



Conjugated polymers containing pyrimidine with electron withdrawing substituents for organic photovoltaics with high open-circuit voltage



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ABSTRACT

Polymers using 6-(2-thienyl)-4H-thieno[3,2-b]indole (TTI) with high planarity were synthesized and utilized for the photovoltaics. Push-pull types of conjugated polymers (**PTTICN**, **PTTICNR** and **PTTIFR**) containing TTI as electron pushing unit and 2-pyriminecarbonitrile or 2-fluoropyrimidine as electron pulling unit were synthesized.

We designed pyrimidine derivatives with strong electron-withdrawing group (C≡N or fluorine) for the generation of strong electron pulling property. By the combination with the electron pushing unit, the pyrimidines with strong electron pulling units will provide low highest occupied molecular orbital (HOMO) energy levels for higher open-circuit voltages (V_{OC}).

For the syntheses of the polymers, the electron pushing and the electron pulling units were combined by Stille coupling reaction with Pd(0)-catalyst. The polymers of **PTTICN** and **PTTICNR** with CN unit show higher V_{OC} than the polymer with fluorine unit. The device comprising **PTTICNR** and PCBM (1:4) with diiodooctane (DIO) additive showed a V_{OC} of 0.82 V, a J_{SC} of 6.38 mA/cm², and a fill factor (FF) of 0.53, giving a power conversion efficiency of 2.81%.

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1. Introduction

Polymer solar cells (PSCs) have been developed caused by their advantages of low cost, flexibility and large area application with solution process. However, the research still has a possibility of advance to improve the unsatisfactory efficiency and stability [1,2]. The major efforts utilizing the bulk heterojunction (BHJ) structure have met with success to resolve various kinds of challenges for the enhancement of efficiency of the PSCs.

To achieve high performance in photovoltaic materials, push–pull type of conjugated polymers, containing electron-rich and deficient units, have been widely used to improve the intramolecular charge transfer (ICT) for the absorbance of the wider

range of the solar spectrum [1–3].

Many types of electron push/pull units, including benzo[1,2-*b*;3,4-*b'*]dithiophene (BDT) [4], carbazole [5], 2,1,3-benzothiadiazole [6], diketopyrrolo[3,4-*c*]pyrrole-1,4-dione [7] and thieno[3,4-*c*]pyrrole-4,6-dione [8], have been reported for high performance of PSCs.

We have designed TTI as the electron pushing unit to augment the ICT for PSCs. By replacing six-membered benzene ring, of the carbazole unit, with five-membered thiophene ring, TTI is expected to reduce the torsional angle and provide stronger electron donating ability [9]. TTI enhanced the planarity to result in more efficient ICT for the red-shift of the absorption spectra and the generation of low band gap [9,10].

The pyrimidine unit, as the electron pulling unit, coupled with dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) unit was reported to provide high efficiency. To improve the electron deficiency of this unit, the electron-withdrawing group (C≡N or fluorine) was introduced at

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C2 position of pyrimidine. By this modification, the pyrimidines coupled with TTI unit will show deep highest occupied molecular orbital (HOMO) energy levels for high open-circuit voltage (V_{OC}) and more efficient ICT effect. In addition to this, the introduction of $C\equiv N$ in the pyrimidine unit will provide higher conjugation and coplanarity [11–14].

In this paper, we report push–pull types of conjugated polymers, **PTTICN**, **PTTICNR** and **PTTIFR**, containing TTI as electron pushing unit and 2-pyriminecarbonitrile or 2-fluoropyrimidine as electron pulling unit [15–17].

By using the Stille coupling condition, TTI and 2-pyriminecarbonitrile/2-fluoropyrimidine fragments were incorporated to synthesize poly(4-{5-[4-(1-octylonyl)-6-(2-thienyl)-4H-thieno [3,2-b]indol-2-yl]-2-thienyl}-6-(2-thienyl)-2-pyrimidine-carbonitrile) (**PTTICN**), poly(4-{4-hexyl-5-[4-(1-octylonyl)-6-(2-thienyl)-4H-thieno [3,2-b]indol-2-yl]-2-thienyl}-6-(4-hexyl-2-thienyl)-2-pyrimidinecarbonitrile) (**PTTICNR**) and poly(2-{5-[2-fluoro-6-(4-hexyl-2-thienyl)-4-pyrimidinyl]-3-hexyl-2-thienyl}-4-(1-octylonyl)-6-(2-thienyl)-4H-thieno [3,2-b]indole) (**PTTIFR**). Novel conjugated polymers showed good solubility at room temperature in various organic solvents. The photovoltaic properties of the polymers were investigated by fabrication of the polymer solar cells with the configuration of ITO/PEDOT:PSS/polymer:PC₇₁BM/Al.

