



Low bandgap polymers with benzodithiophene and bithienylacrylonitrile units for photovoltaic applications

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ABSTRACT

Novel copolymers (**P1** and **P2**) comprising (*E*)-2,3-bis(2-thienyl)acrylonitrile and benzo[1,2-*b*;4,5-*b'*]dithiophene derivatives are designed and synthesized to be applied as an electron donor material in polymer solar cells blended with PC₆₁BM as an electron acceptor. These copolymers show a good thermal stability with a 5% weight loss temperature beyond 340 °C, and their films exhibit a broad absorption band with a low optical bandgap of ca. 1.84 eV. Polymer solar cells based on **P2**, prepared under optimized preparation conditions, are found to exhibit a short-circuit photocurrent of 10.71 mA cm⁻², an open-circuit photovoltage of 600 mV, a fill factor of 65%, and a power conversion efficiency of 4.17% under AM 1.5 illumination conditions, 100 mW cm⁻².

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1. Introduction

Development of clean energy sources capable of replacing environment-polluting fossil fuels, is a very urgent subject for every energy researcher [1,2]. Undoubtedly, solar energy is one of the most environment-friendly, sustainable, and promising resources and various types of photovoltaic devices have been developed for conversion of solar energy to electricity. Among them, bulk heterojunction (BHJ) solar cells or polymer solar cells (PSCs), which consist of a donor-type conjugated polymer and an acceptor-type fullerene derivative, have received a strong interest because of low-cost, lightweight and easy fabrication [3–6]. Energy levels of a polymer to be used as a donor material in PSCs should be tuned so as to have a low-lying highest occupied molecular orbital (HOMO) level to provide a large open-circuit photovoltage (V_{oc}) and a suitable lowest unoccupied molecular orbital (LUMO) level to provide enough offset for light-induced charge separation [7]. In addition to the suitable energy level matching with the fullerene

acceptor, the donor polymer should exhibit broad absorptions with high absorption coefficients toward sunlight, high hole mobility, and appropriate compatibility with the fullerene to form nanoscale bicontinuous interpenetrating network [8–11]. One plausible approach toward this goal is to design alternate copolymers comprising electron-rich (D) and electron-deficient (A) units with some specific functional groups [12–14]. Until now, many candidates for D and A units have been reported. Among them, we have focused our attention on (*E*)-2,3-bis(2-thienyl)acrylonitrile (BTA) as an A unit since BTA possesses a strong electron-accepting cyano group with a thienylene-vinylene moiety which has an extended π -conjugation length responsible for the efficient light harvesting [15–19]. A few D–A type copolymers incorporating a BTA unit have been reported [20–26]. To date, however, PSCs based on the BTA-containing copolymers have failed to yield high power conversion efficiencies (PCEs). To enhance the PCEs of solar cells, other types of D units to be combined with BTA should be developed.

Recently, much attention has been given to benzo[1,2-*b*;4,5-*b'*]dithiophene (BDT) as a D unit. The absorption spectrum of BDT-containing copolymers covers the whole

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visible region from 350 to 750 nm, and the solar cells based on BDT copolymers have yielded high PCEs of 3–6% [27–29]. It is also known that side alkoxy groups attached to the BDT unit play a significant role for enhancing photovoltaic properties by making a bandgap of the polymer narrower and facilitating an electron transfer from the donor polymer to fullerene.

In the present study, we designed two new copolymers consisting of BTA as an electron-deficient group and BDT as an electron-rich group: poly[(4,8-dihexyloxybenzo[1,2-*b*;4,5-*b'*]dithiophene)-*alt*-((*E*)-2,3-bis(2-thienyl)acrylonitrile)] (**P1**) and poly[(4,8-didecyloxybenzo[1,2-*b*;4,5-*b'*]dithiophene)-*alt*-((*E*)-2,3-bis(2-thienyl)acrylonitrile)] (**P2**). The combination of BTA and BDT units is expected to give rise to superior photovoltaic performances by utilizing distinguished characteristics of both BTA and BDT. The synthesis and characterizations of the copolymers are described, together with the performances of PSCs prepared under different conditions with the two polymers blended with PC₆₁BM as the active layer.

