Synthesis and Photovoltaic Properties of Quinoxaline-Based Semiconducting Polymers with Fluoro Atoms

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A new accepter unit, 6,7-difluoro-2,3-dihexylquinonoxaline, was prepared and utilized for the synthesis of the conjugated polymers containing electron donor-acceptor pair for OPVs. New series of copolymers with dioctyloxybenzothiophene as the electron rich unit and 6,7-difluoro-2,3-dihexylquinonoxaline as the electron deficient unit are synthesized. The solid films of poly[2,6-(4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-alt-5,8-(6,7-difluoro-2,3-dihexylquinonoxaline)] (PBQxF) and poly[2,6-(4,8-bis(2-ethylhexyl-oxy)benzo[1,2-b:4,5-b']dithiophene-alt-5,8-(6,7-difluoro-2,3-dihexyl-5,8-di(thiophen-2-yl) quinoxaline)] (PBDTQxF) show absorption bands with maximum peaks at about 599 and 551 nm and the absorption onsets at 692 and 713 nm, corresponding to band gaps of 1.79 and 1.74 eV, respectively. The devices comprising PBQxF with PC71BM (1:2) showed open-circuit voltage (VOC) of 0.64 V, short-circuit current density (JSC) of 1.58 mA/cm2, and fill factor (FF) of 0.39, giving power conversion efficiency (PCE) of 0.39%. To obtain absorption in the longer wavelength region, thiophene units without any alkyl group are incorporated as one of the monomers in PBDTQxF, which may result in low solubility of the polymers to lead lower efficiency.

Key Words: Polymer, OPVs, Synthesis, Fluoro

Introduction

Organic photovoltaics (OPVs) with bulk heterojunction (BHJ) architecture have become an active research area caused by promising alternative renewable energy source.1,2 Polymer solar cells offer the advantages, such as flexible, low-cost fabrication and lightweight plastic substrates.1,3,4 The development of novel materials is necessary to enhance the coverage of the solar spectrum and the absorption coefficients, which can improve the lower power-conversion efficiency and smaller photocurrent as compared to the case of inorganic solar cells.5 To achieve high efficiencies, the active layer of the polymer solar cells should have a broad and strong absorption in the range of solar spectrum.6 The HOMO and LUMO energy levels of the donor, such as lower bandgap conjugated polymer, and PCBM need to have optimal offset to maximize the attainable open circuit voltage (VOC).7,9 Low-bandgap conjugated polymers which absorb in the red and near-IR region can better match the solar photon flux spectrum, which is important for the improvement of the OPV device performance through increases of the short-circuit current (JSC).10

To obtain low bandgap conjugated polymers with planar molecular geometries, various types of aromatic heterocycles have been widely investigated in OPVs.1,6 Many of the low-bandgap (1.4-1.9 eV) conjugated polymers with excellent efficiencies have electron-deficient heterocycles, such as benzothiadiazole (BT),11 quinoxaline12 and benzimidazole,13 and electron-rich moieties, such as carbazole,14,15 thiophene,16 and benzothiadiazole.17 The polybenzothiadiazoles have been much emerged for organic solar cells caused by coplanarity, high hole mobility, and side chain patterns for enhanced solubility.18,19 Quinoxaline-based polymers have been much investigated to give high PCEs in solar cell applications.20 Since F atom is anticipated to minimize the steric interactions, the introduction of electron-withdrawing F atom on the quinoxaline moieties is very attractive to lead planarization of the conjugated backbone.20,21 The fluorination of quinoxaline moieties have been reported to lead high efficiency caused by deeper HOMO, long wavelength absorption and high hole mobility.20,21

New electron deficient unit, 6,7-difluoro-2,3-dihexylquinonoxaline, has been designed and utilized for good solubility of organic solvent. In this study, we report new conjugated copolymers, PBQxF and PBDTQxF for OPV device utilizing a new type of acceptor, 6,7-difluoro-2,3-dihexylquinonoxaline. To the absorption spectrum for the wider coverage of the solar spectrum, these donor-acceptor conjugated poly-
mers were synthesized by Stille coupling reaction of 2,6-bis(trimethyltin)-4,8-dioctyloxybenzo[1,2-b:3,4-b']dithiophene and 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (or 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-dihexylquinoxaline). The photovoltaic properties of the polymers were investigated by fabrication of the polymer solar cells with the configuration of ITO/PEDOT:PSS/polymer:PCBM/Al.

