

Synthesis and Electroluminescence Properties of White-Light Single Polyfluorenes with High-Molecular Weight by Click Reaction

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ABSTRACT: We reported a new way to synthesize single-chain white light-emitting polyfluorene (WPF) with an increased molecular weight using azide-alkyne click reaction. Four basic polymers with specific end-capping, which exhibited high-glass transition temperatures ($T_g > 100$ °C) and excellent thermal stability, were used as foundations of the WPF's synthesis; a blue-light polymer (PFB2) end-capped with azide groups can easily react with acetylene end-capped polymers (PFB1, PFG1, and PFR1, which are emitting blue-, green- and red-light, respectively) to form triazole-ring linkages in polar solvents such as *N,N*-dimethylformamide/toluene co-solvent at moderate temperature of 100 °C, even without metal-catalyst. Several WPFs that

consist of these four basic polymers in certain ratios were derived, and the polymer light-emitting diode device based on the high-molecular weight WPF was achieved and demonstrated a maximum brightness of 7551 cd/m² (at 12.5 V) and a maximum yield of 5.5 cd/A with Commission Internationale de l'Eclairage coordinates of (0.30, 0.33) using fine-tuned WPF5 as emitting material. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 49: 3355–3365, 2011

KEYWORDS: conjugated polymers; copolymerization; light-emitting diodes (LED); polyfluorene

INTRODUCTION In this tough era facing energy crisis, light-emitting diode (LED) has become a new solution for the next-generation solid-state lighting; the lower turn-on voltage and the higher power efficiency bring LED more competitive advantage than the incandescent light bulb. Within the LED technologies, white organic LEDs (WOLEDs) and polymer LEDs (WPLEDs) have drawn many researchers' interests in the past decade because of their potential applications not only in the solid-state lighting but also in full-color flat-panel and liquid-crystal displays' backlight.^{1–3} Despite the high power efficiency of small-molecule WOLEDs, WPLEDs have better advantage for the fabrication of large-area display devices using inexpensive solution processing techniques (e.g., spin-coating and printing technology).^{4–6} Various approaches have been proposed to fabricate white polymeric light-emitting devices; one is to obtain from multilayer device in which each layer emits partial segment of the visible spectrum.^{7,8} Another conventional approach is to use polymer-blend systems containing two or three light-emitting materials as emissive layers, such as polymer/polymer blends^{9–14} or polymer/small-molecule blends.^{15–20} Although WPLEDs can be realized in these two ways, they still face some problems. The first approach could meet some processing challenges, such as thin-film layer adjustment and solvent selection, and the second strategy may suffer from intrinsic phase separation during long-term device operation as well as spectroscopic dependence on the applied voltage.

Recently, studies have developed single-component white polymeric emitter based on insufficient energy transfer by incorporating RGB chromophores into a single polymer chain.^{21–31} This promising method could go through a simple solution process thus make the device fabrication easier. Lee et al. first reported a single fluorene-based copolymer composed of blue-, green-, and red-light emitting units as active material for WPLED, which showed a maximum brightness of 820 cd/m² at 11V with the Commission Internationale de l'Eclairage (CIE) coordinates of (0.33, 0.35).²³ At almost the same time, Wang and coworkers adopted a slightly different synthetic strategy by which green- and red-emitting components were attached to the pendant chain along with blue-emitting polyfluorene backbone.^{28,29} Cao and coworkers synthesized a conjugated silole-containing polyfluorenes, with green- and red-emissive siloles on the blue-emissive polyfluorene backbone. The electroluminescence (EL) device showed a maximum brightness and luminous efficiency of 4102 cd/m² and 2.03 cd/A, respectively.³¹

Although using single white emitting polymers as emitting layer provides an easier way for device fabrication, more efforts should be done in their synthetic strategies. The general synthetic routes for preparing polyfluorenes are organometallic cross-coupling reactions, such as Suzuki coupling or Yamamoto coupling. As a result, however, it is unlikely to remove the metal-catalyst completely from the resultant

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polymers during purification. The azide-alkyne click reaction is a new way to prepare polyfluorenes in mild conditions.^{32–38} Tang and coworkers developed a metal-free, thermally initiated, regioselective 1,3-dipolar polycycloaddition process: simple heating a mixture of arylendiazides (N_3 -Ar- N_3) and arylenediynes ($H-C\equiv C-Ar-C\equiv C-H$) in a polar solvent, such as *N,N*-dimethylformamide (DMF)/toluene mixture, readily furnished a linear poly(1,2,3-triazole) with a high regioregularity (1,4-disubstituted content ratio up to ~92%) in a high yield (up to ~98%).³⁸

In this article, we report two series of polymers: the first contained four fluorene-based polymers with specific end-capping groups (PFs: PFB1, PFB2, PFG1, and PFR1) synthesized via Suzuki polycondensations, and another series involved single-chain white-light polymers (WPFs), which linked via 1,2,3-triazole-ring, obtained by incorporating a small amount of PFG1 and PFR1 into PFB's backbone through azide-alkyne click reaction. The EL spectra of these novel WPFs showed three distinguishable emissions peaks at blue, green, and red area due to the incomplete energy transfer from the blue-emissive (PFB1 and PFB2) to the green- (PFG1) and red-emissive (PFR1). The relative intensities of these three emissions vary in accordance with the relative composition proportion of the four basic PFs. Furthermore, the molecule weight, thermal stability, EL properties (brightness, efficiency, and CIE), and other relevant physical properties of the synthesized polymers were also investigated.

EXPERIMENTAL

Measurements

IR spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer with KBr pellets. The chemical structure is confirmed using ^1H NMR spectra (300 MHz) on a Varian VXR-300 spectrometer. Differential scanning calorimetry (DSC) was recorded on a Perkin-Elmer Pyris Diamond DSC unit operated at heating and cooling rates of 20 and 50 °C min⁻¹, respectively. Samples were scanned from 30 to 300 °C, cooled to 0 °C, and then scanned a second time from 30 to 300 °C. The glass transition temperatures were determined from the second heating scans. Thermogravimetric analyses (TGA) were undertaken on a Perkin-Elmer Pyris 1 TGA instrument to determine the stabilities of samples by measuring their weight losses with a heating rate of 10 °C min⁻¹. UV-visible spectra were measured with an HP 8453 diode array spectrophotometer. PL spectra were obtained on a Hitachi F-4500 luminescence spectrometer, and the PL external efficiency was measured using an integrating sphere. Cyclic voltammetry measurements of the material were done in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scan rate of 80 mV/s. Platinum wire electrodes were used as both the counter and working electrodes, and silver/silver ion (Ag/Ag^+ in 0.1 M $AgNO_3$ solution, from Bioanalytical Systems) was used as a reference electrode. Using ferrocene as an internal standard, the potential values obtained were converted to vs SCE (saturated calomel electrode).

