Novel fluorene-based light-emitting copolymers containing cyanophenyl pendants and carbazole-triphenylamines: Synthesis, characterization and their PLED application

Ying Lin [a,b], Zhi-Kuan Chen [a,*], Teng-Ling Ye [c], Yan-Feng Dai [a,c], Dong-Ge Ma [c], Zhun Ma [a], Qin-De Liu [a], Yu Chen [b,**]

[a] Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore
[b] Department of Chemistry, Lab for Advanced Materials, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People's Republic of China
[c] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Graduate School of the Chinese Academy of Sciences, Changchun 130022, People's Republic of China

ARTICLE INFO

ABSTRACT

A series of novel blue light-emitting copolymers **PCC-1**, **PCC-2**, and **PCC-3**, composed of different ratios of electron-withdrawing segments (spirobifluorene substituted with cyanophenyl groups) and electron-donating segments (carbazole-triphenylamines), has been synthesized and characterized. In order to investigate the effect of hole/electron charge transporting segments, two reference polymers **PSF** and **PCF**, containing only one charge transporting moiety in the polymer backbone, were also synthesized. Incorporation of the rigid spirobifluorene units substituted with cyanophenyl groups into the polymer backbone improved not only the thermal stabilities but also the photoluminescence efficiencies. The polymers except **PSF** possess similar hole injection barriers but different hole transporting abilities. With the device configuration of ITO/PEDOT:PSS/polymers:PBD/CsF/Ca/Al, **PCC-2** showed the best performance with the lowest turn-on voltage of 3.1 V, the highest luminance of 6369 cd/m^2, the highest current efficiency of 1.97 cd/A, and the best power efficiency of 1.40 lm/w.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Since the first report of polymer light-emitting diodes (PLEDs) [1], fabricating ultrathin, full-color, and large-area displays have stimulated intense research interest and tremendous progress in the last decade [2]. The solution processability for PLEDs allows the fabrication of product by printing techniques, e.g. inkjet printing, which is more cost friendly and commercially viable compared with vacuum deposition process [3]. To realize PLED-based displays, high performance blue, green and red light-emitting polymers are required. In comparison with red [4] and green [5] emitters, only a few blue light-emitting polymers show promising applications for PLEDs [6]. Thus, development of stable and efficient blue light-emitting polymers is urgently required.

Among all the conjugated polymers investigated in PLEDs so far, polyfluorenes (PFs) have been recognized as promising candidates

for blue emitters due to their high photoluminescence efficiency, good chemical and thermal stability [7]. In the family of PFs, spirobifluorene with unusual rigid three-dimensional structure exhibits excellent thermal and spectral stability [8]. The properties of spirobifluorene could be easily tuned by attaching different functional groups onto either fluorene unit. In the past decade, a number of spirobifluorene-based light-emitting materials have been developed [9–12].

In the PLED device, the balance of electron/hole transport through the device is critical. It can be achieved by fabricating multilayer devices through incorporating charge transporting layer(s), or doping charge transporting materials into the emissive layer, or introducing electron withdrawing/donating segments into the backbones of emitting polymers [13]. From the synthetic point of view, incorporating electron and/or hole transporting monomers into polymer backbone is a common and effective approach. As for the hole-transporting moieties, triphenylamines (TPAs) and carbazole derivatives have been often used [14]. For the electron-withdrawing segments, a great number of groups have been investigated, such as pyridine [15], oxadiazole [16], cyano group [17], triazole [18], etc. Among them, the cyano group has been widely used because of its strong electron withdrawing property

* Corresponding author. Tel.: +65 6874 4331; fax: +65 6872 0785.
** Corresponding author.
   E-mail addresses: zk-chen@imre.a-star.edu.sg (Z.-K. Chen), chentangyu@yahoo.com (Y. Chen).

