

Fluorine이 도입된 Quinoxaline과 Fluorene 골격을 가진 고분자의 합성 및 특성분석

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Synthesis and Photovoltaic Properties of Copolymers with Fluorinated Quinoxaline and Fluorene Moiety

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초 록

새로운 전자 받개인 6,7-difluoro-2,3-dihexylquinoxaline을 이용하여 유기 태양 전지형 고분자를 개발하였다. Fluorene과 6,7-difluoro-2,3-dihexylquinoxaline으로 Suzuki polymerization방법을 이용하여 낮은 HOMO 에너지를 가지는 PFDTQxF 고분자를 합성하였다. 필름상태의 PFDTQxF은 368과 493 nm에서 두 개의 흡광도를 보였다. PFDTQxF의 HOMO와 LUMO 에너지는 각각 -5.55와 -3.91 eV를 나타내었다. PFDTQxF의 태양전지 소자는 0.47 V의 V_{OC} 와 4.48 mA/cm²의 J_{SC} 와 0.32의 FF 를 가지고 있어 0.78%의 에너지 효율을 나타내었다.

Abstract

New electron deficient moiety, 6,7-difluoro-2,3-dihexylquinoxaline, was developed for the push-pull type copolymer for organic photovoltaics (OPVs). The PFDTQxF with lower HOMO energy level was synthesized using fluorene and 6,7-difluoro-2,3-dihexylquinoxaline by Suzuki polymerization. The PFDTQxF thin film shows two absorption peaks at 368 and 493 nm. The HOMO and LUMO energy levels of PFDTQxF are calculated -5.55 and -3.91 eV, respectively. The device comprising PFDTQxF showed a V_{OC} value of 0.47 V, a J_{SC} value of 4.48 mA/cm², and a FF of 0.32, which yielded PCE of 0.78%, under the illumination of AM 1.5.

Keywords: polymer, quinoxaline, fluorene, fluorine atom, solar cells

1. Introduction

Research on organic photovoltaics (OPVs) has attracted intensive research in industry caused by lightweight plastic substrates, flexible, and low-cost manufacturing[1-3]. The bulk-heterojunction (BHJ) polymer solar cell based on blend of PCBM as the electron acceptor and conjugated polymer as the electron donor have been the most successful device architecture for OPVs[4]. Polymer solar cells have been researched intensively into the syntheses of conjugated polymers with low band gap for more light harvesting of influx photons in matching the solar spectrum[1]. The lower HOMO energy level of conjugated polymer is very significant to leak a high open circuit voltage (V_{OC})

of the polymer solar cell devices[5-8]. The introduction of electron withdrawing group into acceptor unit decreased HOMO energy level of conjugated polymer[9,10].

Research into low-bandgap conjugated polymers with quinoxaline units for OPVs has been recently attracting attention caused by the robust electron-withdrawing ability of the quinoxaline[11]. D-A conjugated polymer by combining with quinoxaline acceptor should be easily structurally deformed caused by high solubility[12]. The fluorinated quinoxaline moiety is the efficacious acceptor units for OPVs due to the strong electron affinity which lead to a broad absorption, high hole mobility, and lower HOMO energy levels, which are significant factors for polymer solar cell[13-15].

In this paper, we present copolymer containing a new acceptor, difluoro-2,3-dihexylquinoxaline units, to show high open circuit voltage. The introduction of fluorine atom into acceptor unit should decrease the HOMO energy level of the PFDTQxF to lead higher open circuit voltages. PFDTQxF was synthesized using 6,7-difluoro-2,3-dihexyl-

