

# Efficient Green-Light-Emitting Diodes from Silole-Containing Copolymers

Michelle S. Liu, Jingdong Luo, and Alex K.-Y. Jen\*

Department of Materials Science and Engineering, Roberts Hall, Box 352120,  
University of Washington, Seattle, Washington 98195-2120

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Two random copolymers based on poly(di-*n*-hexylfluorene-*co*-4,4-diphenyldithienosilole) (PF-DTS) were synthesized by Suzuki coupling reaction. The presence of a small portion (10 mol% for PF9-DTS, 5 mol% for PF19-DTS) of electron-deficient dithienosilole moiety in the copolymers increases their electron affinity and facilitates charge recombination through its function as a charge-trapping site for both holes and electrons. Photoluminescence (PL) studies show that color tuning through efficient Förster energy transfer from the higher-energy fluorene segments to the lower-energy dithienosilole-containing segments can be achieved as well. A double-layer device using PF9-DTS as the emitting layer and an in-situ polymerized bis-tetraphenylenebiphenyldiamine-perfluorocyclobutane (BTPD-PFCB) as the hole-transporting layer demonstrates a low turn-on voltage at 4.6 V, a brightness greater than 25 900 cd/m<sup>2</sup>, and a maximum external quantum efficiency of 1.64%, which could be attributed to both the improved charge injection and charge recombination in this polymer.

## Introduction

The operation of polymer light-emitting diodes (LEDs) involves the injection of both holes and electrons from opposite electrodes, their transport in the bulk material, recombination to form excitons, and the radiative decay of the singlet excitons.<sup>1,2</sup> Because the mobility of electrons and holes in most conjugated polymers are quite different, under a high operating electric field ( $>10^5$  V/cm), a large percentage of the higher mobility carriers can be swept through the polymer without forming excitons, resulting in a low light emission.<sup>3,4</sup> Therefore, an important task to achieve efficient LEDs is to maximize the recombination of injected charge carriers before they get discharged at the electrodes. The efficient capture of electrons and holes can be realized through the charge confinement imposed by a discontinuity in the electronic transporting levels.<sup>5,6</sup> This has been demonstrated by the carrier trapping in polymer blends and dye-doped polymer systems, in which dopants serve as both carrier traps and recombination sites.<sup>7–10</sup> The electrons and/or holes trapped in the dopants cause

a build up in local charge density, which enhances the possibility of attracting oppositely charged carriers. However, the phase separation between two incompatible polymers and the crystallization of small molecules in the polymer host are quite problematic and tend to shorten the device lifetime.

This problem can be circumvented by introducing a small amount of low band gap moieties directly into the polymer main chain.<sup>11–14</sup> The incorporation of these low band gap comonomers by Suzuki coupling reaction creates randomly distributed low energy sites in the polymer chain. Electrons and holes will be trapped at these low-energy sites, where they will have a higher probability of capturing each other. Thus, the yield of singlet exciton formation and electroluminescence (EL) quantum efficiency will be enhanced. In addition, such low-energy sites will also act as effective energy traps for excitons formed at the higher-energy segments. In conjugated polymers, Förster energy transfer is known to be fast and efficient between two chromophore segments of different energy and will shift the emission to longer wavelengths.<sup>15</sup> Employing this approach will not only simplify the material synthesis but will also achieve color tuning for full-color displays.

Among many heteroaromatic ring systems being explored for light-emitting purposes, the silole ring has been demonstrated to possess a particularly low-lying

\* To whom correspondence should be addressed. Phone: 206-543-2626. Fax: 206-543-3100. E-mail: ajen@u.washington.edu.

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lowest unoccupied molecular orbital (LUMO), arising from the orbital interaction between the silicon  $\sigma^*$  and butadiene  $\pi^*$  orbitals.<sup>16</sup> The alternating copolymers containing diaryldithienosilole, a tricyclic system involving a silole ring fused with two thiophene rings, and organosilicon units have been developed.<sup>17,18</sup> However, no detectable light could be observed from their single-layer EL device and these polymers were used as hole-transporting materials. In this paper, a small amount of 4,4-diphenyldithienosilole was introduced into the polyfluorene backbone to increase the electron affinity of the polymers and to function as traps for both charges and excitons. The LED devices based on these polymers were fabricated to evaluate their potential as efficient emitting materials.

