

# Synthesis of a Phenothiazine-Quinoxaline Polymer for Photovoltaic Applications

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Received January 17, 2013, Accepted March 19, 2013

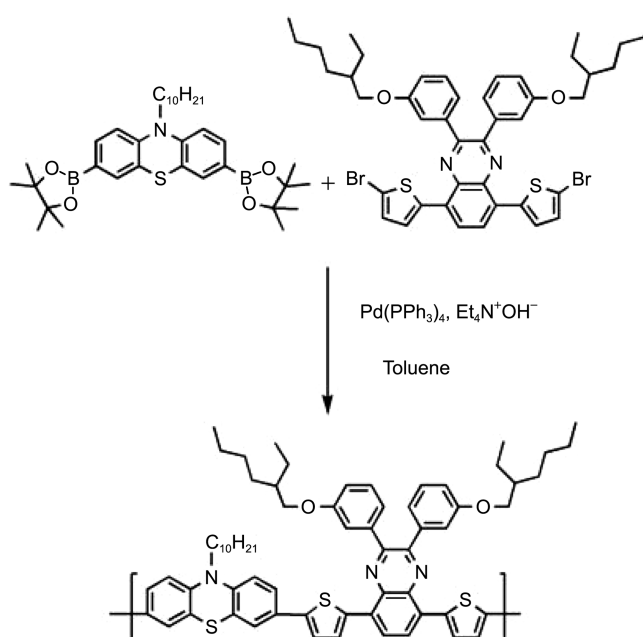
**Key Words:** Phenothiazine, Quinoxalline, Conjugated polymer, Solar cells

Polymer solar cells (PSCs) have attracted considerable attention because of their unique advantages of low cost, light weight, and potential use in flexible devices.<sup>1,2</sup> Based on the concept of a bulk heterojunction (BHJ) structure,<sup>3</sup> PSCs made by blending poly(3-hexylthiophene) (P3HT) as a *p*-type material and [6,6]-phenyl-C61-butyric acid methyl ester (PC<sub>61</sub>BM) as an *n*-type material have been most intensively investigated and have shown power conversion efficiencies (PCEs) up to 5–6%.<sup>4,5</sup>

PCE of photovoltaic devices is proportional to the short-circuit current density ( $J_{sc}$ ), the open-circuit voltage ( $V_{oc}$ ), and the fill factor (FF). The  $J_{sc}$  of a solar cell is strongly affected by the absorption of the active layer, and thus an ideal *p*-type polymer should have a broad and strong absorption spectrum, which requires the polymer to have a low band-gap. The  $V_{oc}$  is tightly related to the energy difference between the highest occupied molecular orbital (HOMO) of the *p*-type polymer and the lowest unoccupied molecular orbital (LUMO) of PCBM. Thus, the *p*-type polymer should have a low band-gap with appropriate energy levels of HOMO and LUMO.<sup>6</sup>

A facile method to synthesize low band-gap polymers is to combine electron-rich (electron-donor, D) and electron-deficient (electron-acceptor, A) monomers, forming alternating D-A type polymers.<sup>7–9</sup> Quinoxaline was reported to be a good acceptor that can be combined with appropriate donors. For example, a thiophene-bis(3-octyloxyphenyl)-quinoxaline polymer (TQ1) exhibited PCEs up to 6.0%.<sup>10</sup> Alternating copolymers consisting of bis(3-alkoxyphenyl)-quinoxaline and either dialkoxybenzene (LBPP) or fluorine (APFO) with a thiophene spacer showed PCEs up to 2.9%.<sup>11</sup> Another alternating copolymers of quinoxaline and either thieno[3,2-*b*]thiophene or carbazole with a thiophene spacer showed PCEs of 2.27% and 1.8%, respectively.<sup>12,13</sup> A copolymer of 2,3-diphenylquinoxaline-based combined with a ladder type oligo-*p*-phenylene with a thiophene spacer showed a PCE of 3.04%.<sup>14</sup> Some other types of quinoxaline-based copolymers with much lower PCEs were also reported.<sup>15,16</sup> Poly(10-hexyl-10*H*-hexylphenothiazine-3,7-diyl) is a very strong electron donor and has a high ionization potential and has thus been used as a hole injection material in polymer light-emitting diodes.<sup>17</sup>

