7.22–7.26 (m, 4H). <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>): δ (ppm) 13.6, 22.4, 26.7, 26.9, 28.6, 29.0, 29.1, 29.3, 29.4, 31.7, 32.9, 48.0, 114.8, 116.7, 126.9, 129.7, 130.0, 144.2

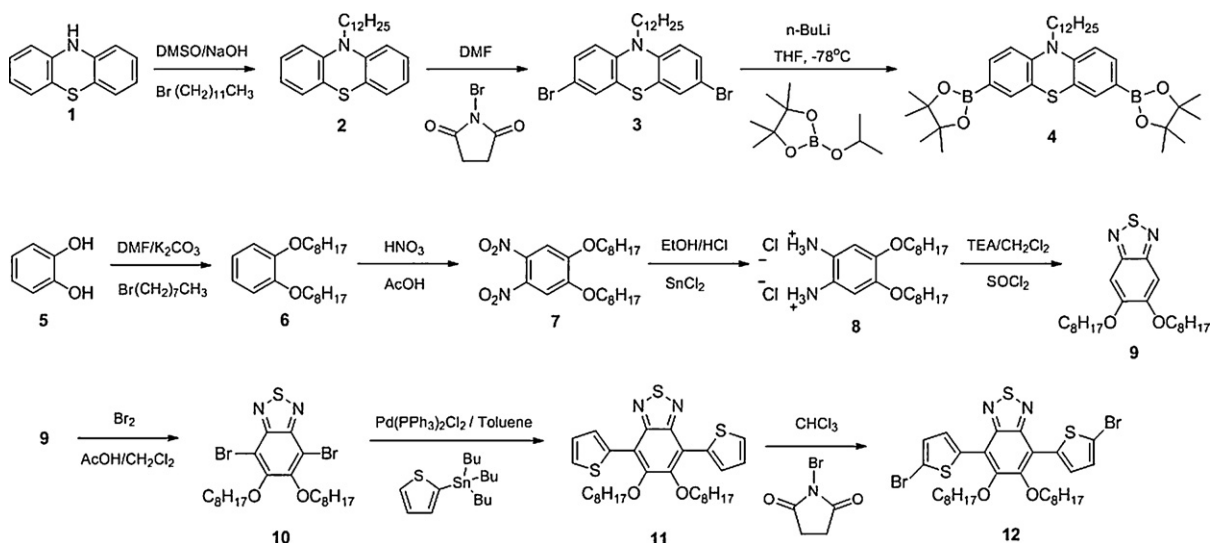
#### 2.4.3. Synthesis of monomer 4

1.0 equiv. monomer 3 diluted in THF was put in a 2-neck flask and stirred for about 20 min at –78 °C. Then 2.2 equiv. *n*-butyllithium was dropped slowly and then stirred for about 1 h. Subsequently 3.0 equiv. 2-iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added quickly and kept overnight at room temperature. When the reaction was complete, water was added to the reactant and extracted with ether. At this time, the organic layer was washed with brine and then dried with MgSO<sub>4</sub>. The solvent was removed through vacuum evaporation and the remnants were recrystallized with acetone to obtain the product [36] (yield: 82.1%).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ (ppm) 0.88 (t, 3H), 1.24–1.40 (m, 42H), 1.77 (m, 2H), 3.84 (t, 2H), 6.82 (d, 2H), 7.51–7.57 (m, 4H). <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>): δ (ppm) 13.7, 22.4, 24.7, 26.8, 27.0, 29.0, 29.1, 29.3, 29.4, 31.7, 47.6, 83.5, 114.6, 115.4, 124.2, 133.7, 133.9, 147.3

#### 2.4.4. Synthesis of P1

1.0 equiv. monomer 4, 1.0 equiv. 5,5'-dibromo-2,2'-bithiophene (13) [42] and 1.5 mol% palladium-tetrakis(triphenylphosphine) were added to a 3-neck flask one by one and then toluene and 2 M



Scheme 1. Synthetic route of monomers.