and good luminescence efficiency [19,20]. Polymers containing only electron-donating segment or only electron-withdrawing segment showed poor device performance. Jenekhe et al. [16e] compared the performances of poly[fluorenevinylene–diphenyloxadiazole], poly[fluorenevinylene–triphenylamine] and the polymer comprised both functional segments, and found that the bipolar copolymer showed better efficiency (1.34 cd/A) over those of poly(oxadiazole–fluorene) (0.83 cd/A) and poly(triphenylamine-fluorene) (0.80 cd/A), when the poly(N-vinylcarbazole) (PVK) was used as the host material. Jin et al [17c] reported three copolymers composed of fluorene units and strong electron-withdrawing cyano groups. The copolymers emitted yellow to orange light rather than blue light. These "hole-only" or "electron-only" materials showed either low efficiencies or undesirable emitting color. Therefore, the polymers containing both electron-donating and electron-withdrawing segments could overcome the drawbacks of the materials discussed above.

In this work, we report a series of fluorene-based copolymers, consisting of cyanophenyl groups as electron transporting pendants and carbazole-triphenylamines comonomer as hole transporting segments. 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-(9H-carbazol-9-yl)-4′,4″-dibromotriphenylamine (**M2**), and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (**M3**). In the monomer **M1** [21], the two cyano groups are attached onto one of the fluorene units in spirobifluorene through a phenylene group. Such a design can enhance the electron transporting property of the polymer but avoid strong intramolecular interaction. Generally, strong intra- and/or inter-molecular interaction will lead to large red shift of emission spectrum and reduced efficiency, and is thus undesirable for blue light emitting materials. **M2**, containing the carbazole-triphenylamine basic structure, has outstanding hole transporting character. These two monomers were conjugated but also separated by the alkyl substituted fluorene (**M3**), which can further reduce the intramolecular interaction. With different feed ratios of **M1** and **M2**, random copolymers **PCC-1**, **PCC-2**, and **PCC-3** were synthesized. For comparison, two reference copolymers **PSF** and **PCF** were also prepared. The electroluminescence (EL) performances of these copolymers were evaluated using two device configurations: ITO/PEDOT:PSS/polymers/CsF/Ca/Al and ITO/PEDOT:PSS/polymers:PBD/CsF/Ca/Al. One used the pure polymer as the emissive layer, and the other used 30% of 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) doped in polymer to form the emissive layer to raise the device performance, such as the color purity and EL efficiency [22]. With the later device configuration, maximum luminance of 6369 cd/m^2 and the highest current efficiency of 1.97 cd/A for **PCC-2** were achieved.

2. Experimental section

2.1. Materials

2,7-Dibromo-9,9′-spirobifluorene (**1**) was purchased from Pacific ChemSource. 4-Carbazol-9-yl-phenylamine (**4**) was synthesized according to the literature reported [14a]. 4-Cyanophenylboronic acid and phenylboronic acid were bought from Boron Molecular. Tetrakistriphenylphosphine palladium [Pd^0(PPh$_3$)$_4$] and palladium acetate [Pd(OAc)$_2$] were purchased from Strem Chemicals. 1-Bromo-4-iodobenzene was bought from Alfa Aesar. 1,1′-Bis(diphenylphosphino)-ferrocene, tetrabutylammonium bromide, and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) were obtained from Aldrich. Sodium *tert*-butoxide and bromobenzene were commercial available from Fluka. All the solvents were A.R. grade and used without further purification.

Synthesis of 2,7-Bis(4′-cyanophenyl)-9,9′-spirobifluorene (**2**) [21]: 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 Na$_2$CO$_3$ (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 with *n*-hexane/ethyl acetate (5:1) as eluent to give **2** as a white powder (1.94 g, 77.5%). ^{1}H NMR (CDCl$_3$, 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). ^{13}C NMR (CDCl$_3$, 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.