## Experimental Section

**Materials.** Commercially available chemicals (Aldrich) were used without further purification. 3,3'-Dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene,<sup>16</sup> 9,9-dihexylfluorene-2,7-dibromide, and 9,9-dihexylfluorene-2,7-di(ethylenyl boronate)<sup>19</sup> were synthesized according to literature procedures. All reactions were performed under a nitrogen atmosphere.

**4,4-Diphenyl-2,6-bis(trimethylsilyl)dithieno[3,2-*b*:2',3'-*d'*]-silole.** To the mixture of 3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (6.75 g, 14.4 mmol) and ether (180 mL) was added a 2.5 M *n*-butyllithium/hexane solution (12.0 mL, 30.0 mmol) at  $-78^\circ\text{C}$ . The resulting mixture was allowed to stir at this temperature for 2 h, and then a freshly distilled dichlorodiphenylsilane (3.4 mL, 16.2 mmol) was added to the mixture. After the addition, the mixture was warmed to room temperature and THF (120 mL) was added. Then the reaction mixture was heated to reflux overnight and hydrolyzed with water. After separating the organic layer, the aqueous layer was extracted with ether. The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated. The resulting mixture was chromatographed on a silica gel column with hexane as eluent to give crude dark yellow semisolids, which were purified by recrystallization from methanol, affording the title product as light yellow crystals. Yield: 4.2 g (60%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.33 (s, 18H), 7.24 (s, 2H), 7.28–7.42 (m, 6H), 7.64 (dd, 4H).

**Dibromodithienosilole.** To 50 mL of an ether solution of compound 4,4-diphenyl-2,6-bis(trimethylsilyl)dithieno[3,2-*b*:2',3'-*d'*]-silole (800 mg, 1.63 mmol) was added dropwise bromine (0.20 mL, 3.8 mmol) at  $-90^\circ\text{C}$ , and the resulting mixture was stirred for 1 h at this temperature. After the solvent was evaporated, the residue was washed with hexane to give white solids, which were recrystallized from chloroform to give dibromodithienosilole as white solids. Yield: 465 mg (57%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.16 (s, 2H), 7.34–7.47 (m, 6H), 7.58 (dd, 4H).

**PF9-DTS.** To a stirred mixture of 9,9-dihexylfluorene-2,7-di(ethylenyl boronate) (149 mg, 0.315 mmol), 9,9-dihexylfluorene-2,7-dibromide (118 mg, 0.24 mmol), 4,4-diphenyldithienosilole (30 mg, 0.06 mmol), tetrakis(triphenylphosphine)palladium (1.5 mg), and Aliquat 336 (15 mg) in toluene (10 mL) was added a 2 M aqueous potassium carbonate solution (0.6 mL). The mixture was heated to reflux for 3 days. The polymerization was end-capped with phenylboronic acid for 6 h, followed by bromobenzene for another 6 h. The reaction

mixture was cooled and added dropwise into a methanol/water (2:1 v/v) solution. The precipitated polymer fibers were collected by filtration. The crude polymer was further purified by redissolving the polymer into THF and reprecipitating in methanol several times. Yield: 70 mg (70%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.79 (t,  $J = 6.5, 5.4\text{Hz}$ ), 1.12 (br, 14.4H), 2.16 (br, 3.6H), 7.67 (m, 5.6H), 7.83 (m, 1H). Anal. Calcd for  $(\text{C}_{24.5}\text{H}_{30.2}\text{Si}_{0.1})_n$ : C, 88.18; H, 9.06; S, 1.92. Found: C, 87.23; H, 9.20; S, 1.93.

