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Synthesis, characterization and photovoltaic properties of dithienobenzodithiophene-based conjugated polymers



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ABSTRACT

Two new donor-acceptor typed conjugated polymers (P1 and P2) based on the large coplanar and moreextended donor dithieno[2,3-*d*:2,3-*d*']benzo[1,2-*b*:4,5-*b*']dithiphene and thienopyrroledione (TPD) units were synthesized. P1 and P2 have the same polymer backbone, but with different side chains, where P1 has 2-ethylhexyl side chains and P2 has the longer branched 4-ethyloctyl side chains. The solubility measurements show that P2 with longer branched 4-ethyloctyl side chain has better solubility in organic solvents than that of P1. The optical, electrochemical and photovoltaic properties were investigated. P1 and P2 show the very same absorption features in both solution and film states indicating an enhanced molecular planarity of the polymer chains in P1 and P2, which benefits from the large coplanar dithieno [2,3-*d*:2,3-*d*']benzo[1,2-*b*:4,5-*b*']dithiphene unit. The band-gaps of P1 and P2 are at 1.83 eV and 1.74 eV, respectively. The solar cells with P1 or P2 as the electron donor component and PC₇₁BM as the electron acceptor were fabricated and measured under AM 1.5G illumination at 100 mW cm⁻². The results show that the P2/PC₇₁BM-based device showed a moderate power conversion efficiency of 2.86%, which is ~50% improvement in comparison with P1/PC₇₁BM-based device.

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1. Introduction

Conjugated polymer solar cells (PSCs) have been investigated intensely as the promising renewable energy source with the advantages of lightweight, low cost, flexibility and the fabrication by printing technology. The most promising and successful PSC is based on the bulk heterojunction (BHJ) photovoltaic cells, the active layer in which contains the blend of a narrow bandgap conjugated polymer (such as poly(3-hexylthiophene), (P3HT)) as the electron donor and a fullerene derivative (such as [6,6]-phenyl C₇₁-butyric acid methyl ester, $PC_{71}BM$) as the electron acceptor [1-6]. There are numerous routes to improve the BHJ photovoltaic performance by either developing the novel narrow bandgap conjugated polymers or optimizing the device processing technology. In term of the development of new conjugated polymers, the most successful strategy in achieving high photovoltaic performance is so-called the donor-acceptor (D-A) approach, where the conjugated polymer backbone consists of an electron-rich donor and an electrondeficient acceptor alternatively. One of the main topics in

* Corresponding author. *E-mail address:* yongzhang@hit.edu.cn (Y. Zhang). polymer solar cells is to develop the novel conjugated polymers with various bandgaps and energy levels and charge carrier mobilities. The recent rapid development in the performance of BHJ photovoltaic cells is also mainly benefiting from the explosion of novel conjugated polymers. Currently, the power conversion efficiencies (PCEs) of over 10% have been achieved through either developing new D-A conjugated polymers or optimizing the device processing technologies [7-11].

Among various types of the narrow bandgap conjugated polymers, the benzo[1,2-*b*:4,5-*b*']dithiophene(BDT)-based polymer is one type of the most attractive and successful polymers and shows very promising photovoltaic properties. The BDT unit was first introduced into polymer photovoltaic materials by Hou and Yu, since then, hundreds of BDT-based polymers have been synthesized and investigated in PSCs with the significant efforts from various research groups. For example, the BDT unit has be copolymerized with thieno[3,4-*b*]thiophene, thienopyrrolidinone, diketopyrrolopyrrole. The PCEs of 8–10% based on these polymers can be easily achieved [12–18]. One of the reasons for the high photovoltaic performance of BDT-based polymers is the large local dipole moment change between ground and excited states, as proved by the theoretical and experimental results, which showed a linear correlation between the dipole change and the PCE. To