Fabrication and Characterization of PLED Devices

The multilayers PLED devices were fabricated as sandwich structures between cathode (Cs) and indium-tin oxide (ITO) anodes in the following configuration: ITO/poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene)(PEDOT:PSS)/TFB(hole-transporting material, which is poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-(4,4'-(*N*-(4-*s*-butylphenyl))diphenylamine)]/light-emitting polymer/Cs/Al. ITO-coated glass substrates were cleaned sequentially in ultrasonic baths of detergent, 2-propanol/deionized water (1:1, v/v) mixture, toluene, deionized water, and acetone. A 50-nm thick hole injection layer of PEDOT:PSS was spin-coated on the top of ITO at 3000 rpm for 40 s and then dried at 150 °C for 1 h under N_2 . TFB was dissolved in toluene of 1.0 wt % and spin-coated at 2000 rpm for 30 s as hole-transporting layer and then dried at 80 °C for 1 h under N_2 . The following construction of the emitting layer may destroy the flatness of the interface between hole-transporting and emitting films due to the TFB, and our active materials are both organic soluble. The method to overcome this shortcoming is the buffer layer technology by using water-soluble ethylene glycol as buffer solvent between two organic-soluble layers. The detailed procedure of buffer layer technology was showed as the following steps: first, the program of spin coater was set for three steps of 5000 rpm for 3 s, 0 rpm for 3.5 s, and 1500 rpm for 30 s in sequence. Second, the program of spin coater started immediately after the ethylene glycol of 60 μ L was dropped from their 1.5 wt % toluene solutions on the PEDOT layer, and then WPFs of 1.5 wt % in toluene were dropped rapidly during the 3.5 s of the spinner was suspended. After the program was finished, the films of WPFs were dried at 100 °C under vacuum for 2 h. The film thicknesses obtained were about 40~50 nm, which were measured by an Alpha-Step 500 surface profiler (KLA Tencor, Mountain View, CA). Finally, 2-nm Cs and 100-nm Al electrodes were thermally evaporated through a shadow mask onto the polymer films using an AUTO 306 vacuum coater (BOC Edwards, Wilmington, MA), typical evaporations being carried out at base pressures lower than 2×10^{-6} Torr. The active area of each EL device was characterized following a published protocol.

Materials

All chemicals, reagents, and solvents were used as received from commercial sources without further purification except tetrahydrofuran (THF) and toluene that have been distilled over sodium/benzophenone. The Suzuki coupling catalyst reagent tetrakis(triphenylphosphine)palladium (0) were purchased from TCI and handled under inert atmosphere.

Monomers, 2,7-dibromo-9,9-di-*n*-hexylfluorene (M1),³⁹ 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-dihexylfluorene (M2),⁴⁰ 4,7-bisbromo-2,1,3-benzothiadiazole (M4),³⁹ *N,N*-di(4-bromophenyl)-*N*-(4-butylphenyl)amine (M3), and 4,7-bis-(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (M5),⁴¹ were synthesized according to literature procedures.

4-(4-Bromophenyl)-2-methylbut-3-yn-2-ol (4)

A solution of 4-bromo-iodobenzene (10.0 g, 35.35 mmol), *trans*-dichloro-bis(triphenyl-phosphine)palladium(II) (0.5 g, 0.71 mmol), and triphenylphosphine (1.87 g, 7.10 mmol) in

triethylamine (150 mL) was stirred at 60 °C for 30 min under N₂. Then copper(I) iodide (1.0 g, 5.26 mmol) and 2-methylbut-3-yn-2-ol (4.36 g, 53.02 mmol) were added into the flask. The mixture was heated to reflux for 16 h under N₂. After cooling, the solution was extracted with ethyl acetate, and the organic phase was dried over magnesium sulfate, filtered, rotary evaporated to remove solvent. The crude product was purified by column chromatography using ethyl acetate/*n*-hexane (1:5, v/v) as eluent to yield **4** as a brown solid (5.91 g, 70.2 %).

¹H NMR (300 MHz, CDCl₃, δ in ppm): 1.61 (s, 6H, —CH₃), 2.01 (s, 1H, —OH), 7.26~7.28 (d, 2H, aromatic protons), 7.42~7.45 (d, 2H, aromatic protons). ¹³C NMR (75 MHz, CDCl₃, δ in ppm): 32.1 (2C, —CH₃), 65.3 (1C, —C(CH₃)₂OH), 80.3 (1C, Ar—C≡C), 93.4 (1C, Ar—C≡C), 121.7, 122.8, 131.3, 134.5 (aromatic carbons). HRMS-EI (*m/z*): [M⁺] calcd. for C₁₁H₁₁BrO, 237.9993; found, 237.9912.

1-Bromo-4-ethynylbenzene (M6)

4-(4-Bromophenyl)-2-methylbut-3-yn-2-ol (**4**) (8.0 g, 33.46 mmol) and potassium hydroxide (5.63 g, 100.38 mmol) were mixed in 150 mL 1,4-dioxane. The mixture was stirred at 120 °C for 3 h. The reactant was cooled to room temperature, and then the solvent was stripped off by evaporation. The residue was mixed with 80 mL of water and extracted with 80 mL ethyl acetate. The extracted solution was dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography (silica gel, eluting with hexane) to yield **M6** as deep brown liquid (5.18 g, 85.5%).

¹H NMR (300 MHz, CDCl₃, δ in ppm): 3.10 (s, 1H, acetylene proton), 7.31~7.34 (d, 2H, aromatic protons), 7.42~7.45 (d, 2H, aromatic protons). ¹³C NMR (75 MHz, CDCl₃, δ in ppm): 82.4 (1C, Ar—C≡C), 79.9 (1C, Ar—C≡C), 121.1, 122.1, 130.5, 134.3 (aromatic carbons). HRMS-EI (*m/z*): [M⁺] calcd. for C₈H₅Br, 179.9575; found, 179.9523.

2-[4-(1-Ethynyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (M7)

To a solution of 2-[4-(1-ethynyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**M6**; 3.0g, 16.57 mmol) in THF (30 mL) was added *n*-butyllithium (8.62 mL, 2.5 M in hexane, 21.55mmol) by syringe under −78 °C. The mixture was then stirred at −78 °C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.39 mL, 21.55 mmol) was added rapidly to the solution, and the resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was poured into water and extracted with ethyl acetate. The solvent was then removed by rotary evaporation, and the residue was purified through column chromatography (silica gel, eluting with *n*-hexane) to yield **M7** as deep brown liquid (2.50 g, 66.2%).

¹H NMR (300 MHz, CDCl₃, δ in ppm): 1.25 (s, 12H, —CH₃), 3.10 (s, 1H, acetylene proton), 7.31~7.34 (d, 2H, aromatic protons), 7.42~7.45 (d, 2H, aromatic protons). ¹³C NMR (75 MHz, CDCl₃, δ in ppm): 21.4 (4C, —CH₃), 83.2 (2C, -boronic ester ring carbons), 82.1 (1C, Ar—C≡C), 79.7 (1C, Ar—C≡C), 121.7, 122.7, 132.3, 133.5 (aromatic carbons). HRMS-EI (*m/z*): [M⁺] calcd. for C₁₄H₁₇BO₂, 228.1322; found, 228.1352.

4-Bromophenyl Azide (M8)

4-Bromoaniline (10.0 g, 58.13 mmol) and 50 mL THF were added into a three-necked flask. Concentrated hydrochloric acid (10.3 mL, 87.2 mmol) was added carefully at 0 °C. A solution of sodium nitrite (6.07 g, 87.2 mmol) in 15-mL THF was added drop-wise within 30 min. Then sodium azide (5.8 g, 87.2 mmol) dissolved in 15-mL THF was added drop-wise within 30 min. Afterward, the mixture was refluxed at 85 °C for 24 h. After the mixture was cooled to room temperature, THF was removed by rotary evaporation, and then the mixture was mixed with 100 mL of water and extracted with 100 mL ethyl acetate. The extracted solution was dried over anhydrous magnesium sulfate. The crude product was isolated by filtration and further purified by column chromatography (silica gel, eluting with *n*-hexane) to yield **M8** as brown liquid (5.23 g, 45.5%).

