Low bandgap polymers synthesized by FeCl₃ oxidative polymerization

Tianqi Cai, Yi Zhou, Ergang Wang, Stefan Hellström, Fengling Zhang, Shiai Xu, Olle Ingaräs, Mats R. Andersson

ABSTRACT

Four low bandgap polymers, combining an alkyl thiophene donor with benzo[c][1,2,5]thiadiazole, 2,3-diphenylquinoxaline, 2,3-diphenylthieno[3,4-b]pyrazine and 6,7-diphenyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline acceptors in a donor–acceptor–donor architecture, were synthesized via FeCl₃ oxidative polymerization. The molecular weights of the polymers were improved by introducing FeCl₃ oxidative polymerization. The optical bandgaps of the polymers vary between 1.0 and 1.9 eV, which is promising for solar cells. The devices spin-coated from an ODCB solution of P1DB:[70]PCBM showed a power conversion efficiency of 1.08% with an open-circuit voltage of 0.91 V and a short-circuit current density of 3.36 mA cm⁻² under irradiation from an AM1.5G solar simulator (100 mW cm⁻²).

1. Introduction

With increasing energy demand, polymer-based solar cells have been attracting considerable attention for their unique advantages, such as low cost, light weight, and potential use in flexible devices. As a result, the development of polymer solar cells has increased rapidly, yielding power conversion efficiencies (PCEs) up to 5–6% [6–11]. In order to produce cheaper electricity, the PCEs of polymer solar cells need further improvement. One of the limiting parameters for PCE of polymer solar cells is the mismatch between the absorption spectrum of the photoactive layer and the terrestrial solar radiation, which leads to only a small portion of solar energy being utilized. Low bandgap polymers (E_g < 1.8 eV) are of interest because their absorption spectra can cover from the visible to the near-infrared region, and have been intensively investigated [12–15]. By using solar cells fabricated from low bandgap polymers, it is possible to capture more of the solar radiation and thereby increase their efficiency. A facile approach to achieve low bandgap polymers is through incorporation of electron-rich units (as donor) with electron-deficient units (as acceptor), forming a donor–acceptor (D–A) structure [16–19]. The interaction between electron-rich units and electron-deficient units results in a compressed bandgap, which can be tuned conveniently by changing one of the units or both of them.

Most low bandgap polymers were synthesized via Suzuki [20–22], Yamamoto [22] and Stille [23,24] coupling polymerizations. Compared with these polymerization methods, ferric(III) chloride (FeCl₃) oxidative polymerization is easy and cheap with mild reaction conditions (at room temperature), thereby making it suitable for large scale production [25]. Here we present four low bandgap polymers that combine an alkyl thiophene donor with four different electron-deficient acceptors. The use of a donor–acceptor–donor (DAD) monomer architecture allows for synthesis via FeCl₃ oxidative polymerization (See Scheme 1). Similar polymers to P1DB have been reported [26,27], and will be compared in this paper. Octyl groups were attached at the 4 position of the thiophene moiety to increase the solubility of the resulting polymers. Benzo[c][1,2,5]thiadiazole, 2,3-diphenylquinoxaline, 2,3-diphenylthieno[3,4-b]pyrazine and 6,7-diphenyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline were used as acceptor units in the alternating polymers. The influence of the acceptor units on photophysical, electrochemical and photovoltaic properties of the resulting polymers were investigated and compared. To improve the molecular weights of the polymers, o-dichlorobenzene (ODCB) was used as the reaction solvent instead of the commonly used solvent, chloroform. As a result, the polymers had improved molecular weights due to their higher solubility in ODCB compared to chloroform.

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2. Experimental

2.1. Materials

All reagents were purchased from Aldrich except for the following chemicals: 3-octylthiophene, benzo[ci][1,2,5]thiadiazole, 2,5-dibromo-3,4-dinitrothiophene, which were bought from Puyang Huicheng Chemical co. Dry tetrahydrofuran (THF) was distilled over sodium with addition of benzophenone. All reactions were performed under nitrogen unless noted.

