Synthesis and Characterization of Quinoxaline-Based Thiophene Copolymers as Photoactive Layers in Organic Photovoltaic Cells

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Received October 5, 2010, Accepted November 23, 2010

A series of new quinoxaline-based thiophene copolymers (PQx2T, PQx4T, and PQx6T) was synthesized via Yamamoto and Stille coupling reactions. The Mₙs of PQx2T, PQx4T, and PQx6T were found to be 20,000, 12,000, and 29,000, with polydispersity indices of 2.0, 1.2, and 1.1, respectively. The UV-visible absorption spectra of the polymers showed two distinct absorption peaks in the ranges 350 - 460 nm and 560 - 600 nm, which arose from the π-π* transition of oligothiophene units and intramolecular charge transfer (ICT) between a quinoxaline acceptor and thiophene donor. The HOMO levels of the polymer ranged from -5.37 to -5.17 eV and the LUMO levels ranged from -3.67 to -3.45 eV. The electrochemical bandgaps of PQx2T, PQx4T, and PQx6T were 1.70, 1.71, and 1.72 eV, respectively, thus yielding low bandgap behavior. PQx2T, PQx4T, and PQx6T had open circuit voltages of 0.58, 0.42, and 0.47 V, and short circuit current densities of 2.9, 5.29, and 9.05 mA/cm², respectively, when PC71BM was used as an acceptor. For the solar cells with PQx2T-PQx6T:PC71BM (1:3) blends, an increase in performance was observed in going from PQx2T to PQx6T. The power conversion efficiencies of PQx2T, PQx4T, and PQx6T devices were found to be 0.69%, 0.73%, and 1.80% under AM 1.5 G (100 mW/cm²) illumination.

Key Words: Organic solar cell, Quinoxaline, Oligothiophene, Thin film transistor, Conjugated polymers

Introduction

Organic electronic devices based on solution-processable organic semiconductors have been increasingly investigated for use in low-cost memory devices, large-area display devices, and flexible electronic devices such as organic thin film transistors (OTFTs).1-3 and organic photovoltaic cells (OPVs).4-7 In particular, organic photovoltaic cells have attracted much scientific and industrial interest because of their significant advantages, including their simplicity, low production cost, and applications in renewable solar energy. The recent development of novel polymers and processing techniques has resulted in dramatic improvements in the performance of OPVs, and an efficiency of more than 7% has been reported.8 In the common device structure of OPVs, a blend of an electron-donor (p-type conjugated polymer) and electron-acceptor (π,π*-transition benzothiadiazole (1), 23 3,6-dibromo-1,2-phenylenediamine (2), 24 1,4-dime-
thylpiperazine-2,3-dione (3), t-bromo-4-(octyloxy) benzene (4), 4,4'-bis(2-octyloxy)benzil (5), 5,8-Dibromo-2,3-bis(4-octyloxyphenyl)quinoxaline (6), 2,2-Bis(4-octyloxyphenyl)-5,8-dithien-2-yl quinoxaline (7), 2,3-bis(4-octyloxyphenyl)-5,8-bis(5'-bromo-dithien-2-yl)quinoxaline (8), 5,5'-bis (trimethylstannyl)-2,2'-bithiophene (9) were prepared with previously described methods.