¹H NMR (300 MHz, CDCl₃, δ in ppm): 6.88~6.91 (d, 2H, aromatic protons), 7.44~7.47 (d, 2H, aromatic protons). ¹³C NMR (75 MHz, CDCl₃, δ in ppm): 123.1, 131.0, 131.7, 143.5 (aromatic carbons). HRMS-EI (*m/z*): [M⁺] calcd. for C₆H₄BrN₃, 196.9589; found, 196.9572.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)aniline (5)

To a solution of 4-bromoaniline (10.0 g, 58.13 mmol) in THF (50 mL) at −78 °C *n*-butyllithium (30.22 mL, 2.5 M in hexane, 75.57 mmol) was added by syringe. The mixture was stirred at −78 °C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.39 mL, 75.57 mmol) was added rapidly to the solution, and the resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was poured into water and extracted with ethyl acetate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, eluting with ethyl acetate/*n*-hexane, 1:5, v/v) to yield **5** as yellow liquid (5.37 g, 42.2 %).

¹H NMR (300 MHz, CDCl₃, δ in ppm): 1.25 (s, 12H, —CH₃), 3.62 (s, 1H, —NH₂), 6.54~6.57 (d, 2H, aromatic protons), 7.21~7.24 (d, 2H, aromatic protons). ¹³C NMR (75 MHz, CDCl₃, δ in ppm): 20.8 (4C, —CH₃), 82.7 (2C, -boronic ester ring carbons), 116.3, 122.0, 134.7, 148.4 (aromatic carbons). HRMS-EI (*m/z*): [M⁺] calcd. for C₁₂H₁₈BNO₂, 219.1431; found, 219.1423.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)phenyl azide (M9)

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl) aniline (**5**) (3.0 g, 13.69 mmol) and 20-mL THF were added into a three-necked flask. Concentrated hydrochloric acid (2.42 mL, 20.53 mmol) was added carefully at 0 °C. Sodium nitrite (1.42 g, 20.53 mmol) dissolved in 8 mL THF was added drop-wise within 30 min. Then a solution of sodium azide (1.36 g, 20.53 mmol) in 8 mL THF was added drop-wise within 30 min. Afterward, the mixture was heated to reflux for 24 h. After the mixture was cooled to room temperature, THF was removed by rotary evaporation, and the mixture was mixed with 50 mL of water and extracted with 50 mL ethyl acetate. The extracted solution was then dried over anhydrous magnesium sulfate. The crude product was filtrated

and further purified by column chromatography (silica gel, eluting with *n*-hexane) to yield M9 as yellow liquid (1.30 g, 38.6%).

^1H NMR (300 MHz, CDCl_3 , δ in ppm): 1.25 (s, 12H, $-\text{CH}_3$), 7.28 (s, 4H, aromatic protons). ^{13}C NMR (75 MHz, CDCl_3 , δ in ppm): 21.2 (4C, $-\text{CH}_3$), 83.1 (2C, $-\text{boronic ester ring carbons}$), 128.8, 132.0, 133.9, 144.5 (aromatic carbons). HRMS- EI (m/z): [M^+] calcd. for $\text{C}_{12}\text{H}_{16}\text{BN}_3\text{O}_2$, 245.1336; found, 245.1321.

Synthesis of Fluorene-Based Conjugated Polymers (PFs)

A typical procedure for the polymerization of PFB2 was given below. Into a three-necked flask were added 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-dihexylfluorene (M2; 0.5 g, 0.85 mmol), 2,7-dibromo-9,9-di-*n*-hexylfluorene (M1) (0.25 g, 0.43 mmol), *N,N*-di(4-bromophenyl)-*N*-(4-butylphenyl)amine (M3; 0.19 g, 0.43 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.015 g, 0.01 mmol), and Aliquat 336 (a small amount) in a dry box. Degassed toluene (7 mL) and aqueous K_2CO_3 (2 M, 3 mL) were then added, by syringe, under an atmosphere of dry argon. The mixture was heated to reflux with vigorous stirring at 90 °C oil bath for 96 h. The end groups were capped by heating the mixture under reflux for 12 h with M8 (0.07 g, 0.35 mmol) and then with M9 (0.08 g, 0.35 mmol) for another 12 h. The reaction mixture was cooled to room temperature and poured into methanol. The precipitation was collected by filtration and washed by acetone to remove oligomers and catalyst residues. The precipitation was then redissolved in THF, reprecipitated in methanol, and finally dried with vacuum oven at 35 °C to give PFB2. PFB1, PFG1, and PFR1 were also synthesized through the above procedure, except the different end-capping reagents (M6 and M7) were used. The yields of these four polymers were in the range of 66~75%.

Synthesis of Single-Chain WPF Copolymers

To diminish the difficulty during purification, we adopted a metal-free, thermally initiated process. With four basic PFs (PFB1, PFG1, and PFR1 with arylenediynes end-capped groups; PFB2 with arylendiazide end-capped group) in hand, a series of novel single WPFs with 1,2,3-triazole-ring linkage were obtained through azide-alkyne click reaction. The mole feed ratios used in the preparation of these new polymers were given in Table 1. A typical procedure for the synthesis of WPF WPF5 was given below. To a solution of PFB2 (0.1 g), PFB1 (0.08 g), PFG1 (0.01 g), and PFR1 (0.01 g) in DMF/toluene (1:1, v/v; 10 mL) was heated to reflux with vigorous stirring under 110 °C oil bath for 72 h at an atmosphere of dry argon. The reaction mixture was then cooled to room temperature and poured into methanol. The precipitation was collected by filtration and dried with vacuum oven at 35 °C to give WPF5. The yields of these four single polymers were in the range of 55~70%.