2.2. Synthesis of monomers

2.2.1. Tributyl(4-octylthiophen-2-yl)stannane (1)

Butyl-lithium in hexane (1.6 mol L⁻¹, 63 mL, 0.10 mol) was slowly added to 3-octylthiophene (19.60 g, 0.10 mol) in anhydrous THF (150 mL) at ~80 °C, after which the mixture was stirred under nitrogen for 1.5 h. After increasing to room temperature for 1 h, the mixture was then cooled to ~80 °C and tributylchlorostannane (35.50 g, 0.11 mol) was added dropwise. The mixture was then stirred at ~80 °C for an additional 1 h, followed by quenching with 2 M aqueous sodium hydrogencarbonate (100 mL). After that, most of THF was removed under reduced pressure and the solution was extracted by CH₂Cl₂ and washed by water. The residue was purified on a column of neutral alumina (hexane as eluent) to give the compound (1) as colorless oil (37.00 g, 76.3%). It was used in the next step without further purification.

2.2.2. 4,7-Dibromobenzo[c][1,2,5]thiadiazole (2)

After a mixture of 2,1,3-benzothiadiazole (20.00 g, 147 mmol) and aq. HBr (48%, 300 mL) was heated to reflux under N₂, Br₂ (70.50 g, 441 mmol, dissolved in 200 mL of 48% aq. HBr) was added dropwise over 1 h. The mixture was refluxed for an additional 6 h. After the reaction, 1 M Na₂S₂O₃ solution was slowly added until the orange solution turned to yellow. The solid was recrystallized in ethanol to yield compound 2 as yellow crystals (30.10 g, 69.3%). ¹H NMR (400 MHz, CDCl₃) δ: 7.71 (s, 2 H), 7.36 (s, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ: 153.08, 132.50, 114.05.

2.2.3. 4,7-Bis(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3)

To the solution of 1 (11.78 g, 24.3 mmol) and 2 (2.95 g, 10.0 mmol) in THF (50 mL) was added Pd(PPh₃)₂Cl₂ (75 mg, 0.11 mmol). The mixture was refluxed overnight under nitrogen. The THF was then removed under reduced pressure, and the residue was extracted with CH₂Cl₂ and washed by water. The organic phase was separated and dried over MgSO₄. After purification by chromatography using CH₂Cl₂:hexane=1:1 as the eluent and recrystallization from ethanol, compound 3 was obtained as orange crystals (2.21 g, 42%). ¹H NMR (400 MHz, CDCl₃) δ: 7.98 (s, 2 H), 7.83 (s, 2 H), 7.04 (s, 2 H), 2.71–2.68 (t, 4 H), 1.72–1.69 (m, 4 H), 1.40–1.29 (m, 20 H), 0.89–0.87 (t, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ: 152.86, 144.60, 139.23, 132.94, 126.24, 125.76, 121.77, 32.18, 30.93, 30.79, 29.74, 29.67, 29.57, 22.96, 14.41.

2.2.4. 5,8-Bis(4-octylthiophen-2-yl)-2,3-diphenylquinoxaline (4)

Compound 3 (1.43 g, 2.72 mmol) was mixed with zinc (1.17 g, 18.0 mmol) in a flask and 50 mL acetic acid was added. The reaction was stirred at 60 °C for 6 h. Upon cooling to room temperature, the solid residue was removed by filtration and then benzil (0.87 g, 4.14 mmol) was added to the solution at once. The mixture was heated to 40 °C and stirred overnight. Then the mixture was poured into water and extracted with CH₂Cl₂ (50 mL x 3). The organic phase was separated and dried over MgSO₄ and then purified by column chromatography using CH₂Cl₂:hexane=1:1 as the eluent. Recrystallization from ethanol yielded compound 4 as orange crystals (1.51 g, 82.7%). ¹H NMR (400 MHz, CDCl₃) δ: 8.09 (s, 2 H), 7.76 (s, 2 H), 7.74 (s, 4 H), 7.38 (s, 4 H), 7.37 (s, 2 H), 7.11 (s, 2 H), 2.70–2.66 (t, 4 H), 1.74–1.67 (m, 4 H), 1.40–1.29 (m, 20 H), 0.90–0.87 (t, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ: 151.55, 142.94, 138.86, 138.54, 137.38, 131.33, 130.61, 129.07, 128.31, 128.17, 127.01, 123.93, 32.09, 30.08, 30.75, 29.69, 29.60, 29.47, 22.86, 14.31.