increase the dipole change, one efficient way is to expand the conjugation system to delocalize the hole so as to lower the local charge density. Considering this proposition, it will be very positive for the photovoltaic performance if the BDT unit is extended with the large coplanar core and conjugation [19]. To this end, dithieno [2,3-*d*:2,3-*d*']benzo[1,2-*b*:4,5-*b*']dithiphene (DTBTD), a notable aromatic analogue of BDT, has been proposed since large aromatic acenes have shown many advantageous physical properties for improving organic photovoltaic performance. Similarly with BDTbased polymers, a few DTBTD-based polymers, which were copolymerized with DTBTD and thienothiophene units, have been reported by Hou, Yu and Yang et al., and PCEs of 3-7% with the improved charge carrier mobilities have been achieved [19-24]. More recently, Sun et al. reported a PDTBTD-based polymer with benzodithiophenedione unit as the electron-deficient unit in conjugated polymer backbone, and the conventional photovoltaic cells and all-polymer solar cells showed the PCEs of more than 9% [25-27]. These achievements demonstrate the bright and promising potential of DTBTD unit in achieving highly efficient PSCs. However, compared to the blooming development and availabilities of BDT-based polymers, the numbers of DTBTD-based polymers are still limited, and there are still a lot of opportunity for developing novel DTBTD-based polymers with promising photovoltaic performance.

Herein, we synthesized two novel DTBTD polymers (P1 and P2, Fig. 1) with a thienopyrroledione (TPD) unit as the electrondeficient acceptor. P1 and P2 have the same polymer backbone, but have different side chains, where P1 has the 2-ethylhexyl chains in DTBTD unit, and P2 has a longer branched 4-ethyloctyl chains. The side chain difference between P1 and P2 allows us to examine how the optical, electrochemical and photovoltaic properties of the polymer were influenced. P1 with the 2-ethylhexyl side chains shows a poor solubility in organic solvents which is believed to be induced by the large coplanar core in DTBTD unit. When the longer branched 4-ethyloctyl unit was introduced, P2 shows an improved solubility in organic solvents compared to P1. The optical and electrochemical properties of both polymers were also influenced by the side chains. The photovoltaic measurements show that the PCE of P2/PC71BM device was improved by ~50% compared with that of P1/PC₇₁BM device.



Fig. 1. Thermogravimetric analysis of P1 and P2.

2. Experimental

2.1. Materials and general characterization method

All reagents were purchased from commercial sources without further purification. Thieno[3,2-*b*]thiophene-3-carboxylic acid (1), 5-octylthieno[3,4-*c*]pyrrole-4,6-dione (8) and 4-ethyloctyl bromide were prepared by following literature procedures [16].

UV–Vis spectra were studied using a Perkin-Elmer Lambda-9 spectrophotometer. The ¹H NMR spectra were collected on a Bruker AV 300 or 500 spectrometer operating at 300 or 500 MHz in deuterated chloroform solution with TMS as a reference. Cyclic voltammetry of polymer films was conducted in acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate using a scan rate of 100 mV/s. ITO, Ag⁺/AgCl and Pt mesh were used as working electrode, reference electrode and counter electrode, respectively. GPC were performed on a Waters 410 differential refractometer with two columns connected in series with a THF (the mobile phase) flowing rate of 1 mL/min. Monodisperse polystyrene samples were used as the standard for the determination of molecular weight. AFM images under tapping mode were taken on a Veeco multimode AFM with a Nanoscope III controller.

2.2. Device fabrication and characterization

The PSCs were fabricated as follows: ITO-coated glass substrates (15 Ω /sq.) were cleaned with detergent, de-ionized water, acetone, and isopropyl alcohol. A thin layer (ca. 40 nm) of PEDOT:PSS (Bavtron[®] P VP AI 4083, filtered at 0.45 µm) was first spin-coated on the pre-cleaned ITO-coated glass substrates at 5000 rpm and baked at 140 °C for 10 min under ambient conditions. The substrates were then transferred into an argon-filled glove-box. Subsequently, the polymer:PC71BM active layer (ca. 100 nm) was spincoated on the PEDOT:PSS layer from a homogeneously blended solution. The solution was prepared by dissolving the polymer at a blend weight ratio of 1:3 in o-dichlorobenzene and filtered with a 0.2 µm PTFE filter. At the final stage, the substrates were pumped down to high vacuum ($<6 \times 10^{-7}$ Torr), and calcium (30 nm) topped with aluminum (100 nm) was thermally evaporated onto the active layer through shadow masks to define the active area of the devices. The un-encapsulated solar cells were tested under ambient conditions using a Keithley 2400 SMU and an Oriel Xenon lamp (450 W) with an AM1.5 filter. A mask was used to define the device illumination area of 10.08 mm² to minimize photocurrent generation from the edge of the electrodes. The light intensity was calibrated to 100 mW/cm² using a calibrated silicon solar cell with a KG5 filter, which has been previously standardized as the National Renewable Energy Laboratory.

