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Synthesis and photovoltaic properties of an alternating polymer based fluorene and fluorine substituted quinoxaline derivatives

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ABSTRACT

An alternating polymer (PFOFTQx) with 9,9-dioctylfluorene (FO) as electron-rich unit and fluorine substituted quinoxaline (FTQx) as electron-withdrawing unit was synthesized and characterized. PFOFTQx showed similar absorption property with that of the counterpart polymer without fluorine atom (synthesized APFO-15). However, the low-lying highest occupied molecular orbit (HOMO) energy level of PFOFTQx was −5.37 eV, about 0.07 eV smaller than that of synthesized APFO-15. In order to study the photovoltaic properties of the materials, polymer solar cells (PSCs) were fabricated with PFOFTQx as donor blended with [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) as acceptor. The power conversion efficiency (PCE) of PSC was 1.77% with a high open-circuit voltage (V_{oc}) of 0.90 V for an optimized PFOFTQx:$PC_{61}BM$ weight ratio of 1:5, in comparison with that of synthesized APFO-15-based device (PCE of 1.60% with V_{oc} of 0.77 V). This study indicated that fluorine substituted quinoxaline-based polymers would be promising material with a higher V_{oc} for the application in polymer solar cells.

1. Introduction

As a solar energy converter, polymer bulk heterojunction (BHJ) solar cells based on conjugated polymers have attracted much attention for their advantages of low cost, roll to roll printing process, and light weight [1–4]. Rapid developments in this field have led to power conversion efficiency (PCE) over 8% and reaching 10% reported recently by Yang [5,6]. However, the efficiency of polymer solar cells is still significantly lower than their inorganic counterparts, such as silicon, CdTe and CIGS, which prevents practical applications in large scale.

There are many factors limiting the performance of BHJ solar cells [7,8]. Among them, the materials of the active layer play an important role in the whole performances of the polymer solar cells (PSCs). Ideally, the polymers should have a broad absorption to ensure effective harvesting of the solar photons and a high hole mobility for charge transport. Furthermore, suitable energy levels of the polymer are required that match those of the fullerene derivatives, the polymer should have a low-lying highest occupied molecular orbit (HOMO) energy level to provide a big open-circuit voltage (V_{oc}) and a suitable lowest unoccupied molecular orbit (LUMO) energy level to provide enough offset for charge separation. In addition, it is imperative that a bicontinuous network of the morphology with a domain size approximately twice that of the exciton diffusion length and a large donor/acceptor interfaces are formed, which favors the exciton dissociation and transport of the separated charges to the respective electrode [9,10].

To satisfy above-mentioned requirements, many kinds of donor–acceptor (D–A) copolymers have been designed for their intramolecular charge transfer from electron-rich unit to the electron-withdrawing unit with tunable energy levels and bandgap. It is an effective way to achieve large V_{oc} through a deeper HOMO energy level material by the introduction of strong electron withdrawing group into the polymer structure. For instance, through replacing the ester with ketone and even more electronegative sulfonyl on thieno[3,4-b]thiophene (TT), rational deeper HOMO energy level and higher V_{oc} of the corresponding devices were achieved [11,12]. As an effective electron withdrawing group, fluorine have attracted broad attention for its high electron affinity, small size and without any deleterious steric effects when introduced into the polymer [13,14]. For example, the two famous high efficiency polymers based on benzodithiophene (BDT) and fluorine

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substituted thieno[3,4-b]thiophene (TT) (PBDTTT-CF and PTB7) were obtained with relatively low-lying HOMO energy level [15,16]. Schroeder also confirmed that the HOMO energy level of SilDT-2FBT was lowered than that of SilDT-BT in their study [17].

As a type of electron-withdrawing unit, quinoxaline has an electron-deficient N-heterocycle, which facilitates tuning the band gap and energy levels. Quinoxaline-based copolymer TQ1 exhibited a high V_{oc} of 0.9 V and a very low-lying HOMO energy level of −5.7 eV [18]. Another polymer with quinoxaline unit (P(T-Qx)) with HOMO energy level of −5.57 eV was reported recently [19]. Among these quinoxaline-based polymers, alternating polymer poly[2,7-(9,9-dioctylflrorene)-*alt*-5,5-(5′,8′-di-2-thienyl-(2′,3′-bis-(3′-octyloxyphenyl)-quinoxaline))] (APFO-15) showed the lowest HOMO energy level of −6.30 eV and highest V_{oc} of 1.0 V [20].

We are interested in the quinoxaline-based polymers due to their good charge-transfer characteristics and stability for device application [21,22]. Through the introduction of fluorine atom into the quinoxaline unit, a promising copolymer poly[6-fluoro-2,3-bis-(3-octyloxyphenyl)quinoxaline-5,8-diyl-alt-thiophene-2,5-diyl] (FTQ) with very deep HOMO energy level (−5.51 eV) and high PCE of 5.3% were achieved [23]. However, the copolymers based on 9,9-dioctylfluorene and fluorine substituted quinoxaline is less reported to the best of our knowledge. In order to decrease the HOMO energy level of APFO-15 and subsequently obtain enhanced photovoltaic performance, in this work, an alternating fluorine substituted quinoxaline copolymer poly[2,7-(9,9-dioctylflrorene)-*alt*-5,5-(5′,8′-di-2-thienyl-(6′-fluoro-2′,3′-bis-(3″-octyloxyphenyl)-quinoxaline))] (PFOFTQx) was synthesized. It is demonstrated that the HOMO energy level of this polymer was lowered to −5.37 eV, about 0.07 eV smaller than that of synthesized APFO-15. As a consequence, V_{oc} and PCE of polymer solar cells based on PFOFTQx:[6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) were enhanced simultaneously in comparison with that of synthesized APFO-15:$PC_{61}BM$-based devices under the same conditions.

