



Synthesis and characterization of difluorophenazine-based conjugated polymers for organic photovoltaics

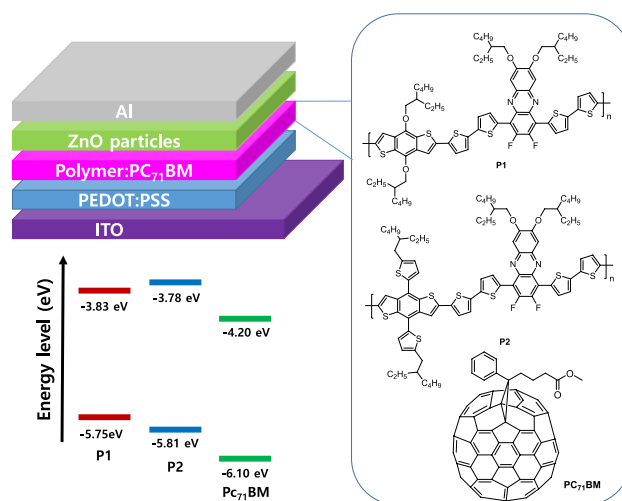
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Abstract

Novel ACCEPTER units, difluorophenazine, were prepared and used for the synthesis of the conjugated polymers incorporating electron donor–acceptor pairs for organic photovoltaics. The introduction of a fluorine atom into the phenazine moiety led to a lowering of the highest occupied molecular orbital (HOMO) energy levels of the polymers. These acceptor units are likely to enhance electron transfer properties within the polymer structure. Conjugated polymers containing difluorophenazine, bithiophene and benzodithiophene, were synthesized using the Stille polymerization reaction to produce **P1** and **P2**. The HOMO/LUMO energy levels of **P1** and **P2** were $-5.75/-3.83$ eV and $-5.81/-3.78$ eV, respectively. **P2**, which incorporates thiophene units into the benzodithiophene backbone, exhibits lower HOMO energy levels to increase the V_{OC} Value. These energy levels are crucial for potentially enhancing the photovoltaic performance of the polymers.

Graphical abstract



Novel acceptor units, difluorophenazine, were prepared and used for the synthesis of the conjugated polymers incorporating electron donor–acceptor pairs for organic photovoltaics. P2, which incorporates thiophene units into the benzodithiophene backbone, exhibits lower HOMO energy levels to increase the V_{OC} Value

Keywords Polymer · Solar cells · Synthesis · Phenazine · Fluorine atom

Extended author information available on the last page of the article

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1 Introduction

Organic solar cells (OSCs) have become a major topic of research because of their high performance and the fact that they can be constructed from non-toxic and inexpensive materials [1–4]. They can be processed via solution processing on lightweight and cost-effective flexible substrates [5]. Extensive research, especially into the design and synthesis of new materials, have led to significant increases in the power conversion efficiencies (PCEs) of OSCs. A critical aspect of OSCs is an interface between an electron-donating polymer and an electron-accepting fullerene derivative [6, 7]. The synthesis of new low-bandgap polymers has substantially improved OSC performance, with reported PCEs reaching 18% in recent years [8].

The modification of polymer chemical structure can lead to changes in the optical, electrochemical, and photovoltaic properties [9]. Benzodithiophene derivatives are one of the most widely used electron-donating units in the polymers of OSCs [10, 11]. Phenazine moiety is an attractive electron-withdrawing moiety due to its coplanar structure resulting from the fusing of multiple aromatic rings [12–14]. Phenazine participates in π - π interactions and exhibits properties of close packing [13–15]. It has also been found that polymers containing phenazine units show expanded absorption areas in their UV–vis spectra, which give enhanced short circuit current densities (J_{SC}) values [13, 14, 16]. Introducing an electron-withdrawing fluorine atom into a low bandgap conjugated polymer lowers its highest occupied molecular orbital (HOMO) energy level. Among the various donor units available, benzodithiophene has elicited much interest with respect to the design of novel conjugated polymers for use in PSCs [17, 18]. Electron-rich thiophene units have generated significant interest because of their capacity to extend conjugation lengths and synthetic multiformity.

In this study, we designed and synthesized polymers based on fluorinated phenazine as the electron-deficient unit and benzo[1,2-*b*:4,5-*b'*]dithiophene and bithiophene units as the electron donor. Conjugated polymers were synthesized as candidates for high-performance OSCs applications via Stille polymerization. To tune the energy levels, we introduced bithiophene to the conjugated polymers. The incorporation of four alkyl chains in the backbone provided high solubility in organic solvents. To assess the photovoltaic properties of the polymers, OSCs with the configuration ITO/PEDOT:PSS/polymer:PC₇₁BM/ZnO particles/Al were fabricated and characterized (see Fig. 1).

