Conjugated Copolymers Comprised Cyanophenyl-Substituted Spirobifluorene and Tricarbazole-Triphenylamine Repeat Units for Blue-Light-Emitting Diodes

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ABSTRACT: A series of conjugated blue-light-emitting copolymers, PTC-1, PTC-2, and PTC-3, comprised different ratios of electron-withdrawing segments (spirobifluorene substituted with cyanophenyl groups) and electron-donating segments (tricarbazole-triphenylamines), has been synthesized. The structures of these polymers were characterized and their thermal, photophysical, electrochemical, and electroluminescence properties were measured. Incorporation of rigid spirobifluorene units into the copolymers led to blue-shifted absorption peaks in dilute toluene solution. Cyclic voltammetric measurement indicated the bandgaps of the polymers were in the range of 2.77–2.94 eV. It was found that increasing cyanophenyl-spirobifluorene content in the polymer backbone lowered both the HOMO and LUMO energy levels of the copolymers, which was beneficial for electron injection/ transporting in the polymer layer of the device. OLED device evaluation indicated that all the polymers emitted sky blue to deep blue light when the pure polymers were used as the emissive layers in the devices with a configuration of ITO/ PEDOT:PSS/polymers/CsF/Ca/AI. The devices have been optimized by doping 30 wt % PBD into the polymer layers. Among the doped devices, **PTC-2** showed the best performance with the turn-on voltage of 3.0 V, maximum brightness of 7257 cd/m², maximum current efficiency of 1.76 cd/A, and CIE coordinates of (0.15, 0.14). © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 292–301, 2010

KEYWORDS: charge transporting; conjugated polymers; cyanophenyl-spirobifluorene; doped devices; fluorescence; photophysics; polymer light-emitting diodes (PLEDs); tricarbazoletriphenylamine; UV-Vis spectroscopy

INTRODUCTION Fluorene-based polymers and oligomers have been considered as the candidates in organic electronic devices,¹ such as light-emitting diodes (LEDs),² solar cells,³ and field-effect transistors (FETs).⁴ Especially in LEDs, polyfluorenes have been broadly used as the emissive materials in polymeric light-emitting diodes (PLEDs) because of their good thermal stability, film-forming ability, and high electroluminescence (EL) efficiencies.² However, the classical poly (alkylfluorene) homopolymers suffer from poor spectral stability associated with keto defects in the polymer backbone or excimer emission.⁵ The common strategies, to address this issue, are introduction of bulky groups to the C-9 position of the fluorene unit, e.g., spirobifluorene, or copolymerization with suitable comonomers.⁶ The structural feature of 90° angle between the two connected fluorene moieties in spirobifluorene can significantly suppress the side effect of molecular packing.⁷ Attachment of additional substituents onto one fluorene unit of the spirobifluorene as the polymer side-chain can further retard the main-chain aggregation. Tang et al.^{7(d)} reported spirobifluorene trimers with peripheral carbazole groups, which exhibited pure blue emission with high quantum yield and good spectral stability. However, the device performance is not high, probably because of the unbalanced charge injection and transport. In this case, injection and transporting of holes are much easier than electrons due to the carbazole segments. To enhance the electron injection and transport, introduction of electronwithdrawing components into the polymers is proven to be effective. Among all the electron-withdrawing groups, cyano group, which possesses strong electron-withdrawing property and excellent luminescence efficiency,⁸ has been well investigated. Taranekar et al.⁹ reported a series of alternated

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SCHEME 1 Synthetic route for M1.

polymers with cyanofluorene groups emitted green to blue light with low turn-on voltages. Very recently, Zhen et al. reported a series of deep blue-light-emitting oligofluorenes containing carbazole-phenylamines and cyanophenyl groups. The carbazole-phenylamine and cyanophenyl segments balanced the hole and electron transport, thus resulted in very high efficient blue-light emission.¹⁰ In fact, carbazole and triphenylamine, as building blocks for light-emitting materials, not only help to enhance hole-transporting property but also improve thermal stability of the materials.¹¹

In this work, we report the synthesis of a series of copolymers PTC-1, PTC-2, and PTC-3, containing cyanophenyl substituted spirobifluorene and tricarbazole-triphenylamine with well-defined chemical structures and the characterization of the thermal, photophysical, electrochemical, and electroluminescent properties of the copolymers. The copolymers were prepared via the Suzuki coupling reaction with three comonomers: 2',7'-dibromo-2,7-bis(4'-cyanophenyl)-9,9'-spirobifluorene (M1), 4-(3,6-(di-9H-carbazol-9-yl)-9H-carbazol-9-yl)-4',4"-dibromotriphenylamine (M2), and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (M3). In M1, two cyanophenyl groups were attached onto one fluorene unit of the spirobifluorene. Such a design can not only enhance the electron transporting property but also suppress the intra- and intermolecular interaction. In M2, two carbazole segments were linked onto C-3 and C-6 positions of another carbazole incorporated with triphenylamine, so called tricarbazole-triphenylamine. The two monomers were not only conjugated but also separated by the alkyl substituted fluorene (M3), which could reduce the intramolecular interaction between the segments containing electron transporting moieties and hole-transporting moieties. With different feed ratios of M1 and M2, random copolymers PTC-1, PTC-2, and PTC-3 were synthesized to optimize the charge transporting properties of the copolymers. For comparison, two reference copolymers PSF and PTCF were also prepared. The electroluminescence (EL) performances of these copolymers were evaluated using two device configurations: ITO/PEDOT:PSS/ polymers/CsF/Ca/Al (**Device A**) and ITO/PEDOT:PSS/polymers:PBD/CsF/Ca/Al (**Device B**). **Device A** used the pure polymer as the emissive layer, and the other doped 30% of 2-(4-*tert*-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) in the emissive layer to further improve the device performance.¹² All the **Device B** exhibited better performance in comparison to **Device A**.

