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The enhanced photovoltaic performance of fluorinated acenaphtho[1,2-b]quinoxaline based low band gap polymer

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ABSTRACT

A new low band gap polymer **P1** with fluorinated acenaphtho[1,2-b]quinoxaline (AQ) as the acceptor unit and benzo[1,2-b:4,5-b′]dithiophene as the donor unit has been designed and synthesized. Comparing with its non-fluorinated analog polymer **P2**, **P1** shows a lower band gap of 1.76 eV with a deeper HOMO energy level of −5.54 eV. Polymer solar cells with the blend of **P1** and $PC_{71}BM$ as the active layer without the additive or annealing showed a PCE of 4.72%, which was higher than **P2** based devices with a PCE of 1.65%. Obviously, **P1** can endow devices with a V_{oc} of 0.77 V and a J_{sc} of 10.75 mA cm^{-2}, which are higher than that of **P2** based devices with a V_{oc} of 0.75 V and **a** J_{sc} of 4.41 mA cm^{-2}, such an enhanced photovoltaic performance can be attributed to the broader absorption, the improvement of film morphology, and the higher charge mobility. Thus, fluorinated AQ can be a useful acceptor unit to construct narrow band gap conjugated polymers. To the best of our knowledge, this is the highest PCE report for AQ based polymer solar cells.

1. Introduction

As a promising next-generation green technology, polymer solar cells (PSCs) based on the bulk heterojunction (BHJ) structure have attracted tremendous attention due to their advantages of low cost, light weight, and roll-to-roll fabrication [1–11]. With the rapid progress over recent years, power conversion efficiencies (PCEs) of around 10% for single-junction polymer solar cells [12] and 11% for tandem cells [13] have been achieved. A major contribution to such significant enhancement of PCEs has come from developing new polymer as donor with a wide absorption range, high charge transport ability and suitable frontier orbital levels matched with fullerene derivative as the acceptor. Another crucial point to obtain high performance for PSCs is the device optimization including controlling the morphology of active layer, developing new interfacial materials, and adopting different device structures [14].

Until now, low band gap polymers with an electron-rich (D) and electron-deficient (A) alternating polymer structure have been considered as the most promising candidate to achieve high performance polymer solar cells (PSCs). Based on this strategy, new donor and acceptor units have been developed to construct series of novel low band gap polymers. Acenaphtho[1,2-b]quinoxaline (AQ), as a more planar quinoxaline derivative, has been used as an electron deficient unit in building low band gap polymers, due to the electron withdrawing property of two imine nitrogen atoms and relatively stable quinoid form [15–18]. However, there are only a few reports about solar cell devices based on polymers containing AQ unit and PCEs are still relatively low (<2%) [19–21]. Recently, fluorinated building blocks have attracted great interest. Fluorinated polymers often exhibited markedly lower HOMO and LUMO energy levels, closer polymer chain packing distance in the solid state, and higher thermal and electrochemical stability [22–27].

Herein, we designed and synthesized a D-A alternating copolymer **P1** with fluorinated AQ as the acceptor unit and benzo[1,2-b:4,5-b′]dithiophene (BDT) as the donor unit. Its non-fluorinated analog **P2** was also synthesized for comparison. The effect of fluorination on photophysical properties of polymers and their photovoltaic device performance was also investigated. The polymer structures are shown in Chart 1. For **P1**, two fluorine atoms were introduced to the 9 and 10 positions of the AQ unit and two

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octyl chains were attached on thiophene units to improve the solubility of the resulting polymer. For **P2,** the two octyloxy chains linked to the 9 and 10 positions of the AQ unit assured a good solubility and planarity. As expected, **P1** shows a lower band gap of 1.76 eV with a deeper HOMO energy level of −5.54 eV than **P2**, which has a band gap of 1.90 eV and a HOMO energy level of −5.43 eV. PSCs with the blend of **P1**:$PC_{71}BM$ (1:3) as the active layer without the additive showed a PCE of 4.72% with an increased V_{oc} of 0.77 V, a J_{sc} of 10.75 mA cm^{-2} and an *FF* of 0.57, which is higher than that of **P2** based solar cells with a PCE of 1.65%, a V_{oc} of 0.75 V, a J_{sc} of 4.41 mA cm^{-2}, and an *FF* of 0.50 under simulated solar illumination of AM 1.5G (100 mW/cm^2). Obviously, fluorinated polymer **P1** can obtain higher V_{oc} than non-fluorinated **P2** without sacrificing J_{sc}, which significantly enhance the photovoltaic performance. Therefore, we can conclude that fluorinated acenaphtho [1,2-b]quinoxaline could be a useful acceptor unit to construct narrow band gap conjugated polymers. To the best of our knowledge, this is the highest PCE report for acenaphtho[1,2-b]quinoxaline based polymer solar cells [19–21].