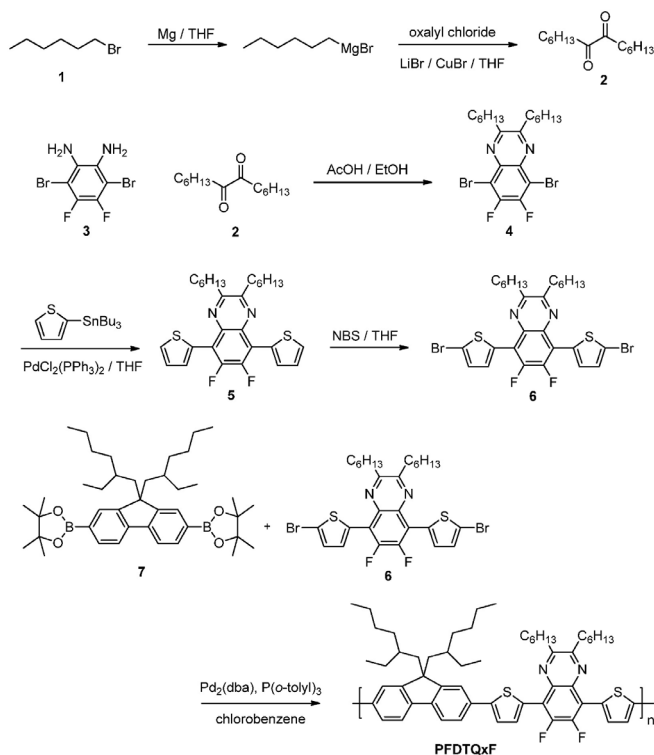
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quinoxaline unit as electron acceptor and alkylated fluorene as electron donor by Suzuki coupling reaction with palladium catalyst. **PFDTQxF** exhibits good solubility, strong absorption and lower HOMO energy level. BHJ device was fabricated with **PFDTQxF** and PCBM with configuration of ITO/PEDOT : PSS/polymer : PC₆₁BM/Al.

2. Experimental

General. 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 JNM ECP-400 (400 MHz, JEOL) 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. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. The UV-vis absorption spectra were recorded by a Varian 5E UV/VIS/NIR spectrophotometer. The cyclic voltammetry was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under argon atmosphere. A platinum electrode (~0.05 cm²) coated with a thin polymer film was used as the working electrode. Pt wire and Ag/AgNO₃ electrode were used as the counter electrode and reference electrode, respectively. The energy level of the Ag/AgNO₃ reference electrode (calibrated by the Fc/Fc⁺ redox system) was 4.8 eV below the vacuum level.

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) : poly(stylenesulfonate) (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-casted from aqueous solution to form a film of 40nm thickness. The substrate was dried for 10 min at 140 °C in air and then transferred into a glove box to spin-cast the charge separation layer. A solution containing a mixture of polymer : PC₇₁BM in DCB solvent with concentration of 7 wt/mL% was then spin-casted on top of the PEDOT/PSS layer. The film was dried for 60 min at 70 °C in the glove box. The sample was heated at 80 °C for 10 min in air. Then, an aluminum (Al, 100 nm) electrode was deposited by thermal evaporation in a vacuum of about 5 × 10⁻⁷ Torr. Current density-voltage (*J-V*) characteristics of the devices were measured using a Keithley 236 Source Measure Unit. Solar cell performance was measured by using an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 1000 W m⁻². An aperture (12.7 mm²) was used on



Scheme 1. Synthetic route for the synthesis of the monomer and polymer.

top of the cell to eliminate extrinsic effects such as cross-talk, waveguiding, shadow effects etc. The spectral mismatch factor was calculated by comparison of solar simulator spectrum with AM 1.5 spectrum at room temperature.

Polymerization of poly[2,7-(9,9-bis(2-ethylhexyl)-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fluorene-*alt*-5,8-(6,7-difluoro-2,3-dihexyl-5,8-di(thiophen-2-yl) quinoxaline)] (**PFDTQxF**) [20].

Carefully purified 9,9-bis(2-ethylhexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fluorene (**7**) [17] (540 mg, 0.84 mmol), 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-dihexylquinoxaline (**6**) [16] (550 mg, 0.84 mmol), P(*o*-tolyl)₃ (40 mol%) and Pd₂(dba)₃ (3 mol%) were dissolved in 5 mL of chlorobenzene. The mixture was refluxed with vigorous stirring for 2 days under argon atmosphere. After cooling to room temperature, the mixture was poured into methanol. The precipitated material was recovered by filtration. The resulting solid material was reprecipitated using 100 mL of THF/1.0 L of methanol several times to remove residual amount of catalyst. The resulting polymer was soluble in THF, CHCl₃, ODCB and toluene.

