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Highly π -extended polymers based on phenanthro-pyrazine: Synthesis, characterization, theoretical calculation and photovoltaic properties

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1. Introduction

The study of narrow bandgap conjugated polymers is an evergrowing research field because of their great promise in application such as polymer solar cells through convenient solutionprocessable method to solve the impending energy crisis [1–4]. Comparing to their inorganic counterparts, soluble polymer semiconductors are generally packed poorly and show low level of order, which leads to the low mobility and power conversion efficiency in photovoltaic devices [5]. Thus, the strategy that generally be applied to design and synthesis conjugated polymers with narrow bandgap includes creating highly planar structure, strengthening the intermolecular interactions, enhancing their molecular orbital overlapping, and using donor-acceptor effects [6–9]. Among many of the building blocks for narrow bandgap organic materials, heterocyclic aromatic units usually provide tendency to form large orbital overlapping and strong intermolecular interaction [10–12]. Recently, dithiophen-thieno[3,4-b] pyrazine [13-15] and dithiophen-quinoxaline moieties [16-18]

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ABSTRACT

Two novel narrow bandgap conjugated polymers containing phenanthro-pyrazine unit have been successfully synthesized by the Stille coupling reaction. Comparing to the common polymers containing dithiophen-quinoxaline or dithiophen-thieno[3,4-b]pyrazine moiety, the conjugation degree of these new polymers is extended through the direction perpendicular to the main chain by introducing phenanthrene-9,10-dione to maintain a rigid conjugated bridge. The obtained polymers exhibit solutionprocessing ability, high thermal stabilities, broad visible absorption bands and narrow optical bandgaps. Theoretical studies disclose that the P2 exhibits wholly coplanar conformation in 1-D and 2-D direction, and the PCE value is 6-folded higher than P1 under the same photovoltaic measurement condition.

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have attracted tremendous interest in the design and synthesis of organic narrow bandgap materials. By rational design of monomers and choosing the suitable polymerization method, kinds of novel polymers are prepared and perform high PCE on account of the intermolecular $\pi - \pi$ stacking and intramolecular charge transfer in D-A system [19,20]. In these works, the dithiophene group in the polymer main chain can be applied as a bridge and the formation of hydrogen bonds between the nitro atoms (in thieno[3,4-b]pyrazine (N-H) or quinoxaline (N-H)) and β -hydrogen atoms (in one or two neighboring thiophene rings (S–H)), can minimize the dihedral angle and strengthen planarity along the main chain direction (1-D conjugation), resulting in strong intramolecular interaction to achieve planar structure (Scheme 1) [21].

In the expectation of broadening the absorption spectra and extending the coplanarity to further promote the intermolecular $\pi - \pi$ stacking of these polymers to get narrow bandgap materials, here, we attempted to extend the 2-dimensional conjugation degree by attaching rigid π -conjugated moieties perpendicular to dithiophen-thieno[3,4-b]pyrazine or dithiophen-quinoxalin unit [22-25]. Phenanthrene-9,10-dione (PQ) was chosen as a basic constructing unit, which could react with diamino monomer to maintain a rigid conjugated bridge and develop the 2-dimensional conjugated polymers [26,27]. The newly formed phenanthropyrazine ring could ensure nearly all atoms be in one plane [28].







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Scheme 1. The structures of dithiophen-thieno[3,4-b]pyrazine, dithiophen-quinoxaline and phenanthro-pyrazine.

In addition, the intermolecular interaction between the electrondonating thiophene unit and electron-accepting phenanthro-pyrazine unit could shorten the distance between the polymer chains to form a higher level of packing order, which would facilitate the charge or carrier transport along the 2-dimensional region. What's more, conceiving the solution processability of the polymer, the dihexyl-fluorene moiety was attached to the 3,6-position of PQ unit, which showed the V-shape conformation and reduced the polymerization steric hindrance to some extent [29,30], and tuned the HOMO level of the polymers [31,32]. The dihexyl-fluorene moiety could simultaneously broaden the absorption spectrum. Here, we report the synthesis and characterization of two new solution-processable narrow bandgap materials, and their primary photovoltaic application.

2. Experimental part

2.1. Materials and measurement

All the reagents and solvents used for the syntheses were purchased from Aldrich or Acros companies and used without further purification. The polymers were collected after Soxhlet extractions with methanol, acetone and n-hexane for 12 h, respectively. All reactions were performed under a dry nitrogen atmosphere.