Synthesis of 2′,7′-Dibromo-2,7-bis(4′-cyanophenyl)-9,9′-spirobifluorene (**M1**) [21]: 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 recrystalization with ethanol to give **M1** (1.12 g, 82.5%). ^{1}H NMR (CDCl$_3$, 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). ^{13}C NMR (CDCl$_3$, 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. Anal. Calcd for C$_{39}$H$_{20}$Br$_2$N$_2$: C, 69.25; H, 2.98; N, 4.14. Found: C, 69.59; H, 3.02; N, 4.20.

Synthesis of 4-(9H-Carbazol-9-yl)-4′,4″-dibromotriphenylamine (**M2**): A mixture of 4-carbazol-9-yl-aniline (**3**) (1.29 g, 5.0 mmol), 1-bromo-4-iodobenzene (3.39 g, 12.0 mmol), Pd(OAc)$_2$ (224.5 mg, 1.0 mmol), 1,1′-bis(diphenylphosphino)–ferrocene (1.11 g, 2.0 mmol) and sodium *tert*-butoxide (1.92 g, 20.0 mmol) was purged with nitrogen, and then dry toluene (20 mL) was added. The mixture was refluxed for 24 h in the dark under nitrogen protection. The suspension was dispersed in 100 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 white solid (464 mg, 16.3%). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, ppm) δ 8.16 (d, J = 7.6 Hz, 2H), 7.45 (m, 10H), 7.30 (m, 4H), 7.09 (d, J = 8.8 Hz, 4H). ^{13}C NMR (CD$_2$Cl$_2$, 100 MHz, ppm) δ 146.39, 146.11, 141.00, 132.66, 132.50, 128.05, 125.90, 125.88, 124.99, 123.25, 120.18, 119.85, 115.95, 109.72. Anal. Calcd for C$_{30}$H$_{20}$Br$_2$N$_2$: C, 63.40; H, 3.55; N, 4.93. Found: C, 64.34; H, 3.70; N, 4.96.

*General Procedures for Suzuki Polymerization Taking **PSF** as an Example*: To a 25 mL round bottom flask charged with **M1** (270.5 mg, 0.40 mmol), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (**M3**) (200.9 mg, 0.40 mmol), potassium carbonate (198.1 mg, 1.45 mmol) and tetrabutylammonium bromide (30.72 mg, 0.10 mmol) was added Pd(PPh$_3$)$_4$ (1.2 mg) in glove-box. Degassed toluene (3.5 mL) and water (0.8 mL) was added into the mixture by syringe. After
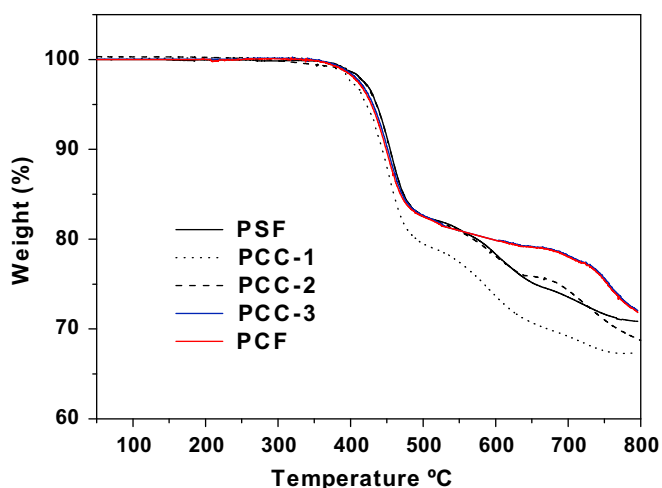
Fig. 1. TGA curves of the polymers recorded under flowing nitrogen conditions.

heating the mixture at 83 °C under nitrogen atmosphere for 42 h, excess phenylboronic acid and bromobenzene were added as end-capping reagents. 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 dried under vacuum to give 283.0 mg of light yellow solid with a yield of 83.3%. GPC (THF) $M_n = 4.6$ kDa, $M_w = 5.9$ kDa, PDI = 1.28. ^{1}H NMR (CD$_2$Cl$_2$, 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 [C$_{64}$H$_{52}$N$_2$]$_n$: C, 90.53; H, 6.17; N, 3.30. Found: C, 90.41; H, 6.41; N, 3.17.