2,3-Bis(4-octyloxyphenyl)-5,8-bis(4'-hexyl-2,2'-bithiophene-5-ly)quinoxaline (9): To a stirred mixture of compound 8 (2.0 g, 2.32 mmol), 4,4,5,5-tetramethyl-2-(4-octyl-thiophene-2-ly)-1,3,2-dioxaborolane (1.5 g, 5.11 mmol), tetrakis(triphenylphosphine) palladium(0) (0.13 g, 0.12 mmol), and Aliquat 336 (2 drops) in 30 mL of toluene and 25 mL of 2 M aqueous sodium carbonate solution was added. The solution was refluxed with vigorous stirring for 20 h at a nitrogen atmosphere. The mixture was poured into water (100 mL) and extracted with CHCl3. The extract was then successively washed with water and brine. After drying over anhydrous MgSO4, the solvent was evaporated and the residue was purified by column chromatography on silica gel with mixture (2:1) as eluent to give compound 9 as a red solid (1.6 g, 64%). 1H NMR (CDCl3, 300 MHz, ppm) 8.04 (s, 2H), 7.77 (d, 4H) 7.75 (d, 2H), 7.20 (d, 2H) 6.93 (d, 4H) 6.84 (s, 2H) 4.00 (t, 4H) 2.62 (t, 4H) 1.81 (m, 4H) 1.65 (m, 4H) 1.48-1.30 (m, 32H) 0.89 (t, 12H) 13C NMR (CDCl3, 80 MHz, ppm) 160.03, 150.99, 144.13, 140.63, 137.67, 137.21, 136.61, 132.04, 131.01, 130.31, 126.60, 125.58, 124.66, 122.80, 118.96, 114.08, 48.06, 31.86, 31.75, 30.61, 30.40, 29.45, 29.34, 29.29, 29.10, 26.13, 22.70, 14.14. Anal. Calcd. for C52H54N2O2S4: C, 72.02; H, 6.28; N, 3.23; O, 3.46; S, 12.64.

2,3-Bis(4-octyloxyphenyl)-5,8-bis(5'-bromo-4'-hexyl-2,2'-bithiophene-5-ly)quinoxaline (10): To a solution of compound 9 (0.81 g, 0.78 mmol) in a CHCl3 (10 mL) was cooled to 0 °C with an ice-water bath. And then NBS (0.27 g, 1.57 mmol) was added. After the reaction was finished, the product was extracted with CHCl3. The organic layer was dried over anhydrous MgSO4 and the solvent removed by rotary evaporation. The crude product was purified by crystallization with MeOH to yield compound 10 as a red solid (0.79 g, 0.75 mmol). 1H NMR (CDCl3, 300 MHz, ppm) 7.95 (s, 2H), 7.71 (d, 4H), 7.66 (d, 2H), 7.10 (d, 2H), 6.92 (s, 2H), 6.89 (d, 4H), 4.00 (t, 4H), 2.56 (t, 4H), 1.80 (m, 4H), 1.62 (m, 4H), 1.50-1.30 (m, 32H), 0.89 (t, 12H) 13C NMR (CDCl3, 80 MHz, ppm) 160.08, 150.99, 144.13, 140.63, 137.67, 137.21, 136.61, 132.04, 131.01, 130.31, 126.60, 125.58, 124.66, 122.80, 118.96, 114.08, 48.06, 31.86, 31.75, 30.61, 30.40, 29.45, 29.34, 29.29, 29.10, 26.13, 22.69, 22.67, 14.13. Anal. Calcd. for C64H76Br2N2O2S4: C, 74.23; H, 7.59; N, 2.71; S, 12.39. Found: C, 74.34; H, 7.58; N, 2.71; S, 12.38.

2,3-Bis(4-octyloxyphenyl)-5,8-bis(4'-hexyl-2,2'-bithiophene-5-ly)quinoxaline-alt-2,2'-bithiophene, PQx4T: A 100 mL Schlenk flask containing anhydrous chlorobenzene (10 mL), compound 8 (0.35 g, 0.460 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.2 g, 0.406 mmol), tri(dibenzylideneacetone)dipalladium (0) (0.036 g, 0.0406 mmol), and tricyclohexylphosphine (0.023 g, 0.0812 mmol) was kept under nitrogen atmosphere at 130 °C for 72 h. When the reaction had finished, the reaction mixture was precipitated from the 10 mL of HCl and 150 mL of methanol. The polymer was dissolved in small amount of toluene and precipitated in methanol. The resulting polymer was further purified by Soxhlet extraction using methanol and then dried in vacuum to give dark-green solid (0.26 g, 80%). Anal. Calcd. for (C72H82N2O2S6)n: C, 72.44; H, 6.87; N, 3.74; S, 14.79. Found: C, 69.98; H, 6.42; N, 2.80; S, 13.64.