2.2.5. 2,5-Bis(3-octylthiophene-5-yl)-3,4-dinitrothiophene (5)

To the solution of 2,5-dibromo-3,4-dinitrothiophene (3.98 g, 11.70 mmol) and compound 1 (12.80 g, 26.40 mmol) in 60 mL of THF was added Pd(PPh₃)₂Cl₂ (0.09 g, 0.13 mmol). The mixture was refluxed overnight. After the reaction, THF was removed under reduced pressure, and the residue was extracted by CH₂Cl₂ (60 mL x 3) and washed by water (60 mL x 3). The organic phase was separated and dried over MgSO₄. After purification by column chromatography using CH₂Cl₂:hexane=1:1 as the eluent and recrystallization from ethanol, compound 5 was obtained as an orange powder (3.89 g, 59.0%). ¹H NMR (400 MHz, CDCl₃) δ: 7.36 (s, 2 H), 7.18 (s, 2 H), 2.64–2.60 (t, 4 H), 1.63–1.61 (m, 4 H), 1.31–1.28 (m, 20 H), 0.90–0.87 (t, 6 H). ¹³C NMR (100 MHz, CDCl₃) δ: 152.86, 144.60, 139.23, 132.94, 126.24, 125.76, 121.77, 32.18, 30.93, 30.79, 29.74, 29.67, 29.57, 22.96, 14.41.
δ: 145.18, 134.23, 132.52, 128.01, 126.29, 115.18, 32.11, 30.61, 30.54, 29.62, 29.48, 22.92, 14.37.

2.2.6. 5,7-Bis(4-octylthiophen-2-yl)-2,3-diphenylthiophene [3,4-b]pyrazine (6)

Compound 5 (1.02 g, 1.8 mmol) was mixed with iron powder (2.20 g, 39.3 mmol) in a flask and 50 mL acetic acid was added. The mixture was stirred at 60 °C for 1 h. After the solution cooled to room temperature, the solid residue was removed by filtration and then benzil (0.62 g, 2.95 mmol) was added to the solution at once. The mixture was heated to 60 °C and stirred overnight. The mixture was then poured into water and extracted with CH2Cl2 (50 mL × 3). The organic phase was separated and dried over MgSO4, and then purified by column chromatography using CH2Cl2:hexane = 1:3 as the eluent. Recrystallization from ethanol yielded compound 6 as a purple powder (0.65 g, 53.3%). 1H NMR (400 MHz, CDCl3): δ: 7.75–7.73 (d, 4 H), 7.50–7.46 (t, 2 H), 7.42–7.34 (m, 6 H), 6.98 (s, 2 H), 2.66–2.62 (t, 4 H), 1.70–1.64 (m, 4 H), 1.42–1.28 (m, 20 H), 0.91–0.87 (t, 6 H). 13C NMR (100 MHz, CDCl3): δ: 152.77, 143.66, 139.22, 137.52, 134.40, 130.15, 129.10, 128.16, 126.06, 125.07, 121.84, 115.17, 32.07, 30.62, 29.63, 29.50, 29.44, 22.86, 14.30.

2.2.7. 4,9-Dibromo-6,7-diphenyl-[1,2,5]thiadiazolo [3,4-g]quinoline (7)

4,7-Dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole (3.89 g, 10.1 mmol) was mixed with iron powder (11.7 g, 208.9 mmol) in a flask and then 350 mL acetic acid was added. The reaction was heated at reflux for 1 h. Upon cooling to room temperature, the solid residue was removed by filtration and then benzil (3.42 g, 16.3 mmol) was added to the solution at once. Then the mixture was heated to 60 °C, and stirred overnight. The mixture was then poured into water and extracted with CH2Cl2 (50 mL × 3). The organic phase was separated and dried over MgSO4 and then purified by column chromatography using CH2Cl2:hexane = 1:1 as the eluent. Recrystallization from ethanol yielded compound 7 as red crystals (2.65 g, 53.2%). 1H NMR (400 MHz, CDCl3): δ: 7.75–7.73 (d, 4 H), 7.50–7.46 (t, 2 H), 7.42–7.39 (t, 4 H). 13C NMR (100 MHz, CDCl3): δ: 156.24, 152.56, 138.28, 137.78, 130.65, 130.50, 128.66, 114.41.