Results and Discussion

Synthesis and Characterization. The general synthetic routes of the monomers and polymers are outlined in Scheme 1. In the first step, 3,6-dibromo-4,5-difluorobenzene-1,2-diamine (3) was cyclized with tetradecane-7,8-dione (2) to obtain 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (4). Stille coupling reaction of 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (4) with tributyl(2-thienyl)stannane were carried out to obtain 6,7-difluoro-2,3-dihexyl-5,8-di(thiophen-2-yl) quinoxaline (5). Compound 5 was brominated with N-bromosuccinimide (NBS) to generate 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-dihexylquinoxaline (6). 2,6-Bis(trimethyltin)-4,8-dioctyloxybenzo[1,2-b:3,4-b']dithiophene (7), as electron-rich moiety, and 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (4) (or 5,8-bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-dihexylquinoxaline (6)) as electron-deficient moiety were copolymerized through Stille coupling polymerization with Pd(0)-catalyst to yield PBQxF (or PBDTQxF). The structures and purities of the monomers were confirmed by 1H-NMR and HRMS. The synthesized polymer, PBQxF, was soluble in various organic solvents such as chloroform, chlorobenzene, THF, dichloromethane and o-dichlorobenzene (ODCB). Table 1 summarized the polymerization results including molecular weight, polydispersity index (PDI) and thermal stability of the polymers. PBQxF and PBDTQxF were determined by GPC to have weight-average molecular weights (Mw) of 15900 and 7600 with polydispersity indexes (PDI, Mw/Mn) of 1.6 and 1.9, respectively. The PBDTQxF has lower molecular weight caused by lower solubility of

Scheme 1. Synthetic route for the synthesis of the monomers and polymers.
chlorobenzene during synthesis process. The thermal properties of the polymers were characterized by thermal gravimetric analysis (TGA) as shown in Figure 1. Thermal gravimetric analysis was performed with TGA 2950 in a nitrogen atmosphere at a heating rate of 10 °C/min to 600 °C. The DSC analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 2920 at heating rates of 10 °C/min. The decomposition temperatures ($T_d$) for PBQxF and PBDTQxF under N$_2$ were determined to be 305 and 316 °C, respectively. The $T_d$ of PBDTQxF was higher than that of PBQxF caused by rigid thiophene unit. The glass transition temperatures of PBQxF and PBDTQxF were not measured in the range of 30-250 °C caused by longer alkyl chain on quinoxaline. The high thermal stability of the synthesized polymer prevents the deformation of the morphology and is important for OPV device applications.

**Optical Properties.** The optical properties of chloroform solution and films of the polymers were investigated by UV-vis absorption spectroscopy. Uniform films were prepared on quartz plate by spin-casting from their ODCB solution at room temperature. The absorption spectra of PBQxF and PBDTQxF were not measured in the range of 30-250 °C caused by longer alkyl chain on quinoxaline. The high thermal stability of the synthesized polymer prevents the deformation of the morphology and is important for OPV device applications.

**Electrochemical Properties.** The electrochemical properties of the polymers were determined from the band gap, which was estimated from the absorption onset wavelength and the HOMO energy level which was estimated from cyclic voltammetry (CV). The CV was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$) (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. The CV spectra are shown in Figure 3, and the oxidation potentials derived from the onsets of electrochemical p-doping are summarized in Table 3. The HOMO and LUMO levels were calculated according to the empirical formula ($E_{\text{HOMO}} = -([E_{\text{onset}}]_{\text{ox}} + 4.8)$ eV) and

![Figure 1. Thermogravimetric analysis of the polymers under N$_2$.](image1)

![Figure 2. UV-visible absorption spectra of polymers in ODCB solution and the solid state.](image2)

![Figure 3. Electrochemical properties of polymers.](image3)

### Table 1. Polymerization Results and Thermal Properties of Polymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>PDI</th>
<th>TGA ($T_d$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBQxF</td>
<td>9800</td>
<td>15900</td>
<td>1.6</td>
<td>305</td>
</tr>
<tr>
<td>PBDTQxF</td>
<td>4000</td>
<td>7600</td>
<td>1.9</td>
<td>316</td>
</tr>
</tbody>
</table>

* 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$_2$.