PCC-1: **M1** (202.9 mg, 0.30 mmol), **M2** (85.2 mg, 0.15 mmol), **M3** (226.0 mg, 0.45 mmol), 299.1 mg of light yellow solid, yield 81.7%. GPC (THF) $M_n = 12.9$ kDa, $M_w = 22.8$ kDa, PDI = 1.77. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, ppm) δ 8.17 (d, $J = 6.8$ Hz, 2H), 8.02–8.12 (m, 8H), 7.30–7.81 (m, 60H), 7.05–7.16 (m, 8H), 1.92–2.09 (m, 12H), 0.93–1.00 (m, 36H), 0.51–0.77 (m, 30H). Anal. Calcd for [C$_{183}$H$_{156}$N$_6$]$_n$: C, 90.11; H, 6.45; N, 3.45. Found: C, 89.78; H, 6.85; N, 3.36.
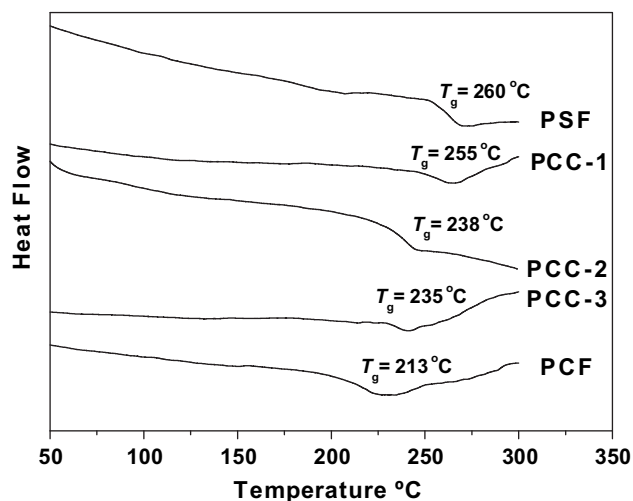
PCC-2:. **M1** (338.2 mg, 0.50 mmol), **M2** (284.1 mg, 0.50 mmol), **M3** (502.3 mg, 1.00 mmol), 435.4 mg of light yellow solid, yield 54.7%. GPC (THF) $M_n = 16.5$ kDa, $M_w = 26.0$ kDa, PDI = 1.57. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, ppm) δ 8.17 (d, $J = 6.8$ Hz, 2H), 8.02–8.12 (m, 4H), 7.31–7.82 (m, 42H), 7.08–7.16 (m, 4H), 1.94–2.10 (m, 8H), 0.93–1.10 (m, 24H), 0.52–0.77 (m, 20H). Anal. Calcd for [C$_{119}$H$_{104}$N$_4$]$_n$: C, 89.56; H, 6.45; N, 3.45. Found: C, 89.88; H, 6.80; N, 3.46.

PCC-3: **M1** (101.5 mg, 0.15 mmol), **M2** (170.5 mg, 0.30 mmol), **M3** (226.0 mg, 0.45 mmol), 214.9 mg of light yellow solid, yield 62.2%. GPC (THF) $M_n = 14.5$ kDa, $M_w = 29.3$ kDa, PDI = 2.02. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, ppm) δ 8.17 (d, $J = 7.2$ Hz, 4H), 8.02–8.12 (m, 4H), 7.31–7.83 (m, 66H), 7.07–7.16 (m, 4H), 1.91–2.10 (m, 12H), 0.92–1.10 (m, 36H), 0.51–0.77 (m, 30H). Anal. Calcd for [C$_{174}$H$_{156}$N$_6$]$_n$: C, 89.65; H, 6.75; N, 3.61. Found: C, 89.50; H, 7.02; N, 3.48.