2.2.8. 4,9-Bis(4-octylthiophen-2-yl)-6,7-diphenyl-[1,2,5]thiadiazolo [3,4-g]quinoline (8)

To the solution of 7 (2.60 g, 5.2 mmol) and 1 (6.07 g, 12.5 mmol) in 25 mL THF was added Pd(PPh3)2Cl2 (0.158 g, 0.23 mmol). The reaction was refluxed overnight. THF was then removed under reduced pressure, and the residue was extracted with CH2Cl2 (50 mL × 3) and washed with water (100 mL × 3). The organic phase was separated and washed with an ether solution of column chromatography using CH2Cl2:hexane = 1:3 as the eluent. Recrystallization from ethanol yielded compound 8 as a green solid (2.10 g, 55.4%). 1H NMR (300 MHz, CDCl3): δ: 8.85 (s, 2 H), 7.82–7.80 (d, 4 H), 7.44–7.39 (m, 6 H), 7.29 (s, 2 H), 2.79–2.76 (t, 4 H), 1.78–1.74 (m, 4 H), 1.40–1.29 (m, 20 H), 0.90–0.87 (t, 6 H). 13C NMR (100 MHz, CDCl3): δ: 153.07, 151.96, 143.15, 138.35, 135.77, 134.96, 134.90, 130.92, 129.72, 128.39, 127.01, 121.36, 32.21, 30.92, 29.82, 29.77, 29.63, 22.98, 14.42.

2.3. Synthesis of polymers

All of the polymers were synthesized in chloroform (CF) and ODCB, respectively, and the corresponding polymers were named PnCF and PnDB (n = 1–4), respectively. Both CF and ODCB were bubbled with N2 for 30 min before use. The same molar ratio of FeCl3 to monomer (5:1) was used in each case with the exception of P2DB, which did not dissolve well in ODCB after purification. The polymer was then synthesized again with a reduced ratio of FeCl3 to monomer in order to limit the molecular weight and increase the solubility.

2.3.1. Poly[4,7-Bis(3-octylthiophene-5-yl)benzo-2,1,3-thiadiazole] in chloroform (P1CF)

To a suspension of FeCl3 (400 mg, 2.47 mmol) in chloroform (5 mL), compound 3 (280 mg, 0.53 mmol) in chloroform (4 mL) was added in one portion under N2. The reaction was stirred for 48 h at room temperature. After that, the mixture was diluted by chloroform and washed with water. Then the organic phase was separated and stirred with ammonia (aq. 20%, 200 mL × 2) for 12 h, and then washed with 0.2 M ethylenediaminetetraacetic acid (EDTA) solution (200 mL × 2) and water (200 mL × 2). The solution was then poured into methanol and the precipitate was collected by filtration. The crude material was purified via Soxhlet with diethyl ether and chloroform. The chloroform solution was then precipitated into methanol and collected by filtration. The polymer was obtained as a red solid (124 mg, 44.3%).

2.3.2. Poly[4,7-Bis(3-octylthiophene-5-yl)benzo-2,1,3-thiadiazole] in ODCB (P1DB)

To a suspension of FeCl3 (240 mg, 1.5 mmol) in ODCB (3 mL), compound 3 (160 mg, 0.3 mmol) in ODCB (3 mL) was added in one portion under N2. The reaction was left stirring for 24 h at room temperature. The reaction mixture was then diluted with ODCB and washed with water. The organic phase was then separated and stirred with ammonia (aq. 20%, 200 mL × 2) for 12 h, followed by washing with 0.2 M EDTA solution (200 mL × 2) and water (200 mL × 2). The solution was then poured into methanol and the precipitate was collected by filtration. The crude material was purified via Soxhlet with diethyl ether and chloroform. The chloroform solution was then precipitated into methanol. After filtration, the polymer was obtained as a red solid (89 mg, 56.0%).

2.3.3. Poly[5,8-bis(4-octylthiophen-2-yl)-2,3-diphenylquinoxaline] in ODCB (P2CF)

P2CF was synthesized by following the same procedure used in Section 2.3.1. After Soxhlet, some solid was left in the thimble, most of which did not dissolve in ODCB. As a result, the yield of this polymer is quite low (12.5%).

2.3.4. Poly[5,8-bis(4-octylthiophen-2-yl)-2,3-diphenylquinoxaline] in dichlorobenzene (P2DB)

P2DB was synthesized by following the same procedure used in Section 2.3.2. After Soxhlet with diethyl ether, the solid residue in the thimble was dissolved in ODCB and filtered through a glass filter and then precipitated into methanol. The polymer was obtained as a red solid by collecting with PTFE filter (yield: 20.0%).