$K_2CO_3$  were added. Aliquat 336 was added as a surfactant, and the reaction took place for 48 h at 90 °C. When the reaction was completed, it was end-capped with bromobenzene. After methanol, acetone, and chloroform were refined using soxhlet one by one, the solvent was removed by collecting chloroform and the product was reprecipitated in methanol [41,42] (yield: 16.8%).

$^1H$  NMR (250 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 0.97 (t, 3H), 1.24–1.48 (m, 18H), 1.68–1.86 (m, 2H), 3.75 (t, 2H), 6.67 (m, 2H), 3.85 (m, 2H), 7.14–7.30 (m, 4H), 7.42–7.51 (m, 2H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 14.329, 22.888, 26.950, 26.960, 27.016, 27.068, 27.108, 29.550, 29.717, 29.733, 29.830, 32.113, 43.945, 47.708

#### 2.4.5. Synthesis of P2

1.0 equiv. monomer 4 and 1.0 equiv. monomer 12 were added to a 3-neck flask and dissolved in toluene. Then 1.5 mol% palladium-tetrakis(triphenylphosphine) was added, followed by 2 M  $K_2CO_3$ . Aliquat 336 was then added for reaction for 48 h at 90 °C. When the reaction was completed, it was end-capped with bromobenzene. After methanol, acetone, and chloroform were purified using soxhlet one by one, the solvent was removed by collecting chloroform and then reprecipitated in hexane to obtain the product [41,42] (yield: 27.8%).

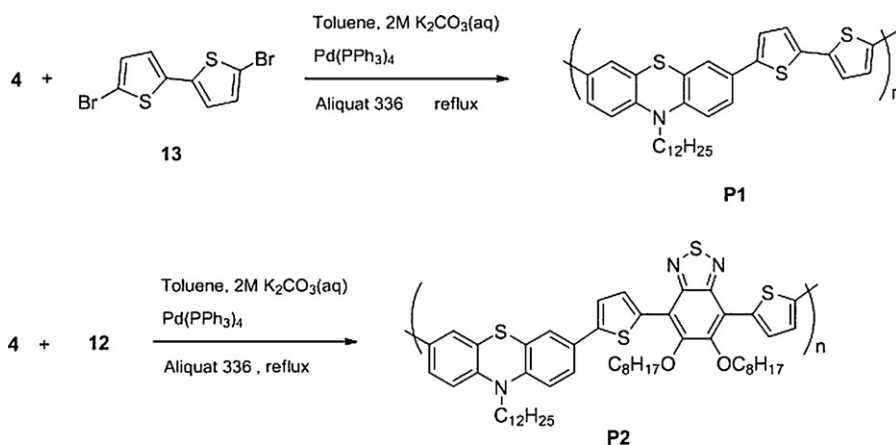
$^1H$  NMR (250 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 0.85–1.02 (m, 9H), 1.26–1.50 (m, 40H), 1.83–2.12 (m, 4H), 3.87 (m, 2H), 4.17 (m, 4H), 6.79–6.96 (m, 2H), 7.14–7.48 (m, 6H), 8.38–8.49 (m, 2H).  $^{13}C$  NMR

(125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 14.338, 14.370, 22.900, 22.926, 26.302, 26.341, 27.033, 27.159, 29.497, 29.564, 29.582, 29.747, 29.770, 29.815, 29.853, 30.688, 32.039, 32.090, 32.126, 47.740, 47.893, 74.657, 74.690, 74.702, 115.539, 115.599, 117.530, 117.558, 122.440, 124.701, 124.762, 124.980, 125.001, 125.093, 125.131, 125.474, 129.241, 132.039, 133.240, 144.305, 144.769, 144.860, 145.037, 150.997, 151.056, 151.769, 151.794, 151.915.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of polymers

