Molecular Design of Efficient White-Light-Emitting Fluorene-Based Copolymers by Mixing Singlet and Triplet Emission

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ABSTRACT: A new strategy to realize efficient white-light emission from a binary fluorene-based copolymer (PF-Phq) with the fluorene segment as a blue emitter and the iridium complex, 9-iridium(III)bis(2-(2-phenyl-quinoline-N,C30)(11,13-tetradecanedionate))-3,6-carbazole (Phq), as a red emitter has been proposed and demonstrated. The photo- and electroluminescence properties of the PF-Phq copolymers were investigated. White-light emission with two bands of blue and red was achieved from the binary copolymers. The efficiency increased with increasing concentration of iridium complex, which resulted from its efficient phosphorescence emission and the weak phosphorescent quenching due to its lower triplet energy level than that of polyfluorene. In comparison with the binary copolymer, the efficiency and color purity of the ternary copolymers (PF-Phq-BT) were improved by introducing fluorescent green benzothiadiazole (BT) unit into polyfluorene backbone. This was ascribed to the exciton confinement of the benzothiadiazole unit, which allowed efficient singlet energy transfer from fluorene segment to BT unit and avoided the triplet quenching resulted from the higher triplet energy levels of phosphorescent green emitters than that of polyfluorene. The phosphorescence quenching is a key factor in the design of white light-emitting polyfluorene with triplet emitter. It is shown that using singlet green and triplet red emitters is an efficient approach to reduce and even avoid the phosphorescence quenching in the fluorene-based copolymers. The strategy to incorporate singlet green emitter to polyfluorene backbone and to attach triplet red species to the side chain is promising for white polymer light-emitting diodes. © 2007 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 453–463, 2008

Keywords: conjugated polymers; light-emitting diodes (LED); molecular design; polyfluorene; synthesis; singlet; triplet; white-light emission

INTRODUCTION

White organic/polymer light-emitting diodes (WOLEDs/WPLEDs) have been attracting extraordinary attention. Great promise has been devoted to them in the applications of full color displays with color filters and lighting sources.1–3 WPLEDs are fabricated utilizing soluble process which is expected to easily make large-area panels at low cost. So far a vast number of efforts have been made to improve the WPLED performance, including device physics investigation, device structure design, and polymer synthesis.4–15 The most common technique to fabricate WPLEDs is based on blend4,5,11–13 or dye-doped polymer systems.7,8,14,15 In these cases, phase separation is easily producible, which generally
leads to color instability at different operating voltages. Furthermore, blending or doping systems often result in the Commission Internationale de l’Eclairage (CIE) coordinates change with driving voltage due to the energy transfer saturation at a high voltage and charge distribution on the trap sites varying with the different voltage. More important, if the emission species in the blend or doping systems possess different aging rates, the emission color will change and be out of white emission, resulting in the diode performance degeneration. Therefore, it is desirable to obtain white-light emission from a single molecule so as to avoid these drawbacks. In the past several years, studies in this field have absorbed increasing interests and made encouraging progress. White-light emitting polymers have been designed and synthesized. Lee et al. reported a single fluorene-based copolymer (PG3R2) containing 3% of green-emitting comonomers (DTPA, 4-(2-[2,5-dibromo-4-[2-(4-diphenylamino-phenyl)-vinyl]-phenyl-vinyl]-diphenylamine) and 2% of red-emitting comonomers (TPDCM, 2-[2-(2-[2-[4-bromo-phenyl]-amino-phenyl]-vinyl)-vinyl]-6-tert-butyl-pyran-4-ylidene)-malononitrile), giving rise to pure white emission with CIE coordinates of (0.33, 0.35), luminous efficiency of 0.1 cd/A, and a maximum luminance of 820 cd/m² at 11 V. Liu et al. have published a polyfluorene-based white-light emitting polymer with a red-emissive unit in main chain and a green-emissive pendant, presenting white emission with blue-, green-, and red emission bands at the CIE coordinates of (0.31, 0.34) and a luminous efficiency of 1.59 cd/A. Sequentially, efficiency of WPLEDs was improved by chemically doping an orange-light emitting unit, 4,7-bis(4-fluorophenyl)-9,9-dioctylfluorene (1). The resulted boronic ester was recrystallized from methanol and further purification by column chromatography (silica gel, 10% ethyl acetate in hexane) to give white solid product (yield, 50%). mp: 128–131°C.