The ¹H NMR and spectra were recorded on AVANCZ 500 spectrometers at 298 K by utilizing deuterated chloroform (CDCl₃) or dimethyl sulphoxide (DMSO) as solvent and tetramethylsilane (TMS) as standard. The elemental analysis was operated by Flash EA 1112, CHNS-O elemental analysis instrument. The MALDI-TOF mass spectra were recorded using an AXIMA-CFR™ plus instrument. Uvvis absorption spectra were recorded on UV-3100 spectrophotometer. Fluorescence measurements were carried out with RF-5301PC. The differential scanning calorimeter (DSC) analysis was determined using a NETZSCH (DSC-204) instrument at 10 °C/min under nitrogen flushing. Cyclic voltammetry (CV) were performed with a BAS 100W Bioanalytical Systems, using a glass carbon disk $(\Phi = 3 \text{ mm})$ as working electrode, a platinum wire as auxiliary electrode and Ag/Ag⁺ as reference electrode. Cyclic voltammetric studies were carried out containing 0.1 M [n-NBu₄][BF₄] as supporting electrolyte. All solutions were purged with nitrogen stream for 10 min before measurement.

2.2. OPV cells fabrication and measurements

The BHJ solar cells were fabricated with the active layer consisting of the Polymer:PCBM with blend ratios (1:1, w/w). ITO glass was cleaned by detergent, acetone and boiled in H₂O₂. A 50 nm layer of poly(3,4-ethylene dioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Bayer PVP AI 4083) as a modified layer was spin-coated onto the pre-cleaned ITO glass substrate and then dried at 120 °C for 15 min on a hot plate. The polymer was dissolved in chlorobenzene to make 10 mg mL⁻¹ solutions, followed by blending with PCBM (purchased from Lumtec. Corp) in blend ratios (1:1, w/w). The active layers were obtained by spin-coating the blend solutions and the thickness of films were about 70 nm, as measured with the Ambios Technology XP-2. Finally, the cathode of LiF (0.5 nm)/Al (100 nm) was thermally deposited to finish the device fabrication. The active area was about 5 mm². Current–voltage (J–V) characteristics were recorded using a Keithley 2400 Source Meter in the dark and under 100 mW cm⁻² simulated AM 1.5 G irradiation (Sciencetech SS-0.5 K Solar Simulator). The spectral response was recorded by a SR830 lock-in amplifier under short circuit conditions when devices were illuminated with a monochromatic light from a Xeon lamp. All fabrication and characterizations were performed under ambient atmosphere at room temperature.

2.3. Synthesis of monomers and polymers

2.3.1. M1

3,6-dibromophenanthrene-9,10-dione (366 mg, 1 mmol), 2-(9,9dihexyl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxabo-rolane (1.15 g, 2.5 mmol) and 23.1 mg Pd(PPh₃)₄ (1% mol) were added in the mixture of 10 mL toluene and 2 mL 2.0 M K₂CO₃, and then the mixture was stirred at 85 °C under the N₂ atmosphere for 24 h. The reaction was stopped by adding water, and the product was extracted by CHCl₃ three times. After dried over MgSO₄, the solvent was removed by rotary evaporation. The product was purified by column chromatography using mixture of CHCl₃ and petroleum ether as the eluent to give the white solid. Yield: 75%. ¹H NMR (500 MHz, CDCl₃, δ): 8.39 (s, 2H), 8.35–8.33 (d, 2H, J = 8.24 Hz), 7.85–7.83 (d, 2H, J = 8.2 Hz), 7.79–7.76 (t, 4H, J = 7.6, 6.7 Hz), 7.34–7.72 (d, 2H, J = 7.9 Hz), 7.66 (s, 2H), 7.40–7.36 (m, 6H), 2.08–2.03 (m, 8H), 1.46– 1.00 (m, 24H), 0.75–0.65 (m, 20H); MALDI-TOF-MS (m/z): [M + H]⁺ calcd for C₆₄H₇₂O₂: 872.5; Found: 873.6; Anal. Calcd. for C₆₄H₇₂O₂: C, 88.03; H, 8.31; O, 3.66; Found: C, 88.00; H, 8.27; N, 3.65.