EXPERIMENTAL

General Information

Molecular weights [number-average (M_n) and weightaverage (M_w)] were determined with a Waters 2690 gel permeation chromatography (GPC) using a polystyrene standard eluting with tetrahydrofuran. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 spectrometer at a resonance frequency of 400 MHz for ¹H and 100 MHz for ¹³C in deuterated solution with a tetramethylsilane (TMS) as a reference for the chemical shifts. Elemental analyses were conducted on a Flash 1112 Series elemental analyzer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using TA instruments TGA-Q500 and DSC-Q100 modules, respectively. The glass-transition temperature (T_g) was recorded on the second heating curve. The UV-vis absorption and photoluminescence (PL) spectra were recorded on a Shimadzu UV-3101 scanning spectrophotometer and on a Perkin-Elmer LS 55 fluorescence spectrometer, respectively. Cyclic voltammetric measurements were conducted on a three-electrode AUTO-LAB (model PGSTAT30) workstation in a solution of $^{n}\text{Bu}_{4}\text{NPF}_{6}$ (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature.



SCHEME 2 Synthetic route for M2.



SCHEME 3 Synthetic route of the conjugated polymers.

3,6-Dibromo-9-(4-nitrophenyl)-9H-carbazole (3) were synthesized according to the literature reported.¹³ 2.7-Dibromo-9.9'spirobifluorene (1) was purchased from Pacific ChemSource. 4-Cyanophenylboronic acid and phenylboronic acid were bought from Boron Molecular. Copper(I) iodine and 1,10-phenanthroline were from Merck and Lancaster, respectively. Tin(II) chloride was obtained from Riedel deHaen. Tetrakistriphenylphosphine palladium(0) [Pd(PPh₃)₄] and palladium (II) acetate [Pd(OAc)₂] were purchased from Strem Chemicals. 1-Bromo-4iodobenzene was bought from Alfa Aesar. Iron(III) chloride, 1,1'-bis(diphenylphosphino)-ferrocene, tetrabutylammonium bromide, and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) were obtained from Aldrich. Bromine was obtained from Spectrum. Carbazole, sodium tert-butoxide and bromobenzene were purchased from Fluka. Sodium carbonate and potassium carbonate were bought from Fisher Scientific. All the solvents were A.R. grade and used without further purification.

Synthesis of Monomers

2,7-Bis(4'-cyanophenyl)-9,9'-spirobifluorene (2)

To a mixture of 2,7-dibromo-9,9'-spirobifluorene (1) (1.76 g, 3.7 mmol) and 4-cyanophenylboronic acid (2.04 g, 13.9 mmol), $Pd(PPh_3)_4$ (0.23 g, 0.20 mmol) was added in argon atmosphere. Toluene (32 mL) and 2 M Na₂CO₃ aqueous solution (16 mL) was added into the mixture and heated to reflux with continuous stirring in the dark for 24 h under the protection of nitrogen. After cooling to room temperature, the organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with water, brine, and dried over sodium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography eluting with nhexane/ethyl acetate (5:1) to give 2 as white powders (1.94 g)77.5%). ¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.98 (d, J = 8.0 Hz, 2H), 7.89 (d, J = 7.6 Hz, 2H), 7.64 (dd, J = 1.6, 8.0 Hz, 2H), 7.60 (d, J = 8.4 Hz, 4H), 7.52 (d, J = 8.4 Hz, 4H), 7.41 (t, J = 7.6 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 2H), 6.94 (s, 2H), 6.80 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 150.43, 147.96, 145.17, 141.85, 141.51, 139.29, 132.39, 128.15, 128.08, 127.63, 127.26, 124.08, 122.76, 120.90, 120.28, 118.79, 110.87, 66.11. Anal. Calcd. for $C_{39}H_{22}N_2$: C, 90.32; H, 4.28; N, 5.40. Found: C, 90.35; H, 4.41; N, 5.53.