PCF: **M2** (340.98 mg, 0.60 mmol), **M3** (301.4 mg, 0.60 mmol), 284.0 mg of light yellow solid, yield 63.9%. GPC (THF) $M_n = 17.6$ kDa, $M_w = 45.0$ kDa, PDI = 2.56. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, ppm) δ 8.17 (d, $J = 7.2$ Hz, 2H), 7.30–7.82 (m, 24H), 2.10 (br, 4H), 1.10 (br, 12H), 0.78 (br, 10H). Anal. Calcd for [C$_{55}$H$_{52}$N$_2$]$_n$: C, 89.15; H, 7.07; N, 3.78. Found: C, 89.04; H, 7.28; N, 3.68.

2.2. Measurement and characterization

^{1}H and ^{13}C NMR spectra were measured using a Bruker 400 spectrometer operating respectively at 400 MHz for ^{1}H and 100 MHz for ^{13}C in deuterated chloroform or methylene chloride solution with a tetramethylsilane (TMS) as a reference for the chemical shifts. Elemental analysis was performed on a Flash 1112
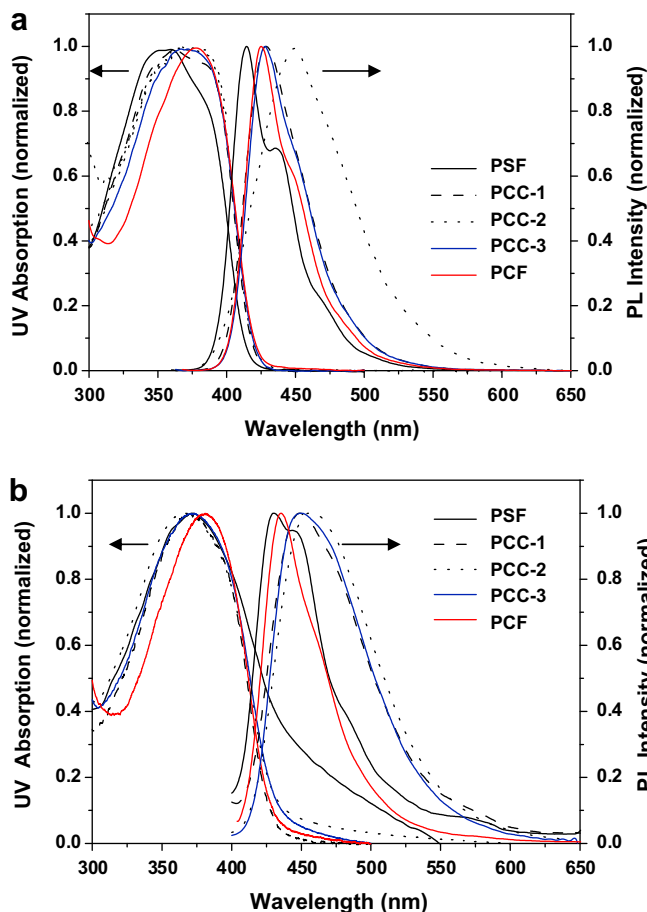

a

b

Fig. 3. UV–vis absorption and PL spectra for the copolymers (a) in dilute toluene solution and (b) in thin film.

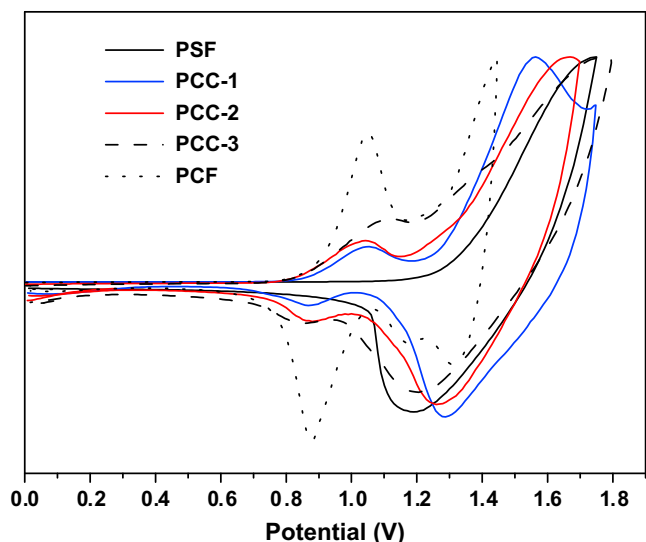**Fig. 2.** DSC measurements of the polymers recorded under flowing nitrogen atmosphere.