2.3. N-(1-Ethylpropyl)-3-thieno[3,2-b]thiophene carboxamide (2)

To a solution of thieno[3,2-*b*]thiophene-3-carboxylic acid (5.3 g, 28.8 mmol) in dry dichloromethane (100 mL) was added oxyl chloride (9 mL) at 0 °C. Then, the mixture was stirred at room temperature for 4 h. After removing the solvent, the intermediate product was dissolved into dry dichloromethane (80 mL) and cooled to 0 °C before adding diethylamine (5 mL, 48 mmol) dropwise. The resulted mixture was stirred at room temperature overnight and then was poured into water. The separated organic phase was dried over Na₂SO₄. The crude product was purified through silica column using dichloromethane as eluent to give a yellow liquid. ¹H NMR (CDCl₃, ppm):7.55 (d, *J* = 1.59 Hz, 1H), 7.48 (dd, J₁ = 5.28 Hz, J₂ = 1.56 Hz, 1H), 7.27 (d, *J* = 5.28 Hz, 1H), 3.61 (q, 4H), 1.29 (t, 6H). ¹³C NMR (CDCl₃, ppm): 164.63, 140.17, 138.31, 129.22, 126.59, 119.05, 60.57, 21.24, 14.38. GC-MS (C₁₁H₁₃NOS₂): *m/z* = 238.

2.4. Benzo[1,2-b:4,5-b']dithieno[3,2-b]thiophene-4,8-dione (3)

Compound 2 (6.1 g, 25.5 mmol) was dissolved into dry THF (150 mL) and cooled to -78 °C. Then, n-BuLi (11 mL, 2.5 M in hexane, 27.5 mmol) was added dropwise to the mixture. The resulted mixture was stirring at room temperature for 12 h and then was poured into water with stirring for several hours. The product was collected by filtration as a brown solid and used in next step without further purification. ¹H NMR (CDCl₃, ppm): 7.80 (d, J = 3.12 Hz, 2H), 7.41 (d, J = 3.12 Hz, 2H). GC-MS (C₁₄H₄O₂S₄): m/z = 331.

2.5. 4,8-Bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithieno[3,2-b] thiophene (4)

Compound 3 (1.5 g, 4.5 mmol), Zn powder (0.70 g, 11 mmol) and NaOH (3 g) were charged into a 100-mL single neck flask, after adding water, the solution was heated up to reflux for 30 min. Then, the 2-ethylhexyl bromide (3 mL, 15.6 mmol) and tetrabutylaminoum bromide (0.5 g, 1.55 mmol) were added into the flask. The resulted solution was refluxed overnight. The mixture was poured into water and extracted with dichloromethane (200 mL), dried over anhydrous Na₂SO₄. After removing the solvent, the crude product was purified through silica column using hexane and dichloromethane as eluent to give the yellow oil (1.3 g, 52%). ¹H NMR (CDCl₃, ppm): 7.58 (d, J = 5.20 Hz, 2H), 7.36 (d, J = 5.20 Hz, 2H), 4.26 (d, *J* = 6.18 Hz, 4H), 2.09–2.05 (m, 2H), 1.46–1.28 (m, 16H), 1.10–0.93 (m, 12H). ¹³C NMR (CDCl₃, ppm): 143.83, 142.28, 139.65, 134.44, 129.30, 120.65, 74.05, 40.10, 32.98, 30.33, 27.69, 23.46, 14.63, 11.05. HRMS (ESI) (M⁺, C₃₀H₃₈O₂S₄): calcd, 558.1755; found, 558.1743.