EXPERIMENTAL

Materials and Characterization

All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Co. and were used as they were received. N NMR spectra were recorded on a Bruker DRX 400 spectrometer operating, respectively, at 400 and 100 MHz, with tetramethylsilane as a reference in deuterated chloroform solution at 298 K. Number-average (Mn) and weight-average (Mw) molecular weights were determined by Waters GPC 2410 in THF via a calibration curve of polystyrene standards. Elemental analysis was performed on Vario EL Elemental Analysis Instrument (Elementar Co.). Cyclic voltammetry (CV) was recorded on a computer-controlled CHI660A electrochemical workstation at a scan rate of 100 mV/s against Ag/AgCl reference electrode in a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu4 NPF6) in acetonitrile (CH3CN). The thin polymer film was coated on a platinum electrode as a working electrode. Cyclic voltammetry of monomers was carried out in the fresh dichloromethane solution. All other conditions were the same as the polymer film. HOMO and LUMO levels were calculated according to an empirical formula (HOMO = −e(Eox + 4.4) (eV) and LUMO = −e(Ered + 4.4) (eV)).

2,7-Dibromo-9,9-dioctylfluorene (1) was prepared according to the published procedures. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (2) was prepared following the published procedure from 2,7-dibromo-9,9-dioctylfluorene (1). The resulted boronic ester was recrystallized from methanol and further purification by column chromatography (silica gel, 10% ethyl acetate in hexane) to give white solid product (yield, 50%). mp: 128–131°C.

1H NMR (CDCl3) δ (ppm): 7.80 (d, 2H), 7.75 (s, 2H), 7.73 (d, 2H) (fluorene ring), 1.96 (m, 4H), 1.35 (s, 24H, −CH3), 1.23–0.99 (m, 20H), 1.35 (s, 24H, −CH3), 1.23–0.99 (m, 20H).
0.82 (t, 6H), 0.54 (m, 4H) (aliphatic); $^{13}$C NMR (CDCl$_3$) $\delta$ (ppm): 150.85, 144.32, 134.06, 129.27, 121.67, 119.75 (fluorene ring), 84.12, 55.56 (C$_9$-fluorene ring), 40.49, 32.15, 30.32, 29.57, 25.33, 23.97, 22.98, 14.47 (aliphatic). Anal. Calcd for C$_{41}$H$_{64}$O$_4$B$_2$: C, 76.74; H, 10.04; Found: C, 76.43; H, 10.33.

4,7-Dibromo-2,1,3-benzothiadiazole (3) was prepared according to the published procedures.$^{27}$ mp: 187–188 °C.

$^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm): 7.83 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm): 153.34, 132.67, 114.31.

3,6-Dibromo-9-(iridium(III)bis(2-phenylquinoline-N,C$_2$)))-14-trifluoro-11,13-tetradecyldiketone)carbazole (4) was synthesized according to the published procedures.$^{27}$