A polymer based on phenothiazine and bithiophene (P1) and a D/A polymer based on phenothiazine and benzothiadiazole (P2) were synthesized through a Suzuki coupling reaction. The synthesis pathways of the monomer and polymer are shown in Schemes 1 and 2, respectively. Polymerization was carried out by using palladium(0) as the catalyst, 2 M  $K_2CO_3$  solution, aliquat 336 as a surfactant, and toluene as a solvent for 48 h at 90 °C. When the reaction was completed, it was end-capped with bromobenzene. Purification of the synthesized polymer was done in the order of methanol, acetone, and chloroform by using soxhlet, and the product was obtained by removing the solvent through chloroform collection and reprecipitation in methanol. The yield was 16.8% and 27.8% for P1 and P2, respectively. The structure of the synthesized compound was



Scheme 2. Synthetic route of polymers.

**Table 1**  
Molecular weights of polymers.

Polymer	$M_n$	$M_w$	PDI	Yield (%)
P1	3896	5466	1.40	16.8
P2	6098	9271	1.52	28.8

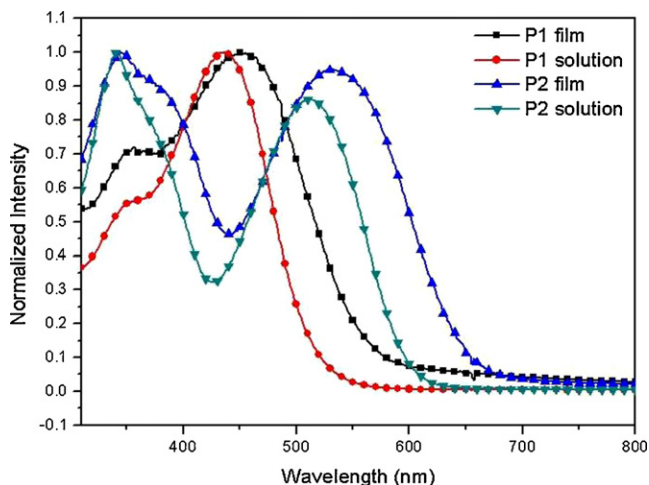


Fig. 1. UV-vis spectra of polymers.

confirmed through  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. An analysis of the  $^1\text{H}$  NMR spectrum confirmed an alkyl group between 0.8 and 4.0 ppm, and an aromatic ring between 6.8 and 7.5 ppm. The synthesized polymer displayed superb solubility for common organic solvents such as toluene, chloroform, THF, and ODCB. The weight of the polymer ( $M_w$ ) was measured by melting the polymer in THF through GPC. Polystyrene was used for the standard material and, as shown in Table 1, the average molecular weights for P1 and P2 were 5400 and 9200, respectively, and the polydispersity indexes (PDI) were found to have narrow distributions of 1.40 and 1.52, respectively. Each polymer showed low polymerization with molecular weights of 5400 and 9200, which is attributable to the rigidity of phenothiazine derivatives and resulting low solubility [49]. In addition, P1 polymer has a lower molecular weight than P2 polymer, and this is because bithiophene does not have an

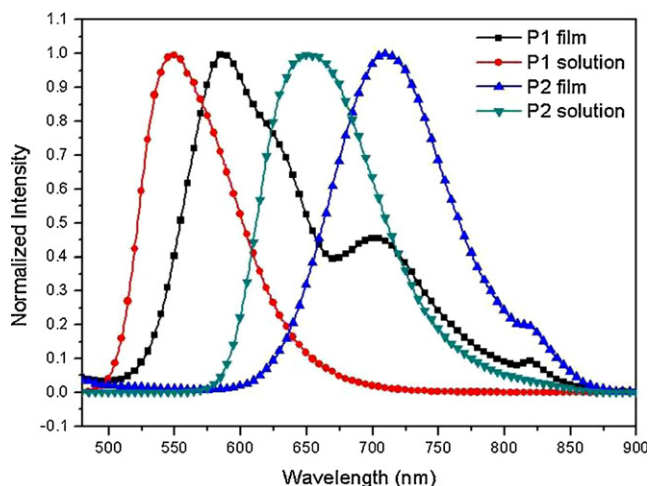


Fig. 2. Photoluminescent spectra of polymers.