2.6. 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithieno[3,2-b]thiophene (5)

To a solution of compound 4 (1.1 g, 1.97 mmol) in THF (15 mL) at -78 °C was added n-BuLi (2.1 mL, 2.4 M in hexane). After the mixture was kept at -78 °C for 1 h, trimethyltin chloride (4.7 mL, 1 M in hexane) was added. Then, the solution was stirring at room temperature overnight. The mixture was extracted with hexane after pouring into water. The organic phase was washed with water and dried over Na₂SO₄. After removing solvent, the title compound was obtained as a brown oil and used without further purification. ¹H NMR (CDCl₃, ppm): 7.36 (s, 2H), 4.24 (d, *J* = 6.09 Hz, 4H), 2.10–2.02 (m, 2H), 1.67–1.43 (m, 16H), 1.08 (t, 6H), 0.97 (t, 6H), 0.47 (s, 18H). ¹³C NMR (CDCl₃, ppm): 144.93, 141.28, 139.86, 130.3, 128.59, 120.61, 74.08, 40.22, 33.48, 30.23, 27.62, 23.26, 14.43, 11.03, -8.86. HRMS (ESI) (M⁺, C₃₀H₅₄O₂S₄Sn₂): calcd, 886.1051; found, 886.1033.

2.7. 4,8-Bis(4-ethyloctyloxy)benzo[1,2-b:4,5-b']dithieno[3,2-b] thiophene (6)

Compound 3 (0.6 g, 1.8 mmol), Zn powder (0.9 g, 13 mmol) and NaOH (1.2 g, 30 mmol) were charged into a 50 mL single neck flask, after adding water, the solution was heated up to reflux for 30 min. Then, the 4-ethyloctyl bromide (2 g, 9 mmol) and tetrabutylaminoum bromide (0.5 g) were added into the flask. The resulted solution was refluxed overnight. The mixture was poured into water and extracted with dichloromethane, dried over anhydrous Na₂SO₄. After removing the solvent, the crude product was purified through a silica column using hexane and dichloromethane as eluent to give the yellow solid (0.52 g, 47%). ¹H NMR (CDCl₃, ppm): 7.58 (d, J = 5.22 Hz, 2H), 7.36 (d, J = 5.22 Hz, 2H), 4.36 (t, J = 6.72 Hz, 4H), 2.06–2.01 (m, 4H), 1.60–1.55 (m, 4H), 1.41–1.33 (m, 20H),

 $0.95-0.90\ (m,\ 12H).\ ^{13}C\ NMR\ (CDCl_3,\ ppm):\ 143.84,\ 137.43,\ 132.17,\ 129.59,\ 125.50,\ 120.14,\ 74.02,\ 38.90,\ 32.99,\ 29.59,\ 29.16,\ 28.03,\ 26.06,\ 23.36,\ 14.38,\ 11.10.\ HRMS\ (ESI)\ (M^+,\ C_{34}H_{46}O_2S_4):\ calcd,\ 614.2381;\ found,\ 614.2374.$

2.8. 2,6-Bis(trimethyltin)-4,8-bis(4-ethyloctyloxy)benzo[1,2-b:4,5-b']dithieno[3,2-b]thiophene (7)

To a solution of compound 6 (0.3 g, 0.49 mmol) in THF (10 mL) at -78 °C was added n-BuLi (0.4 mL, 2.5 M). After the mixture was kept at -78 °C for 1 h, trimethyltin chloride (1.2 mL, 1 M in hexane) was added. Then, the solution was stirring at room temperature overnight. The mixture was extracted with hexane after pouring into water. The organic phase was washed with water and dried over Na₂SO₄. After removing solvent, the title compound was obtained as a brown oil and used without further purification. ¹H NMR (CDCl₃, ppm): 7.36 (s, 2H), 4.35 (t, *J* = 6.75 Hz, 4H), 2.04 (m, 4H), 1.61 (m, 4H), 1.44–1.27 (m, 18H), 0.95–0.88 (m, 12H), 0.47 (s, 18H). ¹³C NMR(CDCl₃, ppm) 145.01, 139.28, 130.21, 127.45, 125.38, 120.01, 74.02, 39.30, 32.78, 29.57, 29.14, 28.05, 26.09, 23.30, 14.35, 11.03, -8.80. HRMS (ESI) (M⁺, C₄₀H₆₂O₂S₄Sn₂): calcd, 942.1677; found, 942.1695.