**PF19-DTS.** To a stirred mixture of 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) (211 mg, 0.42 mmol), 9,9-dihexylfluorene-2,7-dibromide (177 mg, 0.36 mmol), 4,4-diphenyldithienosilole (20 mg, 0.04 mmol), tetrakis(triphenylphosphine)palladium (2.1 mg), and Aliquat 336 (21 mg) in toluene (10 mL) was added a 2 M aqueous potassium carbonate solution (1.5 mL). The mixture was heated to reflux for 3 days. The polymerization was end-capped with phenylboronic acid for 6 h, followed by bromobenzene for another 6 h. The reaction mixture was cooled and added dropwise into a methanol/water (2:1 v/v) solution. The precipitated polymer fibers were collected by filtration. The crude polymer was further purified by redissolving the polymer into THF and reprecipitating in methanol several times. Yield: 144 mg (54%). Anal. Calcd for  $(\text{C}_{24.75}\text{H}_{31}\text{Si}_{0.1}\text{Si}_{0.05})_n$ : C, 89.23; H, 9.38; S, 0.96. Found: C, 89.96; H, 9.31; S, 1.09.

**Characterization.**  $^1\text{H}$  spectra were obtained on a Bruker AF301 (300 MHz) spectrometer and recorded in ppm relative to tetramethylsilane (TMS) ( $\delta = 0$  ppm) as an internal standard. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters Styragel (HR 4E,  $7.8 \times 300$  mm) column with polystyrenes as the standards and THF as the eluent. Thermal properties of polymers were analyzed with a TA Instruments thermal analysis and rheology system (TGA 2950, DSC 2010) under nitrogen at a heating rate of  $10^\circ\text{C}/\text{min}$ . UV-vis spectra were recorded on a Perkin-Elmer spectrophotometer (Lambda 9 UV/vis/NIR). The film thickness was measured with a Dektak surface profilometer (model 3030). PL and EL spectra were obtained with an Oriel Instaspec IV charge coupled device (CCD) camera. Current-voltage ( $I$ - $V$ ) characteristics were measured on a Hewlett-Packard 4155B semiconductor parameter analyzer. The power of EL emission was measured using a Newport 2835-C multifunctional optical meter. Photometric units ( $\text{cd}/\text{m}^2$ ) were calculated using the forward output power and the EL spectra of the devices, assuming Lambertian distribution of the EL emission.<sup>20</sup>

Cyclic voltammetry (CV) was conducted at room temperature in a typical three-electrode cell with a working electrode (ITO glass), a reference electrode ( $\text{Ag}/\text{Ag}^+$ , referenced against ferrocene/ferrocenium (FOC)), and a counter electrode (Pt gauze) under a nitrogen atmosphere at a sweeping rate of 100 mV/s (CV-50W voltammetric analyzer, BAS). CV measurements for polymers were performed in an electrolyte solution of 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram. According to the redox onset potentials of the CV measurements, the HOMO/LUMO energy levels of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum):  $\text{HOMO/LUMO} = -(E_{\text{onset}} - 0.12 \text{ V}) - 4.8 \text{ eV}$ , where the value 0.12 V is for FOC vs  $\text{Ag}/\text{Ag}^+$ .

**Device Fabrication and Testing.** The devices were fabricated on ITO-coated glass substrates (Colorado Concept Coating) that had been ultrasonicated sequentially in detergent, deionized water, methanol, 2-propanol, and acetone, and had been treated with  $\text{O}_2$  plasma for 10 min before use. The hole-injecting poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT, Bayer Corp) layer was spin coated at a spin rate of 4000 rpm from its water solution (1.3 wt %) onto ITO substrates and cured at  $160^\circ\text{C}$  for 10 min under nitrogen.

