

# Synthesis and Characterization of a Fluorene–Quinoxaline Copolymer for Light-Emitting Applications

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A conjugated copolymer based on 9,9-dioctyl-fluorene and 2,3-bis(4-(hexyloxy)phenyl) quinoxaline has been synthesized by the palladium-catalyzed Suzuki coupling reaction. The synthesized polymer was soluble in common organic solvents such as chloroform, THF, and toluene and had good film properties. The polymer was analyzed by <sup>1</sup>H-NMR spectroscopy, UV-vis spectroscopy, GPC, TGA, DSC, and cyclic voltammetry. It had very good thermal properties with high decomposition and glass transition temperatures, 420 °C and 159 °C respectively, and a low band gap of 2.51 eV. The polymer LEDs (ITO/PEDOT:PSS/polymer/LiF/Ca/Al) showed pure green light emission with maximum peaks at 502 nm and CIE coordinates of  $x = 0.28$  and  $y = 0.55$ . The turn-on voltage of the polymer device was 7 V and the maximum brightness was 10.16  $cd/m<sup>2</sup>$  at 14 V. The maximum luminescence efficiency of the polymer was 0.0011 cd/A at 11 V.

Keywords: Fluorene–Quinoxaline Copolymer, Green OLED, Suzuki Coupling Reaction.

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# 1. INTRODUCTION

Conjugated polymers have been used as active materials in several kinds of electronic devices such as transistors, photovoltaic cells (PVCs), and organic light-emitting diodes (OLEDs), including flexible displays.<sup>1–5</sup> They not only combine the physical properties of polymers with those of semiconductors to obtain unique and novel materials but also provide tunable electronic and/or mechanical properties by structure modification.2 Also, it is very important to be controlled these polymer to nanometer scale size.<sup>6</sup>

By the introduction of flexible side chains to the polymer backbone, the solubility and processability of aromatic conjugated polymers can be increased. Flexible side chains also give rise to steric hindrance along the polymer backbone, which controls the effective conjugation length and emission color of the polymers. Conjugated polymers with sterically hindered side chains appended to the polymer backbone have exhibited excellent photoluminescence  $(PL)$  efficiencies in the solid state.<sup>1</sup> Since the discovery of polymer light-emitting diodes (PLEDs) by the Cambridge group, great progress has been made in developing many kinds of conjugated polymers to provide the three primary (RGB) colors for large-area flat panel displays.7

Polyfluorenes (PFs) are of particular interest in various applications ranging from field effect transistors through photovoltaics to light-emitting devices. In particular, PFs have emerged as a promising class of semiconducting polymers for PLEDs.<sup>8,9</sup> They have attracted considerable attention because of their blue light emission with a maximum at about 420 nm, their high photoluminescence (PL) and electroluminescence (EL) efficiency, and their high thermal stability.10 However, the poor electron-transporting property of PF results in a large electron-injection barrier and an imbalance of charge carrier transport in PLEDs application.<sup>2</sup> Poly (9,9-dioctylfluorene) is soluble in toluene. Its films have a PL maximum at 436 nm with well-defined vibronic features, and the PL and quantum efficiency (QE) were approximately 55%. The EL maximum is also at 436 nm. The external QE of a PLED with Ca as the cathode and PBD as the electron transporting layer is about 0.2%.<sup>11</sup>

PF derivates and copolymers with emission colors over the entire visible range have been synthesized by introducing comonomers like benzothiadiazole, pyridine, bithiazole, naphthoselenadiazole, indenofluorene, quinoxaline, and perylene, which act as on-chain excited state energy acceptors. In general, the incorporation of acceptors into the PF backbone lowers the LUMO energy level of the resulting copolymers compared to PF and thus could further improve their electron-accepting ability. The use of

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these acceptors makes it possible to tune the emission of PF copolymers from blue to red, paving the way for copolymers with white light emission. Among other acceptors units, quinoxaline comonomer units appear especially suitable to alter the bandgap of polyfluorene copolymers so as to allowlight emission from blue to yellow–orange. Incorporation of quinoxaline acceptors enhances electrontransport by the copolymers, making them suitable for use in multilayer PLEDs.<sup>10</sup> Donor-acceptor conjugated polymer systems have emerged as promising candidates for flexible organic electronic devices since their electronic and optoelectronic properties can be efficiently described by intramolecular charge transfer  $(ICT).<sup>12</sup>$ 