2.9. 5-(2-Ethylhexyl)thieno[3,4-c]pyrrole-4,6-dione

To a solution of thiophene-3,4-dicarboxylic anhydride (0.60 g, 3.90 mmol) in toluene (20 mL) was added 2-ethylhexylamine (0.70 g, 5.42 mmol). The mixture was refluxed overnight. Then, the solvent was removed under vacuum after cooling to room temperature. The resulted crude was used in next step without further purification. A solution of this crude product was refluxed in thionyl chloride (20 mL) for 4 h. The solvent was removed under vacuum and the resulted yellow solid was further purified by silica column to give the title compound as white solid with 60% yield. FTIR (KBr) ν/cm^{-1} 3080, 2922, 1693, 1513, 1354, 1096, 944, 734, 572. ¹H NMR (CDCl₃, ppm): 7.82 (s, 2H), 3.53 (d, *J* = 7.32 Hz, 2H), 1.83–1.78 (m, 1H), 1.38–1.27 (m, 8H), 0.95–0.91 (m, 6H). ¹³C NMR (CDCl₃, ppm): 163.10, 136.75, 125.61, 42.49, 38.29, 30.61, 28.61, 23.94, 23.16, 14.22, 10.55. HRMS (ESI) (M⁺, C₁₄H₁₉NO₂S): calcd, 265.1136; found, 265.1134.

2.10. 1,3-Dibromo-5-(2-ethylhexyl)thieno[3,4-c]pyrrole-4,6-dione (8)

To a solution of the 5-(2-ethylhexyl)thieno[3,4-*c*]pyrrole-4,6dione (0.50 g, 1.88 mmol) in trifluoroacetic acid (5 mL) and conc. H₂SO₄ (2 mL) was added NBS (1.10 g, 6.18 mmol) in portions. The mixture was stirred at room temperature overnight. Then, water was added and the mixture was extracted with dichloromethane twice. The organic phase was dried over Na₂SO₄. After removing solvent under vacuum, the crude product was purified by silica column to give the title compound as white powder with 75% yield. Mp: 104 °C. FTIR (KBr) ν/cm^{-1} 2956, 2929, 1697, 1535, 1388, 1054, 958,746, 680. ¹H NMR (CDCl₃, ppm): 3.52 (d, *J* = 7.14 Hz, 2H), 1.81–1.77 (m, 1H), 1.38–1.29 (m, 8H), 0.94–0.92 (m, 6H). ¹³C NMR (CDCl₃, ppm): 160.87, 134.90, 113.13, 42.81, 38.36, 30.69, 28.72, 24.00, 23.13, 14.26, 10.55. HRMS (ESI) (M⁺, C₁₄H₁₇Br₂NO₂S): calcd, 420.9347; found, 420.9341.

Polymer P1. Compound 5 (290 mg, 0.33 mmol) and 8 (135 mg, 0.32 mmol) were charged into a 25 mL round bottom flask with a condenser under N₂ protection. After degassing twice, dry toluene (4 mL), DMF (0.5 mL) and Pd(PPh₃)₄ (5 mg) were added into the flask consequently. The resulting mixture was further degassed twice and heated to 120 °C for 24 h. After cooling to room temperature, the mixture was poured into methanol. The precipitate

was collected and washed with acetone for 24 h with a Soxhlet apparatus. The fraction was extracted by chloroform and precipitated into methanol again. The black solid was collected and dried overnight under vacuum (215 mg, 82%). FTIR (KBr) ν/cm^{-1} 2923, 2856, 1742, 1698, 1536, 1349, 1065, 748. $M_n = 14.5$ k, $M_w = 28.2$ k, PDI = 1.94.

Polymer P2. Polymer P2 was synthesized by following the similar procedure with polymer P1. FTIR (KBr) ν/cm^{-1} 2920, 2853, 1695, 1538, 1351, 1006, 748. M_n = 24.5 k, M_w = 32.1 k, PDI = 1.31.

