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New ultra low bandgap thiadiazolequinoxaline-based D-A copolymers for photovoltaic applications

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ABSTRACT

In this communication, we designed two low bandgap D-A copolymers with same fluorinated thiadiazoloquinoxaline (TDQ) as acceptor and different donor units benzo[2,1-b;3,4-b′]dithiophene (**P1**) and benzo[1,2-b:4,5-b′]dithiophene (**P2**). **P1** and **P2** exhibit broad absorption profiles covering from 350 nm to 1150 nm and 350–950 nm, respectively with optical bandgaps of 1.06 eV and 1.18 eV, respectively. Both copolymers showed deep highest occupied molecular orbitals (HOMO), i.e. −5.38 eV and −5.26 eV, for **P1** and **P2**. Their photovoltaic properties were evaluated using conventional devices with a structure of ITO/PEDOT:PSS/copolymer:$PC_{71}BM$/Al. After the optimizations of the copolymer to $PC_{71}BM$ weight ratios, and concentration of the solvent additive (DIO), the devices showed overall power conversion efficiencies of 4.03% and 5.42% for the **P1** and **P2** based devices, respectively. The higher value of PCE of the **P2** based device is attributed to the higher values of J_{sc} and FF, that is related to the higher hole mobility and better exciton dissociation efficiency. Although the PCEs of these devices are moderate, these ultra low band gap copolymers can be used for their potential application in tandem polymers solar cells. Finally, methanol treatment of the active layer was adopted to increase the PCE of the **P2**:$PC_{71}BM$ based polymer solar cells that resulted in an improved PCE up to 6.93%.

1. Introduction

Over the past decade, polymer solar cells (PSC) with bulk heterojunction (BHJ) have attracted attention of researchers as renewable energy sources alternative to inorganic photocells due to their advantages such as low cost, ease of manufacturability, low weight, possibility of flexible large area devices manufacturing, while at the same timenoting significant progress in PSC devices that have achieved power conversion efficiencies (PCEs) exceeding 10% [1–4]. Recently PCEs 11.7% have been reported for PSC after optimization of the active layer processing method [5]. However, PSCs are not yet ready for commercial applications mainly due to low PCE values. A key factor limiting the efficiency of organic solar cells is a discrepancy between the active layer absorption spectrum and the solar radiation spectrum. PSC effectiveness has been greatly improved via simple absorption band extension or via selection of donor polymers absorption. Most successful low band gap polymers exhibit absorption band from 500 nm to 750 nm, which lies exactly at the solar spectrum peak [6–8]. However, the absorbance range of these devices is typically less than ~900 nm, while the solar spectrum extends much further into the near-infrared (NIR) range. A significant portion of the solar spectrum remains unused, that opens great opportunity for further improvement in performance of organic solar cells. It is known that about 50% of the solar energy lies in the NIR solar spectrum range. Using NIR photovoltaic organic materials that absorb low energy photons of the solar spectrum, the PCE of the resulting PSC can be increased further. It is desirable to design low bandgap conjugated polymer that effectively absorb photons of the NIR solar spectrum region. As noted above, photon absorption in the long-wavelength solar spectrum range with large flow of photons, narrow band gap polymers are highly demanded. However, reduction of the bandgap of polymers

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causes LUMO and HOMO levels shift. Since open-circuit voltage (V_{oc}) is proportional to energy difference between donor HOMO and acceptor LUMO, a narrow band gap will inevitably lead to V_{oc} decrease. Therefore, it is essential for ultralow band gap polymers to possess energy levels finely balanced with band gap, to minimize energy loss and to improve overall solar cell performance. Recently, NIR-organic materials have been given significant attention with the aim to improve energy conversion efficiency (PCE) by capturing and converting over 50% of the solar energy from the NIR spectral range (beyond 750 nm). However, photovoltaic characteristics of single-layer based PSCs on the majority of IR-conjugated polymers are still to be improved (PCE $< 2.0\%$) [8–15]. Nevertheless, design and synthesis of materials with good photoresponse beyond 900 nm and significant PCE values in polymer:fullerene solar cells with precisely controlled energy levels are of great demand. Indeed, recently high efficiency of about 6% was achieved by NIR polymers [16]. More recently, there were also reports on tandem NIR-conjugated polymer as a donor polymer with efficiency of 10.6% [17]. Such recent progress inspires us to develop new NIR-absorption polymers for PSC applications. In an effort to develop new NIR-absorption polymers, we started with thiadiazolequinoxaline derivatives as the central acceptor unit. For that purpose, we have prepared two new electron-acceptor monomers based on thiadiazolequinoxaline (TDQ). TDQ is a promising building block for synthesis of polymers with ultra-narrow band gaps due to strong electron-accepting properties due to four imino groups in the TDQ units. On the other hand, we were interested in utilizing **M2** and **M3** electron-donor co-monomers for polymerization because of its beneficial properties, such as high and balanced charge carrier mobility with high absorption capacity in high-energy range of solar spectrum [18,19]. Further correlation studies on thiadiazolequinoxaline alternating polymers structure with different D units and their physicochemical properties may provide some more understanding for design of new narrow band gap polymers [20].