$^1$H NMR (CDCl$_3$) $\delta$ (ppm): 8.31 (d, 1H, quinoline ring), 8.17 (d, 1H, benzene ring), 8.13 (m, 2H), 8.06 (m, 2H) (carbazole ring), 7.92–7.23 (m, 14H), 6.93 (t, 2H), 6.62 (m, 2H), 6.54 (d, 1H), 6.48 (s, 1H), 5.29 (s, 1H, –CH), 4.24 (t, 2H, N–CH$_2$), 2.37 (t, 2H), 1.79–0.84 (m, 16H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 194.12, 186.68 (C-keto form), 160.05, 151.98, 141.01, 132.43, 124.25, 123.92, 122.72, 121.48, 121.32 (quinoline ring), 142.14, 129.83, 129.75, 128.58, 127.79, 126.46, (benzene ring), 141.15 (–CF$_3$), 139.33, 123.88, 123.52, 122.61, 121.97, 110.45 (carbazole ring), 96.42 (–CH), 43.23 (N–CH$_2$), 34.14, 31.46, 29.70, 28.12, 28.04, 27.15, 25.58, 22.61, 22.49. Anal. Calcd for C$_{56}$H$_{47}$Br$_2$N$_3$F$_3$O$_2$Ir: C, 56.60; H, 4.29; N, 3.49. Found: C, 56.60; H, 4.29; N, 3.43.

Mass (ESI), $m/z$: 1202.3 (M$^+$).

General procedures of Suzuki polycondensation taking PF-Phq3 as an example: 2,7-dibromo-9,9-dioctylfluorene (1) (321 mg, 0.5 mmol), 2,7-dibromo-9,9-dioctylfluorene (2) (272 mg, 0.4967 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (3) (1.0 mL, 2.7 mg, 0.003 mmol), with tetrakis-(triphenyl-phosphine)-palladium (5 mg) were dissolved in the mixture of toluene/THF (10 mL), stirred for 0.5 h and with Et$_4$NOH (20%) aqueous solution (4 mL) being added. The mixture was heated to 100 °C and stirred for 2 days in the argon atmosphere. Then the polymer was capped by adding 50 mg of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene followed by stirring for 12 h, and by adding 0.5 mL of bromobenzene followed by heating for another 12 h. The whole mixture was poured into methanol. The precipitated polymer was recovered by filtration and purified by silica column chromatography with toluene to remove small molecular complex and catalyst residue (yield, 50%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.83 (d, 2H), 7.75 (s, 2H), 7.70 (d, 2H), 1.94 (m, 4H), 1.23–0.99 (m, 24H), 0.83 (t, 6H). Anal. Calcd for C$_{56}$H$_{49}$: C, 88.69; H, 10.31; Found: C, 88.82; H, 10.33.

PF-Phq-BT Copolymer: PF-Phq3-BT3 is taken as an example: 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (1) (321 mg, 0.5 mmol), 2,7-dibromo-9,9-dioctylfluorene (2) (272 mg, 0.4967 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (3) (1.0 mL, 2.7 × 10$^{-2}$ M solution in THF), and 3,6-dibromo-9-(iridium(III)bis(2-phenylquinoline-N,C$_2$))-14-trifluoro-11,13-tetradecyldiketone)carbazole (4) (3.6 mg, 0.003 mmol), with tetrakis-(triphenyl-phosphine)-palladium (5 mg) were dissolved in the mixture of toluene/THF (10 mL), stirred for 0.5 h and with Et$_4$NOH (20%) aqueous solution (4 mL) being added. The mixture was heated to 100 °C and stirred for 2 days in the argon atmosphere. Then the polymer was capped by adding 50 mg of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene followed by stirring for 12 h, and by adding 0.5 mL of bromobenzene followed by heating for another 12 h. The whole mixture was poured into methanol. The precipitated polymer was recovered by filtration and purified by silica column chromatography with toluene to remove small molecular complex and catalyst residue (yield, 50%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.85 (d, 2H), 7.78 (s, 2H), 7.72 (d, 2H), 1.96 (m, 4H), 1.21–0.97 (m, 24H), 0.82 (t, 6H). Anal. Calcd for C$_{56}$H$_{49}$: C, 88.69; H, 10.31; Found: C, 89.52; H, 10.30.