PQx6T: PQx6T was synthesized using the same Stille coupling procedure as for PQx4T with compound 9 (0.36 g, 0.302 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.15 g, 0.302 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.027 g, 0.0302 mmol), tri-cyclohexylphosphine (0.017 g, 0.0604 mmol), and chlorobenzene (9.0 mL). Yield (0.30 g, 83%, darkish green color). Anal. Calcd. for (C72H82N2O2S6)n: C, 72.07; H, 6.89; N, 2.33; O, 2.67; S, 16.03. Found: C, 71.49; H, 7.00; N, 2.16; S, 15.84.

Instrumentation. 1H and 13C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer, with tetramethyl silane as an internal reference. The optical absorption spectra were measured on a Shimadzu UV-3100 UV-VIS-NIR spectrometer. The number- and weight-averaged molecular weights of polymers were determined by gel permeation chromatography (GPC) on a Viscotek T60A instrument, using tetrahydrofuran (THF) as eluent and polystyrene as a standard. Thermal gravimetric analysis (TGA) was obtained using a TA Q100 instrument operated under a nitrogen atmosphere. Cyclic voltammetry was performed on an AUTOLAB/PG-STAT12 model system with a three-electrode cell in an acetonitrile solution of Bu4NBF4 (0.10 M) at a scan rate of 50 mV/s. Polymer film coatings on Pt wire electrodes were formed by dipping electrodes into a solution of the appropriate polymer. Atomic force microscopy (AFM) measurements were obtained in tapping-mode using a Multimode IIIa Digital Instrument AFM. Electrical characteristics of the TFTs were measured under ambient conditions using both Keithley 2400 and 236 source/measure units. All measurements were obtained with channel lengths (L) of 100 µm and channel widths (W) of 1000 µm. Field-effect mobilities were extracted in the saturation regime from the slope of the source-drain current.

Fabrication of the Organic Thin Film Transistor Devices. Thin-film transistors were fabricated on silicon wafers using a top contact geometry (channel length L = 100 µm, width W =
1000 μm) under ambient conditions without taking special precautions to exclude air, moisture, or light. A heavily n-doped silicon wafer with a 300 nm thermal silicon dioxide (SiO₂) layer was used as the substrate/gate electrode, with the top SiO₂ layer serving as the gate dielectric. The SiO₂ surface of the wafer substrate was first cleaned with piranha solution (H₂O₂/H₂SO₄) at 130 °C for 20 min, and the cleaned wafer was immersed in a solution of 1.0 mM octyltrichlorosilane (OTS-8) in toluene at room temperature for 2 h under nitrogen. The semiconductor layer was spin-coated at 2000 rpm from a 0.5 wt % chlorobenzene solution, to a thickness of 60 nm. Subsequently, a series of gold source/drain electrode pairs were deposited by vacuum evaporation through a shadow mask. Silicon oxide at the backside of the silicon wafer of the TFT device was removed with HF to provide a conductive gate contact.

**Fabrication of the Organic Photovoltaic Device.** Composite solutions with the quinoxaline based copolymers and PC71BM were prepared using 1,2-dichlorobenzene (DCB). The polymer photovoltaic devices were fabricated with a typical sandwich structure of ITO/PEDOT:PSS/active layer/LiF/Al. The ITO-coated glass substrates were cleaned by a routine cleaning procedure, including sonication in detergent followed by sonication in distilled water, acetone, and 2-propanol. A 45 nm thick layer of PEDOT:PSS (Baytron P) was spin-coated onto a cleaned ITO substrate after exposing the ITO surface to ozone for 10 min. The PEDOT:PSS layer was baked on a hot plate at 120 °C for 60 min. The active layer was spin-coated from the pre-dissolved composite solution after filtering through 0.45 μm PP syringe filters. The device structure was completed by depositing 0.6 nm LiF and then 130 nm Al cathode as the top electrode onto the polymer active layer under a 3 × 10⁻⁶ torr. in a thermal evaporator.