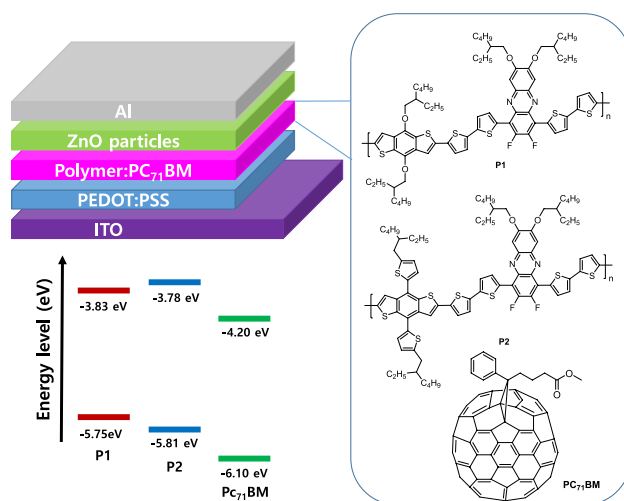
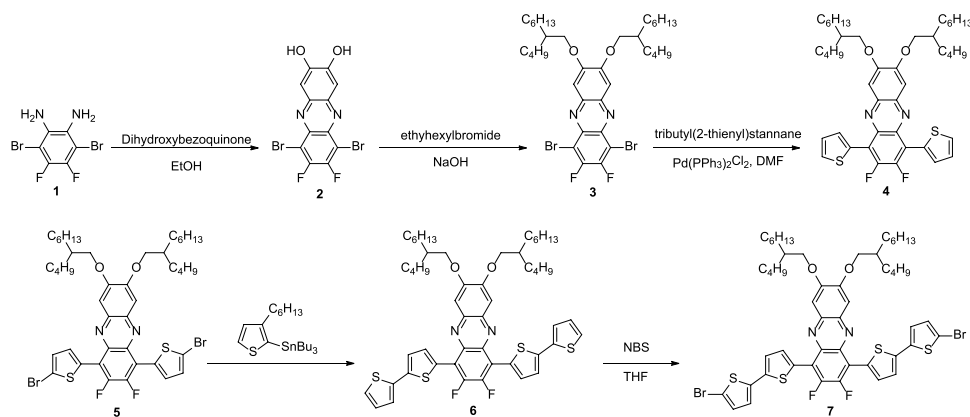
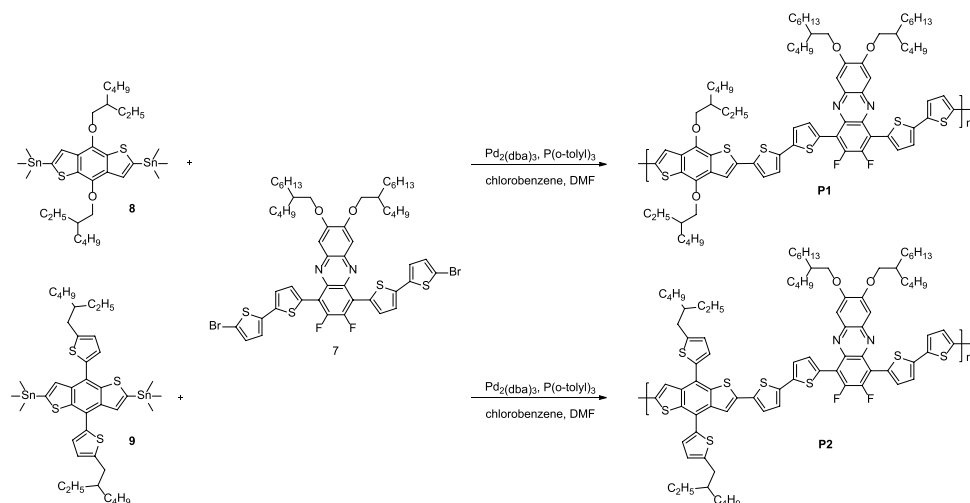


Fig. 1 Molecular structures and energy levels of electron donor and PC₇₁BM and schematic diagram of the PSC device architecture