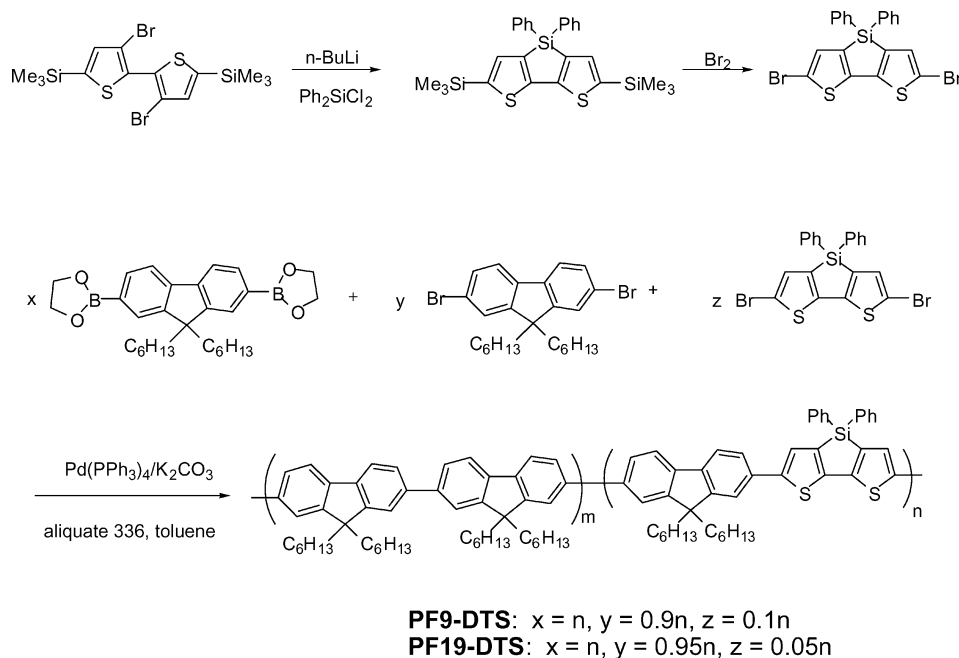
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**Scheme 1. Synthetic Scheme for Monomer and Silole-Containing Copolymers**

An in-situ polymerized hole-transporting bis(tetraphenyl-diamino)biphenyl-perfluorocyclobutane (BTPD-PFCB) layer was fabricated by spin coating dichloroethane solution of its precursor onto ITO substrates and then cured at 225 °C for 45–60 min under nitrogen.<sup>21,22</sup> Then a thin layer of light-emitting polymers (1 wt % in toluene) was spin-coated onto the PEDOT or BTPD-PFCB layer at 1600 rpm. Deposition of the metal electrodes was carried out in a vacuum evaporator inside an argon atmosphere drybox. A layer of 30-nm-thick Ca was evaporated at a pressure below  $10^{-6}$  Torr through a mask, and another layer of 120-nm-thick Ag was evaporated on the top as a protecting layer for Ca. The active emissive area defined by the cathode was about 6.16 mm<sup>2</sup>. All device testing was carried out in air at room temperature.

**Results and Discussion**

**Polymer Synthesis and Characterization.** As shown in Scheme 1, the dithienosilole monomer was obtained by bromination of 4,4-diphenyl-2,6-bis(trimethylsilyl)dithienosilole, which is prepared by the lithiation of 3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene, followed by the reaction with dichlorodiphenylsilane.<sup>16</sup> Two random fluorene copolymers, poly(di-*n*-hexylfluorene-*co*-4,4-diphenyldithienosilole)s (PF9-DTS and PF19-DTS) with a small amount of 4,4-diphenyldithienosilole units (10 mol % for PF9-DTS and 5 mol % for PF19-DTS) were synthesized by Suzuki coupling reaction. The chemical structures of PF-DTS copolymers were verified by NMR spectra. Elemental analysis data indicated that the incorporation ratios of diphenyldithienosilole are in good agreement with the feeding ratios. The weight-average molecular weight ( $M_w$ ) of the polymers, determined by gel permeation chromatography (GPC) using polystyrene as standards, was 146 000 with a polydispersity index of 2.8 for PF9-DTS, and 76 000 for PF19-DTS with a polydispersity index of 2.2.

The polymers are readily soluble in common organic solvents, such as toluene, tetrahydrofuran, and chloroform. Both copolymers are thermally stable with a decomposition temperature (onset weight loss measured by thermogravimetric analysis (TGA)) well above 400 °C. A glass transition temperature ( $T_g$ ) determined by differential scanning calorimetry (DSC) is 100 °C for PF9-DTS, which is slightly higher than that of PF19-DTS (95 °C), due to the higher rigid diphenyldithienosilole content in PF9-DTS (10 mol %).