2.3.2. M2

4,7-dibromobenzo[c][1,2,5]thiadiazole (1.32 g, 4.5 mmol), 2-(thiophen-2-yl)-1,3,2-dioxaborinane (1.68 g, 10 mmol) and 23.1 mg Pd(PPh₃)₄ (1% mol) were added in the mixture of 30 mL toluene and 6 mL 2.0 M K₂CO₃, and then the mixture was stirred at 85 °C under the N₂ atmosphere for 48 h. The reaction was stopped by adding 20 mL water, and the product was extracted by CHCl₃ three times. After dried over MgSO₄, the solvent was removed by rotary evaporation. The product was preliminary purified by column chromatography using petroleum ether as the eluent to give the red solid. Yield: 85%. ¹H NMR (500 MHz, CDCl₃, δ): 8.13 (d, *J* = 3.6, 1.2 Hz, 2H), 7.89 (s, 2H), 7.47 (d, *J* = 5.1, 1.2 Hz, 2H), 7.22 (t, *J* = 5.1, 3.6, 1.2 Hz, 2H).

2.3.3. M3

M2 (300 mg, 1.0 mmol) and Fe powder (1.3 g, 20 mmol) were put into the two-neck bottle, and the 50 mL ice acetate was added. The

mixture was refluxed for 30 min. When the color of the liquid was changed from orange to white, the reaction was stopped. The product does not need to be purified and used as the starting material to synthesize M6.

2.3.4. M4

Tributyl(thiophen-2-yl)stannane (3.73 g, 10 mmol), 2,5-dibromo-3,4-dinitrothiophene (1.1 g, 3.33 mmol) and 77 mg Pd(PPh₃)₄ (1% mol) were put into the two-neck bottle, and the 100 mL toluene was added. The mixture was refluxed for 24 h under N₂ atmosphere. And then the reaction was stopped and cooled to room temperature. The mixture was first purified by column chromatography using THF as the eluent to get orange liquid. And then it was concentrated and purified by column chromatography using petroleum ether as the eluent to get orange solid. Yield: 80%. ¹H NMR (500 MHz, CDCl₃, δ): 7.61–7.60 (dd, 2H, *J* = 5.1, 1.2 Hz), 7.55–7.54 (dd, 2H, *J* = 3.6, 1.2 Hz), 7.19–7.17 (d, 2H, *J* = 5.1, 3.6, 1.2 Hz); MALDI-TOF-MS (*m*/*z*): [M + H]⁺ calcd for C₁₂H₆N₂O₄S₃: 338.0; Found: 339.6; Anal. Calcd. for C₁₂H₆N₂O₄S₃: C, 42.59; H, 1.79; N, 8.28; S, 28.43; Found: C, 42.03; H, 1.68; N, 8.10; S, 28.23.

2.3.5. M5

Under the N_2 atmosphere, M4 (670 g, 2.0 mmol), SnCl₂ (3.8 g, 20 mmol) and HCl (3 mL) were dissolved in 10 mL acetate ether. The mixture was refluxed for 24 h and then poured into water. The product was extracted by acetate ether and 2% NaOH solution. The solvent was removed by rotary evaporation and the concentrated red oil was used directly in the next step to synthesize M8.

2.3.6. M6

M1 (440 mg, 0.5 mmol) and M3 were added to the solution of acetate and refluxed for 12 h at 80 °C. The mixture was then put into the 500 mL methanol, the solid was occurred and filtrated. The product was purified by the column chromatography using petroleum ether as the eluent to give the orange solid. Yield: 95%. ¹H NMR (500 MHz, CDCl₃, δ): 9.62 (s, 2H), 8.91 (s, 2H), 8.24 (s, 2H), 8.13–8.11 (d, 2H, *J* = 8.24 Hz), 7.94 (s, 2H), 7.88–7.85 (m, 4H), 7.81–7.78 (m, 4H), 7.68–7.67 (d, 2H, *J* = 7.9 Hz), 7.62–7.34 (m, 6H), 7.30–7.29 (m, 2H), 2.14–2.04 (m, 8H), 1.26–1.23 (m, 4H), 1.15–1.05 (m, 24H), 0.77–0.72 (m, 20H); MALDI-TOF-MS (*m*/*z*): [M + H]⁺ calcd for C₇₉H₈₂N₂S₂: 1123.6; Found: 1124.4; Anal. Calcd. for C₇₉H₈₂N₂S₂: C, 84.44; H, 7.36; N, 2.49; S, 5.71; Found: C, 83.24; H, 7.06; N, 2.31; S, 5.55.