2.3.5. Poly[5,7-bis(4-octylthiophen-2-yl)-3-diphenylthiophene [3,4-b]pyrazine] in chloroform (P3CF)

P3CF was synthesized by following the same procedure used in Section 2.3.1. After purification, the polymer was obtained as a green solid (yield: 40%).

2.3.6. Poly[5,7-bis(4-octylthiophen-2-yl)-2,3-diphenylthiophene [3,4-b]pyrazine] in ODCB (P3DB)

P3DB was synthesized by following the same procedure used in Section 2.3.2. After purification, the polymer was obtained as a green solid (yield: 53%).
2.3.7. Poly(4,9-bis(4-octylthiophen-2-yl)-6,7-diphenyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline) in chloroform (P4CF)

P4CF was synthesized by following the same procedure used in Section 2.3.1. After purification, the polymer was obtained as a green solid (yield: 42%).

2.3.8. Poly(4,9-bis(4-octylthiophen-2-yl)-6,7-diphenyl-[1,2,5]thiadiazolo[3,4-g]quinoxaline) in ODCB (P4DB)

P4DB was synthesized by following the same procedure used in Section 2.3.2. After purification, the polymer was obtained as a green solid (yield: 28%).

2.4. Measurements

1H-NMR and 13C-NMR spectra were acquired from a Varian 300 MHz and a Bruker Avance 400 MHz spectrophotometer. Tetramethylsilane were used as an internal reference with deuterated chloroform as solvent. Size exclusion chromatography (SEC) was performed on Waters Alliance GPCV2000 with a refractive index detector columns: Waters Styvagel HT GE x 1, Waters Styvagel HMW GE x 2. The eluent was 1,2,4-trichlorobenzene. The working temperature was 135 °C and the resolution time was 2 h. The concentration of the samples was 0.5 mg mL−1, which was filtered (filter: 0.45 μm) prior to the analysis. The molecular weights were calculated according relative calibration with polystyrene standards. UV–vis absorption spectra were measured with a Perkin Elmer Lambda 900 UV–vis-NIR absorption spectrometer. Square-wave voltammetry (SWV) measurements were carried out on a CH-Instruments 650A Electrochemical Workstation. A three-electrode setup was used with platinum wires both as working electrode and counter electrode, and Ag/Ag+ used as reference electrode calibrated with Fc/Fc+. A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu4NPF6) in anhydrous acetonitrile was used as supporting 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu4NPF6) onto the working electrode from ODCB (yield: 28%). After purification, the polymer was obtained as a green solid in Section 2.3.2. After purification, the polymer was obtained as a green solid (yield: 28%).

3. Results and discussions

3.1. Synthesis and characterization

A series of DAD conjugated polymers have been synthesized via FeCl3 oxidative polymerization in chloroform and ODCB, respectively. The synthetic routes for the monomers and polymers are summarized in Scheme 2 and the molecular weights of the polymers can be seen in Table 1. Monomer 3 was obtained via Stille coupling of 4,7-dibromobenzeno[cl,2,5]thiadiazole and tributyl(4-octylthiophen-2-yl)stannane. The reduction of compound 3 with zinc in acetic acid gave the diamine compound, which was then condensed with benzil affording monomer 4. Stille coupling of 2,5-dibromo-3,4-dinitrothiophene and tributyl(4-octylthiophen-2-yl)stannane yielded 5, which was reduced by iron in acetic acid and condensed with benzil to afford monomer 6. 4,7-Dibromo-5,6-dinitrobenzo[c]1,2,5]thiadiazole was reduced by iron and condensed with benzil yielding compound 7 as a red powder. Compound 7 and tributyl(4-octylthiophen-2-yl)stannane were combined via Stille coupling to afford monomer 8. Firstly, all four monomers were polymerized in the commonly used solvent chloroform, with FeCl3 as an oxidant. As shown in Table 1, the molecular weights of the resulting polymers are not high, which can be attributed to the poor solubility of the polymers. It was observed that the polymers precipitated gradually from the reaction solution during the polymerization. According to the mechanism of FeCl3 oxidative polymerization [25], the oxidized polymer chains were complexed with FeCl4⁻ counter ions while growing, which reduced the solubility of the polymers. In order to improve the molecular weights of the polymers, ODCB was used as the reaction solvent instead of chloroform, due to its increased soluble effect for the following polymers. Using the new solvent, the molecular weights of these polymers were improved while the polydispersities (PDI) of P2DB, P3DB and P4DB were reduced. Comparing P84TB (the same structure as P1DB) to P1DB, which was synthesized by Janssen's group via FeCl3 oxidative polymerization in chloroform giving an Mn of 15,500 and Mw of 42,200 [26], is slightly lower than the molecular weight obtained for P1DB with ODCB as the reaction solvent.

