Synthesis and Electroluminescent Properties of Copolymers Based on Fluorene and 2,5-Di(2-hexyloxyphenyl)thiazolothiazole

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Received February 22, 2005; Revised Manuscript Received June 28, 2005

ABSTRACT: A novel series of soluble conjugated random copolymers were synthesized via the Suzuki coupling reaction of 9,9-dihexylfluorene (DHF) and 2,5-di(2-hexyloxyphenyl)thiazolothiazole (TZ), with the TZ composition varying from 5 to 50 mol % in the copolymers. All of the copolymers exhibited good thermal stability and excellent solubility in common organic solvents, such as chloroform, toluene, and tetrahydrofuran. The electrochemical and photophysical properties were characterized in detail. Under UV excitation, these copolymers emitted bright blue fluorescence at around 416–420 nm in CHCl₃ solution and 446–451 nm in thin film form. Light-emitting diodes fabricated with the copolymers emitted bright blue light with external quantum efficiencies of 0.06-0.44%. The electroluminescence (EL) efficiency of the copolymer with a TZ content of 50% was more than 3 times that of the fluorene homopolymer. Preliminary EL studies showed that these copolymers are thus efficient blue emissive materials for polymer light-emitting diodes (PLEDs).

Introduction

Light-emitting conjugated polymers have attracted considerable research interest during the past two decades because of their potential applications in large area flat panel displays¹ and other optoelectronic devices.^{2,3} A large number of conjugated polymers, such as poly(p-phenylene)s, poly(p-phenylenevinylene)s, poly-(9,9-dialkylfluorene)s, polycarbazoles, and polythiophenes, have been synthesized in order to achieve full color emission from polymer light-emitting diodes (PLEDs).^{4–15} Among these polymers, polyfluorene (PFO) and their derivatives show interesting and unique chemical and physical properties because they contain a rigid planar biphenyl unit. Facile substitution at the remote C-9 position can improve the solubility and processability of the polymers without significantly increasing the steric interactions in the polymer backbone.¹⁶ As a result, PFO and its derivatives have emerged as one of the most promising families of light-emitting materials due to their high photoluminescence (PL) quantum efficiency, good chemical and thermal stability, good processability, and facile color tunability.¹⁷⁻²⁸ However, most of the PFO-based polymers have been found to be hole-transport-dominated materials because the hole mobility is much higher than the electron mobility in these materials. As a result, unbalanced rates of electron and hole injection from the respective negative and positive contacts and a shift of the recombination zone toward the region near the polymer/cathode interface are always observed. Electron injection can be improved by introducing a low work function metal, such as Ca and Ba.^{29,30} However, low electron mobility in these materials has limited the efficient recombination of holes and electrons, resulting in a decrease in electroluminescence (EL) efficiency. Attempts have been made

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* To whom correspondence should be addressed: Tel +65-6874-2189; Fax +65-6779-1936; e-mail cheket@nus.edu.sg. to improve the electron-accepting properties of the polymers by introducing electron-deficient moieties into either the side chains or the main chains of the polymers. $^{31-39}$

Thiazolothiazole is a well-known electron-withdrawing heterocyclic molecule, having electron-rich sulfur and nitrogen heteroatoms. Oligomers containing thiazolothiazol moieties have recently found applications in organic thin film transistors because of their good p-type characteristics as well as good stability in air.^{40,41} However, substituted thiazolothiazole compounds have yet to be explored for application in organic lightemitting diodes (OLEDs).

In this work, we report on the synthesis, by the Suzuki coupling reaction,⁴² and characterization of copolymers derived from fluorene and up to 50 mol % of **2**, 5-di(2-hexyloxyphenyl)thiazolothiazole (TZ) (structures shown in Scheme 1). The TZ units were introduced into the main chains of polyfluorene to enhance the electron transport properties and to improve the recombination efficiency of holes and electrons. Devices based on these copolymers can emit bright blue light, with an emission maximum at 480 nm and a quantum efficiency of 0.44%. The efficiency is more than 3 times that of the PFO homopolymer. These copolymers are protentially useful as efficient light-emitting materials arising from their good electron transport properties.