The contents of G (BT) and R (Phq) units in the copolymer are too low to be accurately calculated by elemental analysis and sequential X-ray fluorescence spectrometry (XRF). In our previous publication,$^{28}$ we found that the feed ratio of the monomer (R) was as low as 0.5 mol %, the actual content of R unit in the resulting polymer was 0.41 mol % calculated by the contents of carbon, hydrogen, and iridium in copolymer, which was approximately equal to the feed ratio of the monomer in Suzuki polycondensation. Therefore, we assumed that the actual content of G and R units in the polymers was the same as the feed ratio of the corresponding monomers.
Device Fabrication

The device structure was ITO/PEDOT: PSS/ PVK/copolymers/CsF/Al. A 50-nm thick buffer layer of PEDOT: PSS was spin-coated on a precleaned ITO substrate and dried by baking at 80 °C for 12 h in a vacuum. Then, a 40-nm thick layer of PVK, being used as a hole injection layer, was spin cast from chlorobenzene solution and dried for 1 h at 60 °C. The emissive layer was then spin cast on the PVK film from the p-xylene solution to form an 80 nm thick emissive layer. Profilometry (Tencor Alfa-Step 500) was used to determine the thickness of the films. Then, a thin layer of CsF (1 nm) with a 200 nm thick Al capping layer was deposited through a shadow mask (a defined active area of 0.15 cm²) in a chamber with a base pressure of < 3 × 10⁻⁷ Pa. The layer thickness was monitored on deposition by using a crystal thickness monitor (Sycon). All the polymer film fabrication except that of PEDOT: PSS layer was carried out in a N₂ atmosphere dry-box (Vacuum Atmosphere Co.).

Measurement

Current density (J)-voltage (V)-luminance (L) data were collected using a Keithley 236 source measurement unit and a calibrated silicon photodiode. External EL quantum efficiencies (QE_{ext}) were obtained by measuring the total light output in all directions in an integrating sphere (IS-080, Labsphere). The luminance was calibrated by PR-705 SpectraScan Spectrophotometer (Photo Research). The PL and EL spectra were also recorded using PR-705 SpectraScan Spectrophotometer under the driving of Keithley model 2400 programmable voltage–current source. The PL spectra were obtained under the excitation of the 325 nm HeCd laser.

RESULTS AND DISCUSSION

Molecular Design and Synthesis

The utilization of the phosphorescent emitters allows us to harvest both singlet and triplet excitons, which significantly enhances the efficiency of organic/polymer light-emitting diodes (OLED/PLEDs). Efficient phosphorescent PLEDs from triplet-emitter-doping polymer systems have been reported by several groups. Polyfluorene (PF), an excellent blue-light emitting polymer, has large band gap and good electronic properties. The emission color of PF can be tuned in entire visible region by incorporating low band gap units into the backbone or attaching emitters onto the side chain. However, phosphorescence quenching of the triplet emitter by polyfluorene must be considered when a triplet emitter is introduced into polyfluorene.

It is well known that polyfluorene possesses high singlet energy level (3 eV), but its triplet energy level is commonly less than 2.1 eV, which is lower than those of most phosphorescent materials. Consequently, the fluorene-based copolymers with phosphorescent emitters usually suffer from the reverse energy transfer from the triplet level of guest to that of polyfluorene, leading to a serious phosphorescence quenching and poor emission property. Thompson and coworkers showed that the reverse energy transfer from phosphorescent iridium complexes to a fluorene trimer occurred efficiently in solution mixtures, and proposed that the same process should be less efficient in a solid doping system of an iridium complex and polyfluorene. In addition, Holmes and coworkers found that a spacer between polymer host and phosphorescent guest reduced the reverse triplet energy transfer in the systems with the similar triplet energy levels between host and guest. In fact, some efficient red electrophosphorescence emission has been achieved based on physical- or chemical-doping PF systems but few about green and blue electrophosphorescent emission because the triplet energy levels of green triplet emitters (>2.4 eV) are higher than that of PF, resulting in green and blue phosphorescence emission quenching by PF. We attempted to introduce green iridium complex into the polyfluorene backbone or attach to the side chain, but very poor green emission was observed. However, polyfluorene possesses high singlet energy level and hence efficient singlet energy transfer can occur from polyfluorene to singlet emitters. Green emission from polyfluorenes with fluorescent narrow band gap sites has been observed. The enhancement of efficiency has been reported because of the exciton confinement of the narrow band gap emitters. In principle, to obtain efficient green emission from the fluorene-based copolymers, using fluorescent comonomers as the narrow band gap emitters will be a good choice. Therefore, efficient white-light
emission is expected from the fluorene-based copolymers by attaching a phosphorescent red unit to the side chain and introducing a fluorescent green emitter into the backbone.