a high band gap. Chen et al.<sup>2</sup> synthesized a copolymer  $\text{P}$  use university layer and an ITC with fluorine-quinoxaline as electron acceptor. Although  $\ln$ , 09, 00:14:08 its thermal properties were good, it had low number-in  $\zeta$  essive unrasonic tre A green-emitting material for PLEDs has been much sought after. Leclerc et  $al^{13}$  synthesized PCQ using carbazole and quinoxaline comonomers. Although they obtained a nearly pure green polymer, it had low numberaverage molecular weight, broad polydispersity, a low glass temperature and a high band gap. Tang et al. $^{14}$ synthesized diphenyl polyacetylenes with vinyl and ester groups. Although these polymers were produced by a photopolymerization method, they had low number- and weight- average molecular weights, low thermal stability, and red-shifted emission. Pang et al.<sup>15</sup> synthesized a PPE-PPV hybrid polymer with high weight-average molecular weight, high degree of polymerization, and high yield, but average molecular weight, broad polydispersity, a blueshifted EL spectrum centered at 500 nm, and a high-energy band gap.

In this study, we synthesized a poly (9,9-dioctylfluorene-co-2,3-bis(4-hexyloxyphenyl)quinoxaline) by the Suzuki coupling reaction using the quinoxaline comonomer as an electron acceptor. We characterized the copolymer by  ${}^{1}$ H-NMR and GPC. In addition, the thermal properties of copolymer were verified. The copolymer shows pure green fluorescence in solution and thin films under UV excitation. Subsequently, we fabricated lightemitting diodes. This conjugated polymer shows great promise for the development of stable polymeric green light emitting diodes.

# 2. EXPERIMENTAL DETAILS

# 2.1. Materials and Instruments

All reagents and solvent except toluene were purchased from Aldrich, and used without further purification. Toluene was dried over sodium and distilled under a nitrogen atmosphere. The acceptor monomer 2,3 bis(3-hexyloxyphenyl)-5,8-dibromoquinoxaline was prepared according to literature procedures.<sup>16,17</sup>

<sup>1</sup>H-NMR spectra were measured in a Bruker ARX 400 spectrometer using solutions in  $CDCl<sub>3</sub>$  and chemical shifts were recorded in ppm units with TMS as the internal standard. Thermal decomposition temperatures  $(T_d)$  of the polymer were characterized with a NETZSCH TG 209 F3 thermo gravimetric analyzer (TGA) at a heating rate of 10  $^{\circ}$ C·min<sup>-1</sup>. Differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at a heating rate of  $10^{\circ}$ C·min<sup>-1</sup> using a TA instruments DSC 2310 Modulated DSC. The UV-vis spectra were measured with a HP Agilent 8453 UV-Vis. All GPC analyses used THF as eluant and polystyrene standards as reference. Cyclic voltammetric waves were produced with a Princeton Applied Research Model 273A Potentionstat/Galvanostat in an acetonitrile (substituted with nitrogen for 20 min) solution containing 0.1 M tetrabutylammonium hexafluorophosphorus (TBAPF<sub>6</sub>, Fluka 99.9%) at a constant scan rate of 50 mV/s. A threeelectrode cell with silver/silver chloride [Ag in 0.1 M KCl] as reference electrode was used. Current-voltage characteristics were measured with a computerized Keithley 2400 SourceMeter unit. The luminance and CIE coordinates of the devices were measured with a Spectra Scan PR-670.

# 2.2. EL Device Fabrication and Measurements

For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between an emissive layer and an ITO glass substrate cleaned by successive ultrasonic treatments. The emissive layer was spincoated on top of the thermally dried PEDOT:PSS layer. The sample was annealed at  $125$  °C for 10 min.

# 2.3. Synthesis

# *2.3.1. 2,7-bis(4,4,5,5-tetramethyl-1, 3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (1)*

To a solution of 2,7-dibromo-9,9-dioctylfluorene (10 g, 18.23 mmol) in THF (140 mL) at  $-78$  °C was added by syringe 15.3 mL (38.283 mmol) of n-butyllithium (2.5 M in hexane). The mixture was stirred at −78 °C for 2 h. 2-Isopropoxy-4,4,5,5,-tetramethyl-1,3,2dioxaborolane (9.0 mL, 18.93 mmol) was added to the solution, and the resulting mixture was stirred at  $-78$  °C for 1 h, then warmed to room temperature and stirred for 40 h. The mixture was poured into water, extracted with dichloromethane, and dried over  $Na<sub>2</sub>SO<sub>4</sub>$ . The solvent was removed by evaporation, and the residue was purified by several reprecipitations in hexane to provide 10.763 g  $(91.8\%)$  of the product as a white solid.<sup>18</sup> <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm):  $\delta$  7.78 (d, 2H), 7.72 (s, 2H), 7.70 (d, 2H), 1.97 (m, 4H), 1.37 (s, 24H), 1.18–0.99 (m, 20H), 0.79 (t, 6H), 0.53 (m, 4H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): - 150.45, 143.89, 133.62, 128.89, 119.35, 83.69, 55.16, 40.07, 31.76, 29.91, 29.18, 29.13, 24.92, 23.57, 22.57, 14.05. Anal. Calcd for  $C_{41}H_{64}B_2O_4$ : C, 76.64; H, 10.04. Found: C, 77.00; H, 10.17.