2',7'-Dibromo-2,7-bis(4'-cyanophenyl)-9,9'spirobifluorene (M1)

To a solution of 2,7-bis(4'-cyanophenyl)-9,9'-spirobifluorene (2) (1.04 g, 2.0 mmol) in 25 mL of dichloromethane at 0 °C, 40 mg (0.3 mmol) of iron(III) chloride was added. A solution of bromine (0.71 g, 4.4 mmol) in 10 mL of dichloromethane was added into the stirring mixture dropwise at 0 °C. After stirring at room temperature for 48 h, the solution was cooled to 0 °C again, and an aqueous solution of sodium sulfite was added slowly till the dark color disappeared. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with brine and dried over sodium sulfate. The solvent was removed, and the residue was purified by column chromatography eluting with *n*-hexane/ethyl acetate (5:1) followed by recrystallization with ethanol to give **M1** (1.12 g, 82.5%).

¹H NMR (CDCl₃, 400 MHz, ppm) δ 7.99 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.69 (dd, J = 1.6, 8.0 Hz, 2H), 7.64 (d, J = 8.4 Hz, 4H), 7.53–7.57 (m, 6H), 6.91 (dd, J = 2.0, 6.8 Hz, 4H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 149.75, 148.66, 144.93, 141.37, 139.72, 139.67, 132.47, 131.64, 127.90, 127.72, 127.36, 122.75, 122.20, 121.73, 121.23, 118.74, 111.09, 65.71. m/z: 676 (M⁺, 100%), 679 (15%), 678 (42%), 677 (33%), 675 (19%), 674 (47%), 598 (11%), 597 (24%), 596 (12%), 595 (23%), 516 (15%), 515 (19%). Anal. Calcd. for C₃₉H₂₀Br₂N₂: C, 69.25; H, 2.98; N, 4.14. Found: C, 69.59; H, 3.02; N, 4.20.

3,6-(Di-9H-carbazol-9-yl)-9-(4-nitrophenyl)-9H-carbazole (4)

A mixture of 3,6-dibromo-9-(4-nitrophenyl)-9H-carbazole (**3**) (4.30 g, 9.6 mmol), carbazole (3.67 g, 21.9 mmol), copper(I) iodide (375 mg, 1.97 mmol), 1,10-phenanthroline (710 mg, 3.94 mmol), and potassium carbonate (5.98 g, 43.3 mmol) was purged with nitrogen and 28 mL of anhydrous DMF was added. The mixture was heated to reflux for 24 h. After cooled to room temperature, the dark solution was poured into ice-water. After filtration, the yellow solid obtained was recrystallized in dichloromethane/methanol to give **4** (5.10 g, 85.5%).

¹H NMR (CD₂Cl₂, 400 MHz, ppm) δ 8.61 (d, J = 9.2 Hz, 2H), 8.34 (d, J = 1.6 Hz, 2H), 8.18 (d, J = 8.0 Hz, 4H), 8.02 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 7.70 (dd, J = 1.8, 8.6 Hz, 2H), 7.43 (d, J = 3.6 Hz, 8H), 7.30 (m, 4H). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ 146.62, 143.18, 141.65, 139.71, 131.66, 127.14, 126.74, 125.97, 125.86, 124.87, 123.33, 120.17, 120.02, 119.91, 111.14, 109.56. Anal. Calcd. for C₄₂H₂₆N₄O₂: C, 81.54; H, 4.24; N, 9.06. Found: C, 81.55; H, 4.27; N, 9.01.

4-[(3,6-Di-9H-carbazol-9-yl)-9H-carbazol-9-yl]aniline (5)

To a solution of **4** (3.71 g, 6.0 mmol) in 250 mL of dry THF/ ethanol (1:1), added SnCl_2 (5.69 g, 30.0 mmol). The mixture was heated to reflux for 24 h. The solvent was removed under reduced pressure then the residue was neutralized slowly with cool 40 wt % NaOH. After the mixture became alkaline, 300 mL of toluene was added with stirring. The solid was removed by filtration and the aqueous layer of the filtrate was extracted with toluene twice (150 mL each time). The combined organic layer was washed with brine and dried over sodium sulfate. After the solvent was removed, off-white solid **5** was obtained (3.22 g, 91.4%).

¹H NMR (CD₂Cl₂, 400 MHz, ppm) δ 8.29 (s, 2H), 8.17 (d, 4H, J = 7.6 Hz), 7.62 (d, 4H, J = 1.2 Hz), 7.48 (d, 2H, J = 8.8 Hz), 7.42 (d, 8H, J = 3.6 Hz), 7.29 (m, 4H), 6.99 (d, 2H, J = 8.8 Hz), 4.06 (s, 2H). ¹³C NMR (CD₂Cl₂, 100 MHz, ppm) δ 147.44, 142.28, 141.85, 130.24, 128.82, 127.50, 126.35, 126.27, 123.97, 123.48, 120.53, 120.01, 119.93, 116.24, 111.75, 110.15. Anal. Calcd. for C₄₂H₂₈N₄: C, 85.69; H, 4.79; N, 9.52. Found: C, 85.64; H, 5.20; N, 9.16.