The synthetic route of the copolymers is shown in Scheme 1. The copolymers were synthesized from 2,7-dibromo-9,9-dioctyl-fluorene (1), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (2), 4,7-dibromo-2,1,3-benzothiadiazole (3), and 9-iridium(III)bis(2-(2-phenyl-quinoline-N,C_3O) (11,13-tetradecanedionate))-3,6-dibromocarbazole (4) by Suzuki polycondensation (SPC). To keep the emission color balance, the Phq content of the binary copolymers was tuned within 0.1 to 0.5 mol %, while the contents of benzothiadiazole (BT) and Phq units of ternary copolymers were, respectively, tuned within the range of 0.005 to 0.05 mol % and 0.1 to 0.5 mol %. All the resulted copolymers are soluble in organic solvents and have numerical average molecular weight from 34,300 to 65,500 with polydispersity of 2.1 to 2.7 according to polystyrene standards.

**Optical Properties**

Figure 1 shows the UV-vis absorption spectra of the binary and ternary copolymers in solid film, together with the absorption spectrum of polyfluorene for comparison. All the absorption spectra of these copolymers are the same as that of polyfluorene with a peak of 390 nm. The absorption of Phq and/or BT units is not observed because of their low concentration.

Figure 2 shows the photoluminescence (PL) spectra of all the copolymers. It is seen that,
unlike the absorption spectra resulted from only PF, all the PL spectra possess two emission bands. One is around 440 nm and the other is at 580 nm. The 440 nm emission band comes from the fluorene segment and the 580 nm comes from Phq unit, indicating that there arises the partial energy transfer from fluorene segment to Phq unit. As the Phq concentration increases, more energy is transferred to it, leading to stronger red emission relatively to the blue emission. Similar results are observed for Phq and BT units in the ternary copolymers. In comparison with Figure 2(a), we can see that a 520 nm emission band from BT unit is added in Figure 2(b), indicating that the efficient energy transfer occurs from fluorene to BT. Unlike green phosphorescent dye-doped PF systems, the triplet excited energy is quenched by polyfluorene because of the dominating reverse energy transfer from higher triplet levels of the phosphorescent dyes to lower triplet level of PF.51

In Figure 2(b), the emission of BT unit is remarkably stronger than that of Phq unit though the concentration of BT is much lower than that of Phq. Generally, the energy transfer efficiency is largely related to the distance between host and guest.54 The shorter the distance is, the more efficient the energy transfer is. In this case, the BT unit is inserted into the remarkable backbone and the distance from fluorene segment to BT unit is shorter, while Phq is attached onto the side chain by an octyl-chain and the distance from fluorene to Phq unit is larger. Consequently, more efficient energy transfer occurs from the fluorene to BT than to Phq, leading to stronger emission of BT unit.

Electroluminescence Properties

Devices with the structure of ITO/PEDOT: PSS/ PVK/copolymers/CsF/Al were fabricated. All the EL spectra, shown in Figure 3, present wide spectra covering the whole visible range from 400 to 700 nm. The EL spectra of the binary copolymers exhibit two emission bands of the blue peaked around 440 nm and the red at 580 nm [Fig. 3(a)], respectively, from polyfluorene backbone and Phq unit. For the ternary copolymers, one emission band at 520 nm is added compared
to that of binary copolymers [Fig. 3(b)], which comes from the BT unit. Clearly, the broad emission results from the combination of individual emissions from fluorescent and phosphorescent species. The EL spectrum of PF-Phq2-BT5 [Fig. 3(b)] shows a stronger green emission, although the content of BT (0.05 mol %) is far lower than Phq (0.2 mol %). It is shown that more efficient energy transfer occurs from fluorene segment to BT unit than to Phq, owing to BT units are inserted into the PF backbone and Phq units are attached onto the side chain.