Fig. 4. Cyclic voltammograms of polymer films on Pt in 0.1 M nBu$_4$NPF$_6$ acetonitrile solution at room temperature. Scan rate: 100 mVs^{-1}.

Series elemental analyzer. The molecular weights of the polymers were determined with a Waters 2690 gel permeation chromatography (GPC) using a polystyrene standards eluting with tetrahydrofuran. Thermo gravimetric analysis (TGA) was carried out on a TA TGA-Q500 analyzer with a nitrogen flow at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed on a TA DSC-Q100 modulated DSC instrument at a heating rate of 10 °C/min and a cooling rate of 10 °C/min under nitrogen atmosphere. 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 voltammetry (CV) measurements were conducted on a three-electrode AUTOLAB (model PGSTAT30) workstation in a solution of Bu$_4$NPF$_6$ (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature.

2.3. Device fabrication and performance measurements

The PLEDs were fabricated on indium tin oxide (ITO) coated glass substrates. The substrates were pre-cleaned 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 50 nm of poly(ethylene dioxy)thiophene/poly(styrenesulfonic acid) (PEDOT:PSS), followed by drying at 120 °C in air for 30 min to remove residual water. For

Fig. 5. (a) Current density versus applied bias voltage (inset: device configuration of ITO/PEDOT:PSS/polymers/CsF/Ca/Al); (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.
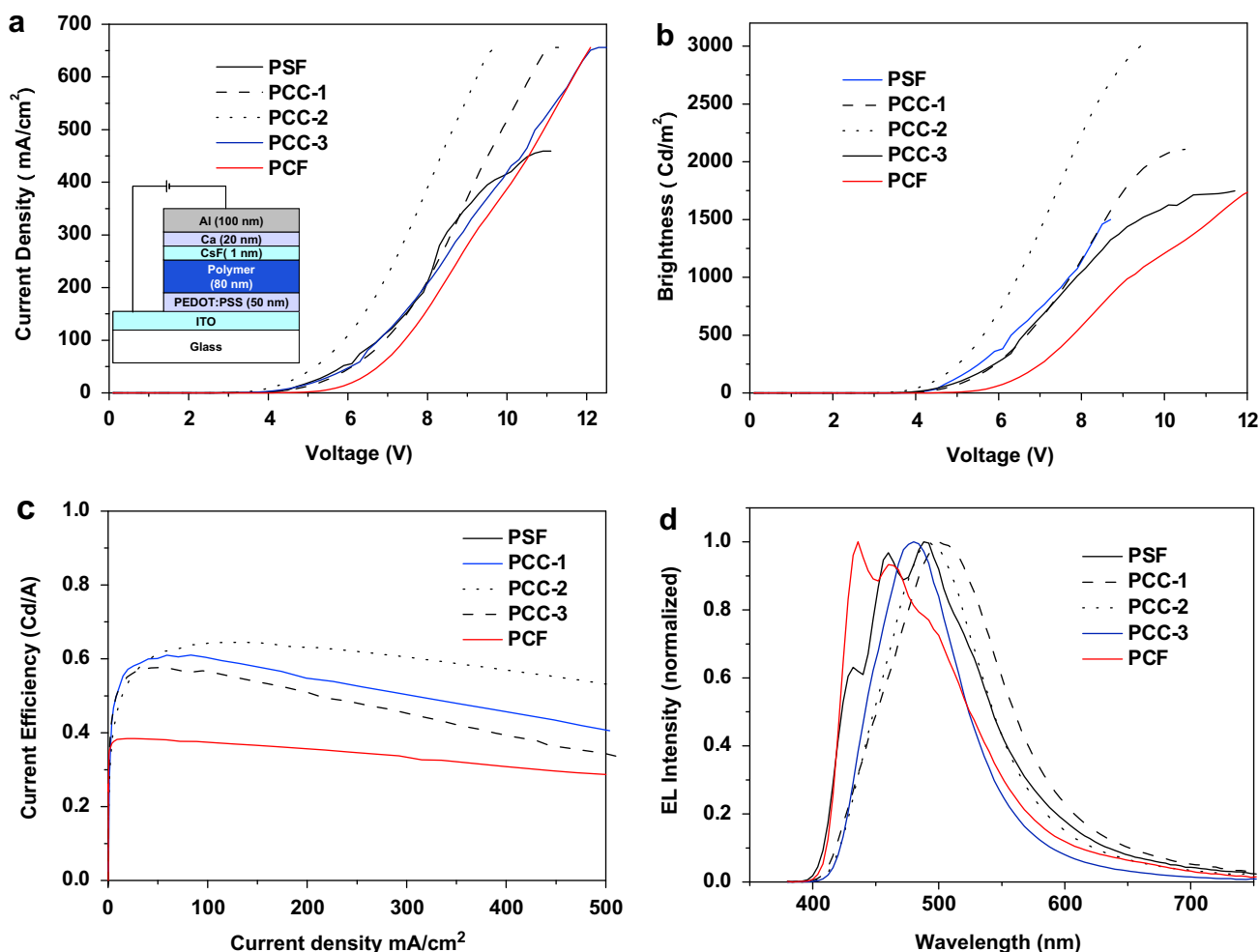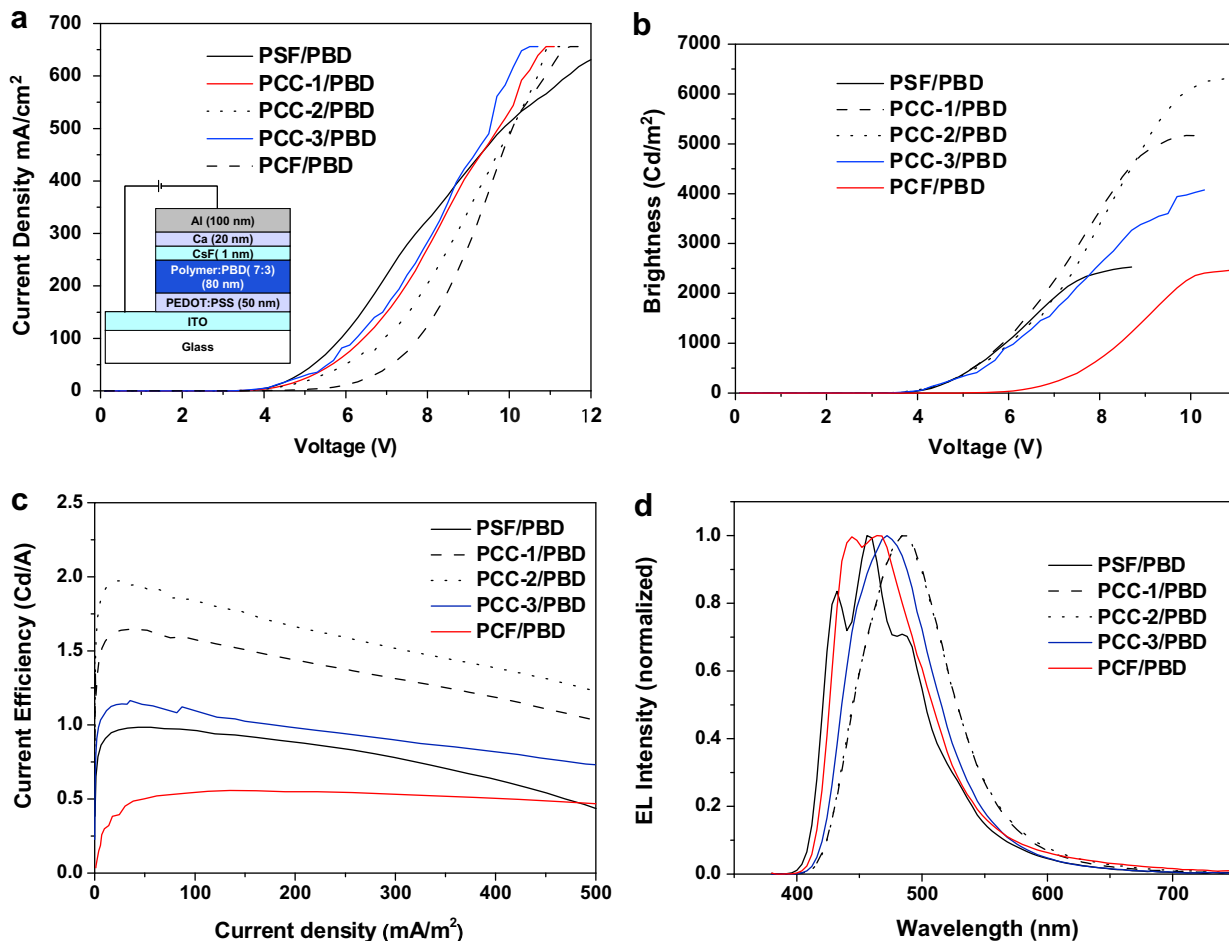
Fig. 6. (a) Current density versus applied bias voltage (inset: device configuration of ITO/PEDOT:PSS/polymers:PBD/CsF/Ca/Al); (b) Luminance versus applied bias voltage; (c) Current efficiency versus current density for devices; and (d) The normalized EL spectra of the polymers mixed with PBD recorded at the voltage of 8 V.

