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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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/cm$^2$, 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 acceptor 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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lquinoloxaline 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. $^1$H and $^13$C 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 60F254 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 cm$^2$) coated with a thin polymer film was used as the working electrode. Pt wire and Ag/AgNO$_3$ electrode were used as the counter electrode and reference electrode, respectively. The energy level of the Ag/AgNO$_3$ 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/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 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 precipitated 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, CHCl$_3$, 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-dihexyl-5,8-di(3(1,3,2-dioxaborolan-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-bromothonphen-2-yl)-6,7-difluoro-2,3-dihexyiquinoxaline (6)[16] (550 mg, 0.84 mmol), P(o-tolyli) (40 mol%) and Pd$_2$(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 precipitated 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, CHCl$_3$, ODCB and toluene.
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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) | $\lambda_{max}^c$ (nm) |
|------------|----------------|-----------------|---------|--------------|------------------------|
| PFDTQxF    | 4000           | 5200            | 1.2     | 385          | 479                   |

Table 2. Electrochemical Potentials and Energy Levels of the Polymer

| Polymer    | Optical band gap$^a$ (eV) | HOMO$^b$ (eV) | LUMO$^c$ (eV) | $E_{ox}^d$ (V) | $E_{red}^d$ (V) | Electrochemical band gap$^e$ (eV) |
|------------|---------------------------|---------------|---------------|---------------|----------------|-------------------------------|
| PFDTQxF    | 2.16                      | -5.55         | -3.91         | 0.75          | -0.89          | 1.64                          |

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.

Figure 3. Electrochemical properties of polymer.

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

Onset decomposition temperature (5% weight loss) measured by TGA under N$_2$.

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

3.2. Photophysical Properties

The photophysical properties of the PFDTQxF 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 $\pi-\pi^*$ 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 PFDTQxF 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 $\pi-\pi$ 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 cyclovoltammogram is shown in Figure 3. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level were obtained from formula $(E_{HOMO} = -[(E_{onset})^\text{ox} + 4.8] \text{ eV})$ and $(E_{LUMO} = -[E_{onset}]^\text{red} + 4.8)$.
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 : PC$_6$BM (100 nm)/Al (100 nm), under illumination with AM 1.5G 100 mW/cm$^2$. 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 PC$_6$BM. The device prepared from PFDTQxf with PC$_6$BM (1 : 2) exhibited short-circuit current density ($J_{SC}$) of 2.65 mA/cm$^2$, 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 though 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/cm$^2$, and FF of 0.32, under the illumination of AM 1.5.

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