

Thienopyrazine or Dithiadiazatrindene Containing Low Band Gap Conjugated Polymers for Polymer Solar Cells^{*}

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Abstract Four new low-band-gap alternating copolymers (**P-1**, **P-2**, **P-3** and **P-4**) based on electron-rich benzodithiophene and newly developed electron-deficient units, thienopyrazine or dithiadiazatrindene derivatives, were synthesized by Stille polycondensation. All polymers exhibit good solubility in common organic solvents and a broad absorption band in the visible to near-infrared regions. The film optical band gaps of the polymers are in the range of 1.28–2.07 eV and the highest occupied molecular orbital (HOMO) energy levels are in the range of –4.99 eV to –5.28 eV. Bulk heterojunction polymer solar cells (PSCs) of the polymers were fabricated with phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) as acceptor material, and a power conversion efficiency of 0.80% was realized with **P-1** as donor material.

Keywords: Low band gap; Conjugated polymers; Electron-deficient aromatics; Polymer solar cells.

INTRODUCTION

Over the past ten years, polymer solar cells (PSCs) have attracted considerable attention of researchers as a new alternative renewable energy sources due to their advantages such as low cost, ease of fabrication, light weight, as well as the possibility of obtaining large-area flexible devices^[1–3]. Among these devices solar cells with bulk heterojunction based on composites of conjugated polymers (donor) and fullerene derivatives (acceptor) are regarded as highly effective system for the rapid dissociation of excitons and charge transport^[4–7]. In comparison with the homopolymers, conjugated polymers with alternating donor-acceptor (D-A) structures exhibit a smaller band gap, which allows extending the absorption region of the conjugated polymers to the near infrared band and increasing the efficiency of PSCs. Currently, the power conversion efficiency (PCE) of PSCs on the basis of new D-A polymers reached about 7%–9%^[8].

To improve the efficiency of PSCs, not only a low band gap, but the specific location of the energy levels of polymers and fullerene derivatives is necessary. The energy levels of polymers depend on the chemical nature of donor and acceptor units, where the highest occupied molecular orbital (HOMO) energy level is mainly determined by the donor, and the lowest unoccupied molecular orbital (LUMO) energy level mainly by the

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electron acceptor^[9, 10]. It is important to control the energy levels of the polymer as it is considered that the difference in LUMO-LUMO gap between the polymer and fullerene is directly related to the efficiency of charge separation. It is assumed that a minimum difference of LUMO-LUMO gap between donor and acceptor, which is required for charge separation at the interface, is ~0.3–0.4 eV^[11, 12]. On the other hand, the energy difference between the HOMO of donor and the LUMO of acceptor determines the maximum achievable open circuit voltage (V_{oc}) of PSCs, and as a result of a direct effect on the maximum power^[13, 14]. Consequently, it is important to specifically locate the energy levels of the polymer relative to the acceptor for the charge separation and quantification of high value V_{oc} , while maintaining a small value of the band gap. In this regard, development of new low band gap conjugated polymers is the actual issue.

Recently, polymers based on benzo[2,1-b:3,4-b']dithiophene (BDT) have attracted considerable attention as a promising electron-donor in polymer solar cells. Copolymers containing BDT structures have a planar structure and show a high mobility of holes. On the other hand, *N*-containing heterocyclic aromatics such as benzothiadiazoles^[15–17] and thienopyrazines (TP)^[18–20] are often used as acceptors in the D-A copolymers. In the current paper, we synthesized four new *N*-containing heterocyclic aromatics, two TP derivatives and two 1H-6,7-dithia-1,3-diazatrindene derivatives, as electron-accepting units. Four D-A conjugated polymers with BDT as donor segment were synthesized, and their photophysical and photovoltaic properties were studied in detail.

EXPERIMENTAL

Materials

THF was dried over KOH for 24 h, then refluxed over Na in the presence of benzophenone to the purple color and distilled under a stream of argon. Toluene was dried over KOH 24 h, then over P₂O₅ for 24 h, after that it was heated in the presence of Na and benzophenone to purple color and distilled under a stream of argon. DMF was dried over KOH for 72 h, then it was distilled over CaH₂ under a stream of argon. Compounds **1**, **6**, **8a**, **b** and **10** were synthesized according to literature methods^[21–26]. Other reagents were used as received without further purification.

Characterization

¹H- and ¹³C-NMR spectra were recorded on a Bruker Avance-400 spectrometer with a frequency of 400.13 MHz and 100.62 MHz correspondingly in CDCl₃. Elemental analysis was conducted on a Carlo Ebra-1106 CHN-elemental analysis system. Thermogravimetric analysis (TGA) measurements were carried out under nitrogen flow on a Perkin-Elmer TGA-7 equipment with a heating/cooling rate of ± 10 K/min. UV-Vis-NIR absorption spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrometer. Molecular weights and polydispersity indices (PDIs) of the polymers were measured by gel permeation chromatography (GPC) on Waters chromatography. Film cyclic voltammetry (CV) was measured in anhydrous acetonitrile with Bu₄NPF₆ (0.1 mol/L) as electrolyte on a CHI660a electrochemical analyzer at a scan rate of 100 mV/s. A glassy carbon electrode with a diameter of 10 mm, a Pt wire and a saturated calomel electrode were used as the working, counter and reference electrodes, respectively. HOMO and LUMO energy levels were estimated by the equations HOMO = $-(4.80 + E_{onset}^{ox})$ eV and LUMO = $-(4.80 + E_{onset}^{re})$ eV, in which E_{onset}^{ox} and E_{onset}^{re} are oxidation and reduction onsets in CV curves, respectively. Atomic force microscopy (AFM) measurements were conducted in tapping mode on a SPA400HV instrument with a SPI 3800 controller (Seiko Instruments).