2.3.7. M7

M6 (480 mg, 0.43 mmol) and NBS (180 mg, 1.0 mmol) were dissolved in 40 mL THF, and the mixture was refluxed for 2 h. The mixture was stopped by pouring into 500 mL methanol. And the deep red solid occurred and filtrated. The product was purified by the column chromatography using petroleum ether as the eluent to give the deep red solid. Yield: 90%. ¹H NMR (500 MHz, CDCl₃, δ): 9.52–9.50 (d, 2H, *J* = 8.24 Hz), 8.90 (s, 2H), 8.14–8.12 (d, 2H, *J* = 8.24), 8.08 (s, 2H), 7.89–7.84 (m, 8H), 7.58 (s, 2H), 7.42–7.35 (m, 6H), 7.20–7.19 (d, 2H, *J* = 4.9 Hz), 2.17–2.06 (m, 8H), 1.18–1.06 (m, 24H), 0.81–0.72 (m, 20H); MALDI-TOF-MS (*m*/*z*): [M + H]⁺ calcd for C₇₈H₇₈Br₂N₂S₂: 1264.4; Found: 1267.7; Anal. Calcd. for C₇₈H₇₈Br₂N₂S₂: C, 73.92; H, 6.20; N, 2.21; S, 5.06; Found: C, 73.62; H, 6.18; N, 2.18; S, 5.00.

2.3.8. M8

M5 was added into the acetate solution of M1 (440 mg, 0.5 mmol) and the mixture was stirred at 80 °C for 2 h. After that, the reaction was stopped by pouring them in 500 mL methanol. A blackish green was precipitated and filtrated. The product was purified by column chromatography using petroleum ether as the eluent to give the blackish green solid. Yield: 80%. ¹H NMR (500 MHz, CDCl₃, δ): 9.29–9.28 (d, 2H, *J* = 7.96 Hz), 8.73 (s, 2H),

7.98–7.66 (d, 2H, J = 7.95 Hz), 7.86–7.84 (d, 2H, J = 7.95 Hz), 7.80–7.72 (m, 6H), 7.70–7.69 (d, 2H, J = 4.0 Hz), 7.48–7.47 (d, 2H, J = 5.1 Hz), 7.42–7.34 (m, 6H), 7.19–7.17 (t, 2H, J = 4.8, 1.0 Hz), 2.14–2.04 (m, 8H), 1.15–1.05 (m, 24H), 0.77–0.72 (m, 20H); MALDI-TOF-MS (m/z): [M + H]⁺ calcd for C₇₆H₇₈N₂S₃: 1114.5; Found: 1115.6; Anal. Calcd. for C₇₆H₇₈N₂S₃: C, 81.82; H, 7.05; N, 2.51; S, 8.62; Found: C, 81.00; H, 7.00; N, 2.20; S, 8.46.

2.3.9. M9

M8 (200 mg, 0.20 mmol) and NBS (90 mg, 0.5 mmol) were dissolved in 25 mL THF and stirred for 2 h at room temperature. After that, the mixture was poured into 200 mL methanol. A blackish green was precipitated and filtrated. The product was purified by column chromatography using petroleum ether as the eluent to give the gray-green solid. Yield: 90%. ¹H NMR (500 MHz, CDCl₃, δ): 8.53–8.51 (m, 4H), 7.84–7.83 (m, 4H), 7.79–7.52 (m, 4H), 7.72–7.70 (d, 2H, *J* = 7.9 Hz), 7.46–7.37 (m, 8H), 6.65 (m, 2H), 2.20–2.01 (m, 8H), 1.22–1.01 (m, 24H), 0.88–0.72 (m, 20H); MALDI-TOF-MS (*m*/*z*): [M + H]⁺ calcd for C₇₆H₇₆Br₂N₂S₃: 1270.3; Found: 1273.8; Anal. Calcd. for C₇₆H₇₆Br₂N₂S₃: C, 71.68; H, 6.02; N, 2.20; S, 7.55; Found: C, 70.98; H, 6.00; N, 2.18; S, 7.22.