2. Experimental section

2.1. Materials and methods

All chemicals and reagents are obtained from Aldrich and Alfa Aesar. THF is dried over Na/benzophenone ketyl and freshly distilled prior to use. 4,7-dibromo-5-fluoro-2,1,3-benzothiadiazole (1) was purchased from Beijing Allmers Chemical S&T Co., Ltd., 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(3-(octyloxy)phenyl)quinoxaline [20] and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene [24] were prepared according to the reported literatures. The synthetic routes of monomers and copolymers are shown in Scheme 1.

2.1.1. 3,6-Dibromo-4-fluoro-1,2-phenylenediamine (1)

4,7-Dibromo-5-fluoro-2,1,3-benzothiadiazole (5 g, 0.016 mol) was dissolved in ethanol (150 ml), then sodium borohydride (12.1 g, 0.32 mol) was added portion wise at 0 °C, and the reactants were stirred for 20 h at room temperature. After evaporation of the solvent, 160 ml water was added, and the mixture was extracted with ethyl acetate. The extract was washed with brine and dried over anhydrous magnesium sulfate. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (25:1) as eluent to afford 3,6-dibromo-4-fluoro-1,2-phenylenediamine (3.5 g) as a pale solid in 78% yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ(ppm): 6.81(d,1H,J = 8 Hz), 3.63(s,4H). ^{13}C NMR(500 MHz, $CDCl_3$): δ(ppm), 154.16, 152.25, 135.75, 135.73, 128.73, 128.71, 109.44, 109.35, 108.83, 108.62, 96.78, 96.58. mp: 94 °C. Anal. Calcd for ($C_6H_5Br_2FN_2$) (%):C25.38, H 1.78, N 9.87. Found (%):C 24.29, H 1.83, N 10.14.

2.1.2. 1,2-Bis(3-(octyloxy)phenyl)ethane-1,2-dione (4)

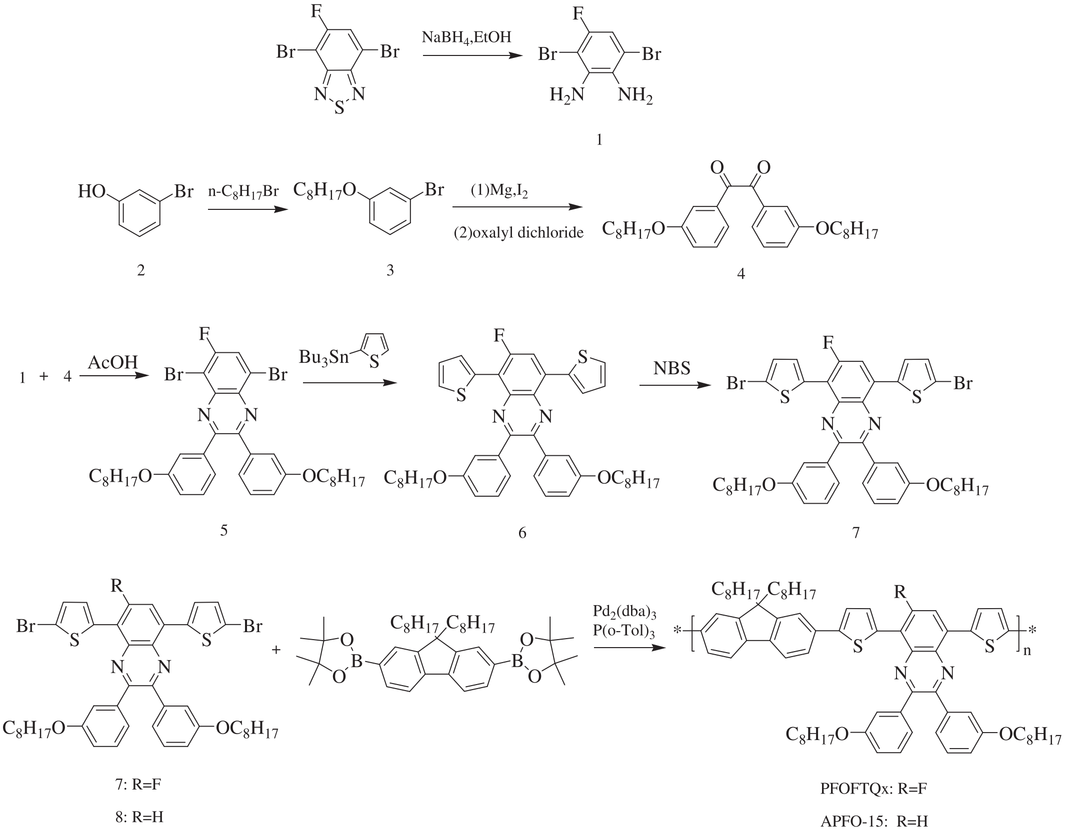
A THF solution of anhydrous LiBr (3.19 g, 36.8 mmol, 15 ml) was added to a suspension of CuBr (2.64 g, 18.4 mmol) in THF (15 ml) under nitrogen. The mixture was stirred at room temperature until it became homogeneous and was then cooled to 0 °C in an ice-water bath. A freshly prepared solution of 3-octyloxybenzene magnesium bromide in THF (5.23 g, 18.4 mmol, 20 ml) was added drop wise to the mixture. After 10 min, oxalyl chloride (1.04 g, 8.22 mmol) was added and the mixture was stirred at 0 °C for 20 min. Then the reaction was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate, the combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using hexane/ethyl acetate (100:1) as eluent to afford compound 4 (2.03 g) as a white solid in yield 53%. ^{1}H NMR ($CDCl_3$, 500 MHz) δ(ppm): 7.51(s,2H), 7.45(m,2H), 7.38(t,2H,J = 8 Hz), 7.19(ddd,2H,J = 5.5 Hz), 4.00(t,4H,J = 6.5 Hz), 1.79(m,4H), 1.46(m,4H), 1.33(m,16H), 0.89(t,6H,J = 7 Hz). ^{13}C NMR(500 MHz, $CDCl_3$): δ(ppm), 194.56, 158.36, 133.91, 129.88, 122.80, 122.15, 113.72, 68.39, 31.81, 29.33, 29.23, 29.13, 26.01, 22.67, 14.11. GC–MS: m/z = 466.