Fabrication and Measurement of Polymer Solar Cells

To fabricate solar cells, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron 4083) with a thickness of ~40 nm was spin-cast on ITO substrates and dried at 120 °C for 30 min in an oven. The polymer:PC₆₁BM layer was then deposited on top *via* spin-casting. Finally, the LiF (1 nm)/Al (80 nm) cathode was thermally deposited. The active area of PSCs was 12 mm². An Oriel 150W solar simulator with an AM 1.5G filter was used to provide an intensity of 100 mW·cm⁻² for illumination of the photovoltaic cells. The light intensity was determined by a calibrated silicon diode with KG-5 visible color filter. Current-voltage (*J-V*) curves were obtained with a Keithley 236 source meter.

Synthesis of Monomers

2,3-Bis(5-octylthiophene-2-yl)-5,7-di(thiophene-2-yl)-thieno[3,4-*b*]pyrazine (**4a**)

In a three-necked 250 mL flask equipped with a reflux condenser, argon introduction and magnetic stirrer were placed 4.33 g (9.69 mmol) of 1,2-bis-(5-octylthiophene-2-yl)ethane-1,2-dione (**2**), 2.7 g (9.69 mmol) of 3',4'-diamino[2,2',5',2'']terthiophene (**1**) and 110 mL of CHCl₃/CH₃OH (9:1). The mixture was stirred at room temperature for 48 h, after which the solvent was evaporated on a rotary evaporator. The product was purified by column chromatography on silica gel (hexane/ethyl acetate 1:1). The product was obtained as dark-green crystals. Yield 4.9 g (73%). M.p. = 110–112 °C. ¹H-NMR (CDCl₃, 400 MHz, δ): 7.60 (d, J = 3.2 Hz, 2H), 7.37 (d, J = 5.0 Hz, 2H), 7.25 (d, J = 3.6 Hz, 2H), 7.09 (t, J = 4.4 Hz, 2H), 6.68 (d, J = 3.7 Hz, 2H), 2.87 (t, J = 7.6 Hz, 4H), 1.75 (m, 4H), 1.42–1.29 (m, 10H), 0.89 (t, J = 7.0 Hz, 6H). Elemental analysis for C₃₈H₄₄N₂S₅ (%): Found, C 66.37; H 6.51; N 3.98. Calculated, C 66.23; H 6.44; N 4.07.

3-Dodecyl-8,10-di(thiophene-2-yl)-9-thia-7,11-diazacyclopenta[*k*]fluoranthene (**4b**)

Synthesized similarly to compound **4a**, using **1** and 4-dodecylenaphthalene-1,2-dione (**3**). The product was obtained as purple crystals. Yield 4.7 g (88%). M.p. = 148–150 °C. ¹H-NMR (CDCl₃, 400 MHz, δ): 8.14 (d, J = 7.1 Hz, 1H), 8.05 (dd, J = 10.3, 8.0 Hz, 2H), 7.66 (m, 3H), 7.46 (d, J = 7.4 Hz, 1H), 7.38 (d, J = 5.2 Hz, 2H), 7.11 (dd, J = 5.1, 3.9 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H), 1.76 (m, 2H), 1.45–1.26 (m, 18H), 0.87 (t, J = 7.0 Hz, 3H). Elemental analysis for C₃₆H₃₆N₂S₃ (%): Found, C 72.81; H 6.07; N 4.63. Calculated, C 72.93; H 6.13; N 4.72.

5,7-Bis(5-bromothiophene-2-yl)-2,3-bis(5-octylthiophene-2-yl)-thieno[3,4-*b*]pyrazine (**5a**)