A comparison between the PL and EL spectra of the copolymer of PF-Phq1-BT2 is shown in Figure 4. The EL spectra are completely different from the PL. The red and/or green emissions contributed to the EL spectra relatively to the blue emission are much larger than that in PL. This phenomenon has been ascribed to the charge trapping which plays an important role in the EL process. White-light emission in EL spectra can be attributed to the individual emission from blue-, green-, and red-emitters with the partial energy transfer from the wide-band gap species to the narrow-band gap species and charge trapping on the narrow-band gap emitters.

The trapping mechanism can also be understood by the energy levels. The hole- and electron-trapping mechanism is most favorable if the HOMO (highest occupied molecular orbital) level of the guest is above (closer to vacuum level) that of the host, and if the LUMO (lowest unoccupied molecular orbital) level of guest is below (farther from vacuum level) that of the host. However, having both the HOMO and LUMO levels of the guest within the gap of the host is not required. As determined by cyclic voltammetry, the HOMO and LUMO of PF and monomers (BTBr₂ and Phq) are −2.1 eV and −5.8 eV, −2.3 eV and −5.9 eV as well as −3.2 eV and −5.3 eV, respectively. HOMO and LUMO levels of the red emitting species (Phq) are within the band gap of the blue emission species (PF). As a result, the large differences of LUMO and HOMO between the red and blue emitters lead to 1.1 eV and 0.5 eV barriers, respectively, for electron and hole, and the electron and hole injected from electrodes are readily trapped on the sites of red emitter. Therefore, triplet excited states will be formed and efficient electrophosphorescence is observed in the EL process of the copolymers. The HOMO level of BT is similar to that of polyfluorene and the LUMO level is only 0.2 eV lower than that of PF, which implies that there are two possibilities of both electron trapping and energy transfer from fluorene segment to benzothiadiazole unit in EL process. The same observation has also been reported in previous articles.

![Figure 3. EL spectra of the copolymers of PF-Phq (a) and PF-Phq-BT (b).](image1)

![Figure 4. PL and EL spectra of the copolymer of PF-Phq1-BT2.](image2)
According to the above discussion, the EL process of the white polymer light-emitting diodes (WPLEDs) comprises three main mechanisms. After charges are injected into copolymers from the electrodes, some of them directly recombine on the fluorene segment to produce blue light emission, and some are trapped on the BT and Phq sites to emit green and red light, and the others are transferred from fluorene segment to BT and Phq units to produce green and red light emission. The broad white light emission combines the emissions from the three emitting species, fluorene segment and BT unit in singlet state and Phq unit in triplet state.