**Results and Discussion**

**Synthesis and Thermal Properties of the Polymers.** The synthetic routes to the monomers are outlined in Scheme 1. The synthetic routes to the polymers PQx2T, PQx4T, and PQx6T are described in Scheme 2. PQx2T was synthesized by a Ni(0)-mediated coupling reaction of compound 8. PQx4T and PQx6T were prepared by a Stille coupling reaction of compound 8. PQx4T and PQx6T are described in Scheme 2. PQx2T was synthesized by a Ni(0)-mediated coupling reaction of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene and either compound 8 or 10. The synthetic routes for the polymers were in reasonable agreement with the theoretical values. The resulting PQx6T showed good solubility in common organic solvents such as chloroform, chlorobenzene, and toluene because of the long alkyl side chain, but PQx2T and PQx4T exhibited relatively poor solubility compared with PQx6T because of the incorporation of the rigid thiophene units into the polymer backbones. The molecular weights and polydispersity indices of the polymers were determined by gel permeation chromatography using THF as the eluent and polystyrene as the standard. The Mn's of PQx2T, PQx4T, and PQx6T were found to be 20,000, 12,000, and 29,000, with polydispersity indices of 2.0, 1.2, and 1.1, respectively. The excellent thermal stabilities of PQx2T, PQx4T, and PQx6T were evident from their TGA profiles, with decomposition temperatures above 350 °C (Figure 1). The weight losses for PQx2T, PQx4T, and PQx6T were 6.9%, 2.7%, and 0.9% at 350 °C, respectively. These results for the synthesized polymers are summarized in Table 1.

**Optical and Electrochemical Properties of the Polymers.** The
The longer wavelength (560 - 600 nm) absorption peak is due to an ICT π-π* transition of the oligothiophene donor.32 The short wavelength absorption peaks of PQx2T, PQx4T, and PQx6T in chlorobenzene solution were observed at 353, 428, and 465 nm, respectively, while those of thin films were observed at 370, 430, and 465 nm, respectively. It was noted that the short wavelength absorption peaks of PQx4T and PQx6T were hugely red shifted (by about 60 - 90 nm) compared with PQx2T in thin solid films. This red shift can be attributed to an elongation of the effective conjugation length upon increasing the number of thiophene rings in the polymer backbone, which would enhance intra/intermolecular orbital overlap, resulting in a red shift in absorption. The long wavelength absorption peaks of PQx2T, PQx4T, and PQx6T in chlorobenzene solution were observed at 561, 601, and 603 nm, respectively, while those of the thin films were observed at 583, 602, and 608 nm, respectively. To gain insight into the performance of solar cell devices based on these polymers, we determined the energy levels of their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) using cyclic voltammetry (CV) (Figure 3, Table 2). The redox behavior of the polymer thin films was estimated from CV measurements of dip-coated thin films on indium-tin oxide (ITO)-coated glass, which formed the working electrode. A platinum rod was used as the counter electrode, and Ag/Ag+ as the reference electrode in acetonitrile with a 0.1 M n-Bu4NPF6 supporting electrolyte solution at a scan rate of 50 mV s⁻¹. The HOMO levels of PQx2T, PQx4T, and PQx6T were estimated to be −5.37, −5.21, and −5.17 eV, respectively, and those of the LUMO levels were estimated to be −3.67, −3.50, and −3.45 eV, respectively. The electrochemical bandgaps, which are defined as the difference between E_HOMO and E_LUMO, are given in Table 2.

Table 1. Physical properties of the PQx2T, PQx4T, and PQx6T

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M_n (g/mol)</th>
<th>M_w (g/mol)</th>
<th>M_w/M_n</th>
<th>T_d (°C)ᵃ</th>
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<tr>
<td>PQx2T</td>
<td>9,900</td>
<td>20,000</td>
<td>2.0</td>
<td>332</td>
</tr>
<tr>
<td>PQx4T</td>
<td>10,000</td>
<td>12,000</td>
<td>1.2</td>
<td>399</td>
</tr>
<tr>
<td>PQx6T</td>
<td>26,000</td>
<td>29,000</td>
<td>1.1</td>
<td>447</td>
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</tbody>
</table>

ᵃTemperature for 5% weight loss.