In a three-necked 250 mL flask equipped with a magnetic stirrer, a thermometer and input for argon were placed 0.888 g (1.57 mmol) of **4a** and 83 mL of dry chloroform. The mixture was cooled to 0 °C and 83 mL of glacial acetic acid and 0.588 g (3.3 mol) *N*-bromosuccinimide (NBS) were added. The reaction mixture was stirred under argon in the dark at room temperature for 1 h, then extracted with a saturated solution of NaHCO₃ and water several times. The organic layer was dried with MgSO₄ and evaporated on a rotary evaporator. The product was purified by column chromatography on silica gel (dichloromethane:hexane = 2:1), and obtained as dark-green crystals. Yield 2.2 g (65%). M.p. = 86–88 °C. ¹H-NMR (CDCl₃, 400 MHz, δ): 7.34–7.16 (m, 4H), 7.02–6.92 (m, 2H), 6.68 (m, 2H), 2.88 (t, J = 7.3 Hz, 4H), 1.79–1.73 (m, 4H), 1.57–1.19 (m, 20H), 0.88 (t, J = 6.6 Hz, 6H). ¹³C-NMR (CDCl₃, 100 MHz, δ): 151.29, 145.63, 139.32, 132.27, 123.15, 115.44, 106.33, 31.79, 31.39, 31.33, 30.35, 29.26, 29.16, 22.59, 14.03. Elemental analysis for C₃₈H₄₂Br₂N₂S₅ (%): Found, C 54.20; H 4.95; N 3.31. Calculated, C 53.89; H 5.00; N 3.31.

8,10-Bis(5-bromothiophene-2-yl)-3-dodecyl-9-thia-7,11-diazacyclopenta[*k*]-fluoranthene (**5b**)

Synthesized similarly to compound **5a** but using **4b** instead of **4a**. The product was obtained as dark-purple crystals. Yield 0.8 g (73%). M.p. = 163–164 °C. ¹H-NMR (C₆D₆, 400 MHz, δ): 8.00 (m, 2H), 7.42–7.07 (m, 4H), 6.82 (m, 1H), 6.40 (d, J = 6.4 Hz, 2H), 2.99 (t, J = 6.8 Hz, 2H), 1.78 (m, 2H), 1.51–1.27 (m, 18H), 0.98 (m, 3H). Elemental analysis for C₃₆H₃₄Br₂N₂S₃ (%): Found, C 57.46; H 4.57; Br 21.55; N 3.60. Calculated, C 57.60; H 4.57; Br 21.29; N 3.73. ¹³C-NMR spectrum was not given due to insufficient solubility of **5b** in the deuterio solvents.

2,7-Dibromobenzo[2,1-*b*;4,5-*b'*]dithiophene-4,5-dione (**7**)

In a two-necked 50 mL flask, equipped with a magnetic stirrer and the introduction of argon, 0.5 g (1.37 mmol) of 2,7-bis(trimethylsilyl)-benzo[2,1-*b*;4,5-*b'*] dithiophene-4,5-dione (**6**) and 10 mL of dry THF were placed, then 0.501 g (2.82 mmol) of NBS was added to a stirred solution and mass stirred at room temperature under an argon atmosphere for 24 h, then 30 mL of distilled water was added. The precipitate filtered, washed with water and ethanol. The product was recrystallized from ethanol and obtained as dark-purple crystals. Yield 0.47 g (92%). M.p. = 235–238 °C. ¹H-NMR (CDCl₃, 400 MHz, δ): 7.45 (s, 2H). Elemental analysis for C₁₀H₂Br₂O₂S₂ (%): Found, C 31.60; H 0.50; Br 42.15. Calculated, C 31.77; H 0.53; Br 42.27.

5,8-Dibromo-2-[4-(2-ethylhexyloxy)phenyl]-1H-6,7-dithia-1,3-diazatrindene (9a)

In a three-necked 25 mL flask equipped with a reflux condenser, an input for argon and a magnetic stirrer were placed 0.5 g (1.32 mmol) of **7**, 0.31 g (1.32 mmol) of 4-(2-ethylhexyloxy)benzaldehyde (**8a**), 1.02 g (13.22 mmol) of ammonium acetate and 10 mL of glacial acetic acid. The mixture was stirred at reflux under a stream of argon for 7 h. The reaction mixture was cooled to room temperature and poured into 100 mL of distilled water, and then extracted with chloroform. The extracts were washed with saturated aqueous NaCl, dried over MgSO₄ and evaporated on a rotary evaporator. The product was purified by column chromatography on silica gel (hexane/ethyl acetate = 1:1) and obtained as beige crystals. Yield 0.58 g (74%). M.p. = 202–204 °C. ¹H-NMR (CDCl₃, 400 MHz, δ): 8.07 (d, J = 8.7 Hz, 2H), 7.78 (s, 2H), 7.05 (d, J = 8.7 Hz, 2H), 3.97 (d, J = 5.6 Hz, 2H), 2.05 (m, 1H), 1.76 (m, 1H), 1.60–1.33 (m, 8H), 0.98–0.89 (m, 6H). ¹³C-NMR (CDCl₃, 100 MHz, δ): 160.79, 149.84, 148.21, 128.77, 127.67, 123.70, 123.17, 121.51, 114.89, 113.03, 70.58, 39.18, 30.34, 28.96, 23.68, 22.94, 14.00, 11.01. Elemental analysis for C₂₅H₂₄Br₂N₂S₂O (%): Found, C 50.49; H 4.00; N 4.58; Br 26.84. Calculated, C 50.68; H 4.08; N 4.73; Br 26.98.