2.3.10. P1

M7 (540 mg, 0.43 mmol), Sn(C₄H₉)₆ (250.0 mg, 0.43 mmol) and $Pd(PPh_3)_4$ 2 mg, 2% was added into the three-neck bottle, and then 1.0 mL toluene, 1.0 mL DMF was added. The mixture was heated to 110 °C and stirred for 48 h under N₂ atmosphere. The reaction was quenched by adding 20 mL HCl (10%). The product was extracted by CHCl₃ and EDTA solution. The organic laver was collected and dried over MgSO₄. The solvent was removed by rotary evaporation. The concentrated oil was precipitated in methanol to form solid. The solid was filtrated and purified by Al₂O₃ column to get rid of Pd catalyst. And then the polymer was finally extracted by soxhlet apparatus. Yield: 55%. ¹H NMR (CDCl₃, 500 MHz): δ 9.50–7.50 (m, 10H), 7.49-7.26 (m, 10H), 7.25-6.50 (m, 6H), 2.30-1.60 (m, 8H), 1.30–0.40 (m, 44H). ¹³C NMR (500 MHz, CDCl₃): $\delta = 151.3, 148.9,$ 147.5, 146.6, 145.8, 143.9, 142.3, 140.2, 139.9, 136.9, 133.3, 132.8, 127.6, 126.3, 125.6, 123.8, 120.8, 119.0, 118.5, 54.3, 39.4, 30.3, 28.9, 22.8, 21.6, 12.3. M_n: 22.0*10³, M_w: 35.2*10³, M_w/M_n: 1.6 (GPC, PS calibration). Anal. Calcd. for (C78H78N2S2)n (%): C, 84.43; H, 7.27; N, 2.52; S, 5.78; Found: C, 80.90, H, 6.89, N, 2.09, S, 5.04.

2.3.11. P2

P2 was synthesized similarly as P1 except that using M9 as the starting material instead of M7. Yield: 50%. ¹H NMR (CDCl₃, 500 MHz): $\delta = 9.50-7.50$ (m, 10H), 7.49–7.26 (m, 8H), 7.25–6.50 (m, 6H), 2.30–1.60 (m, 8H), 1.00–0.80 (m, 24H), 0.70–0.30 (m, 20H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 150.7$, 149.8, 141.4, 140.2, 139.4, 138.5, 135.6, 134.1, 131.7, 126.3, 125.6, 121.9, 120.8, 119.2, 118.7, 54.3, 39.5, 30.5, 28.7, 22.6, 21.6, 12.9. M_{π} : 21.0*10³, M_{W} : 25.2*10³, M_{W}/M_{π} : 1.2 (GPC, PS calibration). Anal. Calcd. for (C₇₆H₇₆N₂S₃)_n (%): C, 81.82; H, 7.05; N, 2.51; S, 8.62; Found: C, 79.40, H, 6.69, N, 2.13, S, 8.11.

3. Results and discussion

3.1. Synthesis

The general synthetic strategy towards the polymers is outlined in Scheme 2. In the present work, the required dibenzo[a,c]phenazine precursor M1 was prepared by Suzuki coupling reaction between 3,6-dibromophenanthrene-9,10-quinone [33] and 2-(9,9dihexyl-9H-fluorene-2-yl)-4,4,5,5-tetramethyl-1,3,2-

dioxaborolane in good yield of 75%. In this way, the soluble alkyl chain and the two active carbonyl units were introduced. M2 was also achieved by Suzuki coupling reaction using 4,7-dibromobenzo



Scheme 2. The synthesis route to the monomers and polymers.

[c][1,2,5]thiadiazole as the starting material, which coupled with 2-(thiophen-2-yl)-1,3,2-dioxaborinane to obtain 4,7-di(thiophen-2yl)benzo[c]-[1,2,5]thiadiazole (M2). And then, the following reduction process was performed in the presence of Fe dust and acetate for 30 min to get the monomer M3. With M1 and M3 in hand, the quinoxaline monomer M6 could be obtained as a yellow powder with a nearly 100% yield by stirring them together at 80 °C for 12 h. M7, the precursor for P1, was then synthesized by bromination of M6 in the presence of NBS in high yield of 90%. For monomer M4, the Stille coupling reaction was first performed to get the yellow crystals of M4 with two nitro reactive group [34]. And it was then reduced to corresponding ortho-diamine compound under SnCl₂ and HCl in solution of ethyl acetate to afford M5 [35]. And then, M9 could be achieved in the similar process as M7 using M1 and M5 as the reactants. After M7 and M9 were successfully prepared, we then tried to polymerize them by Pd(PPh₃)₄, a commonly used catalyst for Still coupling reaction. Polymerization of M7 in the presence of Pd(PPh₃)₄ and Sn₂(C₄H₉)₄ in refluxed DMF/toluene gave a high molecular weight polymer P1 in a reasonable yield [36]. Under the same condition, P2 was also successfully synthesized. The resulting copolymers were characterized, spectroscopically and corresponded well to their expected molecular structures. They were readily soluble in common organic solvent such as toluene, THF and CHCl₃ due to the introduction of