![Table 2. Characteristics of the UV-vis Absorption Spectra](image4)
Table 3. Electrochemical Potentials and Energy Levels of the Polymers

<table>
<thead>
<tr>
<th>polymers</th>
<th>optical band gap&lt;sup&gt;a&lt;/sup&gt; (eV)</th>
<th>HOMO&lt;sup&gt;b&lt;/sup&gt; (eV)</th>
<th>LUMO&lt;sup&gt;c&lt;/sup&gt; (eV)</th>
<th>$E_{oc}$&lt;sup&gt;d&lt;/sup&gt; (V)</th>
<th>$E_{sc}$&lt;sup&gt;d&lt;/sup&gt; (V)</th>
<th>electrochemical band gap&lt;sup&gt;e&lt;/sup&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBQxF</td>
<td>1.79</td>
<td>-5.17</td>
<td>-4.00</td>
<td>0.37</td>
<td>-0.80</td>
<td>1.79</td>
</tr>
<tr>
<td>PBDTQxF</td>
<td>1.74</td>
<td>-5.22</td>
<td>-3.99</td>
<td>0.42</td>
<td>-0.81</td>
<td>1.74</td>
</tr>
</tbody>
</table>

<sup>a</sup>Optical energy band gap was estimated from the onset wavelength of the optical absorption. <sup>b</sup>CALCULATED FROM THE OXIDATION POTENTIALS. <sup>c</sup>CALCULATED FROM THE REDUCTION POTENTIALS. <sup>d</sup>ONSET OXIDATION AND REDUCTION POTENTIALS MEASURED BY CYCLOC VOLTMETRY. <sup>e</sup>CALCULATED FROM THE $E_{ox}$ AND $E_{red}$.

Figure 4. Current density-potential characteristics of the PBDTQxF solar cells under the illumination of AM 1.5, 100 mW/cm<sup>2</sup>.

(E<sub>LUMO</sub> = -(E<sub>ox</sub>)<sub>red</sub> + 4.8 eV), respectively. The band gaps of the PBQxF and PBDTQxF in thin films were determined to be 1.79 and 1.74 eV, which was calculated from the absorption onset wavelengths of 692 and 713 nm, respectively. The polymers exhibited irreversible processes in oxidation scans. The oxidation onsets of the PBQxF and PBDTQxF were estimated to be 0.37 and 0.42 V, which correspond to HOMO energy levels of -5.17 and -5.22 eV, respectively. The reduction onsets of the PBQxF and PBDTQxF were estimated to be -0.80 and -0.81 V, which correspond to LUMO energy levels of -4.00 and -3.99 eV, respectively. The electrochemical band gaps, calculated from cyclic voltammetry data, were determined to be 1.17 and 1.23 eV, which are lower than the optical band gaps estimated from the absorption spectra.

**Polymer Photovoltaic Properties.** The photovoltaic properties of the polymers were investigated by fabricating the OPVs with ITO as positive electrode, the blend with small molecules and PCBM as active layer, and Al as negative electrode. Figure 4 showed the current-voltage (I-V) curves of the OPVs with the configuration of ITO/PEDOT:PSS (40 nm)/polymer:PCBM (100 nm)/Al (100 nm) under AM 1.5G irradiation (100 mW/cm<sup>2</sup>) and summarized in Table 4.

Table 4. Photovoltaic Properties of the Polymer Solar Cells

<table>
<thead>
<tr>
<th>polymers</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBQxF</td>
<td>0.64</td>
<td>1.58</td>
<td>0.39</td>
<td>0.394</td>
</tr>
<tr>
<td>PBDTQxF</td>
<td>0.25</td>
<td>0.007</td>
<td>0.14</td>
<td>0.002</td>
</tr>
</tbody>
</table>

BHJ devices were fabricated by spin-coating of 1% (w/v) ODCB solutions comprising blend of polymers and PC<sub>71</sub>BM. The devices comprising PBQxF with PC<sub>71</sub>BM (1:2) showed open-circuit voltage ($V_{oc}$) of 0.64 V, short-circuit current density ($J_{sc}$) of 1.58 mA/cm<sup>2</sup>, and fill factor (FF) of 0.39, giving a power conversion efficiency (PCE) of 0.39%. The device of PBDTQxF:PC<sub>71</sub>BM (1:2) showed $V_{oc}$ value of 0.25 V, $J_{sc}$ value of 0.007 mA/cm<sup>2</sup>, and FF of 0.14, giving PCE of 0.002%. The device performance of PBDTQxF was not worked caused by lower molecular weight.

**Conclusions**

New polymers, PBQxF and PBDTQxF utilizing 6,7-difluoro-2,3-dihexylquinoxaline, were synthesized at room temperature in organic solvents. The absorption spectra of PBQxF and PBDTQxF exhibited maximum peaks at about 593 and 538 nm in solution, respectively. The solid films of PBQxF and PBDTQxF show absorption bands with maximum peaks at about 599 and 551 nm and the absorption onsets at 692 and 713 nm. The devices comprising PBQxF with PC<sub>71</sub>BM (1:2) showed $V_{oc}$ of 0.64 V, $J_{sc}$ of 1.58 mA/cm<sup>2</sup>, and FF of 0.39, giving PCE of 0.39%.