3. Discussion

3.1. Synthesis

It is known that the branched alkyl chain can provide better solubility than the straight alkyl chain [28]. 2-Ethylhexyl (EH) is one of the best selections as the polymer side chain in order to improve the solubility of the polymer. However, the EH side chains are still not sufficient to provide the good solubility required for the resulting polymer and a longer branched alkyl chain is sometimes required. The chemical structures of P1 and P2 were shown in Scheme 1. For P1, the 2-ethylhexyl side chain in the DTBTD unit was introduced, whereas a longer branched 4-ethyloctyl (EO) side chain was selected in P2. The longer branched EO side chain in P2 is expected to improve the solubility with less steric interactions close to the polymer backbone. Scheme 1 shows the synthetic routes to the monomers and polymers. The key intermediate compound dithieno[2,3-d;2,3-d']benzo[1,2-b;4,5-b']dithiphene (3) was synthesized from thieno[2.3-d]thiophene-3-carboxylic acid (1) via two steps. The alkylation of compound **3** using 2-ethylhexyl bromide under basic condition gave compound 4 according to the reported method in literature [15]. The distannyl compound 5 was prepared from **4** by lithiation with *n*-butyllithium followed by quenching using trimethyltin chloride. The longer branched 4-ethyloctyl bromide derivative was synthesized in a similar manner. Thus alkylation of compound 3 using 4-ethyoctyl bromide provided compound 6 using a similar method of compound 4. Similarly, the distannyl compound 7 from 6 was also synthesized. The thienopyrroledione (8) was prepared by previous reported method [16].

Polymer **P1** and **P2** were synthesized *via* a palladium-catalyzed Stille cross-coupling reaction from **5**, **7** and **8**, respectively [29]. After polymerization, the polymers were collected by precipitating into methanol, and then were purified by Soxhlet extraction with acetone and hexane. The polymer solubility was measured in



Scheme 1. Synthetic routes of monomers and polymers.

organic solvents. P1 has limited solubility in chloroform, and can only be easily dissolved into hot chlorinated solvents, such as chlorobenzene and o-dichlorobenzene. However, P2 shows a better solubility in organic solvents, which is believed to due to the longer branched EO side chains in P2 compared to that of P1. P2 can easily dissolve into chlorobenzene and o-dichlorobenzene, etc. The molecular weights of P1 and P2 were measured by gel permeation chromatography (GPC) using dichlorobenzene as the eluent and polystyrene as the standard. The number-average molecular weights (M_n) of P1 and P2 were 14.5 and 24.5 kDa with a polydispersity index (PDI) of 1.94 and 1.31, respectively. The thermal properties of P1 and P2 were investigated by thermogravimetric analysis (TGA) under a nitrogen atmosphere at a heating rate of 10 °C/min. As shown in Fig. 1, P1 and P2 exhibited a good thermal stability with the decomposition temperature of ~330 °C at the weight loss of >5%.

4. Optical properties

The UV–Vis absorption spectra of P1 and P2 were measured in dilute *o*-dichlorobenzene (DCB) solution and thin film states. As shown in Fig. 2, P1 and P2 exhibited the main absorption spectrum in wavelength range of 350–700 nm. The absorption spectra in solution and film states for P1 and P2 featured two absorption bands: one band in the range of 350–455 nm that was ascribed to the localized π - π * transitions, and the other band with the



Fig. 2. The UV–Vis spectra of P1 and P2 in diluted *o*-dichlorobenzene solution (a) and thin film (b).

vibrionic shoulder in the range of 500-700 nm, which was attributed to intramolecular charge transfer (ICT) peak between the electron-rich donor (DTBTD) and electron-deficient acceptor (TPD) units. In solution, the absorption peak for P1 is at 550 nm with a shoulder at 596 nm, and the absorption peak in film state for P1 is kept almost same with that in solution. The peaks of P2 in solution and film states are at 565 nm and 561 nm, respectively, with a shoulder of ~600 nm. It is interesting that the absorption peaks of P2 in both solution and film states have ~10-15 nm redshift in comparison with that of P1. In the film state, the longer conjugation length will be kept when the film was processing from P2 solution. As it can be seen from Fig. 1, P1 and P2 show the very same absorption features in both solution and film states, which is benefited from the large coplanar DTBTD unit, indicating an enhanced molecular planarity of the polymer chains in P1 and P2 due to intermolecular interactions in the solid state. The optical band-gaps of P1 and P2 are estimated from the onset of absorption in films. The onset of absorption for P1 and P2 in film states are ~678 nm and ~713 nm, corresponding to the optical band-gaps of 1.83 eV and 1.74 eV, respectively. Considering the same conjugated backbone structures in P1 and P2, it can find that the nonconjugated polymer side chain also plays a certain effect on the optical properties by improving the solubility, steric hindrance and polymer backbone stacking [18,30–32].