2 Results and discussion

2.1 Synthesis and characterization

The synthetic routes used to obtain the monomers and polymers are outlined in Schemes 1 and 2, respectively. In the first step, 3,6-dibromo-4-fluorobenzene-1,2-diamine (**1**) was condensed with 1,2-dihydroquinone and then alkylated with ethylhexyl bromide to generate 1,4-dibromo-7,8-bis((2-ethylhexyl)oxy)-2-fluorophenazine (**3**). The Stille coupling reaction of compound **3** with tributyl(2-thienyl)stannane (2.5 eq) was also performed to obtain 7,8-bis((2-ethylhexyl)oxy)-1,4-di(thiophen-2-yl)-2-fluorophenazine (**4**), which was subsequently brominated with *N*-bromosuccinimide (NBS) to generate 1,4-bis(5-bromothiophen-2-yl)-7,8-bis((2-ethylhexyl)oxy)-2-fluorophenazine (**5**). Compound **5** was coupled with tributyl(2-thienyl)stannane (2.5 eq) through a Stille coupling reaction to obtain 1,4-bis((2,2'-bithiophen)-5-yl)-7,8-bis((2-ethylhexyl)oxy)-2-fluorophenazine (**6**), and compound **6** was brominated with NBS to obtain 1,4-bis(5'-bromo(2,2'-bithiophen)-5-yl)-7,8-bis((2-ethylhexyl)oxy)-2-fluorophenazine (**7**). Copolymers based on 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (**8**) [19] and 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)-2-thienyl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**9**) [20] as the electron-donating unit and various 2-fluorophenazine monomers as the electron-accepting moieties were then synthesized via a Pd(0)-catalyzed Stille coupling polymerization reaction in chlorobenzene. It should be noted here that the four alkyl chains in the synthesized polymers were introduced

Scheme 1 Synthetic route of the monomer**Scheme 2** Synthetic route of the polymers**Table 1** Polymerization results and thermal properties of polymers

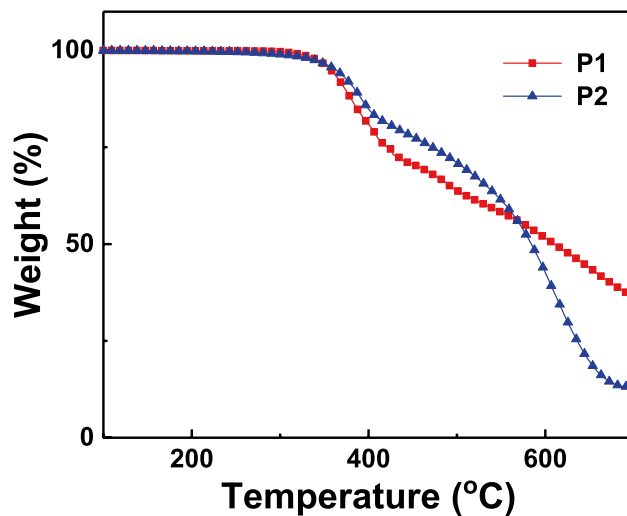
Polymer	M_n^a (g/mol)	M_w^a (g/mol)	PDI ^a	TGA (T_d) ^b
P1	21,000	28,000	1.33	356
P2	13,000	18,000	1.38	362

^aMolecular weight (M_w) and polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards

^bOnset decomposition temperature (5% weight loss) measured by TGA under N_2

to improve the solubilities in organic solvents such as chloroform, THF, chlorobenzene, and *o*-dichlorobenzene (DCB), at room temperature.

Table 1 summarizes the results of the polymerization reactions, including the molecular weights, polydispersity index (PDI) values, and thermal stabilities of the synthesized polymers. Gel permeation chromatography (GPC) of the prepared **P1** and **P2** against a polystyrene standard gave weight-average molecular weights (M_w) of 28,000 and 18,000, respectively, along with polydispersity index (PDI, M_w/M_n) of 1.33 and 1.38, respectively. The thermal

**Fig. 2** Thermogravimetric analysis of the polymers under N_2

properties of the polymers were investigated through thermal gravimetric analysis (TGA) on a Dupont 951 TGA instrument under a nitrogen atmosphere at a heating rate of 10 °C/

min; the samples were heated to 800 °C, as shown in Fig. 2. In the TGA curves, weight decreases of 5% were observed at 356 and 362 °C for P1 and P2, respectively. The high T_d value is desirable in the case of polymers for OSCs.

2.2 Optical properties

The UV–visible absorption spectra of the synthesized polymers in solution and in the solid state (thin films) are shown in Fig. 3. The solutions were prepared using DCB as the solvent and the thin films were spin-coated on a quartz plate from the DCB solutions of the polymers at room temperature. In the solution form, P1 exhibited similar absorption spectra, with absorption maxima at 477 and 589 nm. The absorption peaks of P2 were located at 487 and 657 nm. As

electron density increases from the thiophene introduced on benzodithiophene units, the conjugation length increases to indicate a red shift in the absorption maxima in the solution. The spectra of P1 and P2 in the form of solid films consist of absorption bands of at 472 and 593 nm and 485 and 657 nm and absorption onsets at 734 and 739 nm, corresponding to band gaps of 1.67 and 1.68 eV, respectively. The absorption maxima in solid films are characterized by redshifts and broader absorption bands in the solid state, indicating the further extension of conjugation and possibly different molecular packing in the solid state [21].