Experimental Section

Materials and Measurement. All reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI), unless stated otherwise. They were used without further purification. All solvents were carefully dried and purged with nitrogen. All manipulations involving air-sensitive reagents were performed in a dry argon atmosphere. ¹H NMR spectra were recorded on a Bruker ACF 300 spectrometer with *d*-chloroform as the solvent and tetramethylsilane as the internal standard. Number-average (M_n) and weight-average (M_w) molecular weights were determined on a HP 1100 HPLC system equipped with a HP 1047A RI detector and Agilent PLgel MIXED-C300

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Comonomer ratios: 100/0(PFO), 95/5(PFO-TZ5), 90/10(PFO-TZ10), 75/25(PFO-TZ25), 50/50(PFO-TZ50)

 \times 7.5 mm (i.d.) columns (packed with 5 μ m particles of different pore sizes). The column packing allowed the separation of polymers over a wide molecular weight range of 200-3 000 000. THF was used as the eluent at a flow rate of 10 mL min $^{-1}$ at 35 °C. Polystyrene standards were used as the molecular weight references. Cyclic voltammetry measurements were made on an AUTOLAB potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV/s, with a platinum wire counter electrode and a Ag/AgCl reference electrode in an anhydrous and nitrogen-saturated 0.1 mol/L acetonitrile (CH₃CN) solution of tetrabutylammonium perchlorate (Bu₄NClO₄). The polymers were coated on the platinum plate working electrodes from dilute chloroform solutions. UV-vis and fluorescence spectra were obtained on a Shimadzu UV 1601 spectrophotometer and a Shimadzu RF 5301PC luminescence spectrophotometer, respectively. Thermogravimetric analyses (TGA) were conducted on a TA Instrument TGA 2050 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹ and under an N_2 flow rate of 90 mL min⁻¹. Differential scanning calorimetry (DSC) measurements were carried out on a Mettler Toledo DSC 822e system under N₂ and at a heating rate of 10 °C min⁻¹. The thickness of films was measured using a Dektak surface profilometer.

2-Hexyloxy-5-bromobenzaldehyde (1),³⁹ 9,9-dihexylfluorene-2,7-bis(trimethylene boronates) (3),22 and 2,7-dibromo-9,9dihexylfluorene $(4)^{22}$ were synthesized following the procedures reported in the literature. 2,5-Di(2-hexyloxy-5-bromophenyl)thiazolothiazole (2) was synthesized as follows. A mixture of dithiooxamide (1.5 g, 12.5 mmol) and 2-hexyloxy-5-bromobenzaldehyde (1) (17.79 g, 62.40 mmol) was vigorously stirred at 160 °C for 12 h. Water was removed from the mixture by a Dean Stark trap. The reaction mixture was cooled to room temperature, and 50 mL of ethanol was added. The yellow precipitate was removed by filtration and washed with ethanol several times. The crude product was recrystallized in chloroform to afford a light-yellow solid with a yield of 39% and a mp of 200-201 °C . ¹H NMR (CDCl₃, 300 MHz, δ/ppm): 8.61 (d, 2H), 7.48-7.45 (d, 2H), 6.90-6.93 (d, 2H), 4.23-4.18 (t, 4H), 1.63–0.92 (m, 22H). Anal. Calcd for $C_{28}H_{32}Br_2N_2O_2S_2$: C, 51.54%; H, 4.94%; N, 4.29%; S, 9.83%. Found: C, 51.36%; H, 4.90%; N, 4.48%; S, 9.36%.

Polymer Synthesis. The copolymers were synthesized via the palladium-catalyzed Suzuki coupling reaction.⁴² The procedures for synthesizing the copolymer with 5 mol % TZ in the feed (PFO-TZ5) are given below. Carefully purified 9,9-