One of the difficulties of the FeCl3 polymerization is the removal of the iron salts after polymerization, since a minute amount of metal residue will influence the resulting device performance [28,29]. Here, for purification, we used ammonia and EDTA solutions to wash the polymer solutions, since the complex of the iron ion with the ammonium salt can be dissolved in water and then removed. The polymer purified by washing with ammonia and EDTA solutions showed a much better performance compared to the one without purification.

3.2. Optical and electrochemical measurements

The solution and solid state UV–vis absorption spectra for the polymers can be seen in Fig. 1. All of the polymers showed two distinct absorption bands: the band around 300–400 nm can be assigned to the π–π* transition while the long-wavelength absorption peaks can be attributed to intramolecular charge transfer between the thiophene donor and the acceptor moieties [30,31]. The absorption spectra of the polymers in solid state are red shifted compared to the corresponding spectra in solution, which can be attributed to an increase in the aggregate conformation formed in the solid state. P3DB exhibited a significant absorption into the near-infrared region. The maximum absorption of P3DB is located at ca. 700 nm, which is the highest photon flux of solar radiation, thus more photons are
expected to be absorbed by this material. P4DB showed a strong absorption in the near-infrared, peaking at 884 nm in the solid state, which is blue-shifted compared to PBTTQ reported by Zoombelt et al. [32]. The blue-shift can be attributed to the twist between the head-to-head linked alkylthiophenes in P4DB. The optical bandgaps of the polymers were deduced from the onset of absorption in the solid state, and vary between 1.0 and 1.9 eV, which is promising for solar cell applications. The absorption maximum and optical bandgaps ($E_{op}$) of the polymers are summarized in Table 2.

The HOMO (highest occupied molecular orbital)/LUMO (lowest unoccupied molecular orbital) levels of the polymers are important parameters for investigating their photovoltaic performance. These levels can be estimated using electrochemistry. The polymers were investigated by SWV and the related voltammograms are shown in Fig. 2. For comparison, [60]PCBM was also measured under the same conditions, which showed a peak oxidation potential at 1.45 V and a peak reduction potential at –1.08 V. According to the data summarized in Table 2, the offset of the LUMO levels between the polymers P1DB, P2DB, P3DB and [60]PCBM is larger than 0.3 eV, which indicates there is enough driving force for charge separation in their solar cells [15]. The high ionization potential of P1DB is in favor of achieving a high open-circuit voltage ($V_{oc}$) in the resulting devices [15]. The reduction potential of P4DB (–1.16 V) is very close to that of [60]PCBM (–1.08 V), which might decrease the solar cell performance due to the insufficient driving force for exciton dissociation.

### Photovoltaic studies

All four polymers were investigated in solar cells with a sandwich configuration of Glass/ITO/PEDOT:PSS/Active layer/LiF/Al. The active layer of the solar cells were spin-coated from chloroform.
Due to the poor solubility of P2DB in chloroform, no solar cell data could be obtained. It is reported that the $V_{oc}$ linearly correlates to the energy difference between the HOMO of the donor and the LUMO of the acceptor. The devices from P1DB showed the highest $V_{oc}$ of 1.04 V, which is in accordance with its high oxidation potential. Conversely, P3DB showed a low $V_{oc}$ of 0.55 V, due to its low oxidation potential. As indicated by the low reduction potential of P4DB, the devices from P4DB gave a very poor performance.