5,8-Dibromo-2-[5-(2-ethylhexyl)thiophene-2-yl]-1H-6,7-dithia-1,3-diazatrindene (9b)

Synthesized similarly to compound **9a** starting from **7** and 5-(2-ethylhexyl)thiophene-2-carboxaldehyde **8b**. The product was obtained as yellow crystals. Yield 0.49 g (75%). M.p. = 194–195 °C. ¹H-NMR ((CD₃)₂CO, 400 MHz, δ): 9.85 (s, 1H), 7.79 (c, 2H), 7.56 (d, J = 3.6 Hz, 1H), 6.89 (d, J = 3.5 Hz, 1H), 2.84 (d, J = 6.6 Hz, 2H), 1.66 (m, 1H), 1.45–1.23 (m, 8H), 0.97–0.83 (m, 6H). ¹³C-NMR ((CD₃)₂CO, 100 MHz, δ): 148.08, 146.50, 132.21, 128.80, 127.31, 126.82, 125.47, 113.26, 112.96, 112.69, 42.41, 34.69, 33.21, 29.65, 26.33, 23.75, 14.48, 11.23. Elemental analysis for C₂₃H₂₂Br₂N₂S₃ (%): Found, C 47.18; H 3.64; N 4.48; Br 27.14. Calculated, C 47.43; H 3.81; N 4.81; Br 27.44.

Synthesis of Polymers**Polymer 1 (P-1)**

In a three-necked 25 mL flask equipped with a reflux condenser and a magnetic stirrer were placed 0.7311 g (0.8265 mmol) of 2,6-bis-(trimethylstannyl)-4,8-didodecyloxybenzo[1,2-b;4,5-b']dithiophene (**10**), 0.4764 g (0.8265 mmol) of monomer **5a** and 0.065 g (0.056 mmol) of Pd(Ph₃P)₄ under a stream of argon. Then 15 mL of dry toluene and 2 mL of dry DMF was added. The reaction mixture was stirred at 115 °C for 48 h under argon, after which 0.02 g of 2-bromothiophene and 0.02 g of 2-(tributylstannyl)thiophene were added and stirring was continued for 5 h. The mixture was then cooled to room temperature and landed in 200 mL of methanol and filtered. The polymer was dissolved in chloroform and reprecipitated in methanol, then purified by extraction with methanol, hexane, acetone in a Soxhlet apparatus and dried in a vacuum. Yield 75%. ¹H-NMR (CDCl₃, 400 MHz, δ): 8.02–6.38 (m, 10H), 4.49–4.01 (m, 4H), 3.09–2.57 (m, 4H), 2.05–0.56 (m, 76 H).

Polymer 2 (P-2)

Synthesized similarly to **P-1** using compounds **10** and **5b** as monomers. Yield 73%. ¹H-NMR (CDCl₃, 400 MHz, δ): 8.79–6.85 (m, 6H), 5.76–5.01 (m, 5H), 4.40–3.56 (m, 6H), 2.68–0.64 (m, 69H).

Polymer 3 (P-3)

Synthesized similarly to **P-1** using compounds **10** and **9a** as monomers. Yield 69%. ¹H-NMR (CDCl₃, 400 MHz, δ): 8.66–6.23 (m, 9H), 4.73–3.53 (m, 4H), 2.67–0.38 (m, 63H).

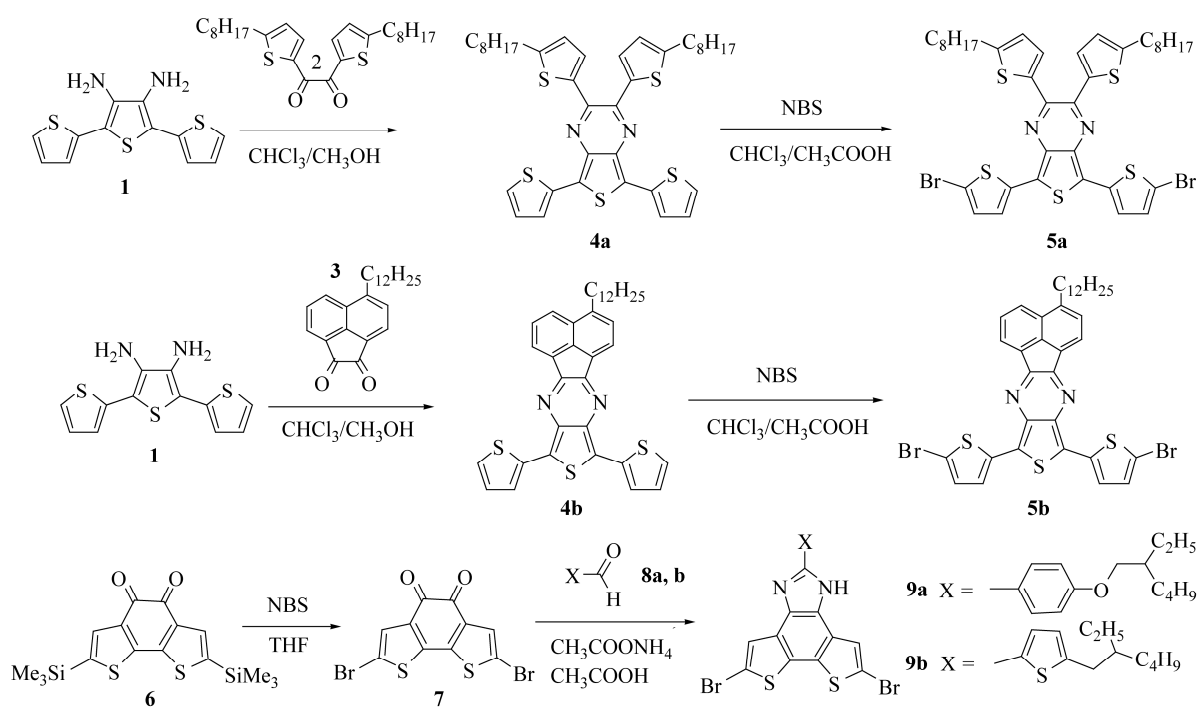
Polymer 4 (P-4)