The device performances with different Phq contents are listed in Table 1. As for the binary copolymers, when the content of Phq unit varies from 0.2 mol % to 0.3 mol %, white light emission is obtained. The efficiency and luminance increase with increasing Phq concentration, which is attributed to the phosphorescence of the iridium complex due to its strong spin-orbital coupling of heavy-metal ions. In addition, an octyl spacer plays an important role in the reduction of the reverse energy transfer from the iridium complex to the polyfluorene backbone. The maximum luminous efficiency of 3.2 cd/A, the maximum luminance of 4105 cd/m², and CIE coordinates of (0.33, 0.32) are obtained for PF-Phq3, and 2.7 cd/A, 1986 cd/m², and (0.30, 0.30) for PF-Phq2. To the red unit, when the Phq content increases from 0.1 mol % to 0.5 mol % in the binary copolymers, the CIE coordinates of the EL change from (0.27, 0.17) to (0.47, 0.35). The emission becomes reddish due to too much red emission contribution. For the ternary copolymers, PF-Phq2-BT3 and PF-Phq3-BT3 emit white light with efficiencies of 2.2 cd/A and 4.6 cd/A and the CIE coordinates of (0.32, 0.33) and (0.31, 0.34), respectively. High-efficient white-light emission is achieved with the maximum luminous efficiency of 6.1 cd/A and the maximum luminance of 10,110 cd/m² for PF-Phq2-BT5. The emission, however, shows a little greenish white light with the CIE coordinates of (0.32, 0.44) due to too much green contribution from BT units. When the BT content is reduced to 0.03 mol %, pure white light emission with the efficiency of 4.6 cd/A and CIE coordinates of (0.31, 0.34) is achieved. It is clearly seen that the EL spectra can be readily tuned by changing the concentrations of Phq and/or BT units. When the concentration of Phq and/or BT units increase, the red and/or green emissions become strong and the blue emission is significantly reduced. We noted that the green emission from BT unit in the ternary copolymers, in comparison with the binary copolymers, improved not only the color purity of the white light, but also the device efficiency (Table 1). This was ascribed to the exciton confinement of the benzothiadiazole unit, which allowed efficient singlet energy transfer from fluorene segment to BT unit and avoided the triplet quenching resulted from the higher triplet energy levels of phosphorescent green emitters than that of polyfluorene. Holmes et al. and Burn et al. concluded that the charge trapping reduces the excited energy loss during the energy transfer or hinder the excitons from migrating to quenching sites. As a result, the introducing of narrow-band gap units into the polymer chain can lead to less concentration quenching and higher efficiency. The direct evidence that the BT unit is confined need to be further confirmed by the photoluminescence tran-

### Table 1. Device Performances From the Copolymers

<table>
<thead>
<tr>
<th>Copolymers</th>
<th>Bias [V]</th>
<th>$J$ [mA/cm²]</th>
<th>LE$_{max}$ [cd/A]</th>
<th>$L_{max}$ [cd/m²]</th>
<th>CIE Coordinates&lt;sup&gt;b&lt;/sup&gt; ($x, y$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-Phq1</td>
<td>8.2</td>
<td>32.7</td>
<td>2.0</td>
<td>3407</td>
<td>(0.27, 0.17)</td>
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<tr>
<td>PF-Phq2</td>
<td>8.6</td>
<td>16.7</td>
<td>2.7</td>
<td>1986</td>
<td>(0.30, 0.30)</td>
</tr>
<tr>
<td>PF-Phq3</td>
<td>7.2</td>
<td>8.7</td>
<td>3.2</td>
<td>4105</td>
<td>(0.33, 0.32)</td>
</tr>
<tr>
<td>PF-Phq5</td>
<td>7.7</td>
<td>8.0</td>
<td>4.8</td>
<td>5230</td>
<td>(0.47, 0.35)</td>
</tr>
<tr>
<td>PF-Phq2-BT05</td>
<td>6.8</td>
<td>2.5</td>
<td>2.8</td>
<td>2170</td>
<td>(0.34, 0.30)</td>
</tr>
<tr>
<td>PF-Phq2-BT1</td>
<td>6.7</td>
<td>5.6</td>
<td>1.9</td>
<td>3585</td>
<td>(0.34, 0.33)</td>
</tr>
<tr>
<td>PF-Phq2-BT3</td>
<td>7.4</td>
<td>5.2</td>
<td>2.2</td>
<td>2410</td>
<td>(0.32, 0.35)</td>
</tr>
<tr>
<td>PF-Phq2-BT5</td>
<td>6.3</td>
<td>2.2</td>
<td>6.1</td>
<td>10,116</td>
<td>(0.32, 0.44)</td>
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<tr>
<td>PF-Phq3-BT3</td>
<td>6.4</td>
<td>2.3</td>
<td>4.6</td>
<td>6035</td>
<td>(0.31, 0.34)</td>
</tr>
</tbody>
</table>

<sup>a</sup> At the maximum luminance efficiency.