In the literature, it is reported that introducing the fluorine atoms into the polymer backbone is an approach for improving the photovoltaic performance of D-A conjugated polymers. New synthesized copolymers **P1** and **P2** possess broad (panchromatic) absorption spectrum between 300 nm and 1200 nm, while initial PSC photovoltaic characteristics exhibit very interesting and promising photovoltaic characteristics such as good fill factor (FF) and open-circuit voltage (V_{oc}). Single bulk heterojunction PSCs based on the optimized active layers (weight ratio 1:2 and using 3% DIO as solvent additive) based **P1** and **P2** as donor and $PC_{71}BM$ showed overall PCE of 4.03% and 5.42%, respectively. The higher PCE of the **P2** based device may be attributed to the better nanoscale morphology of the active layer and exciton dissociation efficiency into free charge carriers and improved balanced charge transport. Finally, methanol treatment of the active layer of the optimized **P2**:$PC_{71}BM$ based device improved up to 6.93%, which is due to the simultaneous enhancement in V_{oc}, J_{sc} and FF.

2. Experimental details

2.1. Synthesis of P1 and P2

All chemicals and reagents were reagent grade and purchased from Aldrich or Acros companies and used without further purification. Toluene, tetrahydrofuran were freshly distilled before use. The co-monomers, 4,9-dibromo-6,7-bis(9,9-didodecyl-7-fluoro-9*H*-fluoren-2-yl) [1,2,5]thiadiazolo[3,4-*g*]quinoxaline (**M1**) [19], bis(trimethylthin)-4,5-bis(undecyl) benzo[2,1-b;3,4-b′]dithiophene (**M2**) [16] and 1,5-bis(trimethylstannyl)-4,8-didodocylbenzo [1,2-b:4,5-b′]dithiophene (**M3**) [11] were prepared according to published procedures.

^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz on Bruker AVANCE spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. The elemental analysis was performed with an Elementar Vario EL III element analyzer for C, H, N, S determination. Absorption spectra were measured with a Shimadzu UV-3600 UV–vis–NIR spectrophotometer. The molecular weights of the polymers were measured by GPC method on Waters 515–2410 with polystyrenes as standard and chloroform as an eluent. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 in a nitrogen atmosphere and at a heating rate of 20° C min^{-1}. The DSC analysis was performed on a DSC Q600 under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Cyclic voltammetry was performed under an inert atmosphere at a scan 0.1 V s^{-1} and 0.1 M Bu_4NPF_6 in acetonitrile as the electrolyte. An ITO glass slide covered with a thin layer polymer (20 nm) was used as the working electrode. The counter and reference electrodes were a Pt wire and Ag/Ag^{+}, respectively. All potentials were referenced against Fc/Fc^{+}. The redox potential of the F_c/F_c^{+} internal reference is 0.4 V vs Ag/Ag^{+}.

2.2. Synthesis of copolymers **P1**

The polymerization was performed by a Stille coupling reaction. In a 50 mL flask monomers **M1** (0.6927 g, 0.5 mmol) and **M3** (0.4428 g, 0.5 mmol) were dissolved in 15 mL of toluene, and the solution was flushed with argon for 15 min, then 27 mg of $Pd(PPh_3)_4$ was added into the solution. The mixture was again flushed with argon for 20 min. The reaction mixture was heated to reflux for 48 h, then cooled to room temperature and added dropwise into 400 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added drop-wise into methanol. Finally, the precipitate was collected and dried under vacuum overnight to get copolymer **P1** as a black solid (0.73 g, yield 82%).^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.71–7.08 (br, 14H, ArH), 4.72 (br, 4H, CH_2–O–Ar) 2.24–2.07 (br, 8H, CH_2–Ar), 1.82–0.70 (br, 138H,CH_3,CH_2). Elem. Anal. for $(C_{116}H_{164}F_2N_4S_3O_2)_n$ Calc: C, 78.24; H, 9.28; N, 3.15;F, 2.13; S, 5.40. Found: C, 77.81; H, 9.00; N, 2.84; F, 1.83; S, 5.02.

2.3. Synthesis of copolymers **P2**

Copolymer **P2** as synthesized by following the same procedure for **P1** but using **M2** instead of **M1**. Monomers **M2** (0.6919 g, 0.5 mmol) and **M3** (0.3130 g, 0.5 mmol) were used as starting materials in the polymerization. Finally, **P2** was obtained as a black solid (0.75 g, yield 87%).^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.56–7.01 (br, 14H, ArH), 3.43 (br,4H,CH_2–Ar), 2.07–2.0 (br, 8H, CH_2–Ar), 1.72–0.63 (br, 134H, CH_3,CH_2). Elem. Anal. for $(C_{114}H_{160}F_2N_4S_3)_n$ Calc: C, 79.60; H, 9.37; N, 3.26; F, 2.21; S, 5.59; Found: C, 79.04; H, 9.02; N, 2.89; S, 5.11.

2.4. Device fabrication and characterization

The device structure was ITO/PEDOT:PSS/active layer/with or without CIL/Al. The indium tin oxide (ITO) coated glass substrates were cleaned with ultrasonication process sequentially in detergent, deionized water, acetone and isopropyl alcohol and then dried in ambient conditions. After filtration through a 0.45 μm filter, PEDOT:PSS (Bay P VP AI 4083, Bayer AG) was spin-coated at 3500 rpm for 60 s to form a thickness of 40 nm thin layer on the cleaned ITO substrate, and baked on a hot plate at 120 °C for about 10 min. A blend film of **P1** or **P2**:$PC_{71}BM$ (different weight ratio of 1:05, 1:1, 1:1.5, 1:2 and 1:2.5) was prepared by spin-coating its mixed solvent of CF/1,8-diiodoctane (DIO) (97:3, v:v) solution