RESULTS AND DISCUSSION

Synthesis and Characterization

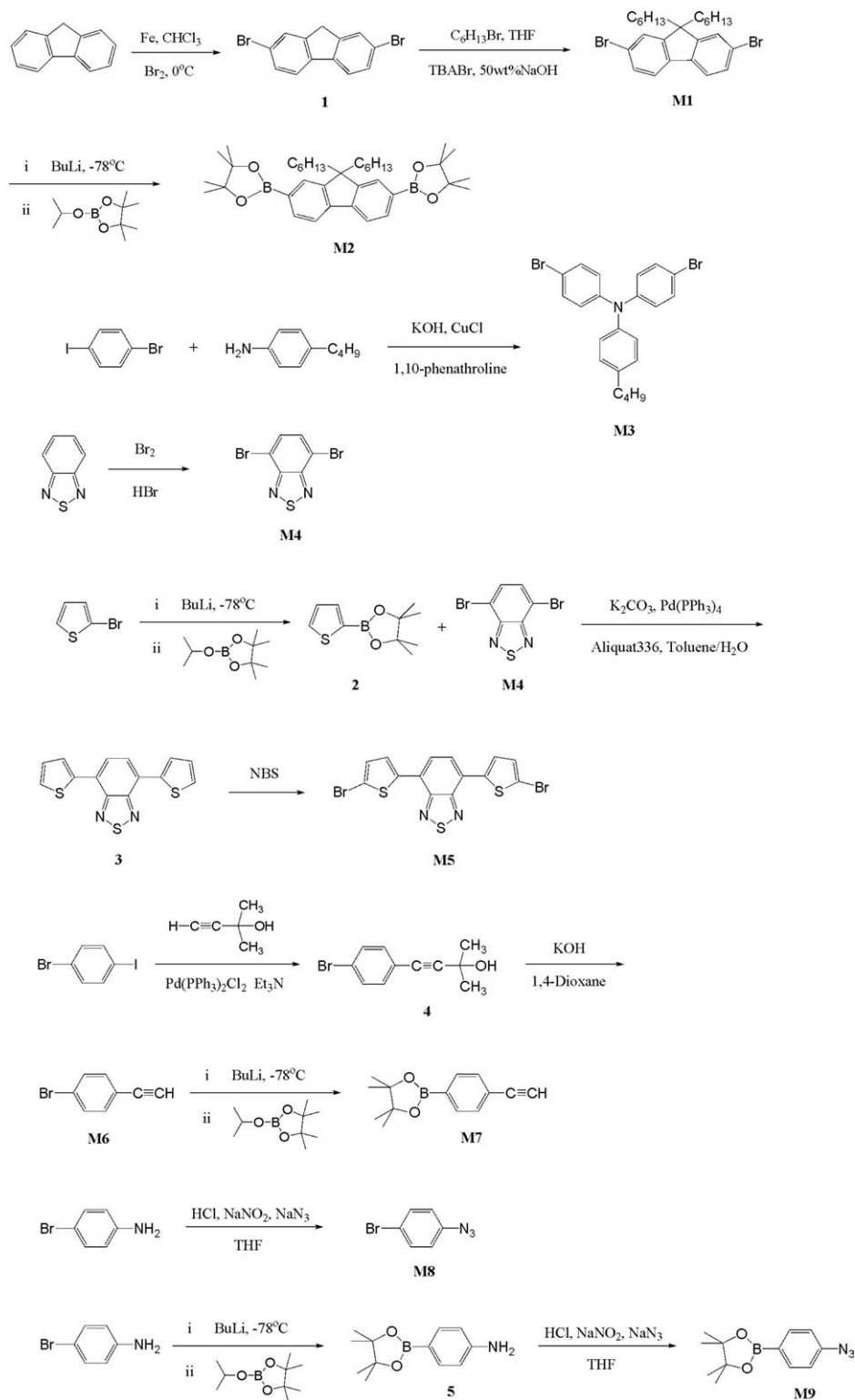
We synthesized two series of polymers successfully; the first is fluorene-based conjugated polymers (PFs), which were

TABLE 1 The Mole Feed Ratios of Basic PFs for Single-Polymers WPFs

	PFB2	PFB1	PFG1	PFR1
WPF1	0.5	0.3	0.1	0.1
WPF2	0.5	0.3	0.06	0.14
WPF3	0.5	0.35	0.05	0.1
WPF4	0.5	0.38	0.04	0.08
WPF5	0.5	0.40	0.05	0.05
WPF6	0.5	0.42	0.02	0.06

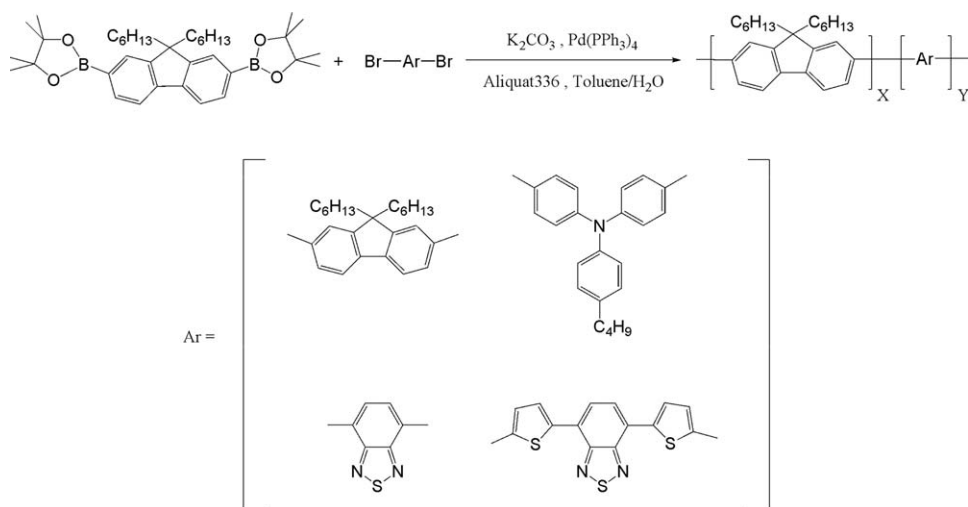
synthesized via Suzuki polycondensations from monomers M1~M5, and another is novel copolymers with 1,2,3-triazole-ring linkage, which were synthesized via azide-alkyne click reaction from aforementioned PFs to afford WPFs. Scheme 1 shows the general synthetic routes toward monomers M1~M9, and the chemical structures of all the monomers were carefully checked with ^1H NMR, ^{13}C NMR, and GC-MS results. Scheme 2 demonstrates the syntheses of the four basic PFs (PFB1, PFG1, PFR1, and PFB2), utilizing palladium-catalyzed Suzuki coupling reaction with an equivalent molar ratio of the diboronic ester monomer (M2) to the dibromo monomers (M1, M3~M5) under argon atmosphere. Monomers (M6 and M7 with arylacetylene end group; M8 and M9 with arylazide end group) were used as the end-capping reagents for Suzuki coupling polymerization.

A new series of WPF polymers were synthesized via an acetylene-azide click reaction by using the specific end-capped polymers as reactants (PFB1 and PFB2 act as host units while PFG1 and PGR1 act as dopants). The chemical structures of these novel WPFs, which were composed of the four PFs in different ratios, are showed in Scheme 3. The mole feed ratios used in the preparation of the WPFs were listed in Table 1. The resulting polymers were characterized by ^1H NMR and FTIR to confirm the polymer structures and to verify the completion of click-reaction. Figure 1 shows the FTIR spectra of polymers PFB1, PFB2, and WPF5; PFB1 absorbs at 3236 and 2102 cm^{-1} due to its $\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$ stretching vibrations, respectively. PFB2 exhibits a strong absorption peak at 2030 cm^{-1} associated with the stretching of its azide group. For the FTIR spectrum of WPF5, all these three absorption peaks disappeared. This suggests that all the acetylene and azide groups of PFs have been transformed to the triazole rings of the polymers WPFs through the click reaction. Although the FTIR spectra support that the click reaction is feasible to obtain a triazole-linked polymer, they offer no information about the regioselectivity (1,4- or 1,5-disubstitution) of the polymers. We used the NMR technique to study this important structural issue. Figure 2 shows the NMR spectra of polymers PFB1, PFB2, and WPF5. The ^1H NMR spectrum of polymer PFB2 exhibited no distinctive peak for azide group. The resonance peak for the acetylene proton of polymer PFB1 was found at δ 3.06. In the spectrum of polymer WPF1, the peak for acetylene group at δ 3.06 became remarkable weaker, and furthermore, a new peak



corresponding to the resonances of triazole ring protons appeared at δ 9.03, which was the characteristic peaks for 1,4-disubstituted 1,2,3-triazole rings. The data of ^1H NMR spectra not only confirmed that the click reaction was achievable but also determined the regioselectivity of the polymer products.