Synthesized similarly to **P-1** using compounds **10** and **9b** as monomers. Yield 63%. ¹H-NMR (CDCl₃, 400 MHz, δ): 8.23–6.26 (m, 7H), 4.78–3.29 (m, 4H), 2.93–0.39 (m, 60H), 0.28–0.16 (m, 3H).

RESULTS AND DISCUSSION

Synthesis of the Monomers and Polymers

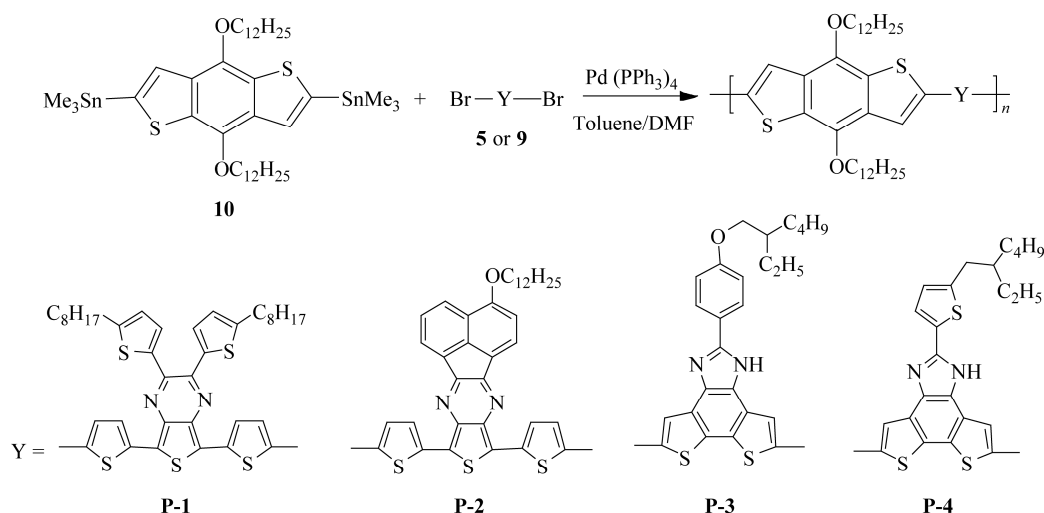
The synthesis of electron-acceptor monomers **5** and **9** is depicted in Scheme 1. For the synthesis of monomers **5a** and **5b** based on thieno[3,4-*b*]pyrazine, the reaction of the diamine **1** with diketone **2** or **3** in a mixture of CHCl_3 : CH_3OH (9:1) at room temperature yielded **4a** and **4b** in yields of 73% and 88%, respectively. This condensation method proposed by us has several advantages compared to the method described in the literature of the cyclization by boiling a mixture of diamine and diketone in acetic acid or ethanol^[27]. Mild reaction conditions allow obtaining significant yields of target compounds, excluding the formation of by-products of amino-groups oxidation at elevated temperatures. The use of volatile solvents methanol and chloroform greatly simplifies the purification of the products. Thieno[3,4-*b*]pyrazine-containing monomers **5a** and **5b** were prepared by bromination of **4a** and **4b** with NBS in a mixture of CHCl_3 : CH_3COOH (1:1). The monomers **9a** and **9b** were obtained through the adaptation and development of the method proposed in the reference^[22]. As shown in Scheme 1, 2,7-dibromobenzo[2,1-*b*;4,5-*b'*]dithiophene-4,5-dione (**7**) was prepared in a yield of 92% through treating **6** with NBS in THF under argon at room temperature. By further condensation of **7** with 4-(2-ethylhexyloxy)benzaldehyde (**8a**) or 5-(2-ethylhexyl)thiophene-2-carboxaldehyde (**8b**) in the presence of ammonium acetate in acetic acid at reflux under argon for 7 h, monomers **9a** and **9b** were obtained in yields of 74% and 75%, respectively.