3. Results and Discussion

3.1. Synthesis and Characterization

The synthesis of the monomer and polymer are shown in Scheme 1. The monomers **6** and **7** were synthesized by reported method [16-17]. 5,8-Bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-dihexylquinoxaline (**6**) [16], as electron-deficient moiety and 9,9-bis(2-ethylhexyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fluorene (**7**) [17], as

Table 1. Polymerization Results, Thermal Property and Optical Property of Polymer

polymer	M_n^a (g/mol)	M_w^a (g/mol)	PDI ^a	T_d^b (°C)	λ_{max} (nm)	
					in solution	in thin film
PFDTQx _n F	4000	5200	1.2	385	479	493

^aMolecular weight (M_n) and polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards.

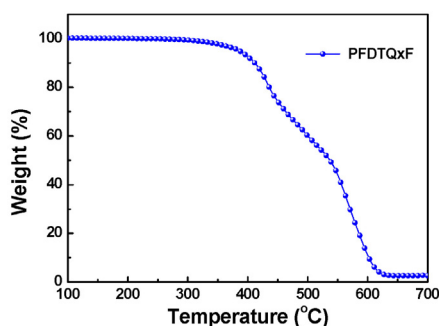
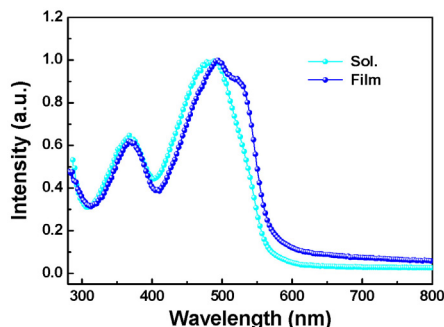
^bOnset decomposition temperature (5% weight loss) measured by TGA under N_2 .

Table 2. Electrochemical Potentials and Energy Levels of the Polymer

polymers	optical band gap ^a (eV)	HOMO ^b (eV)	LUMO ^c (eV)	E_{ox}^d (V)	E_{red}^d (V)	electrochemical band gap ^c (eV)
PFDTQx _n F	2.16	-5.55	-3.91	0.75	-0.89	1.64

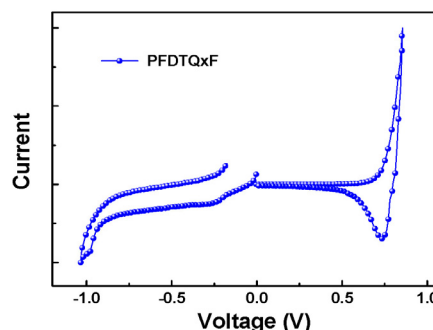
^aOptical energy band gap was estimated from the onset wavelength of the optical absorption. ^bCalculated from the oxidation potentials. ^cCalculated from the reduction potentials.

^dOnset oxidation and reduction potential measured by cyclic voltammetry. ^eCalculated from the E_{ox} and E_{red} .

**Figure 1. Thermogravimetric analysis of the polymer under N_2 .****Figure 2. UV-visible absorption spectra of polymer in chloroform solution and the solid state.**

electron-rich moiety, were copolymerized according to Suzuki polymerization with $Pd_2(dba)_3$ as catalyst for 48 h to give target copolymer PFDTQx_nF.

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) of the synthesized polymer were determined by gel chromatography (GPC) using polystyrene standards with chloroform as eluent and summarized in Table 1. PFDTQx_nF has M_w of 5200 with PDI of 1.2. The thermogravimetric analysis (TGA) of polymer is shown in Figure 1. The onset point of decomposition (T_d) at about 385 °C was determined by the temperature of 5% weight loss under N_2 [18]. The good thermal stability of the polymer is significant for OPV applications in order to prevent the deformation of the morphology. The glass transition temperature (T_g) of

**Figure 3. Electrochemical properties of polymer.**

the polymer was not observed up to 250 °C in differential scanning calorimetry (DSC).