2.3 Electrochemical and theoretical calculations

The electrochemical properties of the polymers were determined from the band gap, which in turn was estimated from the absorption onset wavelength and the HOMO energy level obtained by cyclic voltammetry (CV) measurements in an acetonitrile solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4 , 0.10 M) at a scan rate of 100 mV/s and at room temperature under argon. A platinum electrode ($\sim 0.05 \text{ cm}^2$) coated with a thin polymer film was used as the working electrode, and a Pt wire and an Ag/AgNO₃ electrode were used as the counter and reference electrodes, respectively. The energy level of the Ag/AgNO₃ reference electrode (calibrated by the Fc/Fc⁺ redox system) was 4.8 eV below the vacuum level. Figure 4 shows the CV spectra of the polymers, and the CV parameters are summarized in Table 2. The HOMO and lowest unoccupied molecular orbital (LUMO) levels were calculated according to the empirical formulas ($E_{\text{HOMO}} = -([E_{\text{onset}}]^{\text{ox}} + 4.8) \text{ eV}$) and ($E_{\text{LUMO}} = -([E_{\text{onset}}]^{\text{red}} + 4.8) \text{ eV}$), respectively. The oxidation potential onsets of P1 and P2 were determined to be

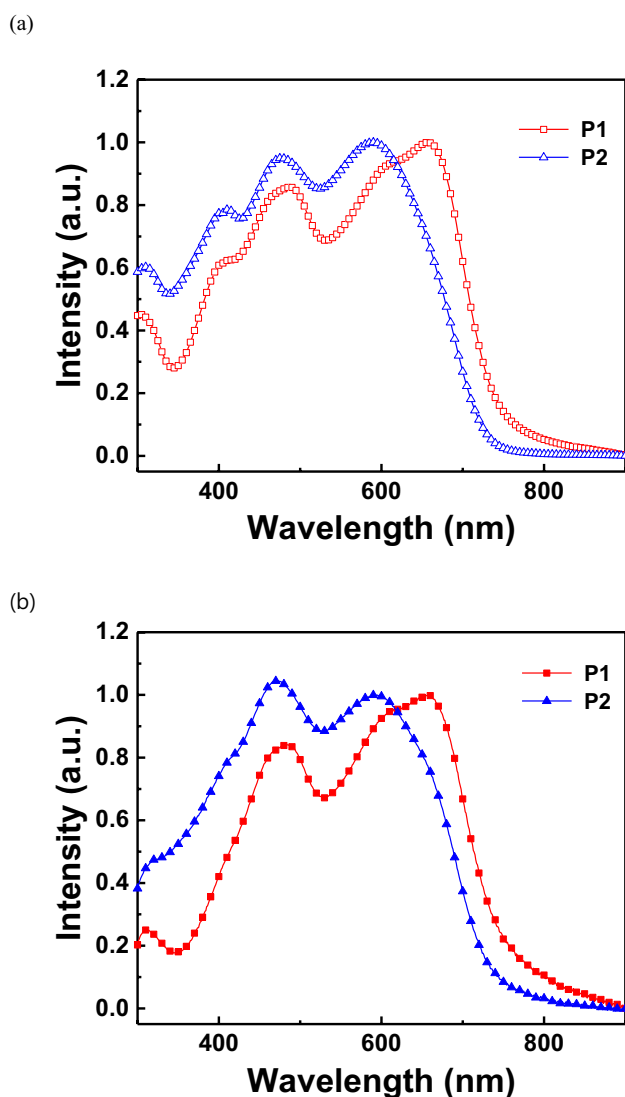


Fig. 3 UV–visible absorption spectra of polymers in dichlorobenzene solution (a) and the solid state (b)

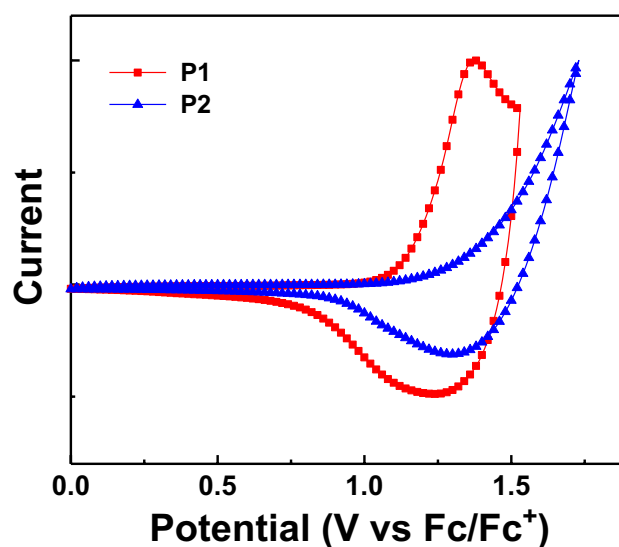


Fig. 4 Electrochemical properties of polymers

Table 2 Electrochemical potentials and energy levels of the polymers

Polymers	optical band gap ^a (eV)	HOMO ^b (eV)	LUMO ^c (eV)	E_{ox} ^d (V)	E_{red} ^d (V)	electrochemical band gap ^e (eV)
P1	1.67	− 5.75	− 3.83	0.95	− 0.97	1.92
P2	1.68	− 5.81	− 3.78	1.01	− 1.02	2.03