Scheme 1 Synthesis of electron-deficient monomers **5** and **9**

As shown in Scheme 2, polymers **P-1**, **P-2**, **P-3** and **P-4** were synthesized by Stille polycondensation under argon in a mixture of toluene and *N,N*-dimethyl formamide (DMF) at 115 °C for 48 h by using $\text{Pd}(\text{PPh}_3)_4$ as a catalyst and 2,6-bis-(trimethylstannyl)-4,8-didodecyloxybenzo[1,2-*b*;4,5-*b'*]dithiophene (**10**) as electron-donor monomer. The resulting polymers **P-1**, **P-2**, **P-3** and **P-4** were purified by re-precipitation twice from solution in methanol and subsequent extraction with methanol, hexane and acetone. The yields of the polymers were in the range of 63%–75%. The structures of the polymers were confirmed by ^1H -NMR spectroscopy. Number-average molecular weights (M_n s) and PDIs of the polymers determined by GPC (eluent: THF; standard: polystyrene)

vary in the range 4.5–35.6 kDa and 1.59–3.94, respectively. **P-2** has low M_n and narrow PDI, which is ascribed to its low solubility in polymerization solvents. All polymers are soluble in common organic solvents such as chloroform, THF and *o*-dichlorobenzene (*o*-DCB). All the synthesized copolymers exhibit relatively high thermal stability. Temperature for 5% weight loss (T_d) of the polymers determined by TGA in argon is in the range of 309–337 °C.



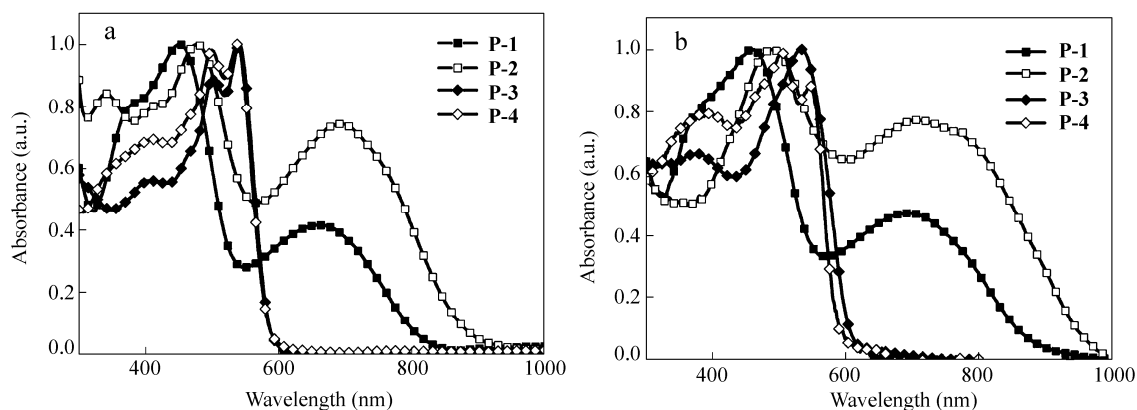
Scheme 2 Synthesis of polymers **P-1**, **P-2**, **P-3** and **P-4**.

Optical and Electrochemical Properties of the Polymers

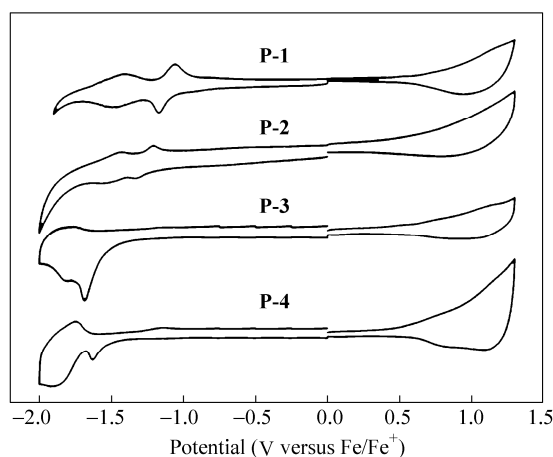
The optical properties of the polymers **P-1**, **P-2**, **P-3** and **P-4** were investigated using UV-Vis-NIR spectroscopy, and the data are presented in Table 1 and Fig. 1. The absorption spectra of the polymers **P-1** and **P-2** in the films exhibit two broad absorption bands in the regions of 400–600 and 600–900 nm, respectively. The long-wavelength bands are attributed to the charge transfer transition state in the D-A segments, which are the most important to cover the spectrum of solar radiation. Maxima of long-wavelength absorption bands of polymers have bathochromic shift in the series: **P-3** < **P-4** < **P-1** < **P-2**, indicating an increasing electron-accepting properties of the co-monomers in the sequence: **9a** < **9b** < **5a** < **5b**. Polymers **P-3** and **P-4** are characterized by the location of the maxima of absorption in a high-energy region due to the weaker electron-accepting properties of the fragments of 1H-6,7-dithia-1,3-diazatrindenes (**9a** and **9b**) in the macromolecules **P-3** and **P-4** compared with the thieno[3,4-b]pyrazine derivatives (**5a** and **5b**). Relatively poorer conjugation of the polymer backbones should also be one of the reasons of the higher band gaps of **P-3** and **P-4**. From the onsets of the film absorption spectra, the optical band gaps of **P-1**, **P-2**, **P-3** and **P-4** were calculated according to the formula $E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}^{\text{abs}}$ [24] (Table 1), which decrease in the series: **P-4** > **P-3** >> **P-1** > **P-2**, indicating an increase in the ability of the monomer to lower the energy gap (HOMO-LUMO) of polymers. As follows from the data, monomers based on the 1H-6,7-dithia-1,3-diazatrindenes **9a** and **9b** had little effect on reducing the polymers band gap as compared to homopolymer based on BDT ($E_g^{\text{opt}} = 2.2$ eV). Electron-acceptor co-monomers **5a** and **5b**, in contrast, had a significant effect on reducing E_g^{opt} of the polymers. The absorption spectra of polymers in solution (chloroform) and in the films are similar (Fig. 1), but the maxima of absorption bands in the films are bathochromic shifted, due to aggregation or the formation of π -stack structures with close packing of the macromolecules in the films.