Fig. 1. The ¹H NMR spectra of P2 and M9.

long alkyl chain on fluorene group. The weight-average molecular weights (M_w) of P1 and P2 determined by gel permeation chromatography (GPC) using THF as the eluent and polystyrene as standard is 35,200 and 25,500, respectively, with a polydispersity index of 1.6 and 1.2.

3.2. NMR characterization

The structure of the polymers was confirmed by NMR, FTIR and elemental analyses. Take P2 as an example, Fig. 1 showed the ¹H NMR spectra of P2 together with its monomer M9. In the spectrum of M9, the absorptions of the CH₂ protons on the long alkyl chain linked with fluorene unit were observed at 2.09, 1.13 and 0.75 ppm, respectively, and P2 showed the similar proton resonances at this area but they became broad in P2. In low field region ($\delta > 8.50$ ppm), the absorptions of the H protons of phenanthrene ring of M9 were observed at 9.29 and 8.73 ppm.

The absorptions of the H protons of thiophene ring were observed at 6.65 and 7.40 ppm indicating that the monomer was successfully formed. P2 also exhibited these proton resonances in this area similar to M9. All this proved that the building block of M9 was inserted to the polymer 2. From 7.10 to 7.90 ppm, the absorptions of the aromatic fluorene hydrogen, aromatic phenanthrene hydrogen and thiophene hydrogen of P2 were hard to distinguish, presumably due to their strong overlapping. No unexpected peaks were found and all the peaks could be readily assigned. Thus, the polymeric product was indeed P2 with a molecular structure as shown in Scheme 2. Similar observations were found in the spectrum of P1 as shown in Supporting Information.

3.3. Thermal properties

Temperature for 5 wt% loss has often been used as a degradation temperature (T_d) to estimate thermal stability of a polymer. Both the polymers were thermally stable and lost little of their weights at a temperature as high as 300 °C (Fig. 2). The T_d was found to be at 385 °C and 395 °C for P1 and P2, respectively. When pyrolyzed at 800 °C, P1 and P2 still kept 63.9% and 62.7% of their original weights, respectively. In DSC heating cycles up to 350 °C, whereas P1 and P2 did not show any thermal transition (as shown in Fig. S6), which was due to their 2-dimensional rigid structure.



Fig. 2. TGA spectra of P1 and P2.

3.4. Photophysical properties

The absorption spectra of P1 and P2 in film state were shown in Fig. 3. The absorption of monomer M9 and P3HT are also measured for comparison purpose in Fig. S7. Absorption of P1 in film was dominated by a series of peaks. The peak around 310 nm came from the dihexylfluorene moiety, while the absorption peak around 400 nm was attributed to the characteristics of π – π * transition of the main chain, and the absorption band around 650 nm was due to the intramolecular charge transfer (ICT) because of the donoracceptor effects. Compared to P3HT, which exhibited main absorption peak at 520 nm, the absorption of P1 was obviously broadened ranging from 400 to 800 nm, and the absorption in the



Fig. 3. Absorption spectra of P1 and P2 in film state.



Fig. 4. The model structure of P1 or P2 and simulation of front molecular orbitals through DFT calculation at a B3LYP/6-31G(d) level.

blue region was improved. P2 also showed the similar absorption peaks at 310, 400 nm, and the absorption of ICT was remarkably red-shifted to 820 nm demonstrating longer conjugation wavelength and stronger CT interaction in the polymer backbone [37]. The onsets of the absorption edge were at 845 nm and 1100 nm, thus the bandgap of P1 and P2 were calculated to be 1.49 and 1.21 eV, respectively. Comparing to the bandgap of P3HT of 1.94 eV, the bandgap of P1 and P2 was obviously decreased, which proved that the narrow bandgap polymers were achieved by our molecular design and endowed their potential application in solar cells.