dihexylfluorene-2,7-bis(trimethylene boronates) (3) (502.31 mg, 1 mmol), 2,7-dibromo-9,9-dihexylfluorene (4) (467.72 mg, 0.95 mmol), 2,5-di(2-hexyloxy-5-bromophenyl)thiazolothiazole (2) (32.63 mg, 0.05 mmol), $Pd(PPh_3)_4$ (12 mg), and several drops of Aliquat 336 were dissolved in a mixture of 5 mL of toluene and 5 mL of 2 M aqueous solution of K₂CO₃. The mixture was kept at 85-90 °C under an argon atmosphere for 48 h. Then, excessive 9,9-dihexylfluorene-2-trimethylene boronates and 2-bromo-9,9-dihexylfluorene were added to end-cap the polymer chain. The entire mixture was poured into a 200 mL mixture of methanol and deionized water (v:v = 10:1). The fibrous solid was filtered and washed with methanol, water, and then methanol, in that order. The resulting polymer was washed with acetone in a Soxhlet apparatus for 24 h to remove the oligomer and catalyst residues, followed by drying under reduced pressure. Yield: 77%. To obtain copolymers of other composition, the TZ content in the feed mixture was adjusted. The sulfur and carbon contents for each copolymer, obtained from elemental analysis, were used for the calculation of actual copolymer composition. Elemental anal. calcd for PFO (fluorene homopolymer): C, 90.30%; H, 9.70%; for PFO-TZ5 (copolymer from 5 mol % TZ in the feed): C, 89.49%; H, 9.58%; N, 0.21%; S, 0.48%; for PFO-TZ10 (copolymer from 10 mol % TZ in the feed): C, 88.71%; H, 9.47%; N, 0.41%; S, 0.94%; for PFO-TZ25 (copolymer from 25 mol % TZ in the feed): C, 86.45%; H, 9.14%; N, 0.99%; S, 2.27%; for PFO-TZ50 (copolymer from 50 mol % TZ in the feed): C, 83.01%; H, 8.66%; N, 1.88%; S, 4.30%. Found: for PFO: C, 88.09%; H, 9.33%; for PFO-TZ5: C, 89.38%; H, 9.55%; N, 0.25%; S, 0.51%; for PFO-TZ10: C, 88.04%; H, 9.42%; N, 0.53%; S, 1.05%; for PFO-TZ25: C, 86.33%; H, 9.53%; N, 0.99%; S, 2.17%; for PFO-TZ50: C, 84.13%; H, 8.65%; N, 1.85%; S, 4.59%.

EL Device Fabrication and Characterization. For the fabrication of electroluminescence (EL) devices, glass substrates coated with indium-tin oxide (ITO) and having a sheet resistance of 100 Ω/\Box (CSG Co. Ltd., Shenzhen, China) were cleaned consecutively in ultrasonic baths of ionic detergent water, acetone, and anhydrous ethanol. Thin layers of commercial PEDOT (Batron-P 4083, Bayer A G, Germany) [PEDOT was poly(ethylenedioxythiophene) doped with poly(styrenesulfonic acid)] and the copolymer (from a 10 mg mL⁻¹ toluene solution of the copolymer) were spin-coated on ITO at 1500 rpm for 30 s in succession. The thickness values of the PEDOT and copolymer layers were about 90 and 80 nm, respectively. Thin layers of Ba (4 nm) and Al (170 nm) were

| Table 1. | Characterization | of the | Copolymers |
|----------|------------------|--------|------------|
|----------|------------------|--------|------------|

| | | | | | DIII/1Z | |
|-----------|--|---|---|--|--|--|
| yield (%) | $M_{ m w}{}^a$ ($	imes$ 10 ³) | $M_{ m w}\!/\!M_{ m n}{}^a$ | $T_{\mathrm{d}}{}^{b}$ (°C) | $T_{\rm g}{}^c(^{\rm o}{ m C})$ | in the feed composition | in the $\operatorname{copolymer}^d$ |
| 75 | 21.2 | 2.83 | 414 | 55 | | |
| 77 | 8.8 | 1.44 | 416 | 56 | 95/5 | 94.6/5.4 |
| 80 | 19.2 | 1.73 | 420 | 63 | 90/10 | 88.7 /11.3 |
| 82 | 17.3 | 1.71 | 421 | 67 | 75/25 | 76.1/23.9 |
| 86 | 32.2 | 2.17 | 425 | 75 | 50/50 | 47.2/52.8 |
| | yield (%) 75 77 80 82 86 | $\begin{array}{c c} \mbox{yield} (\%) & M_{\mbox{w}^a} (\times 10^3) \\ \hline 75 & 21.2 \\ 77 & 8.8 \\ 80 & 19.2 \\ 82 & 17.3 \\ 86 & 32.2 \\ \end{array}$ | $\begin{array}{c cccc} \mbox{yield}(\%) & M_{\rm w}{}^a(\times10^3) & M_{\rm w}/M_{\rm n}{}^a \\ \hline 75 & 21.2 & 2.83 \\ 77 & 8.8 & 1.44 \\ 80 & 19.2 & 1.73 \\ 82 & 17.3 & 1.71 \\ 86 & 32.2 & 2.17 \\ \end{array}$ | yield (%) $M_{\rm w}^a$ (× 103) $M_{\rm w}/M_{\rm n}^a$ $T_{\rm d}^b$ (°C)7521.22.83414778.81.444168019.21.734208217.31.714218632.22.17425 | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ |