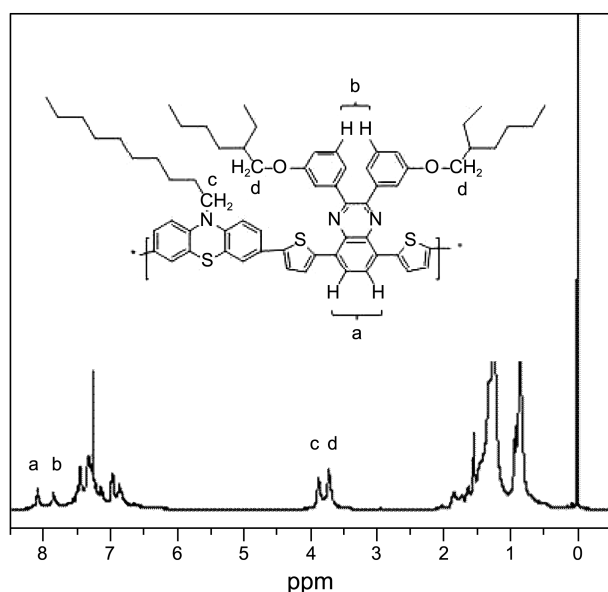
D-A type polymers consisting of phenothiazine and quinoxaline are also expected to be *p*-type materials with low band-gaps, but such polymers have not yet been reported in



**Scheme 1.** Synthesis of PPTQX.

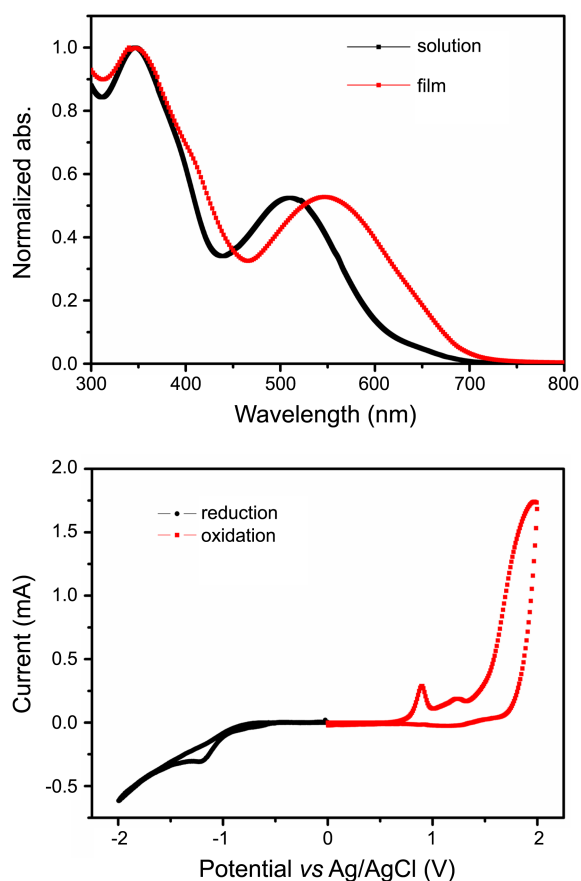
the literature. Thus, we attempted to synthesize a copolymer (PPTQX) consisting of alternating phenothiazine (PT) and dithienylquinoxaline (QX) segments for photovoltaic applications.

As shown in Scheme 1, diboronate ester (compound 1) was reacted with dibromide (compound 2) in the presence of a palladium catalyst *via* Suzuki coupling to give the corresponding polymer, PPTQX. The polymer was purified using a Soxhlet extraction. The <sup>1</sup>H NMR of the isolated polymer is shown in Figure 1, where the two different sets of aromatic protons (a, b) and four aliphatic protons (d) in the QX segment are easily identified along with two aliphatic protons (c) in the PT segment, indicating that PPTQX has been successfully synthesized. The number- and weight-average molecular weights of PPTQX were 7,000 and 12,000, respectively. The relatively low molecular weight of the polymer may be a result of the low reactivity of the QX monomer since its reacting sites are sterically hindered due to the two large alkoxyphenyl substituents. Molecular weights of LBPP and APFO, which were synthesized from QX monomers similar to ours, were also relatively low ( $M_n$  12,000–15,000).<sup>11</sup> The polymer was soluble in common organic solvents such



