CrossMark

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

Haimei Wu [a,b], Bo Qu [c,*], Di Tian [a], Zhiyuan Cong [a], Bowen Gao [d], Jianqun Liu [a], Zhongwei An [a], Chao Gao [a,*], Lixin Xiao [c], Zhijian Chen [c], Qihuang Gong [c], Wei Wei [b,*]

[a] Xi'an Modern Chemistry Research Institute, Xi'an Shaanxi 710065, People's Republic of China
[b] Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing 210003, People's Republic of China
[c] State Key Laboratory for Artificial Microstructures and Mesoscopic Physics, Department of Physics, Peking University, Beijing 100871, People's Republic of China
[d] State Key Laboratory of Transient Optics and Photonics, Xi'an Institute of Optics and Precision Mechanics, Chinese Academy of Science (CAS), Xi'an Shaanxi 710119, People's Republic of China

ARTICLE INFO

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.

© 2013 Elsevier Ltd. All rights reserved.

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

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$_6$H$_5$Br$_2$FN$_2$) (%):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$_4$Cl 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$_2$FN$_2$O$_2$) (%):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-bromo-thiophen-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,