 a Molecular weights and polydispersity indices determined by GPC in THF using polystyrene as standards. b Onset decomposition temperature (5% weight loss) measured by TGA under N₂. c Glass transition temperature measured by DSC under N₂. d Calculated from the results of elemental analysis.

then deposited sequentially on the copolymer film by thermal evaporation under a reduced pressure of 10^{-4} Pa. The active area of the device was about 0.15 cm². The applied dc bias voltages for the EL devices were in a forward direction (ITO, positive; Ba/Al, negative). The current–voltage characteristics were measured on a voltmeter and an amperometer. The EL efficiency and brightness measurements were carried out using a calibrated silicon photodiode. All measurements on the EL devices were carried out in a glovebox at room temperature.

Results and Discussion

Synthesis and Characterization of the Copolymers. The procedures for preparing the monomer and copolymers are outlined in Scheme 1. These copolymers of different compositions were synthesized from 2,7dibromo-9,9-hexylfluorene (DHF), 9,9-dihexylfluorene-2,7-bis(trimethylene boronates), and 2,5-di(2-hexyloxy-5-bromophenyl)thiazolothiazole (TZ) using the wellknown palladium-catalyzed Suzuki coupling method.42 The yields of the copolymers were over 75%. The molar feed ratios of DHF to TZ were 100:0, 95:5, 90:10, 75:25, and 50:50, and the corresponding copolymers were referred to as PFO, PFO-TZ5, PFO-TZ10, PFO-TZ25, and PFO-TZ50, respectively. All the copolymers exhibited excellent solubility in common organic solvents, such as chloroform, toluene, and tetrahydrofuran, arising from the hexyl and hexyloxyl group substituents in the 9-position of fluorene and the 2-position of benzene, respectively. At the end of polymerization, 2,7-dibromo-9,9-hexylfluorene was added to remove boronic acid ester end groups. 9,9-Dihexylfluorene-2-trimethylene boronates as a monofunctional end-capping reagent was added to remove the bromine end group. Boron and bromine moieties could quench emissions and contribute to a red shift in the EL spectra of the resulting PLEDs.43,44

The starting molar ratios of the monomers were adjusted in order to investigate the effect of copolymer composition on the physical and optical properties. The actual molar ratio of DHF/TZ in the copolymer, calculated from elemental analysis, is very close to the actual feed ratio. The results are listed in Table 1. The molecular weights were determined by gel permeation chromatography (GPC), using polystyrene standards. The results are also shown in Table 1. These copolymers have weight-average molecular weights (M_w) of 8770-32 200 with polydispersity indices (M_w/M_n) of 1.44–2.83. The thermal properties of the copolymers were determined by TGA and DSC measurements. All these copolymers show good thermal stability, with onset decomposition temperatures (T_d , 5% weight loss) of 414-425 °C under nitrogen. No weight loss was observed at lower temperatures. Figure 1 shows the representative thermal gravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves of the PFO-



Figure 1. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves of the copolymer PFO-TZ50 (under a nitrogen atmosphere and at a heating rate of 10 °C min⁻¹).

TZ50 copolymer under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Above the decomposition temperature, the weight loss curve falls rapidly, indicating the decomposition of the polymer backbones. Above 600 °C, only 50–55 wt % residues remain. The glass transition temperatures ($T_{\rm g}$) of the polymers range from 55 to 75 °C. Obviously, the $T_{\rm g}$ is effectively improved with increasing TZ content.