2.1.3. 5,8-Dibromo-6-fluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline (5)

A mixture of compound 1 (2.44 g, 8.58 mmol), compound 4 (4 g, 8.58 mmol), and acetic acid (70 ml) was briefly warmed to 60 °C, and the solution was then stirred at room temperature for 2 h. The precipitate was collected by filtration, washed with ethanol, and dried to afford 5,8-dibromo-6-fluoro-2,3-bis (3-(octyloxy) phenyl)quinoxaline 5 (5.83 g) as awhite solide in yield 95.23%. ^{1}H NMR($CDCl_3$, 500 MHz) δ(ppm): 7.94(d,1H,J = 10 Hz), 7.21–7.24(m,4H),7.17(t,2H,J = 10 Hz),6.94(m,2H), 3.86 (t,4H,J = 6.5 Hz), 1.73(m,4H), 1.29–1.42(m,20H), 0.89(t,6H, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$, 500 MHz) δ(ppm): 160.36, 159.09, 158.27, 154.52, 153.29, 139.60, 139.56, 139.00, 138.91, 136.43, 129.36, 122.56, 122.46, 116.72, 115.79, 115.73, 108.21, 108.05, 68.13, 31.56, 29.35, 29.28, 29.12, 26.04, 22.69, 14.12. mp: 89 °C. Anal. Calcd for ($C_{36}H_{43}Br_2FN_2O_2$) (%):C 60.51, H 6.07, N 3.92. Found (%):C 59.96, H 6.14, N 3.97.

2.1.4. 5,8-Bis(5-bromothiophen-2-yl)-6-fluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline (7)

A mixture of 5,8-dibromo-6-fluoro-2,3-bis-(3-octyloxyphenyl)-quinoxaline (1.26 g, 1.76 mmol), 2-(tributylstannyl)thiophene (1.44 g, 3.88 mmol), dichlorobis-(triphenylphosphine)palladium(II) (49 mg), and toluene (100 ml) were heated under reflux overnight. It was then cooled and the toluene was removed under reduced pressure and the residue was recrystallized by hexane and obtained compound 6 (1.01 g) in 80% yield. To a suspension of compound 6 (0.5 g, 0.7 mmol) in THF (20 ml) was added NBS (0.261 g, 0.47 mmol). The mixture was heated at 40 °C for 4 h and poured into methanol, the precipitate was collected by filtration and recrystallized by hexane and afford 5,8-bis(5-bromothiophen-2-yl)-6-fluoro-2,3-bis(3-(octyloxy)phenyl)quinoxaline (0.43 g) in yield 70%. ^{1}H NMR($CDCl_3$, 500 MHz) δ(ppm): 7.90 (d,1H,J = 15 Hz), 7.77(d,1H,J = 3.5 Hz), 7.53(dd,3H,J = 10 Hz), 7.22(ddd,2H,J = 5 Hz), 7.14(dd,2H,J = 5 Hz), 7.09(d,2H,J = 5 Hz), 6.98(d,2H,J = 5 Hz), 4.04(q,4H), 1.80(m,4H), 1.49(m,4H), 1.33(m,16H), 0.89(t,6H,J = 5 Hz). ^{13}C NMR ($CDCl_3$, 500 MHz) δ(ppm): 159.94, 159.40, 157.91, 152.32, 150.98, 139.09, 139.00, 137.98, 137.75, 137.68, 133.60, 133.48, 133.43, 131.25, 131.16, 130.36, 130.21, 129.17, 129.09, 129.06, 126.07, 123.01, 122.90, 118.48, 117.82, 117.79, 117.40, 117.18, 116.23, 116.14, 115.77, 115.53, 115.18, 115.13, 68.36, 31.84, 29.45, 29.35, 29.33, 26.21,



Scheme 1. Synthetic routes of monomers and copolymers.