**Photophysical Properties.** The optical properties of these two silole-containing fluorene copolymers were measured both in solution and in thin film, and the corresponding spectra are shown in Figure 1. PF9-DTS and PF19-DTS display very similar absorption spectra in solution (toluene) with the main absorption peak at 386 nm, which can be assigned to the  $\pi$ – $\pi^*$  transition (Figure 1a). However, the spectrum for PF9-DTS, which has a higher 4,4-diphenyldithienosilole content, also shows a longer wavelength absorption shoulder appearing at 440 nm. This may be due to the stronger charge transfer between 4,4-diphenyldithienosilole and the fluorene units because PF9-DTS has a higher content of 4,4-diphenyldithienosilole than PF19-DTS. The solution photoluminescence (PL) spectrum of PF9-DTS shows two characteristic emission bands (Figure 1a). The one that appeared in the deep-blue region (around 390–450 nm) is attributed to the emission from the fluorene segments. The strong emission band that peaks at 486 nm and has a shoulder at 515 nm seems to arise from the isolated 4,4-diphenyldithienosilole-containing segments. Considering there is only a small amount (10 mol %) of 4,4-diphenyldithienosilole in the copolymer, the strong emission from 4,4-diphenyldithienosilole-containing segments suggests an efficient Förster energy transfer that occurred due to the good overlap between the emission spectrum of fluorene segments and the absorption spectrum of PF9-DTS. Most excitons formed in fluorene units by direct photoexcitation are likely to migrate to the lower energy 4,4-diphenyldi-

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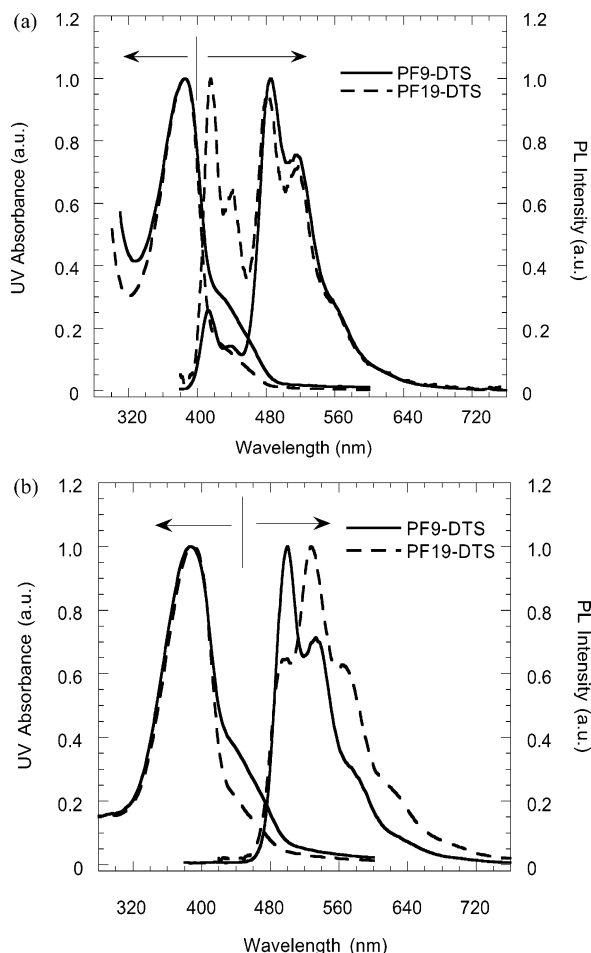
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**Table 1. Performance of Single-Layer and Double-Layer LEDs Based on PF-DTS Copolymers**

device structure <sup>a</sup>	d <sup>b</sup> (nm)	V <sub>on</sub> <sup>c</sup> (V)	B <sub>max</sub> <sup>d</sup> (cd/m <sup>2</sup> )	h <sub>max</sub> <sup>e</sup> (%)	LE <sub>max</sub> <sup>f</sup> (lm/W)	PE <sub>max</sub> <sup>g</sup> (cd/A)
ITO/PF9-DTS/Ca	60	8.4	2 080	0.33	0.33	0.93
ITO/PF19-DTS/Ca	45	6.6	451	0.10	0.10	0.26
ITO/PEDOT/PF9-DTS/Ca	60	5.4	13 100	0.41	0.32	1.03
ITO/PEDOT/PF19-DTS/Ca	40	5.2	7 180	0.16	0.21	0.46
ITO/BTPD-PFCB/PF9-DTS/Ca	45	4.6	25 900	1.64	2.08	4.41
ITO/BTPD-PFCB/PF19-DTS/Ca	35	6.2	7 880	0.32	0.33	0.84