Electrochemical Properties. Cyclic voltammetry (CV) was employed to investigate the electrochemical behavior of the copolymers as well as to estimate the HOMO and LUMO energy levels of the materials. The copolymer film deposited on a platinum plate electrode was scanned both positively and negatively in 0.10 M anhydrous acetonitrile solution of tetrabutylammonium perchlorate (Bu_4NClO_4), using a platinum wire as the counter electrode and Ag/AgCl (0.10 M) as the reference electrode. The energy level of the Ag/AgCl reference electrode (calibrated by the FC/FC+ redox system) was 4.4 eV below the vacuum level. All of the copolymers exhibited partial reversibility in both the p-doping and n-doping processes. The oxidation and reduction potentials derived from the onset of electrochemical p-doping and n-doping are summarized in Table 2. HOMO and LUMO levels were calculated according to the empirical formula $(E_{\text{HOMO}} = -([E_{\text{onset}}]^{\text{ox}} + 4.4)$ (eV) and $E_{\text{LUMO}} = -([E_{\text{onset}}]^{\text{red}} + 4.4)$ (eV)).^{45,46} As shown in Table 2, the HOMO and LUMO levels of the fluorene homopolymer are 5.77 and 2.16 eV, respectively. These values are comparable to those reported by Jenekhe et al.⁴⁷ With the increase in TZ content of the copolymers, the oxidation potential increases and the reduction potential decreases slightly. For example, $E_{\text{HOMO}} = 5.88$ eV and $E_{\rm LUMO} = 2.49$ eV for PFO-TZ50. The changes are

 Table 2. Electrochemical Potentials and Energy Levels of the Copolymers

| copolymers | $\begin{matrix} [E_{\rm onset}^{\rm red}]^a \\ ({\rm V}) \end{matrix}$ | $\underset{(\mathrm{V})}{\overset{\mathrm{onset}}{[E^{\mathrm{ox}}_{\mathrm{onset}}]^b}}$ | LUMO ^c (eV) | $\begin{array}{c} \mathrm{HOMO}^d \\ \mathrm{(eV)} \end{array}$ | $E_{ m g}^{\ e}$ (eV) |
|------------|--|---|---------------------------|---|-----------------------|
| PFO | -2.24 | 1.37 | -2.16 | -5.77 | 3.61 |
| PFO-TZ5 | -2.17 | 1.38 | -2.23 | -5.78 | 3.55 |
| PFO-TZ10 | -1.99 | 1.42 | -2.41 | -5.82 | 3.41 |
| PFO-TZ25 | -1.95 | 1.45 | -2.45 | -5.85 | 3.40 |
| PFO-TZ50 | -1.91 | 1.48 | -2.49 | -5.88 | 3.39 |

^{*a*} Onset reduction potentials measured by cyclic voltammetry. ^{*b*} Onset oxidation potential measured by cyclic voltammetry. ^{*c*} Calculated from the reduction potentials. ^{*d*} Calculated from the oxidation potentials. ^{*e*} Calculated from the LUMO and HOMO energy levels.

attributable to the increase in electron-withdrawing effect of the TZ moieties in the copolymer backbone. The TZ moieties are expected to improve electron injection from the cathode and electron transport in the fluorene polymer. The band gaps (E_g) of these copolymers are estimated from the onset potentials of the oxidation and reduction processes. Also shown in Table 2, E_g decreases with increasing TZ content in the polymer main chain. Apparently, the incorporation of TZ units with nitrogen and sulfur heteroatoms has enhanced the effective π -conjugation length of PFO and given rise to the changes in electrochemical properties.

Photophysical Properties. Photophysical properties of the copolymers were investigated both in CHCl₃ solutions and in thin solid films. The concentration of all the CHCl₃ solutions of the copolymers was fixed at 1×10^{-5} M. Transparent and uniform copolymer films were prepared on quartz plates by spin-casting from their respective toluene solutions (10 mg mL^{-1}) at room temperature. The absorption and emission data for the copolymers are summarized in Table 3. As shown in Figure 2, the absorption spectra of the copolymer solutions and thin films are very similar, with absorption maxima at 379–385 and 378–383 nm, respectively, attributed to the $\pi - \pi^*$ transitions of the copolymers. The absorption maximum underwent a red shift with the increase in TZ content. The optical band gaps of these copolymers are 2.87-2.92 eV, as evaluated from the onsets in the film absorption spectra. These values are close to those obtained from cyclic voltammetry measurements.