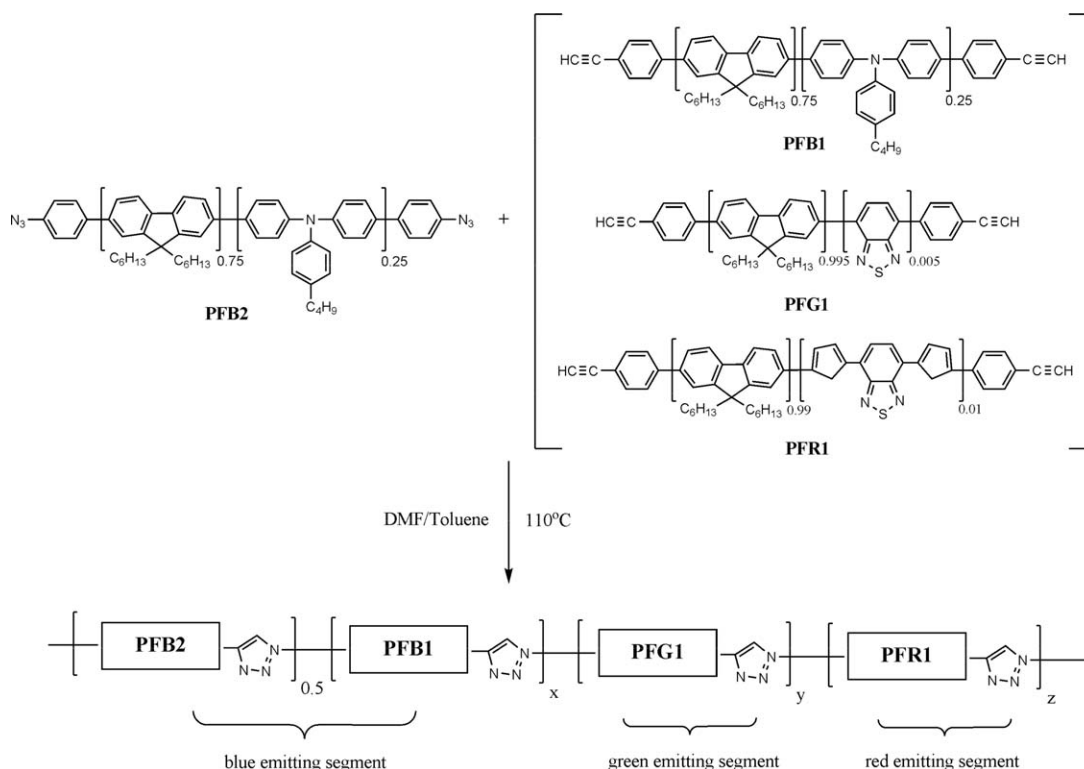
Molecular weights and polydispersity indices of all the polymers were determined by GPC analysis using THF as the eluent and polystyrene as the standard. The number-average molecular weights ($\overline{M}_n$), weight-average molecular weights ($\overline{M}_w$), and the polydispersity indices (PDIs) are summarized in Table 2. The range of the $\overline{M}_n$ and $\overline{M}_w$ for PFs were



SCHEME 2 Polymerization of polymers PFs.

determined to be 15,500–24,300 and 24,200–38,200, respectively, with the PDI range of 1.52–1.70. The $\overline{M}_n$ and $\overline{M}_w$ of all the WPFs were both about four to six times than that of PFs. The higher molecular weights of WPFs compared with PFs suggest successful combination of four basic PFs resulting the novel triazole-linked WPFs. All the polymers are readily soluble in common organic solvents, such as toluene, chlorobenzene, chloroform, and THF at room temperature. Accordingly, uniform thin films of the polymers could easily produced through spin-coating for further study of light-emitting devices.

As good thermal stability is very important for the application of conjugated polymers in flat panel displays, the thermal stability of these polymers was evaluated by TGA and DSC under a nitrogen atmosphere. Table 2 summarizes the glass transition temperatures (T_g) and thermal decomposition temperatures (T_d) of the obtained polymers. Both PFs and WPFs exhibit outstanding thermal stability, with the decomposition temperatures (T_d) higher than 385 °C, and their glass transition temperatures are in the range from 80 to 110 °C, which are similar with those of polyfluorene published in the literature.²³



SCHEME 3 Syntheses of WPFs by click reaction.

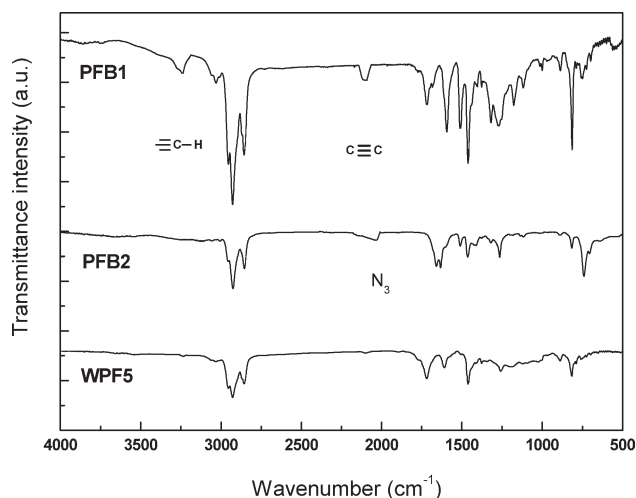


FIGURE 1 FTIR spectra of PFB1, PFB2, and WPF5.

Optical Properties

The fluorescent wavelength of a polymer film fundamentally depends on the band gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which depends on delocalization of π electrons along the polymer backbone. The characteristic peak in the emission spectrum appears when an excited electron relaxes into vibronic energy level of the HOMO level. Because of the coupling of several different vibronic modes, the optical spectra of conjugated polymers are typically broad. UV-vis absorption and photoluminescence spectra of the four PFs polymer in dilute toluene solution and thin film state were showed in Figures 3 and 4, respectively. The polymers PFB1 and PFB2 exhibit similar UV-vis and photoluminescence spectra because of their similar chemical structures (the only discrepancy is in end-capping reagents); they both emitted blue emissions with photoluminescence maxima of about 416 and 428 nm in dilute toluene solution and solid state, respectively. By introducing a small amount of BTMZ group into the main chain of polyfluorene copolymer, the blue emission at 428 nm of polyfluorene could be quenched and dominated by a green- and red-emissive peaked at 532 and 617 nm for PFG1 and PFR1, respectively. This indicates the effectively energy transfer from photogenerated excitons on the polyfluorene segment into BTMZ groups, and the more planar backbone and the smaller band gap were produced. The maximum wavelengths of UV-vis absorption and PL emission for these four polymers in diluted toluene solution and solid state were summarized in Table 3. In comparison with dilute solution, the absorption and emission spectra of PFs in thin film state both showed slightly red-shift, and this phenomenon can be attributed to the aggregation of polymer chains.

Figure 5 shows the photoluminescence spectra of WPFs in thin film state. It can be seen that the absorption spectra of these polymers are practically identical to that of the polymer PFB1 because of the very low contents of polymers PFG1 and PFR1. In the PL spectra of these polymers (Fig. 5), WPF1 exhibits two obvious emission peaks at 429 nm and 558 nm, and the intensity of 558 nm is much stronger than

that of 429 nm to lead to polymer WPF1 emits orange-red light. As shown in Figure 5, the relative intensities of long wavelength peaks decreased gradually for WPF2~WPF6 by decreasing the contents of PFG1 and PFR1. White-light single polymers (WPF3~WPF5) were obtained from polymers containing 85~90 mol % blue-light emitting host and 10~15 mol % green- and red-light emitting dopant. The data of UV-vis and PL spectra were listed in Table 3.