2. Experimental details

2.1. Instrumental characterization

All reagents were purchased from Aldrich or TCI, and used without further purification. Solvents were purified by normal procedure and handled under moisture-free atmosphere. ¹H and ¹³C NMR spectra were recorded with a Varian Gemini-300 (300 MHz) spectrometer and chemical shifts were recorded in ppm units with TMS as the internal standard. Flash column chromatography was performed with Merck silica gel 60 (particle size 230–400 mesh ASTM) with ethyl acetate/hexane or methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F pre-coated aluminum plates with fluorescent indicator UV254. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under electron impact (EI) conditions in the Korea Basic Science Institute (Daegu). Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration and carried out at 35 °C. The DSC analysis was performed on a DSC Q200 at heating rates of 10 °C/min. TGA was performed with a SDT Q600 under nitrogen atmosphere at a heating rate of 10 °C/min to 800 °C in the Korea Basic Science Institute (Busan). The UV–vis absorption spectra were recorded by a Varian 5E UV/VIS/NIR spectrophotometer. Cyclic voltammogram of the polymers was obtained using an Wona-WPG100 at room temperature in a three-electrode cell under a Ar atmosphere at a scan rate of 100 mV/s, with Pt wire as the counter electrode, an Ag/AgNO₃ reference electrode, and 0.1 M tetraethylammonium tetrafluoroborate (TBABF₄) in acetonitrile as the electrolyte. The AFM instrumentation consisted of a Veeco NanoScope AFM and standard silicon cantilever (Veeco; tip radius, 8 nm; normal spring constant, 21–78 N/m; scan rate, 2.0 Hz) at ambient conditions (in air, 20 °C). GIWAXS were measured at the 5A beamline in the Pohang Accelerator Laboratory (PAL, South Korea). 2D GIWAXS patterns were recorded using CCD detector positioned at the end of a vacuum guide tube in which the X-ray pass through the thin films, where operation conditions were set to a X-ray wavelength of 1.0716 Å and a sample-to-detector distance (SDD) of 321.34 mm. The incidence angle (0.13) was carefully chosen to allow for complete X-ray

penetration of the film. The scattering spectra were collected as a 2D image map oriented along the plane of the substrate (q_y) and the plane perpendicular to the substrate (q_z).

2.2. Device fabrication and measurements

The FETs were fabricated on heavily doped *n*-type silicon (Si) wafers each covered with a thermally grown silicon dioxide (SiO₂) layer with thickness of 200 nm. Whole Si substrates were cleaned with ultrasonic bath in acetone and isopropyl alcohol successively, dried over 2 h in the dry oven at 100 °C, and then subjected to UV-ozone treatment for 30 min. The active layer was deposited by spin coating at 2000 rpm. Prior to active layer deposition, SiO₂ surfaces were treated with octadecyltrichlorosilane (OTS) to make surface hydrophobic. All solutions were of 10 mg/ml concentration in dichlorobenzene. The thickness of the deposited films was about 60 nm. Prior to deposition of source drain electrodes, the films were dried at room temperature for 30 min. Source and drain electrodes using Au were deposited by thermal evaporation using shadow mask. The thickness of source and drain electrodes was 50 nm. Channel length (L) and channel width (W) were 50 μm and 3.0 mm, respectively. Electrical characterization was performed using a Keithley semiconductor parametric analyzer (Keithley 4200). All fabrication and measurement processes were carried out in the glove box filled with N₂. The mobility (μ) was determined using the following equation in the saturation regime by

$$I_{\text{sat}} = (\mu WC_i/2L) \cdot (V_{GS} - V_T)^2$$

where C_i is the capacitance per unit area of 15 nF cm⁻² and V_T is the threshold voltage.

Solar cells were fabricated on an indium tin oxide (ITO)-coated glass substrate with the following structure; ITO-coated glass substrate/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)/polymer:PC₇₁BM/Al. The ITO-coated glass substrate was first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. PEDOT:PSS (Baytron PH) was spin-cast from aqueous solution to form a film of 40 nm thickness. The substrate was dried for 10 min at 140 °C in air and then transferred into a glove box to spin-cast the active layer. A solution containing a mixture of polymer:PC₇₁BM in dichlorobenzene solvent with concentration of 20 mg/ml was then spin-cast on top of the PEDOT:PSS layer. The film was dried for 30 min at room temperature in the glove box. Then, an aluminum (Al, 100 nm) electrode was deposited by thermal evaporation in a vacuum of about 3 × 10⁻⁶ Torr. Current density–voltage (J - V) characteristics of the devices were measured using a Keithley 2400 Source Measure Unit. Solar cell performance utilized an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 1000 W m⁻². The spectral mismatch factor was calculated by comparison of solar simulator spectrum with AM 1.5 spectrum at room temperature.

2.3. Synthesis of polymers

The monomers (**6**), (**9**), (**11**), (**15**) and (**17**) were synthesized according to the method as shown in Figure S1.

2.3.1. Synthesis of poly(4-{5-[4-(1-octylonyl)-6-(2-thienyl)-4H-thieno[3,2-b]indol-2-yl]-2-thienyl}-6-(2-thienyl)-2-pyrimidinecarbonitrile) (**PTTICN**)

Carefully purified 4-(1-octylonyl)-2-(trimethylstannyl)-6-[4-(trimethylstannyl)-2-thienyl]-4H-thieno[3,2-b]indole (**6**) (1 eq), 4,6-bis(5-bromo-2-thienyl)-2-pyrimidinecarbonitrile (**10**) (1 eq), P(o-tolyl)₃ (0.4 eq) and Pd₂(dba)₃ (3 mol%) were dissolved in

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