<sup>a</sup> Thickness of PEDOT and BTPD-PFCB layer is 25 nm. <sup>b</sup> Thickness of emitting layer. <sup>c</sup> Turn-on voltage, defined as the voltage needed for brightness of 1 cd/m<sup>2</sup>. <sup>d</sup> Maximum brightness. <sup>e</sup> Maximum external quantum efficiency. <sup>f</sup> Maximum luminous efficiency. <sup>g</sup> Maximum photometric efficiency.



**Figure 1.** (a) Solution absorption and emission spectra of PF9-DTS and PF19-DTS. (b) Film absorption and emission spectra of PF9-DTS and PF19-DTS.

thienosilole-containing sites, from which the emission occurs. For PF19-DTS with 5 mol % 4,4-diphenyldithienosilole incorporated into the polymer, there are very little low energy silole-containing sites distributed in the polymer main chain. As a result, the energy transfer becomes less efficient than that of PF9-DTS, therefore the emission from the fluorene segments becomes dominant. The absorption spectra of these two polymers in solid states follow the same trend as their solution counterparts, although UV absorptions of the films are slightly broadened because of the aggregate formation (Figure 1b). In the films, the emission from the polyfluorene is completely suppressed; instead, the PL spectra reveal only the emission from the 4,4-diphenyldithienosilole-containing segments. The lack of blue emission in the films indicates the complete energy transfer facilitated by both intra- and interchain interaction due

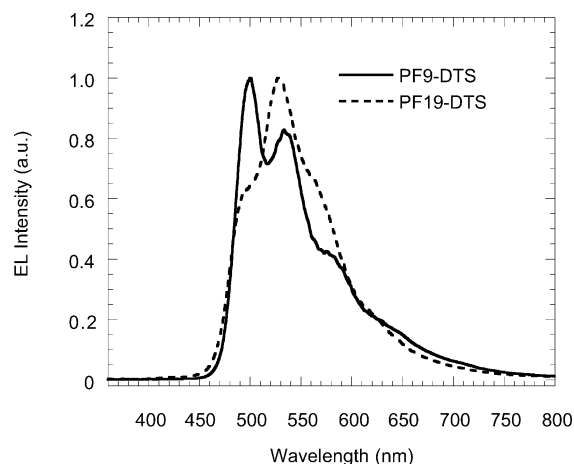
to shorter polymer chain distance in solid state. However, the PL spectrum for PF19-DTS ( $\lambda_{\text{max}} = 527$  nm) is red-shifted and shows different vibronic coupling from that of PF9-DTS ( $\lambda_{\text{max}} = 500$  nm), suggesting the increased interchain interactions in PF19-DTS film.<sup>23</sup> In PF19-DTS, polymer chains are more tightly packed because of less 4,4-diphenyldithienosilole content in the polymer, in which rigid phenyl rings at the 4- position of silole ring serve as the bumper to prevent the chain packing.

**Redox Properties.** The redox behavior of PF-DTS copolymers was investigated by cyclic voltammetry (CV). PF9-DTS undergoes a reversible electrochemical reduction with the onset potential at  $-2.36$  V, which originates from the electron-deficient nature of 4,4-diphenyldithienosilole, while only an irreversible oxidation occurred at  $0.82$  V could be observed. Even with only 5 mol % 4,4-diphenyldithienosiloles, PF19-DTS still demonstrates a reversible reduction wave but with a much lower onset potential at  $-2.50$  V. The highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) energy levels of PF9-DTS were estimated to be at  $-5.50$  and  $-2.32$  eV, respectively, with regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level). Accordingly, the LUMO ( $-2.18$  eV) and HOMO ( $-5.68$  eV) are obtained for PF19-DTS. The high-lying HOMO and low-lying LUMO levels of silole-containing copolymers fall within the HOMO ( $-5.8$  eV) and LUMO ( $-2.12$  eV) of polyfluorene.<sup>24</sup> Thus, the charge-trapping mechanism will play an important role in improving the device efficiency. The higher electron affinity of PF9-DTS could also decrease the energy barrier for electron injection.