4-(3,6-(Di-9H-carbazol-9-yl)-9H-carbazol-9-yl)-4',4"-dibromotriphenylamine (M2)

A mixture of **5** (2.24 g, 3.8 mmol), 1-bromo-4-iodobenzene (2.80 g, 9.9 mmol), $Pd(OAc)_2$ (171 mg, 0.76 mmol), 1,1'-bis (diphenylphosphino)-ferrocene (845 mg, 1.52 mmol), and sodium *tert*-butoxide (1.46 g, 15.2 mmol) was purged with nitrogen and then added dry toluene (35 mL). The mixture was refluxed for 36 h in the dark and cooled to room temperature. The suspension was dispersed in 300 mL toluene and filtered to remove the solid. The filtrate was washed with water, brine, and dried over sodium sulfate. After the solvent was removed, the residue was purified by column chromatography with *n*-hexane/dichloromethane (4:1) to give **M2** as off-white solid (1.76 g, 51.4%).

¹H NMR (CD₂Cl₂, 400 MHz, ppm) δ 8.32 (s, 2H), 8.18 (d, 4H, J = 8.0 Hz), 7.73 (d, 2H, J = 8.4 Hz), 7.63–7.67 (m, 4H), 7.48 (d, 4H, J = 8.8 Hz), 7.42 (d, 8H, J = 4.0 Hz), 7.38 (d, 2H, J =8.8 Hz), 7.28–7.33 (m, 4H), 7.13 (d, 4H, J = 8.8 Hz). ¹³C NMR (CD₂Cl₂, 100 MHz, ppm) δ 146.83, 146.28, 141.84, 140.89, 132.62, 131.78, 130.29, 128.17, 126.16, 126.11, 125.89, 124.83, 123.93, 123.13, 120.17, 119.68, 119.67, 116.28, 111.36, 109.70. m/z (EI) 898 (M⁺, 100%), 902 (11%), 901 (29%), 900 (59%), 899 (56%), 897 (29%), 896 (47%), 822 (6%), 821 (18%), 820 (30%), 819 (19%), 818 (29%). Anal. Calcd. for C₅₄H₃₄Br₂N₄: C, 72.17; H, 3.81; N, 6.23. Found: C, 72.32; H, 4.08; N, 5.95.

Synthesis of Polymers

Taking the preparation of PTC-2 as an example: To a 25-mL round bottom flask charged with M1 (270.6 mg, 0.40 mmol), M2 (359.5 mg, 0.40 mmol), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (M3) (401.8 mg, 0.80 mmol), potassium carbonate (396.2 mg, 2.90 mmol), and tetrabutylammonium bromide (61.4 mg, 0.19 mmol) was added tetrakis(triphenylphosphine) palladium (2 mg) in glove-box. Degassed toluene (6.4 mL) and water (1.5 mL) was added into the mixture by syringe. After heating the mixture at 83 $^\circ\text{C}$ under nitrogen atmosphere for 42 h, excess phenylboronic acid and bromobenzene were added as end-capping reagents sequentially in 12 h interval. The mixture was extracted with chloroform for three times, and the combined organic extracts were washed with water, brine, and dried over sodium sulfate. The salt was filtered off, and the filtrate was concentrated into a small volume. The polymer solution was added dropwise into stirred methanol. After filtration, the collected solid was purified by reprecipitating into methanol and then Soxhlet extraction with acetone. The polymer was then dried under vacuum to give 557.2 mg of pale yellow solid with a yield of 72.4%. GPC (THF) $M_{\rm p} = 29.5$ kDa, $M_{\rm w} = 48.0$ kDa, PDI = 1.63.

¹H NMR (CD₂Cl₂, 400 MHz, ppm) δ 8.32 (s, 2H), 8.18 (d, 4H, J = 7.6 Hz), 8.03–8.09 (m, 4H), 7.29–7.74 (m, 52H), 7.09–7.16 (m, 4H), 1.93–2.01 (m, 8H), 0.92–1.09 (m, 24H), 0.52–0.77 (m, 20H). Anal. Calcd. for [C₁₄₃H₁₁₈N₆]_n: C, 89.43; H, 6.19; N, 4.38. Found: C, 88.81; H, 6.25; N, 4.25.

PSF. M1 (270.5 mg, 0.40 mmol) and **M3** (200.9 mg, 0.40 mmol) were used for preparation of **PSF** and 283.0 mg of light-yellow solid were obtained with a yield of 83.3%. GPC (THF) $M_n = 4.6$ kDa, $M_w = 5.9$ kDa, PDI = 1.28.

¹H NMR (CD₂Cl₂, 400 MHz, ppm) δ 8.01–8.10 (m, 4H), 7.35–7.76 (m, 18H), 7.05–7.15 (m, 4H), 1.92 (br, 4H), 0.92–0.99 (m, 12H), 0.52–0.71 (m, 10H). Anal. Calcd. for [C₆₄H₅₂N₂]_n: C, 90.53; H, 6.17; N, 3.30. Found: C, 90.41; H, 6.41; N, 3.17.

PTC-1. M1 (202.9 mg, 0.30 mmol), **M2** (134.8 mg, 0.15 mmol) and **M3** (226.0 mg, 0.45 mmol) were used for preparation of **PTC-1** and 314.3 mg of pale yellow solid were obtained with a yield of 75.6%. GPC (THF) $M_{\rm n} = 11.0$ kDa, $M_{\rm w} = 16.5$ kDa, PDI = 1.50.