**Table 2**  
Optical and electrochemical properties of polymers.

Polymer	Solution (nm)		Film (nm)		Homo (eV)	LUMO (eV) <sup>a</sup>	Band gap energy (eV) <sup>b</sup>
	UV <sub>max</sub>	PL <sub>max</sub>	UV <sub>max</sub>	PL <sub>max</sub>			
P1	433	547	452	586	-5.27	-3.04	2.23
P2	511	656	533	709	-5.49	-3.57	1.92

<sup>a</sup> LUMO (eV) = -HOMO -  $E_g^{\text{opt}}$ .

<sup>b</sup>  $E_g^{\text{opt}} = 1240/\lambda_{\text{edge}}$ .

alkyl chain, which leads to lower solubility than the benzothiadiazole derivatives with an alkyl chain. Because of this, polymerization could not take place in the solution but was precipitated [5].

### 3.2. Optical and electrochemical characterization of polymers

Fig. 1 shows the absorbance spectrum of the synthesized polymer. The polymer was dissolved in chloroform and measured in the forms of a solution and a film, and the film was fabricated by drop-casting it on a quartz plate. PL was measured using the same method and shown in Fig. 2, and the data are summarized in Table 2. Each polymer showed absorption in an area between 300 and 650 nm. P1 and P2 showed maximum absorption (UV<sub>max</sub>) at 433 nm and 511 nm, respectively, in the solution state, and at 452 nm and 533 nm, respectively, in the film state. The maximum luminescence wavelength (PL<sub>max</sub>) of P1 and P2 were 547 nm and 656 nm, respectively, in the solution state, and 586 nm and 709 nm, respectively, in the film state. Because both the UV-vis and PL spectra had distributions at  $\pi$ - $\pi^*$  transition energy levels, the film state showed a bathochromic shift of about 20 nm compared to the solution state [47]. Moreover, the UV spectrum of P2 was divided into two peaks. The peak absorbing at 300–400 nm is formed because of a delocalized  $\pi$ - $\pi^*$  transition at the polymer chain, and the peak absorbing at 450–650 nm is induced from a localized transition at the state of charge transfer between the donor (phenothiazine unit) and acceptor (benzothiadiazole unit) [46].

Fig. 3 shows an analysis of electrochemical properties of the polymers synthesized through CV. The analytical results are summarized in Table 2. The scan rate is 50 mV/s and Ag/AgCl was used as a reference electrode. The oxidation onset potential for P1 and P2 is 0.92 V and 1.14 V, respectively, and the HOMO energy level of molecules was -5.27 eV and -5.49 eV, which were

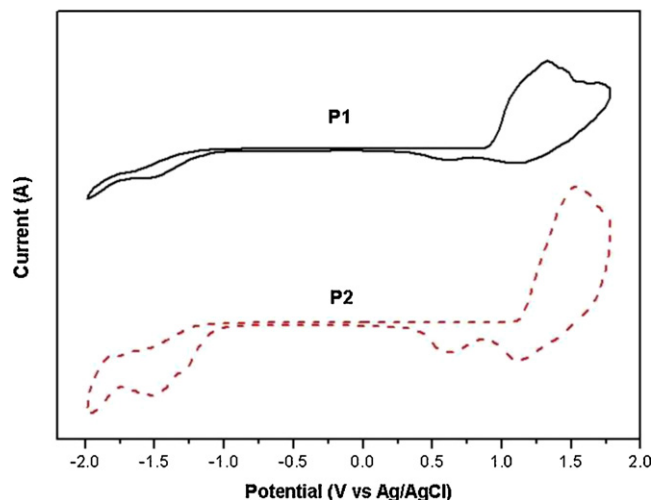


Fig. 3. Cyclic voltammogram of polymers.