^aOptical energy band gap was estimated from the onset wavelength of the optical absorption^bCalculated from the oxidation potentials^cCalculated from the reduction potentials^dOnset oxidation and reduction potential measured by cyclic voltammetry^eCalculated from the E_{ox} and E_{red}

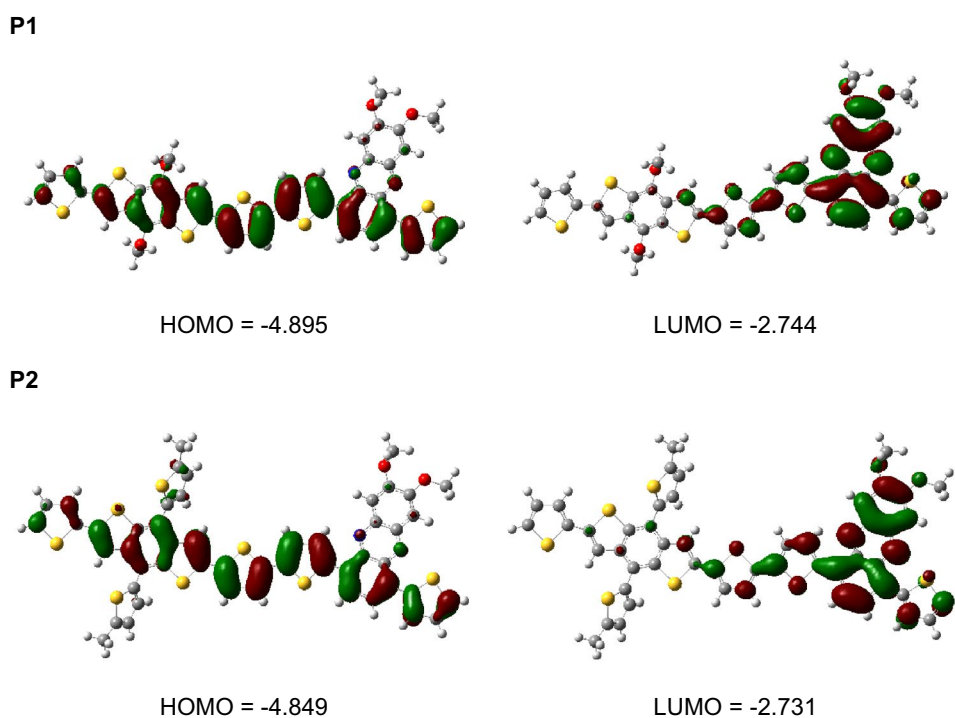
0.95 and 1.01 V, respectively, which correspond to HOMO energy levels of − 5.75 and − 5.81 eV, respectively. The LUMO energy levels of **P1** and **P2** were determined to be − 3.83 and − 3.78 eV, respectively, and so the electrochemical band gap, calculated from the CV data, were 1.92 and 2.03 eV, respectively. When the polymer has low solubility, stronger intermolecular interactions, such as π - π stacking, can occur, which may trap electrons within the polymer, reducing their mobility and consequently lowering the HOMO energy level [22, 23]. P2 exhibited a wider band gap compared to P1 due to the introduction of thiophene units on the benzodithiophene backbone, which influenced the electronic structure.

The optimized geometry for each polymer was then calculated using the B3LYP/6-31G level of theory in the Gaussian 03 package to gain insight regarding their electronic structures. The HOMO and LUMO surfaces were plotted using GaussView version 4.1. To simplify the computations, the

alkyl chains were replaced with methyl groups, and only two repeating units were used for the polymer backbone. We studied the tunability of the HOMO and LUMO energy levels of **P1** and **P2** using computational methods [24–26]. The optimized structures of **P1** and **P2** are shown in Fig. 5, and the HOMO/LUMO levels were determined computationally to be − 4.90/− 2.74 and − 4.85/− 2.73 eV for **P1** and **P2**, respectively. The higher calculated HOMO energy level for P2 can be understood to be an effect of the additional thiophene units on benzodithiophene backbone, which provides increased electron density to the conjugated polymer backbones.