Table 1. Number-average molecular weights (M_n s), polydispersity indices (PDIs), thermal decomposition temperatures (T_d s), optical properties and electrochemical properties of the polymers

Polymer	M_n (KDa)	PDI	T_d (°C)	$\lambda_{\max}^{\text{abs}}$ (nm)		E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	E_g^{cv} (eV)
				solution	film				
P-1	10.4	3.09	330	452, 664	460, 695	1.38	−5.17	−3.45	1.72
P-2	4.5	1.59	337	480, 692	495, 708	1.28	−4.96	−3.28	1.68
P-3	35.6	3.94	309	504, 538	535	2.03	−5.20	−3.02	2.18
P-4	23.7	2.00	317	495, 537	505, 545	2.07	−5.28	−3.01	2.28

**Fig. 1** Solution (a) and film (b) absorption spectra of the polymers **P-1**, **P-2**, **P-3** and **P-4**

The electrochemical properties of polymers **P-1**, **P-2**, **P-3** and **P-4** were examined by CV technique, and the typical CV curves are shown in Fig. 2. The redox potentials were calibrated by the ferrocene/ferrocenium (Fc/Fc^+) pair. All polymers exhibit reversible or partially reversible redox properties. The HOMO and LUMO energy levels were calculated according to the equations $\text{HOMO} = -(4.80 + E_{\text{onset}}^{\text{ox}})$ eV and $\text{LUMO} = -(4.80 + E_{\text{onset}}^{\text{re}})$ eV, in which $E_{\text{onset}}^{\text{ox}}$ and $E_{\text{onset}}^{\text{re}}$ represent oxidation and reduction onset potentials, respectively. The values of the energy band gap (E_g^{cv}) of polymers, found by cyclic voltammetry according to the equation $E_g^{\text{cv}} = (E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{re}})$ are within the range of 1.68–2.28 eV (Table 1).

**Fig. 2** Cyclic voltammograms of polymer films

The measurements were conducted in acetonitrile at a scan rate of 100 mV/s with Bu_4NPF_6 (0.1 mol/L) as electrolyte.

Photovoltaic Properties of the Polymers

PSCs were fabricated from spin-casting with *o*-DCB as solvent and PC₆₁BM as acceptor for studying the photovoltaic properties of the polymers. The weight ratio of polymer:PC₆₁BM was optimized to be 1:2. The main parameters of PSC devices are shown in Table 2, and the corresponding current density-voltage (*J-V*) characteristics are shown in Fig. 3. Photovoltaic devices exhibit short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) in the range of 1.29–3.80 mA/cm² and 0.24–0.58 V, respectively. The fill factor (FF) of solar cells based on the polymers is in the range of 20.9%–48.8%, and PCE varies in the range of 0.15%–0.80% (Table 2). Among these polymers, **P-1** exhibited the best device performance with a PCE of 0.80%. Chloroform and THF were also used as solvents for the fabrication of the PSCs of **P-1**, but PCE is lower than that using *o*-DCB as solvent.

Table 2. Device performance of the PSCs under AM 1.5G illumination at 100 mW/cm²^a

Polymer	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
P-1	0.58	3.80	36.2	0.80
P-2	0.24	1.29	48.8	0.15
P-3	0.52	2.02	31.5	0.33
P-4	0.51	2.53	20.9	0.27

^a Polymer:PC₆₁BM = 1:2 (*W/W*), the thickness of the blend films is ~60 nm.