¹H NMR (CD₂Cl₂, 400 MHz, ppm) δ 8.32 (s, 2H), 8.18 (d, 4H, J = 7.6 Hz), 8.02–8.12 (m, 8H), 7.26–7.76 (m, 70H), 7.07–7.16 (m, 8H), 1.92–2.10 (m, 12H), 0.92–1.05 (m, 36H), 0.63–0.77 (m, 30H). Anal. Calcd. for [C₂₀₇H₁₇₀N₈]_n: C, 89.77; H, 6.19; N, 4.05. Found: C, 89.73; H, 6.32; N, 3.95.

PTC-3. M1 (101.5 mg, 0.15 mmol), **M2** (269.6 mg, 0.30 mmol), and **M3** (226.0 mg, 0.45 mmol) were used for preparation of **PTC-3**, and 339.7 mg of pale yellow solid were obtained with a yield of 75.7%. GPC (THF) $M_n = 15.6$ kDa, $M_w = 25.0$ kDa, PDI = 1.60.

¹H NMR (CD₂Cl₂, 400 MHz, ppm) δ 8.32 (s, 4H), 8.18 (d, 8H, J = 7.6 Hz), 8.05–8.11 (m, 4H), 7.306–7.82 (m, 86H), 7.07–7.16 (m, 4H), 2.01–2.10 (d, br, 12H), 0.92–1.10 (m, 36H), 0.53–0.77 (m, 30H). Anal. Calcd. for [C₂₂₂H₁₈₄N₁₀]_n: C, 89.12; H, 6.20; N, 4.68. Found: C, 89.01; H, 6.34; N, 4.66.

PTCF. M2 (359.5 mg, 0.40 mmol) and **M3** (200.9 mg, 0.40 mmol) were used for preparation of **PTCF**, and 178.6 mg of pale yellow solid were obtained with a yield of 41.7%. GPC (THF) $M_n = 17.1$ kDa, $M_w = 27.4$ kDa, PDI = 1.60.

¹H NMR (CD₂Cl₂, 400 MHz, ppm) δ 8.31 (s, 2H), 8.17 (d, br, 4H), 7.29–7.80 (m, 34H), 2.10 (d, br, 4H), 1.10 (br, 12H), 0.77 (br, 10H). Anal. Calcd. for [C₇₉H₆₆N₄]_n: C, 88.56; H, 6.21; N, 5.23. Found: C, 88.59; H, 6.38; N, 5.06.

Device Fabrication and Performance Measurements

The PLEDs were fabricated on indium tin oxide (ITO)-coated glass substrates. The substrates were precleaned sequentially in detergent solution, distilled water, acetone, and methanol in an ultrasonic bath. The cleaned substrates were treated with oxygen-argon plasma and spin coated with 50nm of (PEDOT:PSS), followed by drying at 120 °C in air for 30 min to remove residual water. For Device A, as shown in the inset of Figure 5(a), the polymers were spin coated from a chloroform solution onto the ITO/PEDOT:PSS surface and annealed at 120 $\,^\circ\text{C}$ for 30 min to form a 80-nm thick emitting layer. For Device B, as shown in the inset of Figure 6(a), a solution of 70 wt % polymer and 30 wt % PBD in chloroform, which was prefiltered through Teflon filter (0.45 μ m), was then spin coated on top of the PEDOT:PSS layer followed by annealing at 120 °C for 30 min to form a 80-nm thick emitting layer. A 1-nm thick CsF buffer layer was grown through thermal sublimation in a vacuum of 1 \times 10^{-5} Pa onto the emitting layer both in **Devices A** and **B**. The cathode was composed of 10 nm Ca and 100 nm Al, which were successively thermally deposited. The corresponding configuration of Device A was ITO/PEDOT:PSS (50 nm)/polymers (80 nm)/CsF (1 nm)/Ca (20 nm)/Al (100 nm), whereas that of Device B was ITO/PEDOT:PSS (50 nm)/polymers:PBD (80 nm)/CsF (1 nm)/Ca (20 nm)/Al (100 nm). The steady-state current-voltage-luminance (I-V-L) characteristics were recorded using a Keithley 2400 source meter with a calibrated Si photodiode. The EL spectra were measured by a PR650 SpectraScan spectrophotometer. All measurements were carried out at room temperature under ambient conditions.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic routes to the monomers (**M1** and **M2**) and polymers are shown in Schemes 1–3. 2,7-Dibromo-9,9'-spirobifluorene (**1**) reacted with 4-cyanophenylboronic acid to afford 2,7-bis(4'-cyanophenyl)-9,9'-spirobifluorene (**2**) using Suzuki coupling reaction at the presence of palladium (0) catalyst. **M1** was obtained through bromination of Compound **2** by using appropriate amount of bromine catalyzed by FeCl₃. 3,6-(Di-9H-carbazol-9-yl)-9-(4-nitrophenyl)-9H-carbazole (**4**) was prepared by the Ullmann reaction between 3,6-dibromo-9-(4-nitrophenyl)-9H-carbazole (**3**) and carbazole. **4** was reduced to 4-[(3,6-di-9H-carbazol-9-yl)-9H-carbazol-9-yl]aniline (**5**) by using SnCl₂. The key monomer **M2** was obtained by Ullmann reaction between **5** and 1-bromo-4-iodobenzene, using palladium(II) acetate as a catalyst. The polymers with different ratios of comonomers were prepared between M1 and M2 were 1:0, 2:1, 1:1, 1:2, and 0:1 in PSF, PTC-1, PTC-2, PTC-3, and PTCF, respectively. The yields were 41.7-83.3%. All the polymers showed good solubility in toluene, dichloromethane, chloroform, and tetrahydrofuran and could be spin coated into high-quality films for device fabrication. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the polymers were in the range of 4600-29,500 and 5900-48,000, respectively, with the polydispersity indexes of 1.28-1.63. PSF, which was composed of M1 and M3, precipitated from solution during the polymerization propagation. It is easy to understand that PSF demonstrated the lowest molecular weight $(M_w/M_n = 5900/4600)$ compared with other polymers due to its poor solubility. The chemical structures of the intermediates and monomers were characterized by ¹H and ¹³C NMR spectra. The ¹H NMR spectra of the copolymers were consistent with their statistic chemical structures. We found that the actual molar ratio of the monomers in each polymer calculated from ¹H NMR is in good agreement with the corresponding feed molar ratio. The ¹H and ¹³C NMR spectra are shown in the Supporting Information (SI). Thermal properties of the polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. The spectra are shown in Figures 1 and 2. The decomposed temperatures ($T_{\rm d}$ s, 5 wt % loss) of the polymers are higher than 400 °C. The first \sim 20% weight loss from 400 to 480 °C is assigned to the decomposition of alkyl groups. The glass-transition temperatures (T_{gs}) are all higher than 250 °C. The TGA and DSC results indicate that the polymers possess extremely good thermal stability. The physical properties of all the polymers are summarized in Table S1.