Table 2. UV-visible maximum absorption wavelength (λ_max), bandgap energy (E_g), and ionization potential (E_HOMO) of the PQx2T, PQx4T, and PQx6T

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λ_max (nm)</th>
<th>ε (L/mol·cm⁻¹)</th>
<th>E_g (eV)</th>
<th>E_HOMO (eV)</th>
<th>E_LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQx2T</td>
<td>561</td>
<td>17 000</td>
<td>1.70</td>
<td>−5.37</td>
<td>−3.67</td>
</tr>
<tr>
<td>PQx4T</td>
<td>601</td>
<td>22 000</td>
<td>1.71</td>
<td>−5.21</td>
<td>−3.50</td>
</tr>
<tr>
<td>PQx6T</td>
<td>603</td>
<td>53 000</td>
<td>1.72</td>
<td>−5.17</td>
<td>−3.45</td>
</tr>
</tbody>
</table>

Measurements preformed in chlorobenzene. ³Absorption coefficient of the polymers at λ_max in chlorobenzene. ⁴Electrochemical band gap. E_g is defined as the difference between E_HOMO and E_LUMO.

UV-visible absorption spectra of the polymers in chlorobenzene solution and as thin solid films are presented in Table 2 and Figure 2. All polymers showed two distinct absorption peaks in the ranges 350 - 460 nm and 560 - 600 nm, which is a common feature of intramolecular donor-acceptor copolymers.29,31 The short wavelength (350 - 460 nm) absorption peak originates from a π-π* transition of the oligothiophene units, while the longer wavelength (560 - 600 nm) absorption peak is due to an ICT π-π* transition between the quinoxaline acceptor and the oligothiophene donor.32
the high HOMO level of the oligothiophene groups.

**Organic Photovoltaic (OPV) Characteristics of the Polymer Thin Film.** Bulk heterojunction solar cells were fabricated with a sandwich structure of ITO/PEDOT:PSS (50 nm)/polymer:PC71BM/LiF (0.6 nm)/Al (130 nm). After deposition of the PEDOT:PSS layer on the top of the anode (ITO), the active materials were deposited via spin coating from a 1,2-dichlorobenzene solution of polymer and PC71BM. The resulting films were dried under vacuum at room temperature for 4 h, and then annealed at 90 °C for 10 min to remove a solvent. In the bulk heterojunction solar cells, the polymers were used as an electron donor and PC71BM was used as an electron acceptor. The J-V characteristics of the polymer solar cells prepared from the polymer (PQx2T, PQx4T, and PQx6T):PC71BM blend materials are shown in Figure 3. For these devices based on the PQx2T-PQx6T:PC71BM (1:3) blend materials, an increase in performance was observed in going from PQx2T to PQx6T. The PCEs of the PQx2T, PQx4T, and PQx6T devices were found to be 0.69%, 0.73%, and 1.80%, respectively. As shown in Table 3, the PQx2T, PQx4T, and PQx6T devices exhibited J_{SC} values of 2.9, 5.29, and 9.05 mA/cm^{2}, when the polymer vs. PC71BM blend ratio was 1:3. The J_{SC} of these polymers was found to increase as the number of thiophene rings in the polymer backbone increased. Because the mobility of the donor polymer is an important parameter that can affect the J_{SC} values, the field-effect hole mobility was measured using an OTFT device with a top contact configuration built on an n-doped silicon wafer. The saturation mobilities of PQx2T, PQx4T, and PQx6T were found to be 9.0 × 10^{-6}, 5.0 × 10^{-7}, and 2.4 × 10^{-8} cm^{2} V^{-1} s^{-1}, respectively (Figure 5). The J_{SC} should generally increase with the increasing hole mobility of the electron-donor polymer, which enhances charge transport in the bulk heterojunctions. Therefore, the above results indicate that increasing the number of thiophene rings in the polymer backbone enhances the hole mobility in the blend films, and thus improves the PCE. In addition, the V_{OC}, which are related to the difference between the HOMO level of the donor polymer and the LUMO level of the acceptor (PCBM), of the PQx2T-PQx6T:PC71BM (1:3) devices were found to be 0.58, 0.42, and 0.47 V, respectively. With the same electron acceptor (PC71BM in this study), electron donors with lower HOMO give higher OC values, however, the trend of V_{OC} for PQx4T does not seem to fit to the electrochemical potentials. This result can be understood in terms of the film morphology of the blended film. Low solubility has an impact on the film mechanical properties, the interface resistance, and the morphology, resulting in a low open-circuit voltage and a low fill factor. To investigate the surface morphology of the blend films, we examined AFM images of PQx2T-PQx6T:PC71BM (1:3) films spin-coated from their corresponding 1,2-dichlorobenzene solutions, identical