2. Experimental section

2.1. Materials and instruments

All chemicals were purchased from commercial suppliers and used without further purification. Toluene was distilled over sodium with benzophenone as an indicator under nitrogen atmosphere. N, N-Dimethylformamide (DMF) was distilled over CaH_2 before use. $Pd(PPh_3)_4$ was prepared according to literature [28]. 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4, 5-b′]dithiophene was purchased from Solarmer Materials. 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[1,2,5]-thiadiazole [29] and 4,7-bis(5-bromothiophen-2-yl)-5,6-difluorobenzo [1,2,5]thiadiazole [30] were prepared by following the literature procedures. All reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) on silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200–300 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer in $CDCl_3$. UV–vis absorption spectra were obtained on a PerkinElmer UV–vis spectrometer model Lambda 750. The electrochemical behavior of polymers was by using cyclic voltammetry (CHI 630A electrochemical analyzer) with a standard three-electrode electrochemical cell in a 0.1 M Bu_4NPF_6 solution in CH_3CN at room temperature with a scanning rate of 100 mV/s. A glassy carbon working electrode, a Pt wire counter electrode, and an Ag/$AgNO_3$ (0.01 M in CH_3CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin–Elmer Diamond DSC instruments, respectively, under a nitrogen atmosphere at a heating rate of 10 °C/min to record TGA and DSC curves. The powder X-ray diffraction (XRD) patterns were collected using a PANalytical X′ Pert PRO MPD diffractometer with Cu KR radiation. Gel permeation chromatography (GPC) measurements were performed at 150 °C on a PL-220 (Polymer Laboratories) chromatography connected to a differential refractometer with 1,2,4-trichlorobenzene as an eluent. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. The thickness of the active layers was determined by a Dektak 6 M surface profilometer.

2.2. Fabrication and characterization of SCLC

Devices used for measuring space charge limited current (SCLC) were fabricated with a configuration of ITO/PEDOT:PSS/Polymer:$PC_{71}BM$/Au. The conductivity of ITO was 20 Ω/square. PEDOT:PSS is Baytron Al 4083 from H.C.Starck and was filtered with a 0.45 μm polyethersulfone (PES) film before use. The PEDOT:PSS was spin-coated on top of cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130 °C for 15 min on a hotplate before transferred into a glove box. The thickness of the PEDOT:PSS layer was about 40 nm. The blend of polymers and $PC_{71}BM$ was dissolved in 1,2-dichlorobenzene (DCB), heated at 110 °C overnight, and then spin-coated onto PEDOT:PSS layer. The top electrode was thermally evaporated, with a 100 nm of gold at a pressure of 10^{-4} Pa through a shadow mask. Dark Current-voltage characteristics were recorded using an Agilent B2902A Source in a dark circumstance with a range of 1.0 V–5.0 V in air without encapsulation. The hole mobilities were calculated according to the Mott–Gurney equation [31]: $\mu = (8d^3/9\varepsilon_0\varepsilon_\gamma)(J/V^2)$, with d the thickness of active layer, ε_0 the vacuum dielectric constant, ε_γ the relative dielectric constant of polymer (usually 3 for polymer).

2.3. Fabrication and characterization of PSCs

PSCs were fabricated in a device configuration of ITO/ PEDOT:PSS/Polymer:$PC_{71}BM$/LiF/Al. ITO glasses with a conductivity of 20Ω/square were cleaned before use. PEDOT:PSS is Baytron Al 4083 from H.C.Starck, and it was filtered with a 0.45 μm PVDF film before use. A thin layer of PEDOT:PSS was spin-coated on top of cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130 °C for 15 min on a hotplate before transferred into a glove box. The thickness of the PEDOT:PSS layer was about 40 nm. The active layer was prepared by spin-coating the solution of polymers and $PC_{71}BM$ on the top of ITO/PEDOT:PSS. The top electrode was thermally evaporated, with a 0.6 nm LiF layer, followed by an 80 nm of aluminum at a pressure of 10^{-6} Torr through a shadow mask. Four cells were fabricated on one substrate with an effective area of 0.04 cm^2. Measurements of devices were conducted in air. The current–voltage (*J*–*V*) measurements of the devices were conducted on a computer-controlled Keithley 236 Source Measure Unit. An AM 1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mW/cm^2 was used as the white light source, and the light intensity was calibrated with a standard single-crystal Si photovoltaic cell. The temperature while measuring the *J*–*V* curves was approximately 20 °C.

2.3.1. Synthesis of 9,10-difluoro-8,11-bis(4-octylthiophen-2-yl) acenaphtho[1,2-b]quinoxaline (3)

A mixture of compound **1** (2.02 g, 3.56 mmol), zinc dust (6.94 g, 106.8 mmol) and acetic acid (60 mL) was heated under reflux for 1.5 h. The reaction mixture was allowed to cool to room temperature and filtered to remove the unreacted zinc dust. A mixture of the filtrate, acenaphthylene-1,2-dione (0.78 g, 4.27 mmol) and acetic acid (20 mL) was stirred at 60 °C for 15 h. Water was added to the mixture, the organic layer was washed with $NaHCO_3$ solution and then extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was chromatographically purified on silica gel eluting with petroleum ether/ dichloromethane (3:1) to give **3** as a yellow solid (1.82 g, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, 2H), 8.10 (d, 2H), 7.88 (s, 2H), 7.83 (t, 2H), 7.28 (s, 2H), 2.75 (t, 4H), 1.75 (m, 4H), 1.48–1.31 (m, 20H), 0.89 (t, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 151.91, 150.37, 150.18, 147.82, 142.55, 136.15, 135.09, 132.41, 132.34, 132.28, 131.51, 130.88, 129.82, 129.53, 128.52, 125.02, 122.69, 118.79, 31.96, 30.67, 30.59,