3.5. Theoretical calculation studies

To gain insight into the electronic structure of two highly π extended polymers, density function theory (DFT) calculations were performed at a B3LYP/6-31G(d) level for the geometry optimization [16,25]. To simplify the calculation, only one to three repeating units of each polymer were subject to the calculation, with alkyl chains removed. The simulated electron density distributions and the calculated HOMO and LUMO levels along with the optimized geometries are shown in Fig. 4 and Fig. S8. The V-shape conformations of the constructing units were observed for P1 and P2, which could reduce the polymerization steric hindrance as expected. And the HOMOs in both polymers were mainly populated over the 1-D main chain, whereas the LUMO had sizable contribution from perpendicular pyrazine fragments. Examination of the frontier orbits of molecules suggests that the HOMO–LUMO excitation would trend to shift the electron density distribution from the central main chain to the pyrazine moieties on side chain to some extent. For extrapolating of HOMO–LUMO gaps for polymers, the linear curve of the HOMO, LUMO and bandgap against the reciprocal of the number of monomer units (1/n) was employed [38]. Alone with the repeat unit (n) increased, the gap was dropped obviously. The modified extrapolation of 1/n afforded HOMO– LUMO gap values of 1.71 and 1.13 eV for P1 and P2 (Table S1), respectively, and this result was very close to the corresponding experimental values obtained from optical absorption edge. Meanwhile, the oligomer for P2 showed narrower bandgap than that for P1, and it was not only due to a stronger CT interaction between donor and acceptor unit in polymer, but also extended conjugation from planar configuration.

In P1, it is also observed that phenanthro-pyrazine unit exhibited the planarity geometry, which was commitment with the design strategy. And the dihedral angel between plane of thiophene and quinoxaline on main chain was calculated to be 25.6° (Dihedral Angel-1). While in P2, the benzene unit in P1 was replaced by thiophene here, the thiophene unit showed alternate arrangement due to the strong hydrogen interactions between two neighboring thiophene rings (S–H), which strengthened coplanarity along the main chain direction (1-D conjugation) [16–18]. The dihedral angel between thiophenes on main chain was decreased to 0.2° , which resulted in the extended conjugation length and further narrower bandgap compared to P1. This was agreed with our observation in absorption spectra. Thus, a higher level of packing order could be formed in this way which would facilitate the charge carrier transport along the two dimensional region [16–21,26,27].

3.6. Electrochemical measurement

The electrochemical behaviors of the polymers were investigated by cyclic voltammogram (Fig. 5). P1 and P2 exhibited quasireversible reduction wave. According to the onset potentials of -1.07 V and -0.98 V, the LUMO level of P1 and P2 were calculated to be -3.65 and -3.73 eV by comparison to ferrocene (4.8 eV vs. vacuum). According to the simulation results of front molecular orbitals, the LUMO energy levels were all mainly originated from the phenanthro-pyrazine unit. Comparing to the benzenepyrazine [13–15] and thiophenepyrazine, [16–18] the onset potentials were decreased nearly 0.3-0.4 eV, indicating the easier injection of electrons. P1 and P2 showed irreversible oxidation wave. The onset potentials were at 1.22 V and 1.27 V, respectively, the HOMO level of P1 and P2 were thus calculated to be -5.93 and -5.99 eV by comparison to ferrocene. The bandgap estimated from the CV were 2.28 eV for P1 and 2.25 eV for P2, which were different from the values calculated from the absorption edge. It was because that the onset potentials in two polymers were not originated from the 1-D main chain as the result DFT calculated, and the oxidation process happened firstly on the peripheral fluorene unit, which was more accessible to the electrode and the redox reaction according diffusion theory in CV measurement [39]. The value of HOMO level was exactly the same as that of the fluorene unit as reported in the literature [40,41]. The values of HOMO levels of both polymers had big difference compared to the results from DFT, and it was because that the fluorene unit was as a substituted group in calculated process, and did not participate in conjugated system and the formation of the frontier molecular orbitals. So, a more reasonable approach from the values of LUMO (-3.65 and -3.73 eV) in CV measurement and the onsets of the absorption edge (1.49 and 1.21 eV) were applied to estimate the values of HOMOs, and they were thus calculated to be 5.14 eV and 4.94 eV for P1 and P2, respectively, which were very close to the DFT predicted values.

3.7. Photovoltaic properties

To demonstrate the potential application of the two conjugated polymers P1 and P2 in OPVs, PCBM was used as electron acceptor,



Photovoltaic parameters of devices based on Polymer:PCBM (1:1).