2. Experimental

2.1. Materials

Thiophene-3-carbonyl chloride, diethylamine, hexyl-*p*-toluenesulfonate, 1-bromodecane, *n*-butyllithium (*n*-BuLi, 1.67 M solution in hexane), trimethyltinchloride (1.0 M solution in hexane), 2-thiophenecarboxaldehyde, tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄), 2-(2-thienyl)acetonitrile, sodium methoxide and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron PH500) were purchased from Tokyo Chemical Industry and used without purification. Tetrabutylammonium bromide (TBAB), *N*-bromosuccinimide (NBS), and tetrabutylammonium hexafluorophosphate (TBAPF₆) were purified by recrystallization. Tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and toluene were dried by CaH₂, Na, and P₂O₅, respectively, under nitrogen. Acetonitrile (CH₃CN) was distilled prior to use.

2.2. Measurement and characterization

The NMR was recorded using a Varian 500 MHz instrument and chemical shifts were recorded in parts per million. The ultraviolet–visible (UV–vis) absorption spectrum was recorded on a Shimadzu UV-3150 spectrophotometer and FT-IR spectra were obtained with a PerkinElmer FT-IR spectrometer. Polymer molecular weights and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) analysis using Shimadzu chromatograph with Shodex KF801, KF802, and KF803L columns at 40 °C with THF as eluent. Thermogravimetric analysis (TGA) was conducted with a SIC model TG/DTA-6200 at a heating rate of 10 °C min⁻¹ under nitrogen flow. Electrochemical measurements were performed at room temperature (RT) using a Hokuto Denko HSV-100 automatic polarization system under an argon atmosphere. A three-electrode cell equipped with a platinum sphere working electrode, an Ag/Ag⁺ (0.01 M in CH₃CN) reference

electrode, and a platinum wire counter electrode was applied. All samples were measured in CH₃CN solutions containing 0.1 M TBAPF₆ as a supporting electrolyte. Ferrocene/ferrocenium redox couple (Fc/Fc⁺) was used as an internal reference.

2.3. Device fabrication and photovoltaic evaluations

Devices with a typical sandwich structure of ITO/PEDOT:PSS/polymer:PC₆₁BM/LiF/Al were fabricated (Fig. 1). Indium-tin oxide (ITO)-coated glass substrates were etched by mixed acidic solution (HCl:HNO₃:H₂O = 4:3:6) and cleaned stepwise under ultrasonication in detergent, alkali solution, de-ionized water, acetone, and 2-propanol for 10 min, respectively, then treated with UV ozone for 30 min. PEDOT:PSS was spin-coated from an aqueous solution on top ITO substrate as buffer layer giving a thickness of about 30 nm, then it was heated on a hot plate at 100 °C for 10 min. Subsequently, a blend solution of polymer/PC₆₁BM (1:1 w/w) with concentration of 15 mg mL⁻¹ in chlorobenzene with or without 1,8-diiodooctane (DIO, 3 vol.%) was spin-coated after being filtrated through a 0.20 μm syringe filter (PTFE) on top of PEDOT:PSS film giving a thickness of about 100 nm, and annealing of the blend film was performed at 150 °C for 10 min. The devices were completed by depositing LiF (0.6 nm) and Al (100 nm) cathode as top electrodes with area defined by a shadow mask under high vacuum (<2 × 10⁻⁶ Torr) and annealed at 150 °C, producing an active area of 25 mm² for each cell. Photocurrent–voltage characteristics were measured under filtered light illumination from an Asahi HAL-302 solar simulator (AM 1.5 G, 100 mW cm⁻²) in an ambient environment. Data were recorded with a computer-controlled Hokuto Denko sourcemeter.

2.4. Synthetic procedures

The synthetic routes of the monomers and copolymers are shown in Scheme 1. The detailed synthetic procedures are as follows:

2.4.1. *N,N*-Diethylthiophene-3-carboxamide (1) [27]

In a 50 mL flask in ice-water bath, diethylamine (6.25 mL, 4.38 g, 60 mmol) and CH₂Cl₂ (10 mL) were

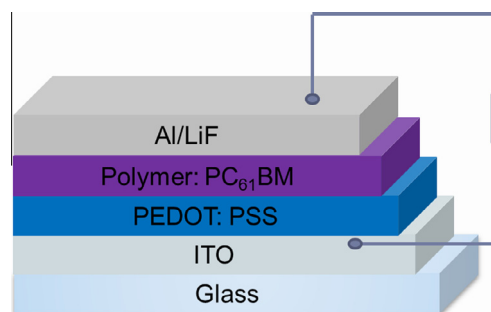


Fig. 1. Schematic device architecture for polymer/fullerene solar cells. The active layer is sandwiched between two electrodes: the ITO electrode covered with PEDOT:PSS layer and the LiF/Al top electrode.

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