<sup>b</sup> Obtained at the current of 2 mA.
sient decay. The efforts are in progress and will be reported in a forthcoming article.

The device stability is very important, especially for commercial applications. As far as the WPLEDs are concerned, the spectra and efficiency stability with increasing voltage and current are the two most important parameters. Figure 5 exhibits the EL spectra and CIE coordinates change with varying voltages for PF-Phq2, PF-Phq3, PF-Phq2-BT3, and PF-Phq3-BT3, respectively. It is shown that all the white light coordinates are in the white region. With the increase of driving voltage, CIE coordinates change from (0.31, 0.30) to (0.27, 0.28) (7–10 V) for PF-Phq2, from (0.36, 0.34) to (0.31, 0.31) (7–10 V) for PF-Phq3, from (0.31, 0.32) to (0.29, 0.30) (8–10 V) for PF-Phq2-BT3, and from (0.31, 0.34) to (0.28, 0.33) (8–10 V) for PF-Phq3-BT3. All those emissions are well located in the white region.

Figure 6 shows the current density ($J$) versus luminous efficiency (LE) and luminance ($L$) characteristics from the copolymers of PF-Phq2, PF-Phq3, PF-Phq3-BT3, and PF-Phq2-BT5. It is clearly seen that the efficiencies decrease very slow with increasing current density, indicating that our white materials and devices have a good stability. At a high current density, the luminance decreases because of the destruction of the active materials under the high electrical field. Anyway, our results indicate that the strategy to realize white light emission by incorporating singlet emission species into the polymer backbone and attaching triplet-emission species onto the side chain of the polymer through an octyl spacer is a promising approach.

CONCLUSIONS

White-light emitting binary fluorene-based copolymers containing phosphorescent emitting species were designed and synthesized. The photo- and electroluminescence properties and the energy transfer of the copolymers have been

*Figure 5.* EL spectra at different voltages from the copolymers of PF-Phq2 (a), PF-Phq3 (b), PF-Phq2-BT3 (c), and PF-Phq3-BT3 (d).

*Figure 6.* J-LE-L characteristics of the copolymers of PF-Phq2, PF-Phq3, PF-Phq3-BT3, and PF-Phq2-BT5.
investigated. The phosphorescence quenching is a key factor in designing white-light emitting polyfluorene with triplet emitter. It is shown that using singlet green and triplet red emitters is an efficient approach to reduce even avoid the phosphorescence quenching in the fluorene-based copolymers.

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REFERENCES AND NOTES


40. Yeh, S.-J.; Wu, M.-F.; Chen, C.-T.; Song, Y.-H.;
42. Zhen, H.; Luo, C.; Yang, W.; Song, W.; Du, B.;
44. Sandee, A. J.; Williams, C. K.; Evans, N. R.; Da-
vies, J. E.; Boothby, C. E.; Köhler, A.; Friend, R. H.;
45. Bernius, M.; Inbasekaran, M.; Woo, E.; Wu, W.;
46. Hou, Q.; Xu, Y.; Yang, W.; Yuan, M.; Peng, J.;
Cao, Y. J Mater Chem 2002, 12, 2887.
47. Yang, R.; Tian, R.; Hou, Q.; Yang, W.; Cao, Y.
Macromolecules 2003, 36, 7453.
48. Inbasekaran, M.; Woo, E. P.; Wu, W. S.; Bernius,
49. Hertel, D.; Setayesh, S.; Nothofer, H.-G.; Scherf,
Thompson, M. E. J Am Chem Soc 2003, 125, 7796.
52. Evans, N. R.; Devi, L. S.; Mak, C. S. K.; Watkins,
S. E.; Pasca, S. I.; Köhler, A.; Friend, R. H.; Williams,
Hou, Q.; Yang, W.; Zhang, C.; Cao, Y. Macromolecules 2005, 38, 244.
54. Shaheen, S. E.; Lippelen, B.; Peyghambarian, N.;
55. Gong, X.; Ostrowski, J. C.; Moses, D; Bazan, G.
56. Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D.