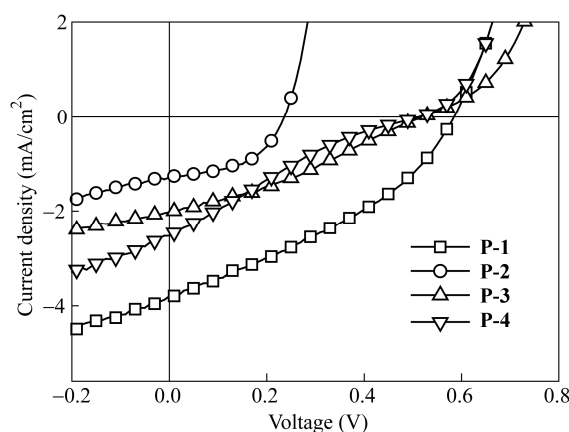
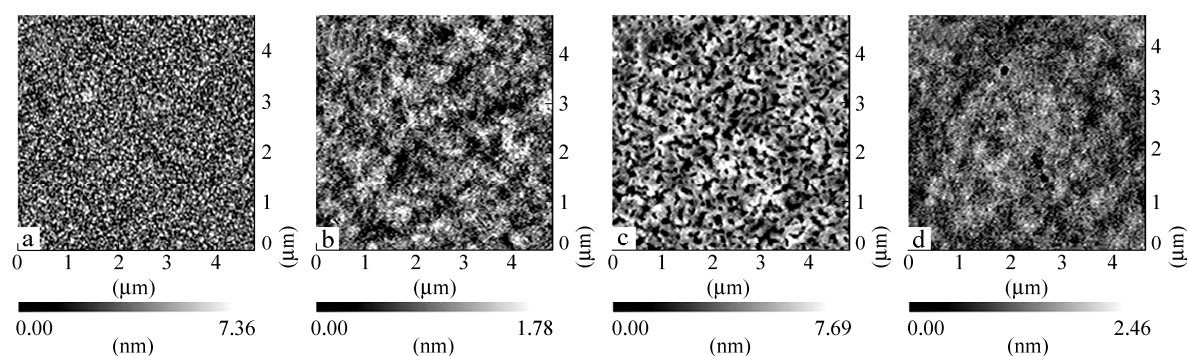


Fig. 3 *J-V* characteristics of PSCs based on the polymers **P-1**, **P-2**, **P-3** and **P-4** with polymer:PC₆₁BM of 1:2 (*W/W*).

The morphology of the active layers (polymer:PC₆₁BM) was studied by AFM in a tapping mode, and images are shown in Fig. 4. The root-mean-square (rms) roughness of the film is 1.52 nm for **P-1**, 0.39 nm for **P-2**, 2.04 nm for **P-3** and 0.44 nm for **P-4**. As shown in Fig. 4, the blend film of **P-3** showed severe phase



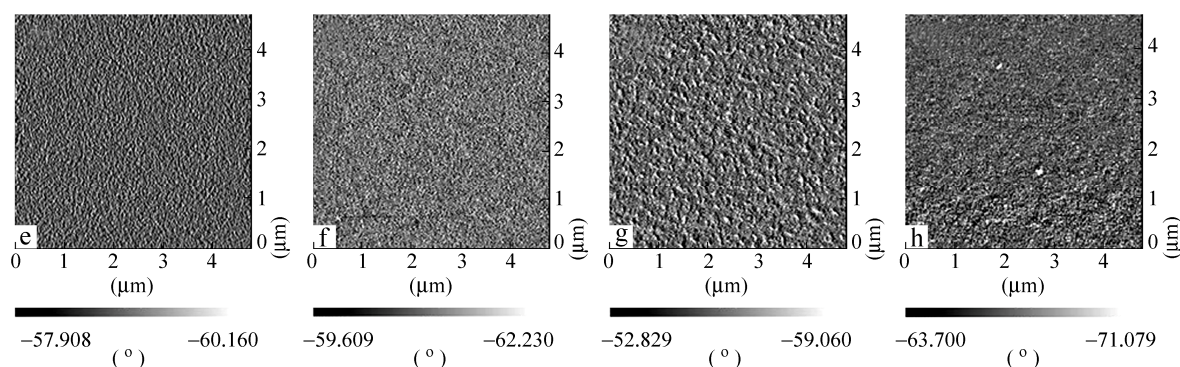


Fig. 4 AFM top (a–d) and phase (e–h) images of the polymer:PC₆₁BM (1:2 *W/W*) films for polymers **P-1** (a, e), **P-2** (b, f), **P-3** (c, g) and **P-4** (d, h)

separation with a domain size of 200–300 nm. Other three polymers all have relatively good miscibility with PC₆₁BM, as indicated by fine structures of the blend films. Therefore, the low PCEs of the PSCs based on these polymers cannot only be attributed to the poor morphology of the films. For polymers **P-1** and **P-2**, relatively low molecular weights might be a reason responsible for the low PCEs of the devices.

CONCLUSIONS

Four conjugated polymers (**P-1**, **P-2**, **P-3** and **P-4**) with benzodithiophene as donor unit and thienopyrazine or dithiadiazatrindene derivatives as acceptor unit were synthesized. The polymers based on dithiadiazatrindenes show the rather larger optical bandgaps of ~2.05 eV. In contrast, polymers with thienopyrazine derivatives as acceptor units exhibit much lower optical band gaps of 1.38 and 1.28 eV for **P-1** and **P-2**, respectively. Moreover, the absorption spectra of the polymers **P-1** and **P-2** cover the whole visible region. These results indicate that newly developed thienopyrazines are promising building blocks for design and synthesis of low band gap D-A conjugated polymers.

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