2.4 Photovoltaic properties of synthesized polymers

To demonstrate the potential application of the synthesized polymers in PSCs, we employed our polymers as the

Fig. 5 Theoretical calculation of the monomers by density functional theory (DFT) at the B3LYP/6-31G level

electron donor and PC₇₁BM as the electron acceptor to fabricate BHJ PSCs with a configuration of ITO/PEDOT:PSS/polymer:PC₇₁BM/Al under AM 1.5G irradiation (100 mW/cm²). Figure 6 shows the current density–voltage plots of the prepared OSCs, while Table 3 lists the open circuit voltages (V_{OC}), short circuit current densities (J_{SC}), fill factors (FF), and PCEs of the devices. The active layers were prepared by spin-coating the blend solutions of **P1** and **P2** as electron donor materials and PC₇₁BM as the electron acceptor materials in DCB. The devices based on **P1**:PC₇₁BM and **P2**:PC₇₁BM showed V_{OC} values of 0.57 and 0.65 V, J_{SC} values of 2.32 and 5.55 mA/cm², and FF values of 0.40 and 0.45, and PCEs of 0.54 and 1.62%, respectively. The superior performance of **P2** is attributed to the incorporation of thiophene into the benzodithiophene backbone, which enhances the electron density and improves the overall efficiency of the device. The incident-photon-to-current efficiency (IPCE) spectra of the photovoltaic devices from the polymer:PCBM blends are presented in Fig. 7. The spectra showed maxima of 16.24% at 440 nm for **P1** and 31.47% at 450 nm for **P2**.

3 Conclusions

The organic low band gap materials with an difluorophenazine as electron deficient and bithiophene and benzodithiophene units as electron-rich units have been synthesized via Stille coupling reaction with Pd catalyst. In solid thin films, the maximum absorption peaks of **P1** and **P2** in solid thin films were at 542 nm and 559 nm, respectively. The HOMO energy levels of the **P1** and **P2** are expected to be −5.75 and −5.81 eV, respectively. As a result, a high PCE of 1.62% was obtained, with V_{OC} of 0.65 V, a J_{SC} of 5.55 mA/cm², an

Table 3 Photovoltaic properties of the polymer solar cells

	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
P1	2.32	0.57	0.40	0.54
P2	5.55	0.65	0.45	1.62

FF of 0.45. These results indicate that the incorporation of thiophene units on benzodithiophene is a feasible approach to improve PCE.

4 Experimental section

General. All reagents purchased from Aldrich or TCI were used without further purification. Solvents were purified by typical procedures and handled under moisture-free atmosphere. ¹H and ¹³C NMR spectra were recorded on a JNM ECP-400 (400 MHz, JEOL) spectrometer, and chemical shifts were recorded in ppm using TMS as the internal standard. Flash column chromatography was performed using Merck silica gel 60 (particle size 230–400 mesh ASTM) with a gradient elution of ethyl acetate/hexane or methanol/dichloromethane unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25-mm silica gel 60F pre-coated aluminum plates with a fluorescent indicator UV254. The molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) with calibration using polystyrene standards. UV–vis absorption spectra were recorded on a Varian 5E UV–VIS–NIR spectrophotometer.

Synthesis of 1,4-dibromo-7,8-bis((2-butyloctyl)oxy)-2-fluorophenazine (**3**).

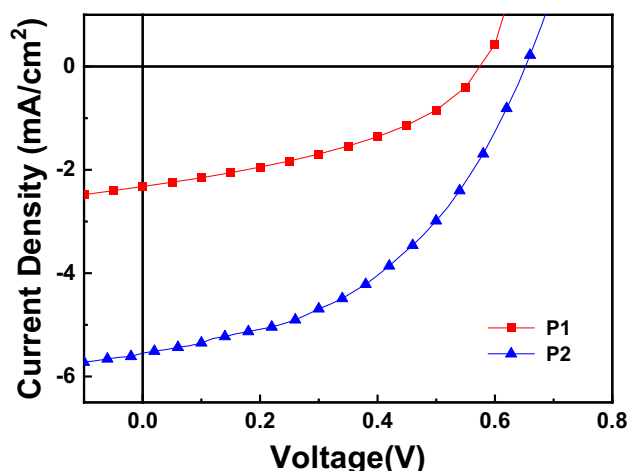


Fig. 6 Current density–voltage characteristics of the polymer solar cells under the illumination of AM 1.5, 100 mW/cm²

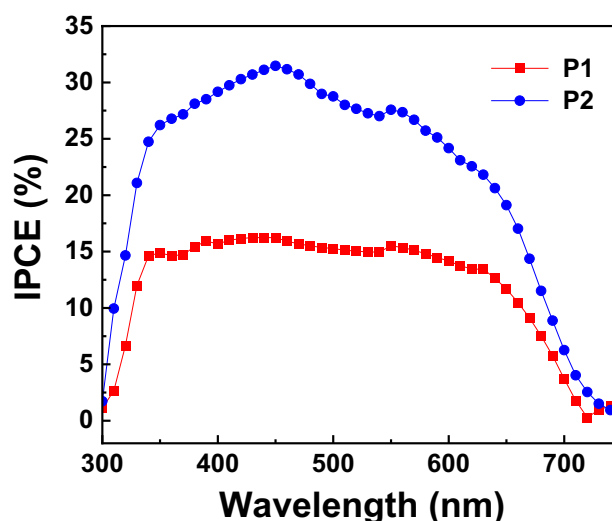


Fig. 7 EQE curves of the polymer-based PSCs under the illumination of AM 1.5, 100 mW/cm²