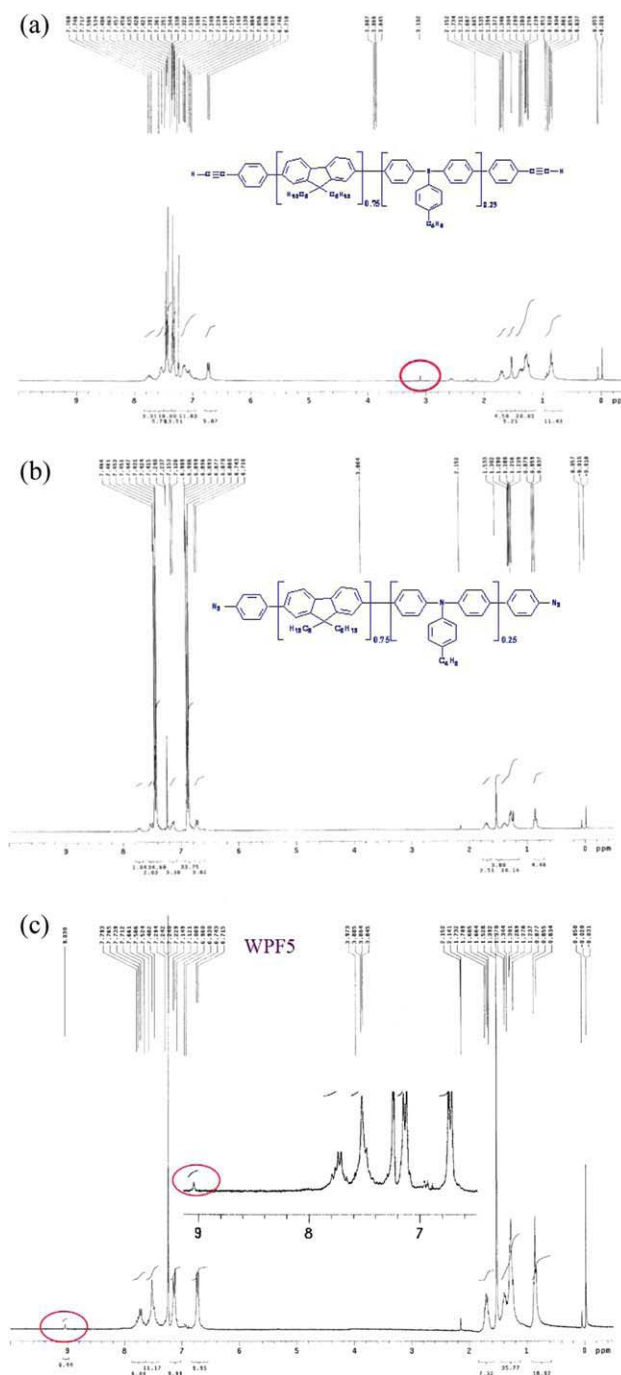
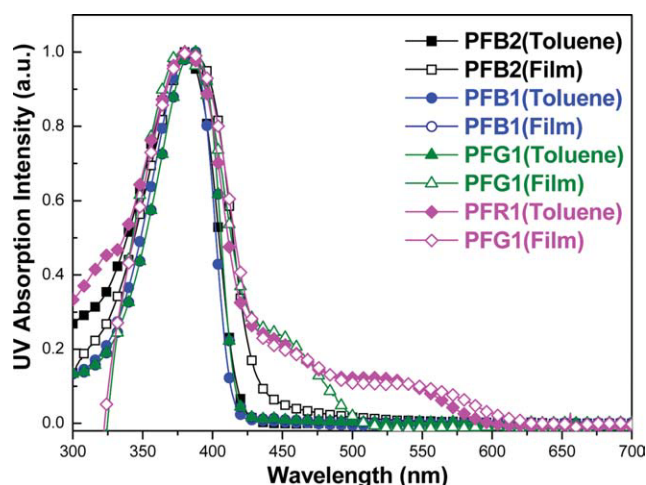
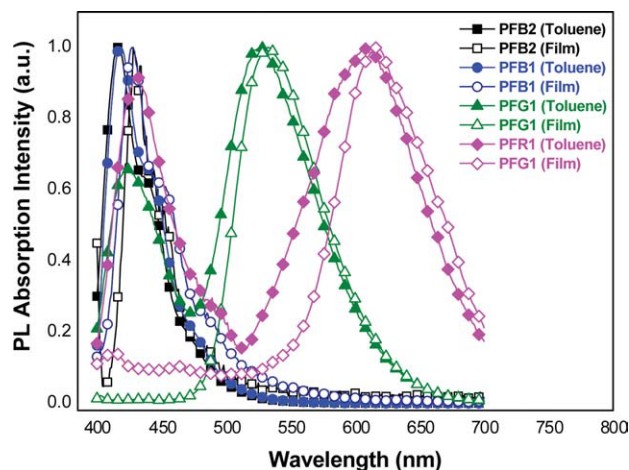


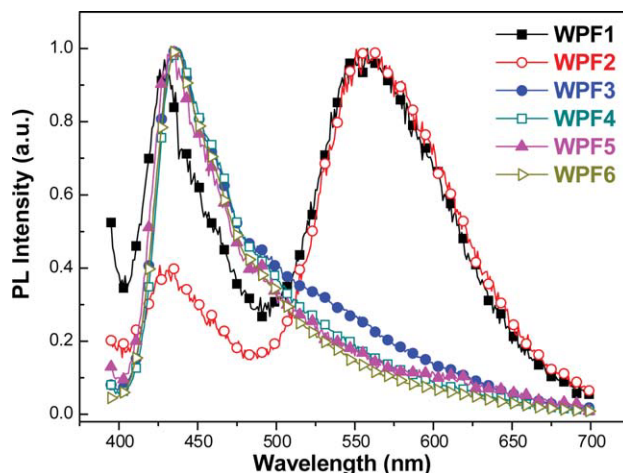
FIGURE 2 ^1H NMR spectra of (a) PFB1, (b) PFB2, and (c) WPF5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 2 Average Molecular Weights and Thermal Properties of Polymers PFs and WPFs

Polymer	$\overline{Mn}^a$ ($\times 10^4$)	$\overline{Mw}^a$ ($\times 10^4$)	PDI ($\overline{Mw}/\overline{Mn}$)	T_d ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)
PFB2	2.4	3.8	1.61	412	82.2
PFB1	1.7	2.6	1.55	406	81.3
PFG1	1.5	2.5	1.70	398	92.5
PFR1	1.6	2.4	1.52	403	95.8
WPF1	8.40	15.8	1.88	393	108.1
WPF2	8.39	16.2	1.93	385	103.9
WPF3	8.73	16.6	1.90	401	99.2
WPF4	8.79	17.5	1.99	409	101.9
WPF5	9.20	18.6	2.02	411	96.6
WPF6	10.56	18.8	1.78	415	93.0