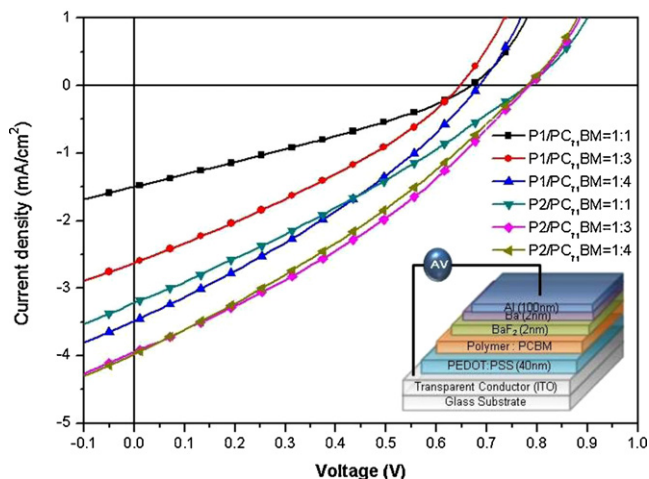


Fig. 4. Voltage-current density ( $J$ - $V$ ) curve of photovoltaic devices.

calculated by using the following equation and ferrocene (0.45 eV under the vacuum) as the correction value [42].

$$\text{HOMO} = [-(E_{\text{onset}} - 0.45)] - 4.8 \text{ eV}$$

Because the LUMO energy level does not clearly show reduction behaviors of the polymers, the optical band gap energy was calculated through a UV-vis graph and the difference from the HOMO energy level was then identified. The optical band gap energy of the synthesized polymers was 2.23 eV and 1.92 eV for P1 and P2, respectively, and the LUMO energy levels were  $-3.04$  eV and  $-3.57$  eV, respectively.

### 3.3. Photovoltaics properties of polymers

In order to confirm the polymer's applicability to OPVs, the polymer, blended with PC<sub>71</sub>BM, was made into a device by preparing a photoactive layer. The device was made as glass/ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM (weight ratio = 1:1/1:3/1:4)/BaF<sub>2</sub>/Ba/Al. The ITO substrate was surface-treated with a UVO (ultra violet ozone) cleaner and then the PEDOT:PSS solution was spin-coated for thermal treatment at 140 °C for 5 min. The photoactive layer was used to dissolve the synthesized polymer and PC<sub>71</sub>BM in ODCB, and was spin-coated over the PEDOT:PSS layer. It was then transferred to a high vacuum chamber for thermal evaporation of BaF<sub>2</sub> (2 nm), Ba (2 nm), and Al (100 nm) sequentially. The photoactive layer of fabricated device was 50–70 nm thick. Fig. 4 shows the current density ( $J$ )-voltage ( $V$ ) curve of the device measured through a solar simulator, and Table 3 summarizes the device's open circuit voltage ( $V_{\text{OC}}$ ), short circuit current density ( $J_{\text{SC}}$ ), fill factor (FF), and power conversion efficiency (PCE) values. The maximum PCE of P1 and P2 was 0.74% and 1.00%, respectively, and at this time,  $V_{\text{OC}}$  was 0.68 V and 0.78 V,  $J_{\text{SC}}$  was 3.5 mA/cm<sup>2</sup> and 3.9 mA/cm<sup>2</sup>, and FF was 31.8% and 32.7%.

Table 3  
Photovoltaic characteristics of polymers.