## *2.3.2. 4,7-dibromo-2,1,3-benzothiadiazole (2)*

A mixture of 10 g (73.438 mmol) of 2,1,3 benzothiadiazole in 33.4 mL of 48% hydrobromic acid was heated under reflux with stirring while 34.309 g (214.686 mmol, 11 mL) of bromine was slowly added. After completion of the bromine addition, the reaction mixture became a suspension of a solid in hydrobromic acid; another 11 mL of hydrobromic acid was added, and the mixture was heated under reflux for another 2.5–3 h. The solid product was filtered, washed well with water, recrystallized from chloroform, and dried to give white needle crystals (15 g, 70%).<sup>19</sup> mp 187–188 °C. <sup>1</sup>H-NMR  $(400 \text{ MHz}, \text{CDCl}_3)$   $\delta$  (ppm): 7.73 (s, 2H). <sup>13</sup>C-NMR (100) MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 153.34, 132.67, 114.31.

#### *2.3.3. 3,6-dibromo-1,2-phenylenediamine (3).*

94–95 °C, <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 3.89 up. 3.24 hillion and team (br. s, 4 H); 6.84 (s, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  hu, duum(0), (PPh<sub>3</sub>)<sub>4</sub>Pd(0). To a suspension of 4,7-dibromo-2,1,3-benzothiadiazole (7.349 g, 25 mmol) in ethanol (250 mL), NaBH<sub>4</sub> (16.69 g, 441.176 mmol) was added portionwise at  $0 °C$ , and the mixture was stirred for 20 h at room temperature. After evaporation in vacuo,  $H<sub>2</sub>O$  (150 mL) was added, and the mixture was extracted with diethyl ether. The organic phase was washed with saturated aqueous NaCl solution and dried ( $Na<sub>2</sub>SO<sub>4</sub>$ ). Evaporation in vacuo gave compound 3 (3.9 g,  $87\%$ ),<sup>19,20</sup> a pale yellow solid, mp (ppm): 109.74; 123.33; 133.83.

## *2.3.4. 2,3-bis-(4-methoxyphenyl)-5,8-dibromoquinoxaline (4)*

A mixture of 3,6-dibromo-1,2-phenylenediamine (2.64 g, 9.93 mmol), 4,4 -dimethoxybenzil (3.22 g, 11.916 mmol), and 3 drops of glacial acetic acid in 40 mL of butanol was stirred under reflux for 5 h. After cooling to 0  $\degree$ C, the precipitate was separated by filtration, washed with hot ethanol, and dried under vacuum to give 2.5 g (50.3%) of 2,3-bis(4-methoxyphenyl)-5,8-dibromoquinoxaline.<sup>17,21</sup> <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 7.85 (s, 2H), 7.65–7.51 (ts, 4H), 6.90–6.88 (ts, 4H), 3.85 (s, 6H).

## *2.3.5. 2,3-bis-(4-methoxyphenyl)-5,8 dibromoquinoxaline (5)*

A mixture of an HCl adduct of pyridine (20.82 g) and 2,3-bis(4-methoxyphenyl)-5,8-dibromoquinoxaline (2.5 g, 4.998 mmol) was stirred for 8 h at 200  $^{\circ}$ C. After cooling to room temperature, 40 mL of 2.5% hydrochloric acid were added, the mixture was stirred for 10 min, and the product was extracted with diethyl ether. The extract was washed with dilute hydrochloric acid and water, and dried over  $Na<sub>2</sub>SO<sub>4</sub>$ . Removal of the solvent by evaporation gave 2.17 g (92%) of 2,3-bis(4-hydroxyphenyl)-5,8 dibromoquinoxaline.<sup>17, 21</sup> <sup>1</sup>H-NMR(CDCl<sub>3</sub>)  $\delta$  (ppm): 8.12

(s, 2H), 7.88–7.86 (dt, 4H), 7.10–7.08 (dt, 4H), 5.16 (s, 2H, OH).

