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Band gap tunable benzodithiophene-based donor-rich semi-random D–A copolymers with active layer thickness tolerance for organic solar cells

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ABSTRACT

A series of donor-rich semi-random copolymers with various benzodithiophene (donor unit)/fluorinated-thienothiophene (acceptor unit) ratios – D2A, D3A, D5A, D7A – were designed and synthesized for use in polymer solar cells (PSCs). The polymer D1A was also synthesized for comparison. The optical and electrochemical properties of these polymers vary with the number of donor units in their polymer backbones. The device containing the polymer D5A exhibits a best power conversion efficiency (PCE) of 5.52% when the active layer thickness is 340 nm, a value that is 80% of its maximum PCE, whereas the best PCE of the D1A-based device is reduced by 32% when the active layer thickness is 310 nm. A large area (6,270 mm²) D5A-based device prepared with the slot die-coating method was found to exhibit a best PCE of 6.54%, which is significantly better than that of the equivalent D1A-based large area device (4.03%).

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1. Introduction

Organic photovoltaic (OPV) solar cells have attracted much attention as promising devices for producing clean and renewable energy because of their potential for low temperature processing and compatibility with various substrates, and because they are thin in film and light in weight. The most important advantage of PSCs over inorganic solar cells is their ease of fabrication, which reduces manufacturing cost [1–6]. One successful technique in this area is the preparation of a solution-processed bulk heterojunction (BHJ) solar cell containing an active layer composed of an electron-donating semiconducting polymer and an electron-withdrawing fullerene derivative. PCEs greater than 9% have been demonstrated for a single junction solar cell based on an active layer consisting of poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-co-3-fluorothieno-[3,4-*b*]thiophene-2-carboxylate] (PTB7-Th) and [6,6]-phenyl C₆₁ butyric acid methyl ester (PC₆₁BM) [7,8]. The performance of large area devices has also rapidly

improved, from less than 3.5% in 2011 to 6.8% in 2013 [4,9]. This significant progress means that researchers in this area are confident that practical uses will be found for organic photovoltaics in the near future.

However, many issues remain that need to be addressed [10]. In particular, new materials are needed with tailored energy levels and the appropriate solubility that are suitable for large area processing. The active layer composites of large area devices can be prepared by using techniques such as inkjet printing, spray coating, gravure coating, and roller casting [11–13]. In these methods, the optimization of the active layer thickness is of particular concern because it is difficult to prepare uniform thin films. To achieve a high performance large area device, the active layer materials must not only exhibit a high PCE but must also provide acceptable performance over a range of thicknesses. Most high efficient new materials exhibit optimal performance in thin films (80–120 nm); only few conjugated polymers have been reported that exhibit high photovoltaic performances when the thickness of the active layer is over 200 nm [14–18].

Yu's group reported a series of alternating ester substituted semiconducting polymers composed of thieno[3,4-*b*]thiophene (TT) and benzo[1,2-*b*:4,5-*b'*]dithiophene units (BDT) [19]. The introduction of fluorine atom into thieno[3,4-*b*]thiophene (TT-F)

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provides a high V_{oc} polymer with a relatively low-lying highest occupied molecular orbital (HOMO) energy level [8,20]. Introducing the 2-ethylhexylthienyl group at the 4 and 8 positions of the BDT moiety to produce BDT-Th improves the coplanarity of the main chain, and an optimized inverted device containing a polymer based on TT-F and BDT-Th was found to exhibit a PCE of 9.35%, an increased V_{oc} and fill factor [7]. These excellent results in the design of new materials containing TT-F and BDT-Th provide a logical starting point for further research.

In this study, we designed novel donor-rich D–A semi-random copolymers based on the TT-F and BDT-Th units, which were found to exhibit reasonable efficiencies for a range of active layer thicknesses. We expect that the BDT-Th-rich sections of the semi-random polymers might give rise to flat regions in their backbones in which charge-separated holes can reside; the hole transport through these flattened polymer backbone is expected to be facile, which will improve the PCEs of associated devices. By varying the number of donor units in the polymer chain, small to medium band gaps can be obtained. This study introduces a promising series of polymers with tuning the band gaps and electrical properties for opto-electronic application.

2. Experimental section

2.1. Synthesis

The detail synthetic procedures and characterizations of monomers and polymers are provided in the Supporting Information.

2.2. General instrumental measurements

^1H NMR and ^{13}C NMR spectra were recorded on the Bruker DRX-300 FT-NMR Spectrometer. Molecular weights were determined with Gel permeation chromatography (GPC) on Viscotek TSA302 Triplet Detector Array system in CHCl_3 using polystyrene standard at room temperature. The elemental analysis was performed on Thermo Scientific FLASH EA-2000 Organic Elemental Analyzer for C, H, N, S determination and Thermo Finigan FLASH EA-1112 Elemental Analyzer for O determination. TGA was measured on the TGA Q5000 V3.13 Build 261.