Active layer		$V_{\text{OC}}$ (V)	$J_{\text{SC}}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
P1/PC <sub>71</sub> BM (w/w)	1:1	0.68	1.5	29.9	0.30
	1:3	0.64	2.6	31.9	0.53
	1:4	0.68	3.5	31.8	0.74
P2/PC <sub>71</sub> BM (w/w)	1:1	0.72	2.1	28.9	0.44
	1:3	0.78	3.9	32.7	1.00
	1:4	0.78	3.9	30.6	0.94

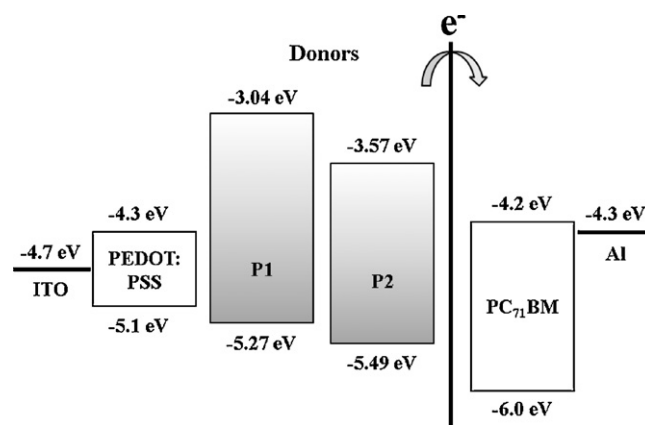


Fig. 5. Band diagram of polymers.

Fig. 5 shows the energy band diagram of P1 and P2. P2 was found to have a lower energy level than P1, and this is because its structure has benzothiadiazole derivatives attracting electrons, and the HOMO and LUMO showed lower energy levels due to the use of phenothiazine as a donor and the even stronger effect of induced charge transfer (ICT) [48]. Therefore,  $V_{\text{OC}}$  of the synthesized polymers was 0.68 V and 0.78 V, respectively, confirming that the P2 polymer with a lower HOMO energy level had a greater  $V_{\text{OC}}$  value. Moreover, the  $J_{\text{SC}}$  value was larger in the P2 polymer; this is attributed to its  $D/A$  structure, which makes it easier to transfer electron-holes as compared to P1.

## 4. Conclusion

Through this study, two new polymers, poly[(N-10'-dodecyl-phenothiazin-3,7-ylene)-*alt*-(2,2'-bithiophen-5-yl)] (P1) and poly[(N-10'-dodecyl-phenothiazin-3,7-ylene)-*alt*-(5',6'-dioctyloxy-benzothiadiazole-bithiophene)] (P2), which employ phenothiazine derivatives, thiophene, and benzothiadiazole as basic units, were synthesized by using a Suzuki coupling reaction and their applicability as OPVs was confirmed. The optical and electrochemical properties of the synthesized polymers were analyzed through UV-vis, PL, and CV, while their photovoltaic characteristics were analyzed by creating a device in the form of BHJ. Each polymer showed absorption in a section between 300 and 650 nm, and P1 and P2 showed low band gap energy of 2.23 eV and 1.92 eV, respectively. As for photovoltaic characteristics, the synthesized polymers and PC<sub>71</sub>BM were blended and used as a photoactive layer for measurement. As a result,  $V_{\text{OC}}$  was measured to be over 0.6 V and 0.7 V for P1 and P2, respectively. Meanwhile,  $J_{\text{SC}}$  was 1.5–3.5 mA/cm<sup>2</sup> for P1 and 2.1–3.9 mA/cm<sup>2</sup> for P2, and FF was 29.9–31.8% for P1 and 28.9–32.7% for P2. The maximum PCE of the device based on P1 was 0.74% (P1/PC<sub>71</sub>BM = 1:4, w/w,  $V_{\text{OC}}$  = 0.68 V,  $J_{\text{SC}}$  = 3.5 mA/cm<sup>2</sup>, FF = 31.8%) and as for P2, the maximum PCE was 1.00% (P2/PC<sub>71</sub>BM = 1:3, w/w,  $V_{\text{OC}}$  = 0.78 V,  $J_{\text{SC}}$  = 3.9 mA/cm<sup>2</sup>, FF = 32.7%). These results confirm that a material with a  $D/A$  structure to which benzothiadiazole derivatives are applied provides better photovoltaic performance. They also suggest the need for further development of polymers using materials with new structures that can be applied to OPVs.

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