3.2. Photophysical Properties

The photophysical properties of the PFDTQx_nF were studied by UV-vis absorption in chloroform solution and thin film on quartz plate by spin-casting from ODCB solution as shown Figure 2. The photophysical properties of the conjugated polymer are summarized in Table 1. The absorption peak of the polymer is observed at 368 nm, which correspond to the π - π^* transition of conjugated polymer chain in solution. The broad absorption band at about 479 nm was attributed to the intramolecular charge transfer (ICT) interaction[19]. The thin film of PFDTQx_nF has two peaks at 368 and 493 nm, which was shifted toward the long wavelength area as compared with corresponding solution state due to the intermolecular interaction from π - π stacking of polymer backbone.

3.3. Electrochemical Properties

The electrochemical properties of the synthesized polymer were determined by cyclic voltammetry using tetrabutylammonium tetrafluoroborate in acetonitrile. The oxidation and reduction potentials are summarized in Table 2, and the cyclic voltammogram is shown in Figure 3. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level were obtained from formula ($E_{HOMO} = -([E_{onset}]^{ox} + 4.8)$ eV) and ($E_{LUMO} = -([E_{onset}]^{red} + 4.8)$

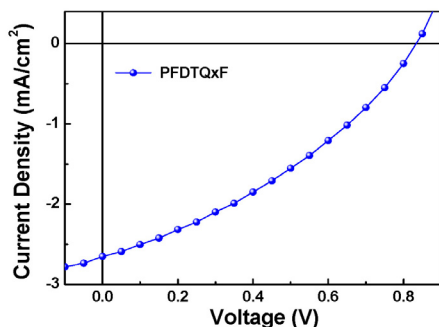


Figure 4. Current density-potential characteristics of the polymer solar cells under the illumination of AM 1.5, 100 mW/cm².

eV), respectively. The onset potential was 0.75 eV for **PFDTQxF**. The corresponding HOMO energy level of **PFDTQxF** is calculated -5.55 eV. The reduction onset value of the **PFDTQxF** was calculated roughly to be -0.89 V. The corresponding LUMO energy level was determined at -3.91 eV. The electrochemical band gap was determined to be 1.64 eV. The optical band gap of the **PFDTQxF** was 2.14 eV, which was estimated using the absorption onset at about 574 nm in thin film. The optical band gap is higher than the electrochemical band gap measured by cyclic voltammetry.

3.4. Polymer Photovoltaic Properties

The photovoltaic performances of polymer were investigated in the device structure ITO/PEDOT : PSS (40 nm)/polymer : PC₆₁BM (100 nm)/Al (100 nm), under illumination with AM 1.5G 100 mW/cm². The current density-voltage (*J-V*) curve of the device based on **PFDTQxF** is displayed in Figure 4. BHJ device was produced by spin-coating of 2 % (w/v) ODCB solution of **PFDTQxF** and PC₆₁BM. The device prepared from **PFDTQxF** with PC₆₁BM (1 : 2) exhibited short-circuit current density (J_{sc}) of 2.65 mA/cm², open-circuit voltage (V_{oc}) of 0.84 V, and fill factor (*FF*) of 0.35, giving a power conversion efficiency (PCE) of 0.78%. The higher V_{oc} was attributed to deeper HOMO energy level of **PFDTQxF**.

4. Conclusions

We have synthesized new conjugated polymer, **PFDTQxF**, containing fluorene and 6,7-difluoro-2,3-dihexylquinoxaline units through the Suzuki polymerization with palladium catalyst. **PFDTQxF** had good solubility, thermal stability and lower HOMO energy level. The onset oxidation potential of the **PFDTQxF** was calculated roughly to be 0.75 V, which accorded to deeper HOMO energy level of -5.55 eV. The PCE of the photovoltaic device based on **PFDTQxF** showed 0.78% with V_{oc} of 0.47 V, J_{sc} of 4.48 mA/cm², and *FF* of 0.32, under the illumination of AM 1.5.

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