22.67, 14.15. mp: 134 °C. Anal. Calcd for ($C_{44}H_{47}Br_2FN_2O_2S_2$) (%):C 60.14, H 5.39, N 3.19. Found (%):C 59.75, H 5.30, N 3.14.

2.1.5. For 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(3-(octyloxy)phenyl)quinoxaline (8)

(Yield 77%) ^{1}H NMR($CDCl_3$, 500 MHz) δ(ppm): 8.07(s,2H), 7.55(dd,4H,*J* = 5 Hz). 7.22(t,2H,*J* = 10 Hz), 7.11(dd,4H,*J* = 10 Hz), 6.98(ddd,2H,5 Hz), 4.04(t,4H,6.5 Hz), 1.81(m,4H), 1.42(m,20H), 0.85(t,6H,*J* = 5 Hz).

2.1.6. Synthesis of APFO-15 and PFOFTQx

In a 50 ml dry flask, monomer 7 (175.7 mg, 0.2 mmol) or 8 (172.2 mg, 0.2 mmol) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (128.5 mg, 0.2 mmol) were dissolved in a mixture of 20% aqueous tetraethylammonium hydroxide(1.5 ml) and degassed toluene (10 ml), the mixture was flushed with nitrogen for 30 min, tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (3.7 mg) and tri(o-tolyl)phosphine (P(o-Tol)$_3$) (6.5 mg) were added, flushed with nitrogen again. Then the mixture was vigorously stirred at 100 °C for 72 h under a nitrogen atmosphere. The polymer was end-capped by adding phenyl boronic acid (2.4 mg) and bromobenzene (2.2 μL) at the end of polymerization. After cooling to room temperature, the solution was poured into methanol. The obtained polymer was then subjected to Soxhlet-extracted with methanol, hexane and chloroform successively. The chloroform solution was concentrated to a small volume, and precipitated by pouring this solution into methanol. Finally, the polymer was collected by filtration, dried under vacuum at 50 °C overnight.

For APFO-15 (184 mg, yield 84.7%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ(ppm): 8.22(br,2H), 7.98(br,2H), 7.72(br,6H), 7.48(br,4H), 7.36(br,4H), 7.00(d,2H,*J* = 8 Hz), 3.90(t,4H,*J* = 6 Hz). GPC (tetrahydrofuran, polystyrene standard): M_n = 22.23 kDa, M_w = 38.42 kDa, PDI = 1.73. Anal. Calcd for ($C_{73}H_{88}N_2O_2S_2$)$_n$ (%):C 80.4, H 8.14, N 2.57. Found (%):C 79.68, H 8.28, N 2.12.

For PFOFTQx (190 mg, yield 85.7%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ(ppm): 8.11(br,1H), 8.00(br,2H), 7.74(br,6H), 7.50(br,4H), 7.38(br,4H), 7.00(d,2H,*J* = 8 Hz), 3.91(t,4H,*J* = 6 Hz). GPC (tetrahydrofuran, polystyrene standard): M_n = 37.13 kDa, M_w = 102.69 kDa, PDI = 2.76. Anal. Calcd for ($C_{73}H_{87}N_2O_2FS_2$)$_n$ (%):C 79.16, H 7.92, N 2.53. Found (%):C 78.31, H 7.94, N 1.84.

2.2. Measurement and characterization

All compounds were characterized by nuclear magnetic resonance spectra (NMR) recorded on a Bruker AV 500 spectrometer in $CDCl_3$ at room temperature. Molecular weights and distributions of the copolymers were estimated by gel permeation chromatography (GPC) method, THF as eluent and polystyrene as standard. The absorption spectra were determined by a Unico UV-2102 scanning spectrophotometer. Thermogravimetric analysis (TGA) of the polymers was investigated on a Universal V2.6D TA instruments. Differential scanning calorimetry (DSC) measurements were performed on DSC Q20 V24.9 Build 121 with a heating rate of 20 °C/min. The electrochemical cyclic voltammetry was conducted on a CHI 660D Electrochemical Workstation with Pt disk, Pt plate, and Ag/Ag$^+$ electrode as working electrode, counter electrode, and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. Polymer thin films were formed by drop-casting chloroform solution (analytical reagent, 1 mg/mL) onto the working electrode, and then dried in the air. Atomic force microscopy (AFM) images were collected in air under ambient conditions using the MultiMode scanning probe microscope (Agilent Technologies 5500).