**Experimental Section**

**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. <sup>1</sup>H and <sup>13</sup>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 60F pre-coated aluminum plates with fluorescent indicator UV254. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer. 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.
scence spectra measurements.

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(styrenesulfonate) (PEDOT:PSS)/polymer: PCBM/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 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 charge separation layer. A solution containing a mixture of polymer:PCBM in ODCB solvent with concentration of 7 wt/mL % was then spin-casted on 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.

Synthesis of 5,8-Dibromo-6,7-difluoro-2,3-dihexylquinoxaline (4). A solution of tetradecane-7,8-dione (2) (1.8 mL, 7.95 mmol), 3,6-dibromo-4,5-difluorobenzene-1,2-diamine (3) (2.03 g, 6.62 mmol), and ethanol (150 mL) was heated at 70 °C overnight. After cooling to room temperature, the reaction mixture was treated with water and ethyl acetate. The aqueous phase was extracted with ethyl acetate and combined organic layer was dried with MgSO₄. After concentration of the organic phase under reduced pressure, the residue was purified by column chromatography to give compound 4 as white solid. ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, 6H, J = 7.0 Hz), 1.33-1.40 (m, 12H), 1.88 (quin, 4H, J = 7.8 Hz), 3.04 (t, 4H, J = 7.5 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 14.06, 22.60, 27.43, 29.12, 31.73, 34.57, 109.15, 135.61, 149.5 (d, J = 254 Hz, C-F), 158.03. HRMS (m/z, EI') calecd for C₂₅H₂₀Br₂F₂N₂ 490.0431, found 490.0435.

Synthesis of 6,7-Difluoro-2,3-dihexyl-5,8-di(thiophen-2-yl) quinoxaline (5). A solution of 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (4) (5.63 g, 11.44 mmol) and tributyli(2-thienyl)stannane (17.08 g, 6.42 mmol) in 250 mL of THF at room temperature was treated with dichlorobis-(triphenylphosphine)palladium(II) (2 mol %). The reaction mixture was stirred for 12 h at 110 °C, concentrated under reduced pressure, and the residue was purified by flash column chromatography to give compound 5 as a red solid. ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, 6H, J = 7.0 Hz), 1.35-1.48 (m, 12H), 1.97 (quin, 4H, J = 7.7 Hz), 3.07 (t, 4H, J = 7.5 Hz), 7.21 (d of d, 2H, J = 5.4 and 4.0 Hz), 7.59 (d, 2H, J = 5.4 Hz), 7.99 (d, 2H, J = 3.8 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 14.10, 22.63, 27.88, 29.29, 31.78, 34.63, 117.24, 126.12, 129.37, 130.22, 130.99, 134.31, 148.68 (d, J = 255 Hz, C-F), 154.87.

Synthesis of 5,8-Bis(5-bromothiophen-2-yl)-6,7-difluoro-2,3-dihexylquinoxaline (6). 6,7-Difluoro-2,3-dihexyl-5,8-di(thiophen-2-yl) quinoxaline (5) (0.7 g, 1.4 mmol) was brominated with N-bromosuccinimide (NBS) (0.5 g, 2.8 mmol) in THF (10 mL) at room temperature. After stirring for 24 h, water (100 mL) and ethyl acetate (200 mL) were added. The organic phase was washed with 3 × 200 mL of water. The organic phase was concentrated under reduced pressure and the residue was purified by flash column chromatography to give compound 6 as a red solid. ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, 6H, J = 7.0 Hz), 1.38-1.48 (m, 12H), 1.98 (quin, 4H, J = 7.5 Hz), 3.09 (t, 4H, J = 7.5 Hz), 7.15 (d, 2H, J = 4.3 Hz), 7.75 (d, 2H, J = 4.3 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 14.21, 22.59, 27.52, 29.42, 31.91, 34.88, 115.58, 118.52, 128.49, 129.68, 132.13, 132.45, 147.91 (d, J = 256 Hz, C-F), 154.50.

Polymerization of Poly[2,6-(4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene)-alt-5,8-(6,7-difluoro-2,3-dihexylquinoxaline)] (PBQXF). Carefully purified 2,6-bis(trimethylsilyl)-4,8-dioctylbenzo[1,2-b′:3,4-b′]dithiophene (7) (628 mg, 0.81 mmol), 5,8-dibromo-6,7-difluoro-2,3-dihexylquinoxaline (4) (400 mg, 0.81 mmol), P(o-toly1) (40 mol %) and Pd₃(dbda) (5 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.

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References