^a Determined by GPC, relative to polystyrene standards.**FIGURE 3** UV-vis spectra of polymers PFs in dilute toluene and film state.**FIGURE 4** Photoluminescence spectra of polymers PFs in dilute toluene and film state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**TABLE 3** UV and PL Peaks of Polymers PFs

polymer	PL [λ_{max} (nm)]				PL _{eff} (%) ^a	
	Toluene	Film	Toluene	Film	Toluene	Film
PFB2	380	384	416	428	82.2	55.3
PFB1	383	388	419	427	80.7	50.7
PFG1	388	380(455)	422,529	532	86.6	42.8
PFR1	381	382	429,609	617	70.7	37.1
	(455,525)	(458,530)				

^a The PL external efficiency was measured using an integrating sphere.**FIGURE 5** Photoluminescence spectra of white-light polymers WPFs in film state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Electrochemical Properties

The electrochemical behavior of these polymers was investigated by cyclic voltammetry (CV). The corresponding HOMO energy levels were estimated from the oxidation onset potentials. HOMO levels of all the polymers were calculated according to the empirical formula $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.4)$ (eV). Polymers coated on a Pt wire from toluene solution were performed in an electrochemical cell with a Pt counter electrode and an Hg reference electrode. From the difference of the onset potentials and the band gaps (E_g) calculated from the onsets of UV absorption spectra, the energy levels

TABLE 4 Energy Levels of Polymers PFs

	$E_{\text{ox,onset}}$ (V) ^a	Energy Level (eV)		
		HOMO ^b	LUMO ^b	E_g ^c
PFB2	1.25	5.65	2.71	2.94
PFB1	1.23	5.63	2.69	2.94
PFG1	1.41	5.81	3.16	2.65
PFR1	1.37	5.77	3.62	2.15

^a The E_{ox} stands for the onset potentials of oxidation.^b Calculated from the empirical formula, $E_{\text{(HOMO)}} = -(E_{\text{ox}} + 4.40)$ (eV), $E_{\text{(LUMO)}} = -(E_{\text{red}} + 4.40)$ (eV).^c The energy gap (E_g) was estimated from the onset wavelength (value in parentheses) of UV-vis spectra of the polymer film.

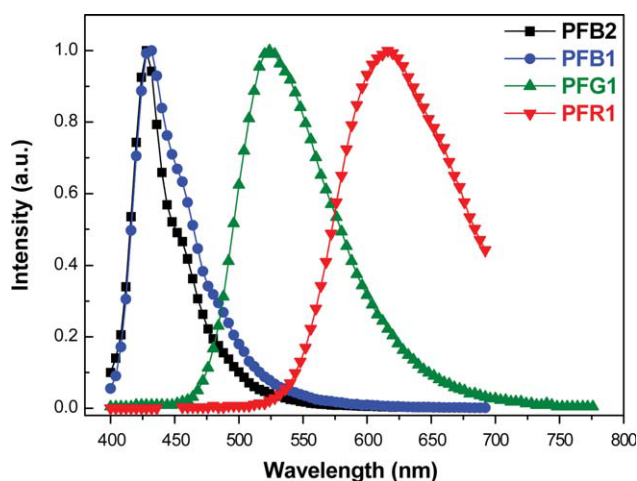


FIGURE 6 Electroluminescence spectra of polymers PFs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were determined and displayed in Table 4. It can be seen that polymers PFB1 and PFB2 possess the similar electrochemical properties to homo-polyfluorene. The reversible oxidation curve of PFB1 and PFB2 with onset at 1.23 and 1.25 V, respectively (in agreement with data reported previously for polyfluorene homopolymer) that could be assigned to the oxidation potential of polyfluorene main chains and indicated that the end-capping group made no effect to electrochemical properties of polymers PFs. When compared with polyfluorene homopolymer (E_g of PFO were 2.95 eV), the E_g of polymers PFG1 and PFR1 show a less value because the incorporation of the electron-rich BTMZ moiety.³⁹ As BTMZ moiety has a smaller band gap than polyfluorene, the excitation energy on the fluorene segments can transfer to the BTMZ units with high efficient green and red lights. The difference in chemical structure between the WPFs and the basic polymers (PFs) is the particular triazol-ring. As the results in Table 4, polymers WPFs all exhibited the very similar electrochemical behavior with that of the basic polymers PFs, indicating that the triazol-ring leads to little change in the resulting polymers' redox properties.

TABLE 5 Device Performance of All the Polymers

Polymer	CIE(x,y) ^a	$V_{\text{turn on}}$ (V)	Luminance (cd/m^2) ^b	Yield (cd/A) ^b	Yield (cd/A) ^c	Yield (cd/A) ^d
PFB2	(0.19,0.18)	5	3,955	1.62	1.21	0.86
PFB1	(0.20,0.18)	5	4,341	1.83	1.27	1.66
PFG1	(0.28,0.49)	6	10,186	5.62	2.92	4.6
PFR1	(0.63,0.31)	5	2,383	1.16	0.59	0.95
WPF1	(0.42,0.45)	5	3,644	5.24	1.10	4.15
WPF2	(0.45,0.40)	5	3,483	3.06	1.54	2.02
WPF3	(0.30,0.32)	5	6,697	3.66	1.93	3.37
WPF4	(0.31,0.31)	5	7,174	5.47	2.11	4.79
WPF5	(0.30,0.33)	5	7,551	6.21	1.73	5.46
WPF6	(0.22,0.22)	5	6,412	4.16	2.14	3.83

^a CIE coordination at 8 V.

^b Maximum luminance and yield.

^c Yield with current density at 300 mA/cm^2 .

^d Yield with luminance at 100 cd/m^2 .

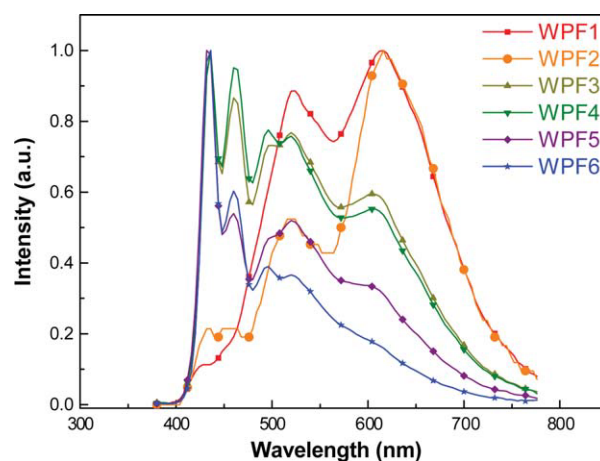


FIGURE 7 Electroluminescence spectra of white-light polymers WPFs at 8 V. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Electroluminescence

For evaluating the EL properties of these single WPFs, the devices with a configuration of ITO/PEDOT:PSS (30 nm)/TFB (15 nm)/light-emitting polymer (50~60 nm)/Cs (2 nm)/Al (100 nm) were fabricated. Figures 6 and 7 show the EL spectra of PLED devices with polymers PFs and WPFs as active layers, respectively. PFBs, PFG1, and PFR1 exhibited blue ($\lambda_{\text{max}} = 428$), green ($\lambda_{\text{max}} = 528$), and red ($\lambda_{\text{max}} = 618$) emissions, respectively. WPFs all exhibited simultaneous blue, green, and red emissions originating from the polyfluorene backbone, 2,1,3-benzothiadiazole unit, and 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole unit, respectively. The feed ratios of RGB PFs significant tuned the color of WPFs devices, and the white emission was achieved by fairly balance of RGB emissions. For EL spectra of polymers WPF1~2, the intensity of green and red peaks was much stronger than blue peak, leading to CIE coordinates in yellow light region (see Table 5). This might be attributed to the higher contents of green and red derivative units that introduced. Similarly, polymer WPF6 with higher content of blue derivative unit exhibited blue emission with CIE coordinates of (0.22, 0.22) presumably. The EL spectra of WPF3~5 showed white emission with