5. Electrochemical properties

The electrochemical behaviors of the polymers were investigated by cyclic voltammograms (CV). The HOMO and LUMO energy levels of P1 and P2 were calculated from the onset potential of the 1st oxidation and reduction peaks by using the following equation, where ferrocene was used as an internal reference. [33,34].

 $HOMO = -[E_{ox} - E_{ferrocene} + 4.80] \text{ eV}$

 $LUMO = -[E_{red} - E_{ferrocene} + 4.80] \text{ eV}$

Fig. 3 shows the CV curves of both P1 and P2. The detailed measurement is shown in the experimental section. The oxidation peaks of P1 and P2 are located at 0.74 V and 0.87 V, respectively, with good reversible curves. The reduction peaks are at -1.01 V



Fig. 3. The CV curves of P1 and P2.

and -0.99 V for P1 and P2, respectively. The HOMO and LUMO energy levels of P1 were determined to be -5.14 eV and -3.39 eV, respectively, and the HOMO and LUMO energy levels of P2 were calculated to be at -5.27 eV and -3.41 eV, respectively. Considering polymer P1 and P2 possess the same conjugated backbone but different side chains, it is therefore expected that the HOMO and LUMO energy levels of both polymers would be similar because the molecular orbital of the conjugated polymer is only delocalized across the conjugated backbone and the side chain has little effect on the molecular orbital. So the slight difference on the HOMO energy levels between P1 and P2 should be ascribed to the side chain effect, which may have the different Coulombic interactions between the polycationic chains and the anions as the different alkyl chain [35]. The LUMO energy levels are almost same for P1 and P2. In addition, the LUMO level of $PC_{71}BM$ is at -3.80 eV, the offset between the LUMOs of donor P1/P2 and PC71BM should be able to provide an enough driving force for efficient exciton dissociation, and thus energetically favorable electron transfer should be expected.

The electronic structures and HOMO/LUMO energy levels of P1 and P2 were carried out by performing density functional theory (DFT) calculations at B3LYP/6-31G(d) level of Gaussian 09 [36]. To simplify the calculation, the side chains (ethylhexyl and ethyloctyl for P1 and P2, respectively) were replaced with methyl groups during calculation. Fig. 4 shows frontier molecular orbitals obtained from DFT calculation with optimized geometries. Since P1 and P2 have the same conjugated backbone, the frontier molecular orbital for P1 and P2 are identical. As shown in Fig. 4, both the electron wave functions of HOMO and LUMO for P1 and P2 were delocalized entirely over the electron-donating and electron-accepting units. The HOMO was predominantly distributed over the electrondonating unit and the electron density of the LUMO was located mainly on the electron-accepting unit, although some of electron density of LUMO was also delocalized on the electron-donating unit (vice versa). This electron delocalization of the HOMO and LUMO are very similar to those of other benzodithiophene-based polymers [37,38]. The calculated HOMO and LUMO energy levels are at -5.20 eV and -2.65 eV, respectively, for both P1 and P2.

6. Photovoltaic properties

The photovoltaic properties of the polymers were investigated by fabricating bulk heterojunction solar cells with the device structure of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. The active



Fig. 4. The HOMO/LUMO wave function of P1/P2 obtained from DFT calculations.



Fig. 5. The J-V (a) and EQE (b) curves of P1/PC71BM and P2/PC71BM devices.