**Figure 1.**  $^1\text{H}$  NMR spectrum of PPTQX in  $\text{CDCl}_3$ .

as chloroform, THF, chlorobenzene, and *o*-dichlorobenzene. The thermal transition behavior of the polymer was investigated by DSC, but no thermal transition was detected in the temperature range from 25  $^\circ\text{C}$  to 250  $^\circ\text{C}$  (data not shown), indicating that the polymer is amorphous in this temperature

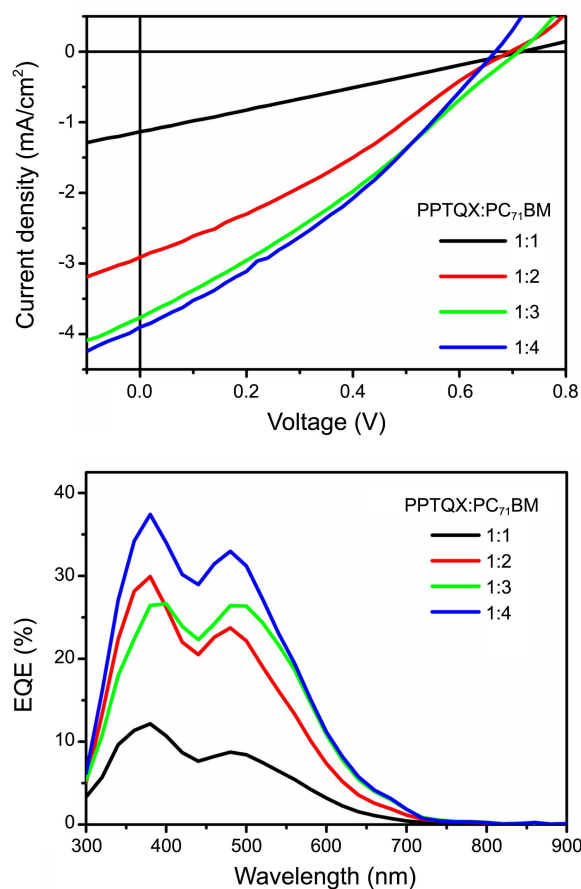


**Figure 2.** Normalized UV-visible absorption spectra (up) and cyclic voltammograms (down) of PPTQX.

range. The TGA results of PPTQX revealed that a thermal degradation of 5 wt % loss occurred around 320  $^\circ\text{C}$ .

An absorption maximum in the visible region for PPTQX in solution and film occurred at 508 and 546 nm (Fig. 2), respectively, indicating that the absorption of the film was red-shifted compared to that of the solution due to the closer  $\pi$ - $\pi$  interactions in the film. The optical band-gap calculated from the absorption onset (704 nm) of PPTQX in the film was 1.76 eV, which is slightly larger than that of TQ1 (1.70 eV),<sup>10</sup> but lower than those of LBPP (1.8 eV) and APFO (2.0 eV).<sup>11</sup> The oxidation onset potential of PPTQX was 0.80 V, corresponding to its HOMO level of  $-5.20$  eV,<sup>18</sup> which is higher than those of TQ1 ( $-5.7$  eV), LBPP ( $\sim -5.5$  eV) and APFO ( $-5.8$  eV). The LUMO energy level of PPTQX, calculated from the optical band gap and HOMO energy level, was  $-3.47$  eV.<sup>19</sup> This comparison clearly indicates that for a given A segment, D segments can significantly affect the HOMO/LUMO levels and band-gaps of the resulting D-A type polymers.

The J-V characteristics of solar cells fabricated using PPTQX and  $\text{PC}_{71}\text{BM}$  are shown along with EQE curves in Figure 3, and the results are summarized in Table 1. The PCE of the devices increased slightly as the ratio of PPTQX to  $\text{PC}_{71}\text{BM}$  increased from 1:1 to 1:4, mainly due to the increase in the  $J_{\text{sc}}$  value. The increase in the  $J_{\text{sc}}$  value with



**Figure 3.** Current density-voltage (J-V) (up) and external quantum efficiency (EQE) curves (down) of PPTQX-based photovoltaic devices.