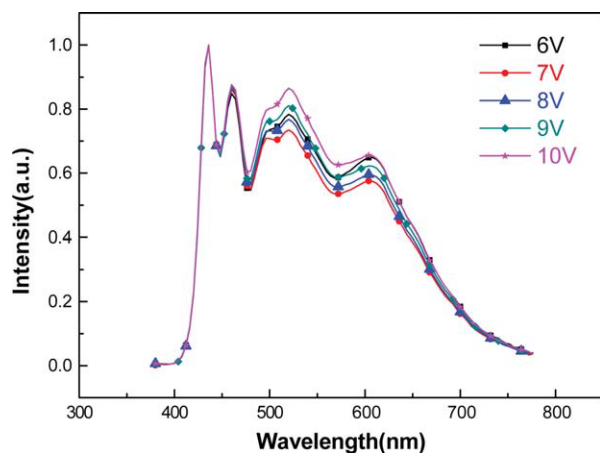


FIGURE 8 Electroluminescence spectra of white-light polymers WPF3 during bias scanning. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1931 CIE coordinates close to that (0.33, 0.33) of standard white emission [WPF3~5 at (0.30, 0.32), (0.31, 0.31) and (0.30, 0.33) at 8 V, respectively]. It is noteworthy that these white-light devi-

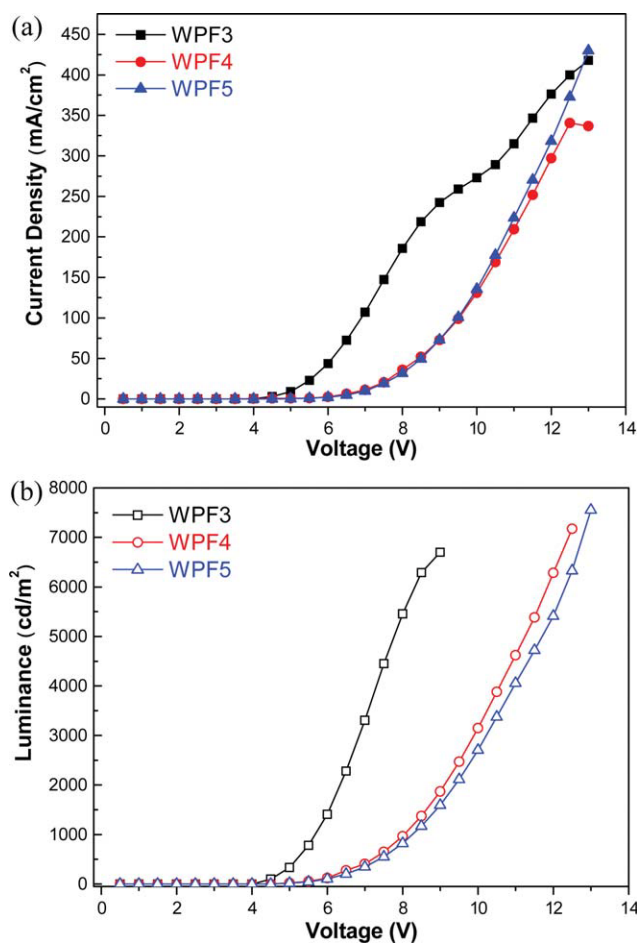


FIGURE 9 (a) Current density-voltage and (b) Luminance-voltage characteristics of white-light polymers WPF3~5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

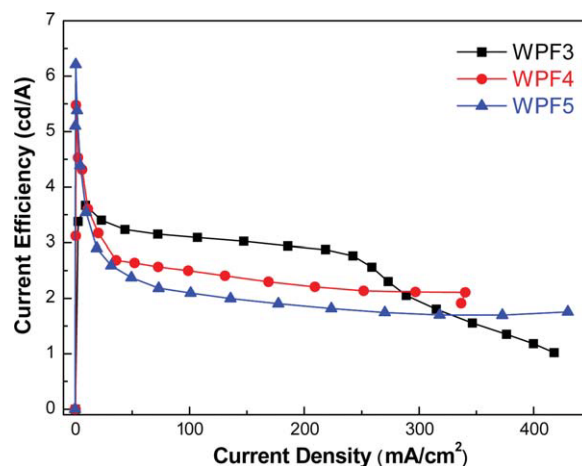


FIGURE 10 Current efficiency-current density characteristics of white-light polymers WPF3~5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ces displayed good color stability during the bias scanning. For example, as showed in Figure 8, the EL spectrum of WPF3 almost unchanged during the device operated from 6 to 10 V. As the result of fine tune for the emissive color, we will pay much attention to WPFs WPF3~5 in the following discussions.

Table 5 summarizes the device performances of all the polymers in the same fabricated condition. Figure 9 displays EL performance of white-light emitting devices using polymers WPF3~5 as emissive layer. A maximum brightness of 6697 cd/m^2 (at 10 V) and a maximum yield of 3.66 cd/A were performed from WPF3, while a maximum brightness of 7174 cd/m^2 (at 12.5 V) and a maximum yield of 5.47 cd/A were achieved by WPF4. WPF5 showed the highest brightness of 7555 cd/m^2 (at 13 V) and the maximum yield of 6.21 cd/A . As the presentation in Figure 10, the luminous efficiency-current density-brightness curves of these three white-light devices indicated the good stability of EL efficiency. For instance, device WPF4 demonstrated the maximum EL efficiency of 4.79 cd/A with the brightness of 100 cd/m^2 at the current density of 2.5 mA/cm^2 . Moreover, its EL efficiency still held at a good performance of 2.11 cd/A even with a high current density of 300 mA/cm^2 and brightness of 6335 cd/m^2 .

CONCLUSIONS

In this article, we have developed synthetic approaches to single-chain WPFs with 1,2,3-triazole-ring linkage through azide-alkyne cycloaddition (click reaction) using polyfluorene derivatives with azide and alkyne end-capped groups as reactants. The chemical structures of all the polymers were confirmed by ^1H NMR and FTIR spectra, and the results of these measurements also showed evidences to determine that the 1,2,3-triazole-ring linkages were formed within the resulting single-chain WPFs. The molecular weight of these novel polymers (WPFs) were about four to six times (even up to 18.8×10^4) than that of PFs due to the successful combination of four basic PFs. Electroluminescent devices have been constructed with a ITO/PEDOT/TFB/light-emitting polymer/Cs/Al configuration, in which hole-transporting TFB were coated by buffer-layer

technology to achieve convenient and inexpensive solution process for device fabrication. The devices fabricated from resulting polymers displayed white-light with blue, green and red emissions simultaneously; moreover, the EL spectra of these WPFs not only exhibited the CIE coordinates close to standard white light (0.31, 0.31) but also showed color and EL stability during the bias scanning. In all of our WPLED devices, the best EL performance with a maximum brightness of 7551 cd/m² and luminous efficiency as high as 6.21 cd/A was obtained on the device using polymer WPF5 as emitting material.

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