**LED Characteristics.** LEDs with configurations of ITO/polymer/Ca, ITO/PEDOT/polymer/Ca, and ITO/BTPD-PFCB/polymer/Ca were fabricated to study the electroluminescence properties of copolymers. The device performances are summarized in Table 1. The EL spectra of the devices based on these two copolymers are almost identical to their PL spectra, indicating that the same energy transfer process is involved in EL as well as in PL (Figure 2). Surprisingly, the single-layer device with only PF9-DTS already demonstrates a very efficient green emission, with a maximum external quantum efficiency of 0.33% at 32 cd/m<sup>2</sup> and 11.8 V bias. The maximum luminance is 2080 cd/m<sup>2</sup> at a drive voltage of 20.4 V and a current density 0.50 A/cm<sup>2</sup>. The high efficiency demonstrated from the single-layer

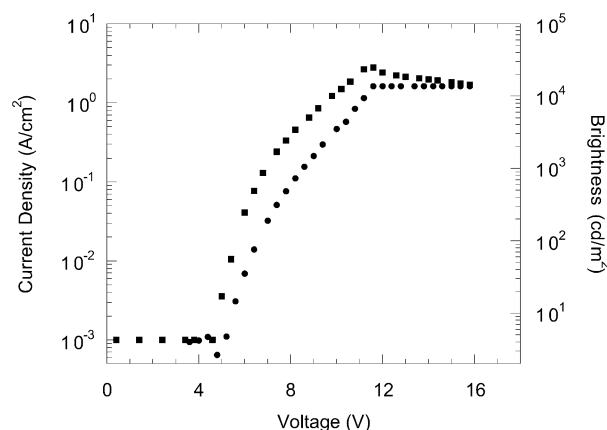
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**Figure 2.** EL spectra of PF9-DTS and PF19-DTS from ITO/polymer/Ca devices run at 10 V.

device indicates that the efficient recombination has been achieved at the dithienosilole-containing segments. By incorporating [poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate)] (PEDOT) as the hole-injecting layer, the device can be turned on at a relatively low voltage (5.4 V), because of the decrease of hole injection barrier. The maximum quantum efficiency of this device (0.41%) is only slightly higher than that of the single-layer device. However, the maximum luminance is 6 times higher than that of the single-layer device, reaching 13 100 cd/m<sup>2</sup> at a bias of 14.2 V and a current density of 1.62 A/cm<sup>2</sup>. When we use an in-situ thermally polymerized BTPD-PFCB as the hole-transporting layer,<sup>22,23</sup> the maximum external quantum efficiency increases to 1.64% at a brightness of 254 cd/m<sup>2</sup>. The maximum luminance for bright green emission as depicted in Figure 3 is found to be 25 900 cd/m<sup>2</sup> at a bias of 11.6 V and for a current density of 1.53 A/cm<sup>2</sup>. The photometric and luminous efficiencies at this luminance are 1.69 cd/A and 0.51 lm/W, respectively. The significant increase in efficiency and brightness are due to balanced charge injection and transport. All devices based on the PF9-DTS possess much higher efficiency than the devices with PF19-DTS as the emitting layer. This could be attributed to the more



**Figure 3.** Current density (solid circles) and luminance (solid squares) versus applied voltage of ITO/BTPD-PFCB/PF9-DTS/Ca/Ag device.

efficient charge trapping, higher electron affinity, and less chain packing for PF9-DTS with 10 mol % 4,4-diphenyldithienosiloles.

### Conclusion

In conclusion, two random copolymers of 9,9-*n*-hexylfluorene and 4,4'-diphenyldithienosilole have been synthesized. Optimizing the amount of low band gap 4,4-diphenyldithienosilole moieties into polymer not only enhances the electron affinity but also results in efficient charge recombination and energy transfer. Efficient green emission has been demonstrated from both the single-layer and the double-layer LED devices.

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