2.3. Solar cell device fabrication and characterization

The organic photovoltaic cells were fabricated with ITO glass as the anode, Al as the cathode and the blend films of polymer: $PC_{61}BM$ as the active layer. The ITO glass was pre-cleaned and modified by a thin layer of PEDOT:PSS, which was spin-coated from a PEDOT:PSS aqueous solution (Bayer), and the thickness of the PEDOT:PSS layer was about 40 nm. The photosensitive layer was prepared by spin-coating a blend solution of the polymer and $PC_{61}BM$ in chlorobenzene (CB) with the concentration of 15 mg/ml on top of ITO/PEDOT:PSS substrate and the thickness of the active layer was about 80 nm. Then the blend system was put in glove box overnight. Finally, 0.5 nm-thick LiF layer and 85 nm-thick Al layer were evaporated in sequence under the vacuum of 3×10^{-6} Torr. The effective area of the device was 0.0314 cm^2. The current density–voltage (J–V) curves were obtained using a Keithley 2611 source-measure unit. The photocurrent was measured with a solar simulator (Newport Thermal Oriel 69911 300W, 4 in. × 4in. beam size) with AM 1.5G illumination at 100 mW/cm^2. A calibrated mono silicon diode is used as a reference.

3. Results and discussion

3.1. Thermal properties

The thermal properties of polymers were determined by using TGA (Fig. 1) and DSC (Fig. 2), the thermal decomposition temperature (5% weight loss) were 370 °C for synthesized APFO-15 and 340 °C for PFOFTQx, respectively. Consequently, the thermal properties of the two polymers are adequate for application in photovoltaic solar cells and other optoelectronic devices. From the DSC measurement, synthesized APFO-15 showed a glass transition temperature about 142 °C. However, no transition was observed for PFOFTQx.

3.2. Absorption properties

The absorption properties of polymers were investigated both in $CHCl_3$ solution and film state as shown in Fig. 3. The two copolymers showed very similar absorption curves with two main absorption peaks, the band in short-wavelength near 390 nm can be assigned to the π–π^* transition of their conjugated backbone, while the other peak of 525 nm for synthesized APFO-15 and 521 nm for PFOFTQx could be ascribed to the strong intramolecular charge transfer between donor and acceptor. In the solid state, the main absorption peak became broader and shifted toward longer wavelength at 542 nm for synthesized APFO-15 and 540 nm for PFOFTQx. The red shift about 20 nm from solution to film, which indicated that π stacked structure in the solid state might be

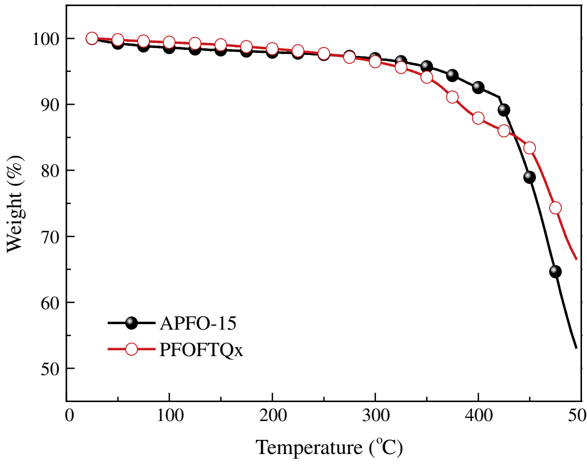


Fig. 1. Thermalgravimetric analysis curves of polymers with a heating rate of 10 °C/min in nitrogen.

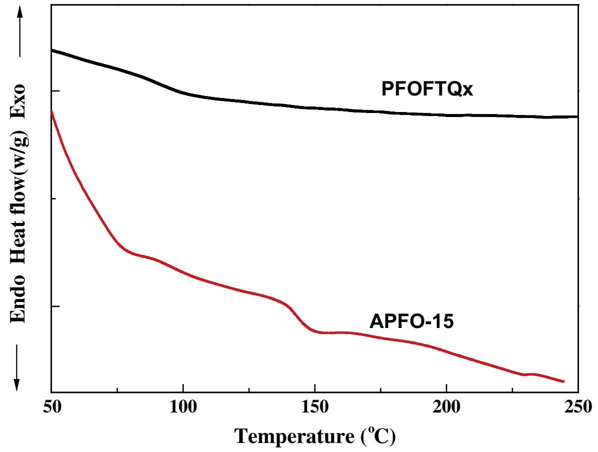


Fig. 2. DSC scans of polymers at a heating rate of 20 °C/min in nitrogen.

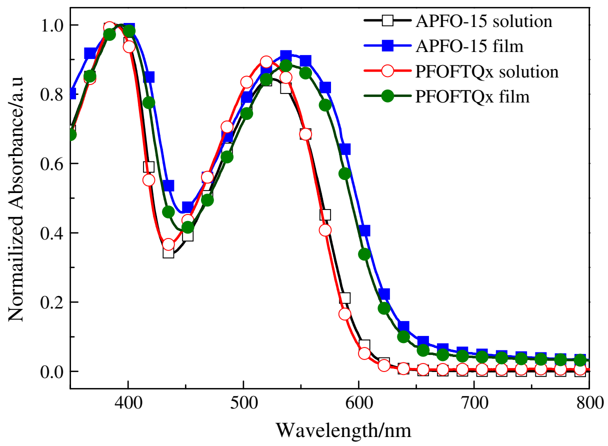


Fig. 3. Absorption spectra of polymers solution and film.