The 3,6-dibromo-4-fluorobenzene-1,2-diamine (**1**) (2.03 g 7.17 mmol) was added to ethanol (120 mL), then 1,2-dihydroquinone (1.18 g 10.75 mmol) put into round-bottomed flask. Then, the solution was stirred for 24 h at reflux condition. After that, the solution was dried under vacuum condition and collected red-dark powder (3.21 g) was dissolved using dimethylformamide (100 mL). Then put in 2-butyloctylbromide (3 mL) and K_2CO_3 (3.20 g, 23.11 mmol). This solution stirred 24 h at reflux condition. After that, dried DMF and extracted with chloroform twice. The collected organic solution was dried over anhydrous $MgSO_4$. After removing the solvent, purified by a column chromatography using a solvent gradient of 10% dichloromethane in hexane as the eluent, which afforded 1.54 g (yield 35.13%) of an orange sticky solid the product. 1H -NMR ($CDCl_3$, 400 MHz, δ): 7.90 (d, 2H), 4.11 (d, 2H), 4.09 (d, 2H), 1.98–1.83 (m, 2H), 1.63–1.28 (m, 32H), 0.90 (m, 12H).

Synthesis of 7,8-bis((2-butyloctyl)oxy)-1,4-di(thiophen-2-yl)-2-fluorophenazine (**4**).

The 1,4-dibromo-7,8-bis((2-butyloctyl)oxy)-2-fluorophenazine (**3**) (1 g, 1.64 mmol) was added to toluene (100 mL), then 2-(tributylstannyl)thiophene (1.52 g, 4.10 mmol) and Pd catalyst that tris(*o*-tolyl)phosphine (0.015 g, 0.049 mmol) and $Pd_2(dba)_3$ (0.045 g, 0.0049 mmol) put into flask. This solution was stirred 24 h at reflux condition. After that, the solvent was dried and extracted with chloroform twice. The collected organic solution was dried over $MgSO_4$. After removing the solvent, purified by a column chromatography using a solvent gradient 10~20% dichloromethane in hexane as the eluent, which afforded 0.72 mg (yield 60.4%) of a red sticky solid. 1H -NMR ($CDCl_3$, 400 MHz, δ): 7.85 (s, 2H), 7.71 (d, 2H), 7.68 (d, 2H), 7.24 (t, 2H), 4.18 (m, 2H), 3.92 (m, 2H), 2.35 (m, 4H), 0.65–1.53 (m, 44H).

Synthesis of 1,4-bis(5-bromothiophen-2-yl)-7,8-bis((2-butyloctyl)oxy)-2-fluorophenazine (**5**).

The 7,8-bis((2-butyloctyl)oxy)-1,4-di(thiophen-2-yl)-2-fluorophenazine (**4**) (0.88 g, 1.41 mmol) was added to chloroform (60 mL), then NBS (0.73 g, 4.23 mmol) into flask. Then, the solution was stirred 24 h at room temperature. After that, the solution was extracted with chloroform twice. The collected organic solution was dried over $MgSO_4$. After removing the solvent, purified by column chromatography using a solvent gradient 10~20% dichloromethane in hexane as the eluent, which afforded 0.66 g of a red–orange sticky solid. 1H -NMR ($CDCl_3$, 400 MHz, δ): 7.85 (s, 2H), 7.46 (d, 2H), 7.35 (d, 2H), 7.24 (t, 2H), 4.14 (m, 2H), 3.92 (m, 2H), 2.35 (m, 4H), 0.65–1.43 (m, 44H).

Synthesis of 1,4-bis((2,2'-bithiophen)-5-yl)-7,8-bis((2-butyloctyl)oxy)-2-fluorophenazine (**6**).

The 1,4-bis(5-bromothiophen-2-yl)-7,8-bis((2-butyloctyl)oxy)-2-fluorophenazine (**5**) (1 g, 1.26 mmol) was added to toluene (100 mL), then 2-(tributylstannyl)thiophene (1.41 g,

3.78 mmol) and Pd catalyst that tris(*o*-tolyl)phosphine (0.045 g, 0.138 mmol) and $Pd_2(dba)_3$ (0.135 g, 0.0147 mmol) put into flask. This solution was stirred 24 h at reflux condition. After that, the solvent was dried and extracted with chloroform twice. The collected Organic solution was dried over $MgSO_4$. After removing the solvent, purified by column chromatography using a solvent gradient 10~20% dichloromethane in hexane as the eluent, which afforded 0.89 g of a red solid. 1H -NMR ($CDCl_3$, 400 MHz, δ): 7.83 (d, 2H), 7.66 (d, 2H), 7.54 (d, 2H), 4.25 (m, 2H), 3.92 (m, 2H), 2.35 (m, 2H), 0.65–1.53 (m, 44H).