![Figure 3. Cyclic voltammograms of the three polymer films on ITO glass at a scanning rate of 50 mV s^{-1} in acetonitrile containing 0.1 M n-Bu_{4}NBF_{4}.](image)

![Figure 4. J-V characteristics of photovoltaic cells prepared from polymers:PC_{71}BM (1:3) blend active materials under an illumination of AM 1.5G, 100 mW/cm^2.](image)

![Figure 5. (a) Transfer characteristics of the polymer TFT devices with an OTS-modified surface and annealed at 100 °C, where V_{DS} = -60 V. (b) Output characteristics of PQx6T based TFT devices.](image)

<table>
<thead>
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<th>Table 3. Photovoltaic properties of the polymer:PC_{71}BM devices</th>
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<tbody>
<tr>
<td>Polymer:PC_{71}BM ratio (wt.)</td>
</tr>
<tr>
<td>PQx2T (1:3)</td>
</tr>
<tr>
<td>PQx4T (1:3)</td>
</tr>
<tr>
<td>PQx6T (1:3)</td>
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</table>
to the procedure used to fabricate the active layers of the solar cell devices. We observed coarse phase separation in the images of these polymer blends. Coarse phase separation was evident in the images of the PQx6T:PC71BM (1:3) films, whereas the PQx2T-PQx4T:PC71BM (1:3) films showed a smoother and more homogeneous surface. The root-mean-square (RMS) roughness of the PQx2T, PQx4T, and PQx6T blends was 0.56, 1.32, and 1.28 nm, respectively. These results suggest that the roughness of the PQx2T:PC71BM device shows relatively high photoconversion efficiency over the wavelength range 400 - 700 nm, with EQE values above 30% and a maximum EQE of almost 40% at around 480 nm. In particular, the PQx6T:PC71BM device yielded an EQE plot that was similar to the absorption spectrum of PQx6T in the longer wavelength region, indicating that excitons are mainly generated in the polymer phase. The photovoltaic study of quinoxaline-based thiophene polymers shows it to be a promising donor material for BHJ solar cells.

Conclusions

In summary, we have synthesized new solution-processable quinoxaline-based low bandgap polymers using the Yamamoto and Stille coupling reactions. PQx6T showed good solubility in common organic solvents such as chloroform and chlorobenzene because of the long alkyl side chain, but PQx2T and PQx4T showed relatively poor solubility because of the rigid thiophene units in the polymer backbones. PQx2T, PQx4T, and PQx6T exhibited long wavelength UV-visible absorption peaks at 583, 602, and 608 nm, respectively. A photovoltaic device using a PQx6T:PC71BM (1:3) film as the active layer exhibited an open circuit voltage of 0.47 V, a short circuit current density of 9.05 mA/cm², a fill factor of 0.42, and a power conversion efficiency of 1.80% under AM 1.5 G (100 mW/cm²) illumination.

Acknowledgments. This work was supported by a grant from the cooperative R&D Program (B551179-08-03-00) funded by the Korea Research Council Industrial Science and Technology, Republic of Korea, and also supported by the Catholic University of Korea, Research Fund, 2010. This study was supported by a grant (M2009010025) from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy (MKE), Republic of Korea.

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