Polymer	Thickness ^a (nm)	$V_{\rm oc}^{\ b}(V)$	J _{sc} ^c (mA/cm ²)	FF ^d (%)	η ^e (%)	$V_{\rm oc}{}^{\rm f}({\rm V})$	V _{oc} ^g (V)
P1	95	0.70	1.0	32	0.20	1.63	0.84
P2	100	0.66	3.6	53	1.26	1.69	0.64.

^a The thickness of active layer.

^b The open-circuit voltage.

^c The short-circuit current density.

^d The fill factor. ^e The power conversion efficiency.

^f Theoretical V_{oc} from the electrochemistry HOMOs according to Brabec theory (V).

 g $V_{\rm oc}$ measured from the optical HOMOs.

and a device configuration of indium tin oxide (ITO)/PEDOT:PSS (40 nm)/active layer (\approx 100 nm)/LiF(1 nm)/Al (100 nm) was utilized to evaluate the photovoltaic performances of OPVs. The polymer and PCBM blend films were prepared from chlorobenzene solution, while the LiF interlayer and Al was thermally deposited to finish the device fabrication. The photovoltaic performance characteristics of the OPVs were summarized in Table 1.

Fig. 6 depicted the current density—voltage (J–V) curves of the OPVs measured under the illumination of simulated AM 1.5G conditions (100 W m⁻²) in P2 device. As shown in the atomic force microscopy (AFM) images (Fig. 7) of the blend films, the morphologies of the blend films were moderately homogeneous and there was no large phase separation, indicating that both of the two polymers possessed good miscibility with PCBM. Polymer P1 exhibited device performance of $V_{oc} = 0.70 \text{ V}$, $J_{sc} = 1.0 \text{ mA/cm}^2$ and FF = 0.32, resulting in PCE = 0.20%. Polymer P2 exhibited an improved performance of $V_{oc} = 0.66 \text{ V}$, $J_{sc} = 3.6 \text{ mA/cm}^2$ and FF = 0.53, resulting in PCE = 1.26%. The value is comparable to those for some low-bandgap NIR-absorbing organic polymer diodes reported [42,43].

Though P1 exhibited a higher V_{oc} , its PCE was just about sixth of P2. The better performance of P2 originated from two aspects. Firstly, P2 showed broader absorption and covering the solar spectrum better than P1. As shown in Fig. 8, the IPCE curves of the OPV based on P2 exhibited a broad response covering 380–700 nm, and the EQE was near 20% in the spectral region from 380 to 600 nm, higher and broader than that of P1 [44]. Secondly, the dihedral angel between thiophenes on P2 main chain was only 0.2°



Fig. 6. Current density–voltage (J-V) curves of the polymer solar cell with P2:PCBM (1:1) active layers under simulated AM 1.5 solar irradiation.



Fig. 5. Cyclic voltammogram of P1 and P2.



Fig. 7. AFM images (10*10 µm²) of the active layers from the polymers (polymer:PCBM).



Fig. 8. EQE curves of the photovoltaic cells with polymer:PCBM system illuminated by monochromatic light.

and P2 exhibited wholly coplanar conformation as revealed by DFT, which showed higher level of packing order and benefited for the transport of carriers, resulting improved FF and nearly 6-folded higher PCE than P1.

Additionally, there was large difference between the obtained V_{oc} in OPV device and the V_{oc} from the electrochemistry HOMOs according to Brabec theory. And the difference was little from that achieved by optical method [45]. A reasonable explanation was that the fluorene unit only had a substituted effect and did not participated in the formation of the frontier molecular orbital as described in DFT.

4. Conclusions

In summary, two 2-dimensional narrow bandgap conjugated polymers based on the dithiophen and phenanthro-pyrazine units have been successfully designed and synthesized by the Still coupling reaction. The obtained polymers show good solubilities in common organic solvent, high thermal stabilities, and broader visible absorption bands and narrower optical bandgap than P3HT. The optical bandgap is calculated to be 1.49 and 1.21 eV for P1 and P2 from the onsets of the absorption spectra. P2 exhibits wholly coplanarity conformation in 1-D and 2-D direction as revealed by the theoretical studies, and a higher PCE value of 1.26% of P2/PCBM device than P1 is finally achieved under simulated AM 1.5 conditions. The 6-folded improved PCE value in P2/PCBM device may be originated from tuning the dihedral angel between dithiophen and phenanthro-pyrazine from 25.6° for P1 to 0.2° for P2.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.09.015.

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