Figure 3 shows the photoluminescent (PL) spectra of the copolymers in $CHCl_3$ solutions and in thin films. The solution and thin film PL spectra exhibit a slight red shift, arising from the decrease in HOMO–LUMO energy gap with increasing TZ content. The PL spectra of the copolymer solutions exhibit similar vibronic features with a narrow bandwidth and emission maxima at around 416–420 and 437–441 nm. In general, the presence of well-defined vibronic features in the emission spectra indicates that the polymer has a rigid and well-defined backbone structure.^{29,48} In contrast to the



Figure 2. (a) UV–vis absorption spectra of the copolymers in the CHCl₃ solution (concentration = 1×10^{-5} mol/L). (b) UV–vis absorption spectra of the copolymers in thin film form (thickness = 80 nm).

PL spectra of the copolymers in solution, the PL spectra of the copolymer films show only an emission maximum in the 446-451 nm region. The emission maximum at around 416-420 nm, observed in CHCl₃ solutions, was not discernible in the copolymer films, suggesting the presence of aggregation of polymer main chains in the solid state. The phenomenon is commonly observed in polyfluorenes, arising from the inherent rigid nature of their backbones.⁴⁹

Electroluminescence (EL) Properties. Lightemitting diodes (LEDs) based on these copolymers and with the configuration of ITO/PEDOT/PFO-TZ/Ba/Al were fabricated in a glovebox under a nitrogen atmosphere. PEDOT with a thickness of about 90 nm was used as the hole injection and transport layer. The thickness of the emissive layer was around 80 nm. A thin layer of Ba (4 nm) was employed as the cathode because the work function of Ba does not match well

Table 3. Absorption and Emission Data for the Copolymers

| | solutio | on $\lambda_{\max} (nm)^a$ | film $\lambda_{max}(nm)$ | | | |
|------------|---------|----------------------------|--------------------------|-----|----------------------------|------------------------|
| copolymers | abs | em | abs | em | optical band $gap^{b}(eV)$ | $fwhm\ (film)^c\ (nm)$ |
| PFO | 379 | 417 (440) | 378 | 446 | 2.92 | 70 |
| PFO-TZ5 | 383 | 416 (437) | 378 | 446 | 2.91 | 55 |
| PFO-TZ10 | 383 | 417 (439) | 379 | 446 | 2.91 | 47 |
| PFO-TZ25 | 384 | 418 (440) | 382 | 450 | 2.89 | 57 |
| PFO-TZ50 | 385 | 420 (441) | 383 | 451 | 2.87 | 59 |

^{*a*} The data in the parentheses are the wavelengths of shoulders and subpeaks. ^{*b*} Optical band gap was estimated from the onset wavelength of the optical absorption. ^{*c*} Full width at half-maximum of the film PL spectra.



Figure 3. (a) PL spectra of the copolymers in the CHCl₃ solution (concentration = 1×10^{-5} mol/L) under 320 nm excitation. (b) PL spectra of the copolymers in thin film form (thickness = 80 nm) under 320 nm excitation.

with the LUMO of these large band gap copolymers. The electron transport properties of the copolymers can be readily compared to those of the fluorene homopolymer in terms of the external quantum efficiency of the devices with the Ba cathode. The Ba layer was coated with a 170 nm layer of Al. Bright blue emission was obtained from all of the copolymers. The EL spectra of the copolymers are presented in Figure 4. The EL spectra exhibit a maximum in the region of 445-450 nm. All these spectra also show a broad emission maximum, red-shifted to about 520 nm. The green emission does not appear to be affected by the presence of TZ units. It is probably attributable to the excimer emission and/or keto effect, which is an emission phenomenon commonly observed in polyfluorenes.^{7,50–55} The performance of the devices fabricated from the copolymers is compared in Table 4. Preliminary device data are promising. The performance of the copolymer devices, based on the standard configuration of ITO/ PEDOT/PFO-TZ/Ba/Al, varies with the copolymer com-



Figure 4. EL spectra of devices with the configuration of ITO/ PEDOT/copolymer/Ba/Al.