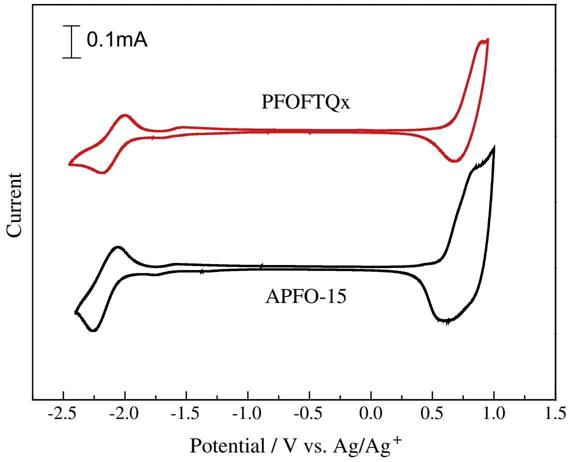


Fig. 4. Cyclic voltammograms of polymer films on a platinum electrode in 0.1 M Bu_4NPF_6/CH_3CN solution at room temperature.

Table 1
Electrochemical and optical properties of the polymers.

Polymer	E_{ox} (V)	E_{red} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{ec} (eV)	E_g^{opt} (eV)[a]
Synthesized APFO-15	0.58	−1.61	−5.30	−3.11	2.19	1.90
PFOFTQx	0.65	−1.50	−5.37	−3.22	2.15	1.91

[a] Optical band gaps were estimated from the onset of electronic absorption of the polymer films $\left(E_g^{opt} = 1240/\lambda(\text{nm})\right)$.

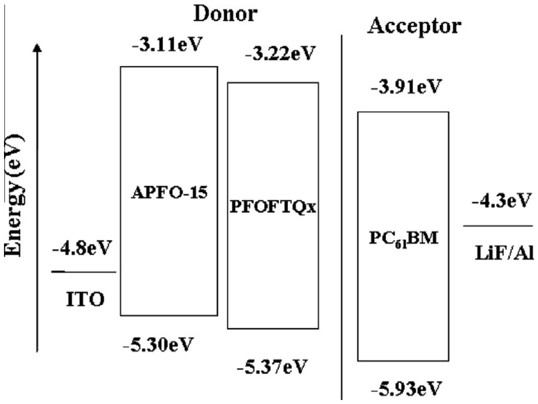


Fig. 5. Energy level diagrams of synthesized APFO-15, PFOFTQx and $PC_{61}BM$.

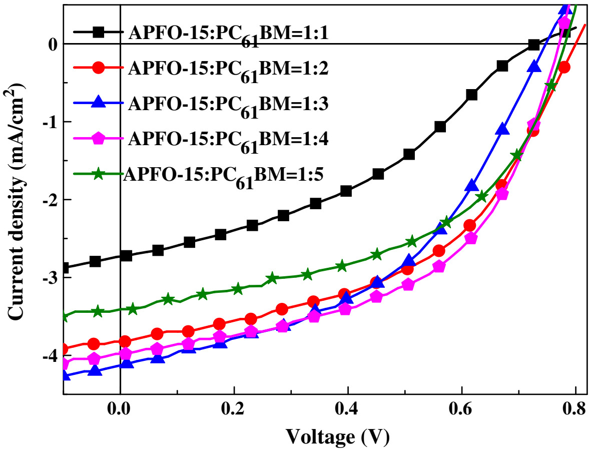


Fig. 6. *J–V* curves of the PSCs based on synthesized APFO-15:$PC_{61}BM$ with different donor/acceptor weight ratios (1:1, 1:2, 1:3, 1:4 and 1:5), under illumination of AM1.5G, 100 mW/cm^2.

formed. The optical bandgap of two copolymers can be calculated about 1.90 eV for synthesized APFO-15 and 1.91 eV for PFOFTQx from the absorption edges of the films.

3.3. Electrochemical properties

Fig. 4 shows the cyclic volatmmograms of polymer films on Pt electrode. The HOMO and LUMO energy levels of the polymers were determined from the onset oxidation potentials (E_{ox}) and the onset reduction potentials (E_{red}) and by assuming the energy level of ferrocene/ferrocenium (Fc/Fc$^+$) to be −4.72 eV below the vacuum level. The formal potential of Fc/Fc$^+$ was measured as 0.09 eV against Ag/Ag$^+$. The energy gap $\left(E_g^{ec}\right)$ of the polymer was calculated from the HOMO and LUMO energy levels. The calculating equations are as follows:

$$E_{HOMO} = -e(E_{ox} + 4.72) \tag{1}$$

$$E_{LUMO} = -e(E_{red} + 4.72) \tag{2}$$

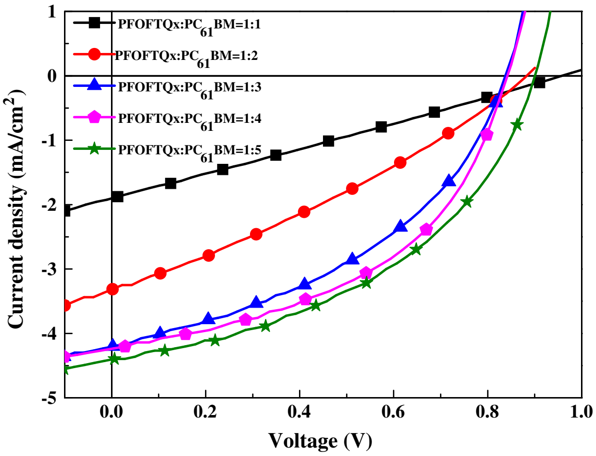


Fig. 7. *J–V* curves of the PSCs based on PFOFTQx:PC61BM with different donor/acceptor weight ratios (1:1, 1:2, 1:3, 1:4 and 1:5), under illumination of AM1.5G, 100 mW/cm^2.