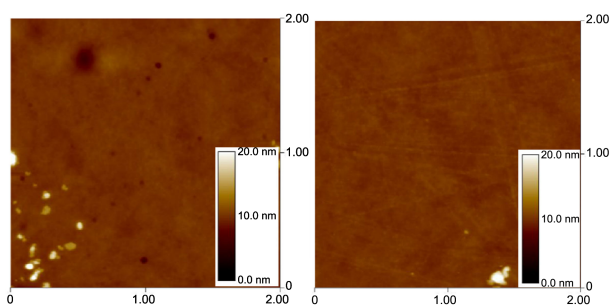
**Table 1.** Performances of photovoltaic devices (ITO/PEDOT:PSS/PPTQX:PC<sub>71</sub>BM/LiF/Al)

PPTQX :PC <sub>71</sub> BM	$J_{sc}$ (mAcm <sup>-2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
1:1	1.14	0.72	0.25	0.21
1:2	2.91	0.70	0.30	0.60
1:3	3.76	0.71	0.30	0.79
1:4	3.90	0.67	0.32	0.83

increasing PC<sub>71</sub>BM content is mainly due to the more efficient harvesting of light, especially in the visible range.<sup>20</sup> The EQE curves of the solar cells show that the PCE value increased as the ratio of PPTQX to PC<sub>71</sub>BM increased, which is in good agreement with the J-V characteristic results. The shapes of the EQE curves resemble the UV-visible spectrum of PPTQX, which is a common observation for polymer solar cells.

AFM images showed that the root mean square (rms) roughness of PPTQX/PC<sub>71</sub>BM films with 1:2 or 1:4 ratios were 0.82 nm and 0.55 nm, respectively (Fig. 4). The PPTQX/PC<sub>71</sub>BM (1:4) film appears to be more homogeneous. These results indicate that uniform mixing with small rms roughness in a 1:4 blend film may be beneficial for obtaining high  $J_{sc}$  and FF. However, PPTQX seems to be almost completely mixed with PC<sub>71</sub>BM at the molecular level in both cases as nanostructured domains are not seen. This suggests that the morphology of the blend films might largely contribute to the low  $J_{sc}$  and FF values of PPTQX/PC<sub>71</sub>BM-based devices, since efficient dissociation of excitons and charge mobility generally result from active layers of interpenetrated nanostructures.<sup>21</sup> Their efficiency is expected to be enhanced through better morphology control by using mixed solvents, thermal treatment, and additives.

UV-visible absorption spectra of PPTQX and P3HT were measured at the same concentration in chloroform. The maximum absorbance in the visible region of the PPTQX solution was approximately 30% of that of P3HT. In general, a low absorption coefficient of a *p*-type polymer results in a low concentration of excitons in the active layer of photovoltaic devices, leading to a low  $J_{sc}$  value. The comparison of the absorption coefficients of the two polymers explains, at least partly, why the  $J_{sc}$ , and consequently the PCE values, of the PPTQX-based devices are low.

**Figure 4.** AFM images of PPTQX/PC<sub>71</sub>BM films: 1:2 (left) and 1:4 (right).

In summary, a new polymer, PPTQX, was successfully synthesized in this work. The polymer has a low band-gap of 1.76 eV with a HOMO level of -5.20 eV. The PPTQX-based photovoltaic devices exhibited PCEs of 0.21-0.83% under AM 1.5G illumination conditions. The unexpectedly low PCE values of the PPTQX-based devices were attributed primarily to the low absorption coefficient of the polymer and the good miscibility of the polymer and PCBM without the formation of a nanostructured morphology.

## Experimental Section

**Materials.** Phenothiazine and 3-bromophenol were purchased from TCI. Other chemicals were purchased from Aldrich. All reagents were used without further purification. Solvents were purified by normal procedures and handled under a moisture-free atmosphere.

**10-Decyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazine (1).** This compound was prepared in three steps starting from phenothiazine according to procedures reported in the literature.<sup>22</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.55-7.53 (d, 2H), 7.51 (s, 2H), 6.81-6.79 (d, 2H), 3.85-3.82 (t, 2H), 1.80-1.73 (m, 2H), 1.44-1.36 (m, 2H), 1.31 (s, 24H), 1.28-1.25 (m, 4H), 0.87-0.84 (t, 3H). Calc'd: C, 69.0; H, 8.7; N, 2.4; S, 5.4. Found: C, 67.7; H, 8.1; N, 2.6; S, 5.3.