## *2.3.6. 2,3-bis-(4-hexyloxyphenyl)-5,8 dibromoquinoxaline (6)*

A mixture of KOH (0.57 g, 10.1 mmol) and 2,3-bis-(4-methoxyphenyl)-5,8-dibromoquinoxaline (1.2 g, 2.54 mmol) in ethanol (17 mL) was allowed to react under reflux. 1-Bromohexane (1.294 g, 7.837 mmol) was then added, and the reaction mixture was stirred under reflux for 24 h. After cooling to  $-20$  °C, the precipitate was collected by filtration, washed with a small amount of methanol, recrystallized from methanol, and dried to give 0.90 g (55.3%) of 2,3-bis(4-hexyloxyphenyl)-5,8 dibromoquinoxaline.<sup>17, 21</sup> <sup>1</sup>H-NMR (CDCl<sub>3</sub>)</sub>  $\delta$  (ppm): 7.84 (s, 2H), 7.66–7.62 (d, 4H), 6.89–6.85 (d, 4H), 4.00–3.97 (t, 4H), 1.83–1.76 (m, 4H), 1.53–1.43 (m, 4H), 1.36–1.32 (m, 8H), 0.93–0.89 (t, 6H).

## *2.3.7. Poly(9,9-dioctylfluorene)-co-(2,3-bis-(4 hexyloxyphenyl)-quinoxaline), PFHOPQ (7)*

Copyright: American Sdissolved in a mixture of dry toluene  $(20 \text{ mL})$  and aque-Monomers 1 (0.2 g, 0.312 mmol), and 6 (0.2 g, 0.312 mmol) and tetrakis(triphenylphosphine) palladium(0),  $(PPh_3)_4Pd(0)$ ,  $(3.605 \text{ mg}, 1 \text{ mol\%})$  were ous 2M K<sub>2</sub>CO<sub>3</sub> (13 mL). The solution was refluxed with vigorous stirring under a nitrogen atmosphere for 48 h. The polymerization solution was poured into methanol with stirring, and the resulting precipitate was dissolved in  $CHCl<sub>3</sub>$  and washed with dilute HCl. The organic layer was separated using a separatory funnel and evaporated. The solid residue was dissolved again in toluene for reprecipitation. The precipitated polymer was filtered off, and dissolved again in  $CHCl<sub>3</sub>$ . The polymer solution was slowly poured into 500 mL of intensively stirred methanol. The precipitated polymer was filtered off and washed with dilute HCl,  $NH<sub>4</sub>OH$ , and water. The crude polymer was washed for 24 h in a Soxhlet apparatus using methanol, acetone, hexane, and chloroform to remove oligomers and catalyst residues.<sup>22</sup>

## 3. RESULTS AND DISCUSSION

Scheme 1 shows the general synthesis routes toward monomers and polymer. The product copolymer, synthesized by the palladium-catalyzed Suzuki coupling reaction, was a yellowish powder. It was completely soluble in organic solvents such as CHCl<sub>3</sub>, THF, DMF, acetonitrile and toluene at room temperature and formed good films. The  ${}^{1}$ H-NMR spectra of the polymer in CDCl<sub>3</sub> is shown in Figure 1. The signals in the ranges of 0.76–4.02 and



6.84–7.97 ppm are assigned to the hexyl, octyl, and phenyl protons. The number of protons estimated from the integration of the peaks was in good agreement with the proposed structures. The number-average molecular weight  $(M_n)$  and the weight-average molecular weight  $(M_w)$  of the synthesized polymer were 40,400 and 60,500 with a polydispersity of 1.49 as determined by GPC using THF as the eluant and polystyrene as the standard.

The thermal properties of the polymer were determined by DSC and thermal gravimetric analysis (TGA) under a nitrogen atmosphere at a heating rate of  $10 °C/min$ . Figure 2 shows the TGA and DSC (inset figure) curves of the polymer. The polymer shows a glass transition at 159 °C and loses less than 5% of its weight on heating to 430.7 °C. These  $T_{\rm g}$  and  $T_{\rm d}$  are higher than those of other



Fig. 1. The <sup>1</sup>H-NMR spectra of synthesized polymer in CDCl<sub>3</sub>.



Fig. 2. The TGA curve of the polymer at a heating rate of  $10 \text{ °C/min}$ under a nitrogen atmosphere. The insert shows the DSC curve of polymer at a heating rate of 10 °C/min under a nitrogen atmosphere.

Table I. The result of polymerization and optical properties of PFHOPQ.