$$E_g^{ec} = e(E_{ox} - E_{red}) \tag{3}$$

where the units of E_{red} and E_{ox} are *V* vs. Ag/Ag$^+$. The electrochemical potentials and energy levels of polymers as shown in Table 1, the onset potentials (E_{ox}/E_{red}) of synthesized APFO-15 and PFOFTQx are 0.58/−1.61 and 0.65/−1.50 V, respectively. From the E_{ox} and E_{red} values of the polymers, the corresponding HOMO, LUMO energy levels and the electrochemical bandgap $\left(E_g^{ec}\right)$ of the polymers were calculated and listed in Table 1. As expected, compared to synthesized APFO-15, a lower HOMO energy level of −5.37 eV was obtained for PFOFTQx, which was advantageous to the V_{oc} for the corresponding polymer solar cells. In addition, the LUMO energy level of PFOFTQx was significantly higher than that of $PC_{61}BM$ (−3.91 eV, as shown in Fig. 5), the relative large offset facilitate electron transferring from the polymer to the $PC_{61}BM$. It should be noted that the HOMO energy level of APFO-15 was −6.30 eV [20], which was too deep to understand. However, a rational HOMO of −5.30 eV for synthesized APFO-15 was obtained in this work.

3.4. Photovoltaic properties

To investigate the photovoltaic properties of the copolymers, polymer solar cells were fabricated with a general device structure of ITO/PEDOT:PSS/polymer:$PC_{61}BM$/LiF/Al. Synthesized APFO-15/PFOFTQx was used as electron donor and $PC_{61}BM$ as electron acceptor, chlorobenzene as solvent. The weight ratio of donor and acceptor in the bulk-heterojunction (BHJ) layer was tuned from 1:1 to 1:5, and the corresponding *J–V* curves of the devices were shown in Figs. 6, 7 and summarized in Table 2. For synthesized APFO-15, a reasonable V_{oc} (0.77 V), J_{sc} (3.98 mA/cm^2), FF (0.52) and PCE (1.60%) were obtained by the optimized weight ratio 1:4. However, this is inferior to the reported 3.7% [20]. It is well known that the morphology of the active layer plays an important role in the properties of the photovoltaic devices, so the morphology of blend films (from 1:1 to 1:5) spin-coated from

Table 2
Photovoltaic results of the PSCs based on synthesized APFO-15, PFOFTQx and $PC_{61}BM$ with different weight ratio under the illumination of AM1.5G (100 mW/cm^2).

Polymer	D/A ratio	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
Synthesized APFO-15	1:1	0.73	2.73	0.38	0.76
	1:2	0.75	4.13	0.46	1.42
	1:3	0.75	3.82	0.52	1.49
	1:4	0.77	3.98	0.52	1.60
	1:5	0.78	3.41	0.51	1.33
PFOFTQx	1:1	0.96	1.91	0.26	0.47
	1:2	0.88	3.32	0.30	0.90
	1:3	0.84	4.21	0.42	1.48
	1:4	0.84	4.25	0.47	1.69
	1:5	0.90	4.40	0.45	1.77