via the Suzuki coupling reaction. The feed molar ratios

Optical and Photoluminescence Properties

The normalized UV-vis absorption and photoluminescence (PL) spectra of the polymers in dilute (10^{-6} M) toluene solution are shown in Figure 3(a). The absorption maxima are in the range of 359–372 nm corresponding to the π - π * transition of the polymer backbone. The absorption bands are red shifted gradually with increasing the content of tricarbazoletriphenylamines. Thus, PTCF, which is composed of only tricarbazole-triphenylamine repeating unit and 9,9-dihexylfluorene repeating unit, shows the absorption maximum at 372 nm, which is the longest wavelength among the polymers, suggesting relatively longest π -conjugation.¹⁴ The absorption shoulders at about 346 nm of PTC-1, PTC-2, PTC-3, and PTCF could be ascribed to the carbazole absorption.¹⁵ In PL emission spectra, PSF has the shortest emission peak at 414 nm with a vibronic shoulder at around 436 nm. The other four polymers have the main emission peaks at 422-423 nm with small shoulders at 443 nm. From the absorption and PL emission spectra, the Stokes shifts of PTC-1, PTC-2, and PTC-3 were calculated to be 61, 57, and 54 nm, respectively, which are larger than that of PSF and PTCF. The larger Stokes shifts in the three copolymers might suggest that incorporation of both M1 and M2 into the polymer backbone causes a larger geometric conformation change from the



FIGURE 1 TGA curves of the polymers recorded under flowing nitrogen conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ground states to excited states in solutions:¹⁶ higher content of **M1**, larger geometric conformation caused. The corresponding fluorescence quantum yields (Φ_f) of the polymers were determined by using quinine sulfate ($\Phi = 0.55$) as a reference according to the method reported.¹⁷ The fluorescence and absorption of quinine sulfate were measured in a 0.1 M sulfuric acid aqueous solution. PL quantum yields of the polymers were measured in dilute toluene solution. As shown in Table S1, the fluorescence quantum yields of **PSF**, **PTC-1**, **PTC-3**, and **PTCF** are 0.79, 0.75, 0.82, 0.66, and 0.60, respectively.

Figure 3b shows the normalized UV-vis and PL spectra of the copolymers in thin films. The absorption maxima are in the range of 370–375 nm. The maximum absorption wavelength shifts of **PSF**, **PTC-1**, **PTC-2**, **PTC-3**, and **PTCF** from dilute solutions to thin films are 13, 10, 5, 2, and 3 nm, respectively, indicating that weak aggregation effect existed in the **PSF** film could be fully suppressed by incorporation of



FIGURE 2 DSC measurements of the polymers recorded under flowing nitrogen atmosphere.