position. The turn-on voltages of the devices decrease from 11.2 to 7.3 V with increasing TZ content. Although the hole injection barrier becomes higher (the HOMO level increases, as shown in Table 2) as the TZ content increases, the LUMO level decreases and becomes closer to the work function of Ba (about 2.7 eV). Thus, the electron injection will become more efficient. Since hole injection and transport are more efficient than those of electrons in most conjugated polymers, including polyfluorenes, a more balanced injection and transport of both types of carriers will lead to a decrease in the turnon voltage of the LEDs. As expected, the external quantum efficiency has been markedly improved with increasing TZ content. The highest EL quantum efficiency of 0.44% at 10.2 V, with a current density of 97.3 mA $\rm cm^{-2}$ and a luminance of 142.9 cd $\rm m^{-2},$ was obtained in a device configured from PFO-TZ50 (TZ content of about 50%). The efficiency is more than 3 times that of the device based on the PFO homopolymer. The turn-on voltage of PFO is lower, and external quantum efficiency higher, than those of the PFO-TZ copolymers with TZ contents less than 25%. Thus, the device performance was probably controlled by electron and hole injection, rather than carrier mobility, at low TZ contents. The reverse was true with increasing TZ content. The I-V and L-V characteristics of the device with PFO-TZ50 are shown in Figure 5. The significant increase in efficiency over that of the fluorene homopolymer is due to a more balanced charge injection and transport. Although the thiazolothiazole derivatives are p-type materials, they contain electron-accepting imine structures,⁴⁰ similar to pyridine and its derivatives.⁵⁶ The electron transport properties of the thiazolothiazole derivatives are, therefore, expected to be superior to those of the PFO homopolymer. In accordance with the improved electron transport properties, the incorporation of TZ moieties has given rise to a more efficient recombination of holes and electrons, or an improved EL quantum efficiency, in the copoly-

Table 4. EL Performance of the PFO-TZ Copolymers in Device Configuration of the Form ITO/PEDOT/PFO-TZ/Ba/Al

| copolymers | $\lambda_{EL,max}\left(nm\right)$ | turn-on voltage (V) | voltage $^{a}(V)$ | current density ^{a} (mA cm ^{-2}) | $luminance^a \ (cd \ m^{-2})$ | $QE_{ext}\left(\%\right)$ |
|------------|-----------------------------------|---------------------|-------------------|---|-------------------------------|---------------------------|
| PFO | 445 | 7.8 | 10.6 | 92 | 116 | 0.13 |
| PFO-TZ5 | 445 | 11.2 | 15.4 | 91 | 74 | 0.06 |
| PFO-TZ10 | 446 | 9.0 | 13.2 | 77 | 107 | 0.08 |
| PFO-TZ25 | 448 | 8.6 | 10.1 | 76 | 177 | 0.23 |
| PFO-TZ50 | 450 | 7.3 | 10.2 | 97 | 143 | 0.44 |

^a Measured under the condition of maximum external quantum efficiency.



Figure 5. Current-voltage and luminance-voltage curves of PFO-TZ50 in a device with the configuration of ITO/PEDOT/ PFO-TZ50/Ba/Al.

mers. The preliminary results on EL devices indicate that these copolymers are novel materials for efficient blue emission in polymer light-emitting diodes. Further improvement on the EL performance can be expected to come from improvement and optimization in device fabrication, configuration, and encapsulation.

Conclusions

A series of novel conjugated copolymers, composed of random 9,9-dihexylfluorene and thiazolothiazole units, were prepared via the palladium-catalyzed Suzuki coupling reaction. All the copolymers exhibited good solubility in common organic solvents, such as chloroform, toluene, and tetrahydrofuran. The introduction of TZ moieties improved the electron transport properties of polyfluorene. Light-emitting diodes were fabricated using these copolymers as the emitting layer. These devices were capable of bright blue emission with an external quantum efficiency of 0.44%. The highest EL efficiency obtained in a device fabricated from PFO-TZ50 (TZ content of 50%) was more than 3 times that of the device fabricated from polyfluorene. Preliminary EL results show that these copolymers are novel candidates for efficient blue emission in polymer LEDs. Further improvements in performance of these copolymers could be expected to come from the subsequent optimization of the device configuration.

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MA050378N