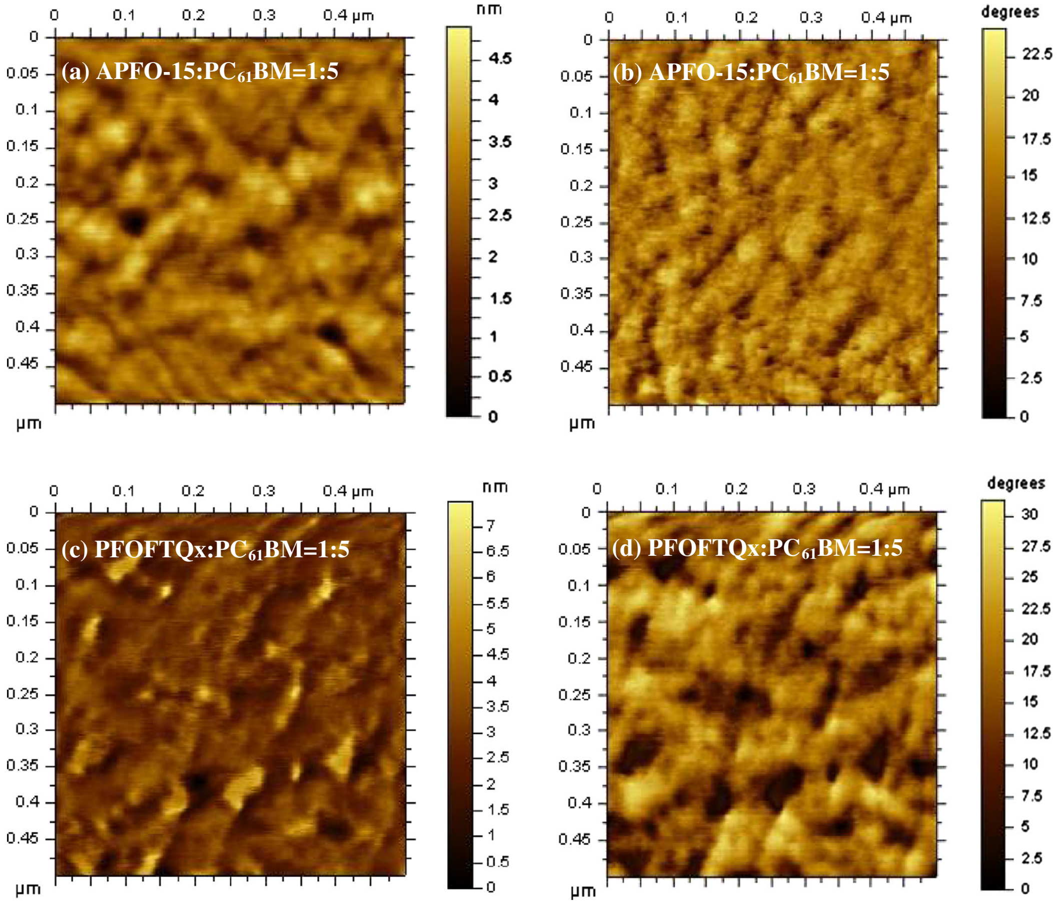


Fig. 8. AFM images for polymer:PC61BM films (1:5) (0.5 µm × 0.5 µm). (a and c) The topography of polymer film. (b and d) The corresponding phase images.

chlorobenzene were investigated by atomic force microscopy (AFM) (Fig. S14 and Fig. 8). Films 1:2 and 1:4 showed a much more uniform than others but still had an average large domain size of 20–60 nm, which is disadvantageous to exciton dissociation and charge transfer, and this might be the main reason for the difference of PCE with reported material [20].

As expected, it is notable that every device based on PFOFTQx has a larger V_{oc} than that of synthesized APFO-15-based device under the same conditions as shown in Table 2. As illumination above, the HOMO energy level of PFOFTQx was 0.07 eV smaller than that of synthesized APFO-15 through introduction the fluorine atom into the polymer, which could contribute to enhancement of V_{oc} and the PCE. In addition, both the J_{sc}, FF and PCE vary monotonically with increasing $PC_{61}BM$ content (from 1:1 to 1:5), this increase as a function of $PC_{61}BM$ content might be attributed to improved carrier transport, the formation of appropriate hole and electron percolation paths that is advantageous to efficient charge collection to electrodes and decreasing in bulk resistance, in addition to efficient dissociation of excited states [25,26]. When the weight ratio of PFOFTQx:$PC_{61}BM$ reached 1:5, reasonable V_{oc} (0.90 V), FF (0.45), J_{sc} (4.40 mA/cm^2) and PCE (1.77%) were obtained.

In order to further study the difference in the photovoltaic performance between PFOFTQx and synthesized APFO-15, the morphology of PFOFTQx:$PC_{61}BM$ (1:5) and synthesized APFO-15:$PC_{61}BM$ (1:5) were selected, carried out and shown in Fig. 8. The PFOFTQx:$PC_{61}BM$ film showed a much more uniform and finer domain structure with an average domain size of 20–40 nm (Fig. 8c and d), which was not ideal but suitable for the exciton diffusion to some extent. While the average domain size of synthesized APFO-

15 blended film was 30–70 nm (Fig. 8a and b), which indicated the increase of the exciton diffusion length and recombination rate of charges. So, if further improvement of the morphology can be adopt (such as thermal annealing, solvent annealing and additives) [27,28] to obtain idea morphology and domain length, enhanced photovoltaic performance might be anticipated for the devices.

4. Conclusions

An alternating polymer (PFOFTQx) with 9,9-dioctylfluorene as electron-rich unit and fluorine substituted quinoxaline as electron-withdrawing unit was synthesized. In comparison with the counterpart polymer without fluorine atom (synthesized APFO-15), PFOFTQx showed the similar absorption spectrum but with a deeper HOMO energy level of −5.37 eV, about 0.07 smaller than that of synthesized APFO-15. Polymer solar cells (PSCs) were fabricated with PFOFTQx/synthesized APFO-15 as donor and $PC_{61}BM$ as acceptor. Enhanced power conversion efficiency of 1.77% with a high V_{oc} of 0.90 V was achieved for an optimized PFOFTQx:$PC_{61}BM$ (1:5), compared to 1.60% (0.77 V) for its non-fluorinated counterpart (synthesized APFO-15). These results demonstrated that fluorine substituted quinoxaline based D–A conjugated polymer might be promising materials with a higher V_{oc} for bulk heterojunction photovoltaic cells. However, ideal phase separation of active layers has not been obtained in this work, if the morphology of blend film can be further optimized, improved photovoltaic performance is prospective.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym.2013. 07.015.

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