FIGURE 3 UV-Vis absorption and PL emission spectra for the polymers (a) in dilute toluene solution (10^{-6} mol/L) and (b) in thin film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tricarbazole-triphenylamine segments into the polymer backbone. In the emission spectra, 10–23 nm of red shifts were observed in the solid states compared with that in dilute solutions, indicating the excitons could transfer the energy to lower energy site before radiation occurred in the solid state.¹⁸ The copolymer **PTC-1**, **PTC-2**, and **PTC-3** showed more red-shifted emissions and larger Stokes shifts than both **PSF** and **PTCF**, which could be ascribed to larger geometric conformation change from the ground states to excited states in thin films as explained above. Moreover, the red shifts of **PTC-1**, **PTC-2**, and **PTC-3** in comparison with the homopolymers are only observed in emission spectra but not in absorption spectra and also suggest that no intramolecular charge transfer (ICT) from the electron-donating component to electron-withdrawing component exists in the copolymers.¹⁹

Electrochemical Properties

Cyclic voltammetry (CV) experiments were carried out to investigate the electrochemical properties of the polymers. The CV curves of **PSF**, **PTC-1**, **PTC-2**, **PTC-3**, and **PTCF** are shown in Figure 4. Both the reduction and oxidation cycles of the polymer films were measured in acetonitrile conducting with tetrabutylammonium hexafluorophosphate as the electrolyte. Polymer solutions were coated on the surface of



FIGURE 4 Cyclic voltammograms of the polymers in solid states, collected in 0.1 M nBu_4NPF_6 acetonitrile solution at room temperature. Scan rate: 100 mV s⁻¹.

the working electrode by drop-casting method. All the polymers displayed reversible reduction and oxidation processes, suggesting good electrochemical stability for the electronwithdrawing/donating segments in the polymers. The onset oxidation potentials of the polymers measured from the CV traces are in the range of 0.89-1.42 V. The onset reduction potentials of the polymers changed from -1.35 to -2.04 V with decreasing content of cyanophenyl-spirobifluorene units. The PSF, whose structure is dominated by the electron-withdrawing units, has the highest onset reduction potential of -1.35 V, indicating the strongest electron-withdrawing property. PTC-2, PTC-3, and PTCF, containing more tricarbazole-triphenylamine units than cyanophenyl-spirobifluorene units, demonstrate very close onset reduction/ oxidation potentials, indicating they have similar charge injecting and transporting properties. The bandgaps of the polymers were calculated based on the onset reduction and onset oxidation potentials and found to be from 2.77 to 2.94 eV. The bandgaps were tuned by the ratios of M1 and M2: the polymer without M2 had the lowest bandgap whereas incorporation of M2 into the polymer backbone could raise the bandgaps compared with PSF. This indicates that incorporation of M2 moieties into the polymer backbone can improve the color quality for blue-light emission. With ferrocene as the external standard ($E_{\text{onset}}^{\text{ox}}$ was found to be 0.51 V), the HOMO levels of the polymers were calculated to be

from -5.18 to -5.71 eV using the equation of HOMO= -4.8 – ($E_{\text{onset}}^{\text{ox}}$ – 0.51) eV. Meanwhile, the calculated LUMO levels of the polymers lay between -2.25 and -2.94 eV. The electrochemical measurement results were summarized in Table S2. When tricarbazole-triphenylamine units were incorporated into the copolymers, both HOMO and LUMO levels increased significantly, compared with homopolymer **PSF**. The HOMOs and LUMOs for **PTC-1**, **PTC-2**, and **PTC-3** are in the range of -5.18 to -5.32 eV and -2.25 to -2.41 eV, respectively, which are lowered by about 0.5 eV and 0.7 eV than that for **PSF**, suggesting that the HOMO/LUMO energy levels of the copolymers are dominated by the electron-donating moieties in the polymer backbones.

Electroluminescence Properties

To investigate the electroluminescence properties of the polymers, two types of devices were fabricated: one used pure polymer films as the emissive layer and the other used PBD-doped polymers. The corresponding device structures are ITO/PEDOT:PSS/polymers/CsF/Ca/Al (Device A) and ITO/PEDOT:PSS/polymers:PBD/CsF/Ca/Al (Device B). In both device configurations, poly (ethylenedioxy)thiophene mixed with poly(styrene sulfonic acid) (PEDOT:PSS) was used as the hole injection layer (50 nm). The emissive layer was 80 nm, and cesium-fluoride (CsF) (1 nm) was used as the electron-injection layer. The 20 nm of Ca and 100 nm of Al were deposited onto CsF layer as the cathode. With the configuration of Device A, as summarized in Table S3, the reference polymer PTCF presented the highest turn-on voltage and brightness but the lowest maximum current efficiency and power efficiency, which should be ascribed to the poor electron transporting property of the polymer. Another reference polymer PSF showed the lowest maximum luminance because of poor hole transporting. Incorporation of both M1 and M2 into the polymers facilitates the tunability of the electroluminescence properties such as the turn-on voltages, luminance, current and power efficiencies, EL spectra, and CIE coordinates. Among the five polymers, PTC-1 showed the highest current efficiency of 0.99 cd/A, which is \sim 50% higher than that for the devices based on the two reference polymers, suggesting relatively balanced electron/ hole transportation. All these polymers exhibit good spectral stability during device operated at different voltages. Figure 5(d) shows the EL spectra of these polymers at the applied voltage of 8 V. It can be observed that the EL maxima of the polymers are all red shifted compared with their PL spectra in thin films. The difference between the PL and EL spectra is caused by the different emission mechanism: the PL emission only involves exciton migration and relaxation, but in EL both charge migration and energy transfer are involved.²⁰ In addition, the formation of eximers could be another reason. The EL maxima of PSF (488 nm), PTC-1 (488 nm), and PTC-2 (484 nm) are in the sky blue region.