	Molecular <sup><math>a</math></sup> weight		Thermal <sup>b</sup> properties		Optical properties		
					State	UV $\lambda_{\text{max}}$ PL $\lambda_{\text{max}}$	
					<b>PFHOPQ</b> $M_n$ 40,400 $T_g$ (°) 159 Solution (nm) 329 (399)		514
		PDI 149			$M_{\rm w}$ 60,500 $T_{\rm d}$ (°) 421 Film (nm) 327(397) $E_{\sigma}^{\rm opt}$ (eV) <sup>c</sup>	2.57	501

<sup>a</sup>Molecular weight  $(M_n, M_w)$  and polydispersity (PDI) of the polymer was determined by gel permeation chromatography (GPC) in THF using polystyrene standards.  ${}^b$ Glass transition temperature measured by DSC under N<sub>2</sub> and decomposition temperature (5% weight loss) measured by TGA under  $N_2$ . <sup>c</sup>Calculated from the onset of the absorption spectra in thin film.

conjugated polymers, suggesting that the thermal properties of polyfluorene can be improved by incorporating the acceptor moiety, quinoxaline, into the polymer backbone. This could be valuable in device applications; the high thermal stability of the copolymer prevents deformation of the polymer morphology and degradation of the polymer by the applied electric field of a PLED (Table I).

film are 329 and 327 nm, respectively. The  $\lambda_{\text{max}}$  values are  $\text{Pur}_\text{were}$  estimated by evelic blue-shifted compared to the solution values. This feature  $\frac{1}{2}$  formed with a solution suggests increased disruption of  $\pi$ -conjugation caused by  $\Gamma$  Suppression (TRAP) The UV-visible absorption spectra of the polymer are shown in Figure 3 and the corresponding absorption maxima  $(\lambda_{\text{max}})$  are summarized in Table I. The solution was prepared using chloroform as the solvent and the thin film was prepared by depositing drops of the polymer solution on quartz plates. The  $\lambda_{\text{max}}$  of the polymer solution and the hexyloxyphenyl substitution.<sup>23, 24</sup> or a consequence of H-aggregation.25–27

The optical band gap  $(E_g)$  of the polymer, calculated from the onset of the absorption band in the thin film, is 2.57 eV. This optical band gap is lower than that of the fluorene-quinoxaline copolymer, 2.64 eV. Two distinct absorption bands are observed. The absorption peak of about 330 nm is due to the fluorene segments and a side peak of about 390 nm can be assigned to the absorption of the quinoxaline unit (Fig. 3). According to decrease quinoxaline ratio, the absorption of the quinoxaline was disappeared and the absorption peak of 385 nm due to the fluorene segments was inspected<sup>2, 19</sup> The low band gap of this polymer is probably due to intramolecular charge transfer,  $\pi$ -electron delocalization in twodimensional direction, between fluorene and the electron acceptor, quinoxaline,<sup>28</sup> or to backbone planarity. However, the decrement of band gap of copolymer is not consistent with the increasing order of the acceptor strength because of the backbone planarity.

The PL emission spectrum of polymer in chloroform solution shows a maximum peak at 514 nm, but in the thin film, the peak is blue-shifted 13 nm to 501 nm. Since the substituted hexyloxyphenyl groups in the quinoxaline units can increase the conjugation length, the polymer had low energy level and then the emission was red-shifted. The polymer had more blue shifted absorption and emission peaks than other fluorene-co-quinoxaline polymer which has no substitution. Because the  $\lambda_{\text{max}}$  peak of its PL spectrum is at 501 nm, the polymer emits a purer green.

The electrochemical properties and the redox potential of the polymer were determined from the optical band gap, which was estimated from the wavelength of absorption onset, and the HOMO energy levels, which were estimated by cyclic voltammetry (CV). CV was performed with a solution of tetrabutylammonium hexafluorophosporus (TBAPF<sub>6</sub>) (0.1 M) in acetonitrile at a scan rate of 100 mV/s at room temperature. A Pt wire and a Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. ITO glass ( $\sim$ 1 cm<sup>2</sup>) coated with a thin polymer film was used as the working electrode. Figure 4 shows the cyclic voltammogram of the polymer. It exhibits quasi-reversible oxidation and reduction. The absorption onset wavelength of the polymer was 482 nm in solution, which corresponds to a band gap of 2.57 eV.



Fig. 3. UV-vis absorption and PL emission spectra of polymer in solution and solid thin film.



Fig. 4. Cyclic voltammograms of polymer film on a ITO electrode in acetonitrile solution containing  $TBAPF<sub>6</sub>$  as the electrode.



From Figure 4, the n-doping onset point was 1.38 V and the *p*-doping onset point was  $-1.13$  V.