Considering that the asymmetric structure of [70]PCBM can absorb more solar radiation than [60]PCBM, the cells from P1DB and P3DB increased at least 1 mA cm$^{-2}$ (Table 3), which is also confirmed by the obviously enhanced intensity of their EQE profiles (see Fig. 4). The cells from P1DB:[70]PCBM gave the highest PCE of 1.08%, and benefited from a reasonably high $V_{oc}$ of 0.91 V. Although the efficiencies of the cells from P3DB were low, limited by its low $V_{oc}$, the $J_{sc}$ is reasonably high due to its broad absorption spectrum. It’s not clear why the cells from P2DB showed an even lower $V_{oc}$ than that of P3DB, even though the oxidation potential of P2DB is higher than that of P3DB. The poor solubility and low molecular weight ($M_n=9000$) of P2DB may be the main reasons.

### 4. Conclusion

Four low bandgap polymers that combine an alkyl thiophene donor with different electron-deficient units forming a DAD structures were synthesized via FeCl$_3$ oxidative polymerization with chloroform and ODCB as solvents. The devices spin-coated $J$–$V$ characteristics of the devices from polymer:[70]PCBM and P1DB:[60]PCBM are shown in Fig. 3 and the $V_{oc}$, short-circuit current density ($J_{sc}$), fill factor (FF) and PCE data are summarized in Table 3. To confirm the device performance, external quantum efficiencies (EQEs) from the cells of polymer:[70]PCBM were measured under monochromatic light and the EQE profiles can be seen in Fig. 4.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_{\text{op}}^g$ (eV)</th>
<th>$E_{\text{ox}}$ (V)</th>
<th>$E_{\text{red}}$ (V)</th>
<th>$E_{\text{ec}}^g$ (eV)</th>
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<tr>
<td>P1DB</td>
<td>331,515</td>
<td>335,536</td>
<td>1.78</td>
<td>0.70</td>
<td>-1.71</td>
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<tr>
<td>P2DB</td>
<td>333,501</td>
<td>338,527</td>
<td>1.88</td>
<td>0.55</td>
<td>-1.82</td>
<td>2.37</td>
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<tr>
<td>P3DB</td>
<td>368,651</td>
<td>370,682</td>
<td>1.33</td>
<td>0.33</td>
<td>-1.57</td>
<td>1.90</td>
</tr>
<tr>
<td>P4DB</td>
<td>363,810</td>
<td>385,884</td>
<td>1.00</td>
<td>0.48</td>
<td>-1.16</td>
<td>1.64</td>
</tr>
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![Fig. 1. UV-vis absorption spectra of the polymers (a) in solution and (b) in the solid state.](image)

<table>
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<th>Potential (V) vs. Fc/Fc$^+$</th>
<th>Normalized Current (a.u.)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>P1DB</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>2.0</td>
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</tbody>
</table>

![Fig. 2. SWV measurements of the polymers and [60]PCBM in film.](image)

![Fig. 3. J–V characteristics of the devices from polymer:[70]PCBM and P1DB:[60]PCBM.](image)
had a photoresponse up to absorption spectrum that peaked at around 700 nm and its EQE indicated that ODCB is a promising solvent in the FeCl₃ oxidative polymerization for obtaining high molecular weight conjugated polymers.

Table 3

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymer:PCBM (wt%)</th>
<th>JSC (mA cm⁻²)</th>
<th>VOC (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1DB</td>
<td>1:4 (60:PCBM)</td>
<td>2.08</td>
<td>0.91</td>
<td>0.35</td>
<td>1.08</td>
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<td>P2DB</td>
<td>1:3 (70:PCBM)</td>
<td>3.36</td>
<td>0.39</td>
<td>0.37</td>
<td>0.56</td>
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<tr>
<td>P3DB</td>
<td>1:4 (60:PCBM)</td>
<td>2.12</td>
<td>0.55</td>
<td>0.34</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>1:3 (70:PCBM)</td>
<td>3.17</td>
<td>0.57</td>
<td>0.34</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Fig. 4. The EQE profiles of the polymer solar cells.

from ODCB solution of P1DB:[70]PCBM showed a PCE of 1.08% with VOC of 0.91 V and JSC of 3.36 mA cm⁻² under AM 1.5 G solar simulator (100 mW cm⁻²) conditions. P3DB had a promising absorption spectrum that peaked at around 700 nm and its EQE had a photoresponse up to ~800 nm, but the low Voc limited its PCE. The molecular weights of the polymers were improved by using ODCB as the solvent instead of chloroform. These results indicate that ODCB is a promising solvent in the FeCl₃ oxidative polymerization for obtaining high molecular weight conjugated polymers.

Acknowledgments

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References