2.3. Thin film characterizations

Absorption spectra were recorded on a Shimadzu UV-3600 UV–vis spectrometer. The samples for UV–vis absorption measurements were prepared by spin-coated the solution of polymer in chloroform on cleaned quartz glass substrates. The thickness of various layers was measured by contact surface profile meter (Alpha Step IQ). Cyclic voltammetry (CV) was measured by using IviumStat instrument. CV is conducted with a scan rate of 50 mV s^{-1} at room temperature under the protection of argon with 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile as the electrolyte. A platinum electrode was coated with a thin copolymer film and used as the working electrode. A Pt wire was used as the counter electrode, and a Ag/Ag^+ electrode was used as the reference electrode.

2.4. Hole and electron mobilities measurements

OTFT devices bottom contact structure ($W/L = 120\ \mu\text{m}/12\ \mu\text{m}$) were fabricated from 0.5 wt% chloroform solution of polymer. In SCLC method, hole and electron mobilities of the interlayers were determined using the hole and electron only device ITO/Al₂O₃/copolymer:PC₇₁BM/MoO₃/Ag and ITO/ZnO/copolymer:PC₇₁BM/Ca/Al, respectively, along with the use of SCLC equation for the calculation.

2.5. Solar cell fabrication and measurements

The structure of small and large area BHJs devices are similar, with the configuration of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)/polymer: [6,6]-phenyl C₇₁ butyric acid methyl ester (PC₇₁BM) (1:1.5 w/w)/Ca/Al.

2.5.1. Small area device fabrication

To fabricate small area PSCs, first, ITO coated glass slides were cleaned by detergent, followed by ultrasonic washing in deionized (D.I.) water, acetone and isopropanol, and subsequently dried in an oven overnight. After UV-ozone treatment for 10 min, PEDOT:PSS solution (Clevious P) was spin-coated onto the ITO substrate at 5000 rpm for 40 s and then annealed at 140 °C for 10 min. For deposition of the active layer, blend solutions of polymer:PC₇₁BM (1:1.5 w/w) dissolved in chlorobenzene (CB) containing 3% 1,8-diodooctane (DIO) were spin-cast on top of the PEDOT:PSS layer in a nitrogen-filled glove box. Finally, metal top electrode, Ca and Al were sequentially deposited onto BHJ active layer in vacuum ($< 10^{-6}$ Torr) by thermal evaporation. The active area of the small devices is 9 mm^2 .

2.5.2. Large area module fabrication

Patterned ITO glass substrates ($12\text{ cm} \times 12\text{ cm}$) for slot-die coating were washed with D.I. water, acetone and isopropanol three time each and dry in oven at 140 °C overnight. After 15 min UV-Ozone treatment, a solution of PEDOT:PSS (Clevious P) diluted with IPA (1:1.5) was coated on the substrate with flow rate $100\ \mu\text{m s}^{-1}$ at 80 °C. Slot-die coated PEDOT:PSS layer was dried at 140 °C for 20 min in air to get average thickness of 25 nm. A solution of polymer and PC₇₀BM with total concentration of 25 mg mL^{-1} dissolved in chlorobenzene (CB) containing 3% DIO was coated on PEDOT:PSS at 80 °C with flow rate of $60\ \mu\text{m s}^{-1}$ to get average thickness of 95 nm. Each module was fabricated with 11 cells. Finally, for the series connections of the cells tap-mask was used and Ca/Al (2/100 nm) metal electrode was deposited by thermal evaporator.

2.5.3. Measurements

The J – V characteristics of the small area devices and large area sub-module were recorded by using a computer-controlled Keithley 236 source measure unit (Keithley Instruments). The characterization of un-encapsulated solar cells was carried out in air under illumination of AM 1.5 G, 100 mW cm^{-2} , using a solar simulator (Newport) with xenon light source. Small devices are measured with mask. Illumination intensity was set using an NREL certified silicon diode with an integrated KG5. The external quantum efficiency (EQE) was measured using a reflective microscope objective to focus the light output from a 100 W halogen lamp outfitted with a monochromator and optical chopper (PV Measurements, Inc.).

3. Results and discussion

3.1. Synthesis and characterization of the polymers

As shown in Scheme 1, all the copolymers were synthesized with Stille coupling reactions that used toluene and N,N -dimethylformamide (4:1, v/v) as the solvents and tetrakis(triphenylphosphine)palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) as the catalyst. We obtained the polymers in yields of 64–82%. All these polymers are sufficiently soluble in common organic solvents such as toluene, chloroform, CB, and dichlorobenzene for the fabrication of PSCs. The molecular weight and polydispersity index (PDI) of each polymer were

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