HOMO and LUMO levels were calculated according to the empirical formula:

HOMO (or LUMO) (eV)

$$
=-4.8 - (E_{\text{onset}} - E_{1/2}(\text{Ferrocene}))^{29}
$$

Using this formula, the HOMO and LUMO level of the polymer were determined to be  $-5.76$  and  $-3.25$  eV, respectively. The LUMO and HOMO levels of this polymer are smaller than those of other fluorene-coquinoxaline polymers because this quinoxaline monomer has an hexyloxyphenyl side chain which contributes to resonance effects. (LUMO =  $-2.65$  eV, HOMO =  $-5.51$  eV). The electrochemical band gap estimated from the difference between HOMO and LUMO levels is 2.51 eV, similar to the optical band gap. Table II summarizes these results.

tion glass/ITO/PEDOT:PSS/polymer/LiF/Ca/Al. Figure 5  $\frac{1}{9}$  Sq  $\frac{2}{9}$  m for 30 s EL devices with the studied polymer used as the emissive layer were fabricated in the configurashows electroluminescence characteristics of the EL device. The PEDOT:PSS hole injection layer was spincoated on an ITO-coated glass at 2000 rpm for 30 s to obtain a thickness of 30 nm. Then it was annealed for 10 min. To fabricate the polymer emissive layer devices,



Fig. 5. Electroluminescene (EL) characteristic of ITO coated glass/PEDOT:PSS/the copolymer/LiF/Ca/Al.



Fig. 6. Current density(line-closed black square) and brightness(dash line-open blue square) characteristics of EL device.

the polymer solution was spin-coated under different conditions. Therefore, the polymer emissive layers had different thicknesses. A 1 wt% polymer solution in THF was used to make the emissive layers; this solution was spincoated on the PEDOT:PSS film at 1,000 rpm, 2,000 rpm, 3,000 rpm or 4,000 rpm for 30 s. Then lithium fluoride  $(1 \text{ nm}, 0.18 \text{ Å/s})$ , calcium  $(50 \text{ nm}, 1.1 \text{ Å/s})$  and aluminum (100 nm, 2 Å/s) were thermally deposited on the polymer film.

died epotymer nused to: PurduAll of the EL devices emitted green light. Among ated in the configura<sup>-</sup> hu, these EL devices, we focused on the one spin-coated at 4,000 rpm for 30 s. As shown in Figure 5, its emission maximum was at 500 nm, a pure green emission similar to the PL from the thin film. The current density–voltage– luminescence (J–V–L) characteristics and electroluminescence efficiency of the devices fabricated from the studied polymer are shown in Figures 6 and 7. In forward bias, the turn-on voltage of the polymer was 7 V and the maximum brightness was  $10.16$  cd/m<sup>2</sup> at 14 V. The maximum luminescence efficiency of the polymer was 0.0011 cd/A



Fig. 7. Luminous efficiency of EL device as a function of current density.

at 11 V. The EL properties of the monolayer device are shown in Figure 5. Because of quinoxaline unit with hexyloxyphenxyl side chain, the emission maximum of the EL device was 502 nm, which was blue-shifted rather than other fluorene-quinoxaline copolymers. The emission color of the device was green with CIE coordinates of  $x = 0.28$ ,  $y = 0.51$ . Although this polymer device exhibits lower brightness and luminescence, it is noteworthy that it produces much purer green light than other green-emitting materials.

## 4. CONCLUSION

gle layer PLED EL devices with different emissive layer  $\frac{P}{\text{UIC}}$  State Patent No. 7368510 ( thicknesses by spin-coating. An EL device with the config- $\frac{1}{18}$ . N. S. Cho, J.-H. Park, S. Exercise to the country of the company of the N.S. Cho, J.-H. Fauration ITO/PEDOT:PSS/copolymer/LiF/Ca/Al had been In conclusion, we present here the synthesis of a conjugated polymer, which could be used in a green PLED, by copolymerization of fluorene with quinoxaline units bearing side chains using the Suzuki coupling reaction. Since the quinoxaline side chain is a strong electron acceptor, the copolymer emission is red-shifted to around 500 nm, in the green region of the spectrum. The polymer has a glass transition temperature of  $159 °C$  and high thermal stability up to  $420$  °C, so it is suitable for making PLEDs. This polymer has lower HOMO and LUMO levels than other PFs. As a result, the polymer's energy levels are matched to the energy levels of electrode materials. Therefore, charge carrier entry is easier. We fabricated sinfabricated and emitted green light with an maximum at 502 nm. One of these devices emits green light of high purity with CIE 1931 coordinates of  $x = 0.28$  and  $y = 0.51$ . It has a turn-on voltage of 7 V, and a maximum brightness of 10.16  $cd/m<sup>2</sup>$  at 14 V. This study suggests that tuning of electronic and optoelectronic properties can be achieved by incorporating quinoxaline with alkoxy phenyl side chains as electron acceptors into polyfluorenes to produce a good candidate material for green PLEDs. The EL efficiency of PFHOPQ should be improved if the quinoxaline unit had other side chain. Future study will focus on modification of the polymer structure to improve the charge injection characteristics of the hybrid material.