To obtain higher performance, devices with optimized structures (**Device B**) with the configuration of ITO/PEDOT:PSS/ polymers:PBD/CsF/Ca/Al were fabricated in which the emissive layer contained 70% of polymers and 30% of PBD [5biphenyl-2-(4-tert-butyl)phenyl-1,3,4-oxadiazole)], because



FIGURE 5 (a) Current density versus applied bias voltage (inset: device configuration of ITO/PEDOT:PSS/polymers/CsF/Ca/AI); (b) luminance versus applied bias voltage; (c) current efficiency versus current density; and (d) the normalized EL spectra of the polymers recorded at the voltage of 8 V.



FIGURE 6 (a) Current density versus applied bias voltage (inset: device configuration of ITO/PEDOT:PSS/polymers:PBD/CsF/Ca/ AI); (b) luminance versus applied bias voltage; (c) current efficiency versus current density for devices; and (d) the normalized EL spectra of the polymers mixed with PBD recorded at the voltage of 8 V.

PBD can help to confine the holes in the emissive layer by blocking the holes migrating to cathode side. In addition, PBD can narrow the emissive spectrum to achieve better color quality for blue emission.¹² The results of the devices doped with PBD were summarized in Table S4 and the I-V-L plots were shown in Figure 6(a-c). As expected, the doped devices exhibited improved performances in comparison with the pure polymer-based devices: higher luminance, higher current efficiencies and power efficiencies, and deeper blue EL spectra. Except PTC-1, all the polymers showed lower turn-on voltages. Compared with the pure polymerbased devices, the maximum brightness has been raised by 25-174%; the highest current efficiencies were improved by 0.3-1.3 times. Among them, PTC-1 and PTC-2 demonstrated similar current efficiency. However, PTC-2 showed higher luminance and better power efficiency. The EL spectra of the optimized devices driven at 8 V are shown in Figure 6(d). All the polymers showed blue-shifted emissions. The x + yvalues of the CIE coordinates of the undoped devices are in the range of 0.36-0.53. The values are significantly reduced to 0.26-0.40 in Device B. All the polymers, except PTC-1, emitted pure blue to deep blue light in Device B. All the results indicated that doping PBD was an effective approach to improve the device performance and suppress the formation of excimers in the emissive layer. Among the polymers, PTC-2 showed the best performance with the turn-on voltage of 3.0 V, maximum brightness of 7257 cd/m^2 , current efficiency of 1.76 cd/A, power efficiency of 1.30 lm/W, and EL emission peak at 460 nm with the CIE coordinates of (0.15, 0.14).

CONCLUSIONS

A series of conjugated blue-light-emitting copolymers PTC-1, PTC-2, and PTC-3 containing cyanophenyl substituted spirobifluorenes and tricarbazole-triphenylamines has been designed and synthesized. For comparison, two reference polymers PSF and PTCF were also prepared. The feed ratios of two monomers (2',7'-dibromo-2,7-bis(4'-cyanophenyl)-9,9'-spirobifluorene and 4-(3,6-(di-9H-carbazol-9-yl)-9Hcarbazol-9-yl)-4',4"-dibromotriphenylamine) in PSF, PTC-1, PTC-2, PTC-3, and PTCF were varied from 1:0, 2:1, 1:1, 1:2, to 0:1, respectively. TGA and DSC analyses indicated that all the polymers had good thermal stabilities: the decomposed temperatures (T_d s, 5 wt % loss) and the glass-transition temperatures (T_{os}) of the polymers are higher than 400 °C and 250 °C, respectively. The fluorescence quantum yields of the polymers measured in dilute toluene solution are in the range of 60-82%. Investigation of the cyclic voltammetric behaviors of the polymer films revealed that the band gaps of the polymers are from 2.77 to 2.94 eV. The higher the content of the cyanophenyl-spirobifluorene, the lower HOMO and LUMO energy levels were obtained. The EL performances of the three copolymers and two reference polymers were evaluated with two device configurations: ITO/PEDOT:PSS/polymers/CsF/ Ca/Al (Device A) and ITO/PEDOT:PSS/polymers(70%):PBD (30%)/CsF/Ca/Al (**Device B**). The polymers emitted sky blue light when the pure polymers were used as the emissive

layers. In comparison with the pure polymer-based devices, the polymers in **Device B** with 30 wt % of PBD in the active layers showed improved device performance. The maximum current efficiencies were improved by 0.3–1.3 folds, and the brightnesses were increased by 25–174%. In addition, all the polymers emitted deep blue light with x + y values of about 0.30. Among all the polymers, **PTC-2** demonstrated the best performance with the highest brightness of 7257 cd/m², maximum current efficiency of 1.76 cd/A, power efficiency of 1.30 lm/w, and CIE coordinates of (0.15, 0.14).

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