layer was spin-cast from a solution of the polymer:PC71BM mixtures in o-dichlorobenzene. The photovoltaic performances of the photovoltaic cells were measured under simulated AM 1.5G 1 sun illumination (100 mW/cm²). Details of the fabrication is shown in the experimental section. Fig. 5a shows the J-V curves of P1/PC71BM and P2/PC71BM devices and the characteristic device data are summarized in Table 1. The P1/PC₇₁BM device showed a V_{oc} of 0.77 V, a short-circuit current density (J_{sc}) of 6.22 mA cm⁻², and a fill factor (FF) of 0.40, corresponding to a PCE of 1.92% (Table 1). P2/ PC₇₁BM device gave a better PCE of 2.86% with a V_{oc} of 0.75 V, a J_{sc} of 7.30 mA cm^{-2} and a FF of 0.52 (Table 1), benefiting from the improved J_{sc} and FF. It is well known that the V_{oc} of the device is largely dependent on the offset between the HOMO energy level of polymer donor and the LUMO energy level of PC₇₁BM acceptor [39]. Since the HOMO energy levels of P1 and P2 are very similar, therefore a similar Voc for P1/PC71BM and P2/PC71BM devices are expected. The slight difference between their Vocs is because of other factors such as interface resistance and excition nonradiative

Table 1The device performances of P1 and P2.

Polymer/PC71BM	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
P1/PC ₇₁ BM	0.77	6.22	0.40	1.92
P2/PC ₇₁ BM	0.75	7.30	0.52	2.86



Fig. 6. The AFM images of P1/PC71BM and P2/PC71BM blend films.

recombination [40-43].

Fig. 5b shows the external quantum efficiencies (EQEs) of P1 and P2 devices. As shown in Fig. 5b, P1/PC₇₁BM device shows a low photoresponse in all wavelength region, EQE values of P1 device are less than 40% over the range of 350 nm–750 nm. By contrast, the EQEs of P2 device are beyond 40% from 350 nm to 600 nm. It is known that the important contribution to the J_{sc} in solar cell is the photon absorption under sunlight of the polymer/PCBM. The EQE spectra of the device mainly reflected the photon absorption properties of each polymer/PCBM blend. The EQE results indicate that P2/PC₇₁MB device has better photon absorption than that of P1/PC₇₁MB device. The EQE values are in line with a lower J_{sc} for P1/PC₇₁MB device and a higher J_{sc} for P2/PC₇₁MB device, indicating the accuracy of the measurements.

In order to gain insight into the surface morphology of polymer and PC₇₁BM blend, atomic force microscopy (AFM) were carried out. As shown in Fig. 6, it can be found that P1/PC₇₁BM blend film has a larger roughness than that of P2/PC₇₁BM, and also a more uniform blend film with more evenly distributed domains was also found in P2/PC₇₁BM. It is known that the smooth morphology of a film may be more favorable to the bicontinuous, interpenetrating networks, which is required for the efficient charge separation and transport in polymer solar cell [44]. Considering the structural difference between P1 and P2, it is believed that the better solubility from the longer branched alkyl chains will make P2 have a better miscibility with fullerene, and therefore producing a smoother blend film and partially contributing to the higher current density and FF in P2/PC₇₁BM device.

7. Conclusion

We have designed and synthesized two new donor-acceptor type conjugated polymers (P1 and P2) based on the large coplanar and more-extended donor dithieno[2,3-*d*:2',3'-*d*']benzo [1,2-*b*:4,5-*b*']dithiphene and thienopyrroledione units *via* Stille polymerization. P1 and P2 have the same polymer backbone, but have different side chains. P1 has the 2-ethylhexyl side chain and P2 has the longer branched 4-ethyoctyl side chain. The results from the solubility measurements show that P2 with longer branched 4-ethyloctyl side chain has a better solubility in organic solvents than that of P1. The optical measurement shows that P1 and P2 showed strong π - π stacking as a result of the large coplanar DTBTD donor unit in P1 and P2 backbone. The band-gaps of P1 and P2 are

measured at 1.83 eV and 1.74 eV, respectively, the difference is ascribed to the effect of different side chain. The HOMO and LUMO energy levels of P1 and P2 were measured to be at -5.14 eV to -5.27 eV and -3.39 eV to -3.41 eV, respectively. The photovoltaic cells with P1 or P2 as the electron donor and PC₇₁BM as the electron acceptor were fabricated and measured under AM 1.5G illumination at 100 mW/cm². The P2/PC₇₁BM-based solar cell showed a PCE of 2.86%, which is ~50% improvement in comparison with that of P1/PC₇₁BM-based solar cell. These results indicate the promising potential of dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-b'] dithiphene unit for high efficient polymer solar cells, and also show the importance of the longer branched alkyl chains in solution processing, the miscibility of polymer/fullerene and photovoltaic performance.

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