# References and Notes

- 1. Y. E. Jin, J. Y. Kim, S. Song, Y. Xia, J. Kim, H. Y. Woo, K. Lee, and H. Suh, *[Polymer](http://www.ingentaconnect.com/content/external-references?article=0032-3861(2008)49L.467[aid=8969936])* 49, 467 (2008).
- 2. W.-C. Wu, C.-L. Liu, and W.-C. Chen, *[Polymer](http://www.ingentaconnect.com/content/external-references?article=0032-3861(2006)47L.527[aid=8969935])* 47, 527 (2006).
- 3. D. K. Moon, J.-Y. Yun, K. Osakada, T. Kambara, and T. Yamamoto, *Molecular Crystals and Liquid Crystals* 464, 177 (2007).
- 4. J. Y. Lee, Y. J. Kwon, J.-W. Woo, and D. K. Moon, *Journal of Industrial and Engineering Chemistry* 14, 810 (2008).
- 5. D.-K. Moon, A. B. Padias, H. K. Hall, T. Huntoon, and P. D. Calvert, *[Macromolecules](http://www.ingentaconnect.com/content/external-references?article=0024-9297(1995)28L.6205[aid=8969933])* 28, 6205 (1995).
- 6. K. Ariga, J. P. Hill, M. V. Lee, A. Vinu, R. Charvet, and S. Acharya, *[Science and Technology of Advanced Materials](http://www.ingentaconnect.com/content/external-references?article=1468-6996(2008)9L.014109[aid=8603878])* 9, 014109 (2008).
- 7. Q. Peng, Z.-Y. Lu, Y. Huang, M.-G. Xie, D. Xiao, S.-H. Han, J.-B. Peng, and Y. Cao, *[J. Mater. Chem.](http://www.ingentaconnect.com/content/external-references?article=0959-9428(2004)14L.396[aid=8969932])* 14, 396 (2004).
- 8. Y.-H. Kim, S.-J. Park, J.-W. Park, J. H. Kim, and S.-K. Kwon, *Macromolecular Research* 15, 216 (2007).
- 9. M. A. Karim, Y.-R. Cho, J. S. Park, K.-J. Yoon, S. J. Lee, S.-H. Jin, G.-D. Lee, and Y.-S. Gal, *Macromolecular Research* 16, 337 (2008).
- 10. A. Tsami, X.-H. Yang, F. Galbrecht, T. Farrell, H. Li, S. Adamczyk, R. Heiderhoff, L. J. Balk, D. Neher, and E. Holder, *[J. Polym. Sci.,](http://www.ingentaconnect.com/content/external-references?article=0887-624x(2007)45L.4773[aid=8969930]) [Part A: Polym. Chem.](http://www.ingentaconnect.com/content/external-references?article=0887-624x(2007)45L.4773[aid=8969930])* 45, 4773 (2007).
- 11. D. Y. Kim, H. N. Cho, and C. Y. Kim, *[Prog. Polym. Sci.](http://www.ingentaconnect.com/content/external-references?article=0079-6700(2000)25L.1089[aid=7548822])* 25, 1089 [\(2000\)](http://www.ingentaconnect.com/content/external-references?article=0079-6700(2000)25L.1089[aid=7548822]).
- 12. W.-Y. Lee, K.-F. Cheng, T.-F. Wang, C.-C. Chueh, W.-C. Chen, C.-S. Tuan, and J.-L. Lin, *[Macromol. Chem. Phys.](http://www.ingentaconnect.com/content/external-references?article=1022-1352(2007)208L.1919[aid=8969929])* 208, 1919 (2007).
- 13. J.-F. Morin and M. Leclerc, *[Macromolecules](http://www.ingentaconnect.com/content/external-references?article=0024-9297(2002)35L.8413[aid=8969928])* 35, 8413 (2002).
- 14. W. Z. Yuan, A. Qin, J. W. Y. Lam, J. Z. Sun, Y. Dong, M. Haussler, J. Liu, H. P. Xu, Q. Zheng, and B. Z. Tang, *[Macromolecules](http://www.ingentaconnect.com/content/external-references?article=0024-9297(2007)40L.3159[aid=8969927])* 40, 3159 [\(2007\)](http://www.ingentaconnect.com/content/external-references?article=0024-9297(2007)40L.3159[aid=8969927]).
- 15. Q. Chu, Y. Pang, L. Ding, and F. E. Karasz, *[Macromolecules](http://www.ingentaconnect.com/content/external-references?article=0024-9297(2003)36L.3848[aid=8969926])* 36, 3848 [\(2003\)](http://www.ingentaconnect.com/content/external-references?article=0024-9297(2003)36L.3848[aid=8969926]).