Synthesis of 1,4-bis(5'-bromo(2,2'-bithiophen)-5-yl)-7,8-bis((2-butyloctyl)oxy)-2-fluorophenazine (**7**).

The 1,4-bis((2,2'-bithiophen)-5-yl)-7,8-bis((2-butyloctyl)oxy)-2-fluorophenazine (**6**) (1.0 g, 1.25 mmol) was added to chloroform (60 mL), then NBS (0.78 g, 4.5 mmol) put into flask. Then, the solution was stirred 24 h at room temperature condition. After that, the solution was extracted with chloroform twice. The collected organic solution was dried over $MgSO_4$. After removing the solvent, purified by column chromatography using a solvent gradient 10~20% dichloromethane in hexane as the eluent, which afforded 0.66 g (yield 94.9%) of a red solid the product 1.07 g. 1H -NMR ($CDCl_3$, 400 MHz, δ): 7.92 (d, 2H), 7.89 (d, 2H), 7.61 (s, 2H), 7.18 (d, 2H), 7.11 (d, 2H), 4.18 (m, 2H), 3.73 (m, 2H), 2.18 (m, 2H), 0.65–1.48 (m, 44H).

Polymerization of poly[2,6-(4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene)-*alt*-1,4-((2,2'-bithiophen)-5-yl)-7,8-bis((2-butyloctyl)oxy)-2-fluorophenazine] (**P1**).

The 2,6-bis(trimethyltin)-4,8-bis(2-butyloctyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (**8**) (0.242 g, 0.313 mmol) was added to chlorobenzene (20 mL), then 1,4-bis(5'-bromo(2,2'-bithiophen)-5-yl)-7,8-bis((2-butyloctyl)oxy)-2-fluorophenazine (**7**) (0.3 g, 0.313 mmol) and Pd catalyst that tris(*o*-tolyl)phosphine (0.080 g, 0.0246 mmol) and $Pd_2(dba)_3$ (0.0226 g, 0.0246 mmol) put into flask. This solution was stirred for 48 h at 100 °C condition. After cooling to room temperature, this solution was put into stirred methyl alcohol at 0 °C one by one. The polymer was filtered and washed with methanol. The collected polymer was soxhlet-extracted with methanol, acetone, chloroform and chlorobenzene. Then, chloroform and chlorobenzene solutions were put into stirred methanol for reprecipitation. The purified polymer was collected by filtration to give 210 mg.

Polymerization of poly[2,6-(4,8-bis(5-(2-ethylhexyl)-2-thienyl)benzo[1,2-*b*:4,5-*b'*]dithiophene)-*alt*-1,4-((2,2'-bithiophen)-5-yl)-7,8-bis((2-butyloctyl)oxy)-2-fluorophenazine] (**P2**).

By following the similar method used for **P1**, **P2** was synthesized with, 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)-2-thienyl)benzo[1,2-*b*:4,5-*b'*]dithiophene (0.283 g, 0.313 mmol) and 1,4-bis(5'-bromo(2,2'-bithiophen)-5-yl)-7,8-bis((2-butyloctyl)oxy)-2-fluorophenazine (**7**) (0.3 g,

0.313 mmol). The purified polymer was collected by filtration to give 270 mg as violet solid.

The solar cell fabrication. Solar cells were fabricated on an indium tin oxide (ITO)-coated glass substrate with the following structure: ITO-coated glass substrate/ poly(3,4-ethylenedioxythiophene):poly(stylenesulfonate) (PEDOT:PSS)/ polymer:PCBM/Al. The ITO-coated glass substrate was first cleaned using a detergent and ultrasonicated in acetone and isopropyl alcohol, followed by drying overnight in an oven. PEDOT:PSS (Baytron PH) aqueous solution was spin-cast to form a 40 nm thick film. The substrate was dried for 10 min at 140 °C in air and then transferred into a glove box to spin-cast the charge separation layer. A solution containing a mixture of polymer:PCBM in dichlorobenzene as solvent was then spin-casted on top of the PEDOT/PSS layer. Then, the film was dried for 60 min at 70 °C in the glove box. The sample was heated at 80 °C for 10 min in air. Then, an aluminum (Al, 100 nm) electrode was deposited by thermal evaporation under a vacuum of approximately 5×10^{-7} Torr. Current density–voltage (*J*-*V*) characteristics of the devices were measured using a Keithley 236 source measure unit. Solar cell performance was measured using an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 1000 W m^{-2} . An aperture (12.7 mm^2) was used on top of the cell to eliminate extrinsic effects such as cross-talk, and waveguiding, shadow effects. The spectral mismatch factor was calculated by the comparison of the solar simulator spectrum with the AM 1.5 spectrum at room temperature.

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