**5,8-Bis(5-bromothiophen-2-yl)-2,3-bis(3-(2-ethylhexyloxy)phenyl)-4a,8a-dihydroquinoxaline (2).** This compound was prepared in several steps starting from thiadiazine according to previously reported procedures.<sup>23,24</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.0 (s, 2H), 7.57 (d, 2H), 7.56 (d, 2H), 7.48 (d, 4H), 6.98 (d, 2H), 6.97 (d, 2H), 3.92 (t, 4H), 1.98 (m, 2H), 1.2-1.6 (16H, 8CH<sub>2</sub>) 0.80-1.0 (12H, 4CH<sub>3</sub>). Calc'd: C, 61.2; H, 5.8; N, 3.2; S, 7.4. Found: C, 60.4; H, 5.2; N, 3.4; S, 7.8.

**Poly[3-(5-(2,3-bis(3-(2-ethylhexyloxy)phenyl)-8-(thiophen-2-yl)-4a,8a-dihydroquinoxalin-5-yl)thiophen-2-yl)-10-decyl-10*H*-phenothiazine] (PPTQX).** Tetrakis(triphenylphosphine) palladium (0) (13.4 mg, 0.012 mmol) and degassed tetraethylammonium hydroxide (0.9 mL, 20% by weight in H<sub>2</sub>O) were added under argon to a stirred solution of diboronic ester monomer (137 mg, 0.232 mmol) and dibromide monomer (200 mg, 0.232 mmol) in toluene (10 mL). After being stirred at room temperature for 5 min, the reaction mixture was stirred at 90 °C for 48 h. The reaction mixture was poured into methanol/HCl (10:1) (220 mL), and the dark blue precipitates were collected by filtration. The resulting polymer was dissolved in chloroform and precipitated by slowly adding methanol (200 mL). The precipitated polymer was collected by filtration and purified by Soxhlet extraction in acetone for 12 h to remove oligomers and catalyst residue. After drying under reduced pressure at room temperature, 180 mg of PPTQX was obtained (dark blue powder).

**Measurements.** Proton NMR spectra were recorded using a Varian Gemini-300 (400 MHz) spectrometer with trimethylsilane as an internal standard. The molecular weight of the polymer was determined by gel permeation chromatography with a Viscotec GPC system (Model 350 HTGPC) in

chloroform. Differential scanning calorimetry was performed on a TA Instruments DSC 2920 at a heating rate of 10 °C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed with a TA Instruments TGA 2950 at a heating rate of 10 °C/min under a nitrogen atmosphere. UV–visible absorption spectra were recorded on a Varian Cary 1 spectrophotometer. Cyclic voltammograms of the polymer were obtained in a solution of tetrabutylammonium tetrafluoroborate (0.10 M) in acetonitrile at room temperature under an argon atmosphere using a Wona-WPG100 in a three-electrode cell at a scan rate of 50 mV/s. All measurements were calibrated against ferrocene, and the ionization potential of the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox system value is 4.4 eV.<sup>25</sup> Polymer films were deposited on ITO glass using polymer solution in chlorobenzene. A platinum wire and an Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively.

**Fabrication of Photovoltaic Devices.** Photovoltaic devices with an active area of 9 mm<sup>2</sup> were fabricated with the following configuration: ITO/PEDOT:PSS/PPTQX:PC<sub>71</sub>BM/LiF/Al. Patterned ITO glasses (2 × 2 cm) were ultrasonically cleaned with acetone and isopropyl alcohol and were then treated with O<sub>2</sub>-plasma. Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS, Baytron P VP AI 4083, Bayer AG) was spin-coated onto the ITO glass (30 nm) and dried at 90 °C for 20 min under nitrogen. A blend of PPTQX and PC<sub>71</sub>BM in *o*-dichlorobenzene was spin-coated on to the substrate in a nitrogen-filled glove box (thickness ~ 80 nm). LiF (1.0 nm) and Al (150 nm) layers were deposited by thermal evaporation under vacuum (1 × 10<sup>-6</sup> torr). The current density-voltage (J-V) characteristics of the photovoltaic devices in the dark and under white light illumination were measured using an AM 1.5G solar simulator (Newport) at 100 mW/cm<sup>2</sup>, adjusted with a standard PV reference cell (2 × 2 cm monocrystalline silicon solar cell, calibrated at NREL, Colorado, USA) with a Keithley 2400 source-measurement unit. The external quantum efficiency (EQE) was determined using a Polaronix K3100 spectrometer.

**Acknowledgments.** This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant No. 2010-0011626).

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