- 16. F. S. Mancilha, B. A. Dasilveira, N. A. S. Lopes, P. F. Moreira, Jr., F. H. Quina, R. S. Gongalves, and J. Dupont, *[Eur. J. Org. Chem.](http://www.ingentaconnect.com/content/external-references?article=1434-193x(2006)2006L.4924[aid=8969925])* [2006, 4924](http://www.ingentaconnect.com/content/external-references?article=1434-193x(2006)2006L.4924[aid=8969925]) [\(2006\)](http://www.ingentaconnect.com/content/external-references?article=1434-193x(2006)2006L.4924[aid=8969925]).
- 17. B. L. Lee, K. M. Han, J. H. Shin, S. Y. Lee, and E. J. Jeong, United State Patent No. 7368510 (11/073,691) (2006).
- 18. N. S. Cho, J.-H. Park, S.-K. Lee, J. Lee, H.-K. Shim, M.-J. Park, D.-H. Hwang, and B.-J. Jung, *[Macromolecules](http://www.ingentaconnect.com/content/external-references?article=0024-9297(2006)39L.177[aid=8969924])* 39, 177 (2006).
- 19. R. Yang, R. Tian, J. Yan, Y. Zhang, J. Yang, Q. Hou, W. Yang, C. Zhang, and Y. Cao, *[Macromolecules](http://www.ingentaconnect.com/content/external-references?article=0024-9297(2005)38L.244[aid=8969923])* 38, 244 (2005).
- 20. M. J. Edelmann, J.-M. Raimundo, N. F. Utesch, F. Diederich, C. Boudon, J.-P. Gisselbrecht, and M. Gross, *[Helvetica Chimica Acta](http://www.ingentaconnect.com/content/external-references?article=0018-019x(2002)85L.2195[aid=8969922])* [85, 2195](http://www.ingentaconnect.com/content/external-references?article=0018-019x(2002)85L.2195[aid=8969922]) (2002).
- 21. T. Yamamoto, B.-L. Lee, H. Kokubo, H. Kishida, K. Hirota, T. Wakabayashi, and H. Okamoto, *[Macromol. Rapid Commun.](http://www.ingentaconnect.com/content/external-references?article=1022-1336(2003)24L.440[aid=8969921])* 24, 440 [\(2003\)](http://www.ingentaconnect.com/content/external-references?article=1022-1336(2003)24L.440[aid=8969921]).
- 22. M. Ranger, D. Rondeau, and M. Leclerc, *[Macromolecules](http://www.ingentaconnect.com/content/external-references?article=0024-9297(1997)30L.7686[aid=7548825])* 30, 7686 [\(1997\)](http://www.ingentaconnect.com/content/external-references?article=0024-9297(1997)30L.7686[aid=7548825]).
- 23. J. A. Mikroyannidis, *J. Lumin.* [128, 1137](http://www.ingentaconnect.com/content/external-references?article=0022-2313(2008)128L.1137[aid=8969920]) (2008).
- 24. S.-H. Jin, H.-J. Park, J. Y. Kim, K. Lee, S.-P. Lee, D.-K. Moon, H.-J. Lee, and Y.-S. Gal, *[Macromolecules](http://www.ingentaconnect.com/content/external-references?article=0024-9297(2002)35L.7532[aid=8969919])* 35, 7532 (2002).
- 25. M. C. Mccairn and M. L. Turner, *[Tetrahedron Lett.](http://www.ingentaconnect.com/content/external-references?article=0040-4039(2007)48L.1045[aid=8969918])* 48, 1045 (2007).
- 26. A. Facchetti, M.-H. Yoon, C. L. Stern, G. R. Hutchison, M. A. Ratner, and T. J. Marks, *[J. Am. Chem. Soc.](http://www.ingentaconnect.com/content/external-references?article=0002-7863(2004)126L.13480[aid=7844153])* 126, 13480 (2004).
- 27. X. Zhang, J. P. Johnson, J. W. Kampf, and A. J. Matzger, *[Chem.](http://www.ingentaconnect.com/content/external-references?article=0897-4756(2006)18L.3470[aid=8969917]) Mater.* [18, 3470](http://www.ingentaconnect.com/content/external-references?article=0897-4756(2006)18L.3470[aid=8969917]) [\(2006\)](http://www.ingentaconnect.com/content/external-references?article=0897-4756(2006)18L.3470[aid=8969917]).
- 28. L. Huo, Z. A. Tan, X. Wang, Y. Zhou, M. Han, and Y. Li, *[J. Polym.](http://www.ingentaconnect.com/content/external-references?article=0887-624x(2008)46L.4038[aid=8969916]) [Sci., Part A: Polym. Chem.](http://www.ingentaconnect.com/content/external-references?article=0887-624x(2008)46L.4038[aid=8969916])* 46, 4038 (2008).
- 29. H. S. Lee and J. H. Kim, *Polymer Science and Technology* 18, 487 (2007).

Received: 10 July 2008. Accepted: 8 December 2008.