device 1, as shown in Fig. 5a, the polymers were spin-coated from a chloroform solution onto the ITO/PEDOT:PSS surface and annealed at 120 °C for 30 min to form a 80 nm-thick emitting layer. For **device 2**, as shown in Fig. 6a, a solution of 70 wt.% polymer and 30 wt.% PBD in chloroform, which was pre-filtered through Teflon filter (0.45 µm), 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 1×10^{-5} Pa onto the emitting layer both in **device 1** and **2**. The cathode was composed of 10 nm Ca and 100 nm Al, which were successively thermally deposited. The corresponding configuration of **device 1** was ITO/PEDOT:PSS (50 nm)/polymers (80 nm)/CsF (1 nm)/Ca (20 nm)/Al (100 nm), whereas that of **device 2** 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.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1–3 show the chemical structures and the synthetic routes to the monomers and copolymers. The synthesis starts with commercially available 2,7-dibromo-9,9′-spirobifluorene (**1**) by Suzuki coupling reaction to get the intermediate compound **2**. The key monomer **M1** was obtained by bromination of compound **2** using bromine with the catalyst of iron(III) chloride [21]. Compound **3** was converted to **M2** by reacting with 1-bromo-4-iodobenzene using the Ullmann reaction. In an attempt to select the optimal ratio of the monomers, copolymers with different ratios of monomers were prepared via Suzuki-coupling reactions. The feed molar ratios between **M1** and **M2** were 1:0, 2:1, 1:1, 1:2, and 0:1 in **PSF**, **PCC-1**, **PCC-2**, **PCC-3**, and **PCF**, respectively. The copolymers were purified by reprecipitation of polymer chloroform solution in methanol and Soxhlet extraction by acetone. The yields were 54.7–83.3%. The number-average molecular weights (M_n) of the polymers were determined by gel permeation chromatography (**GPC**) against
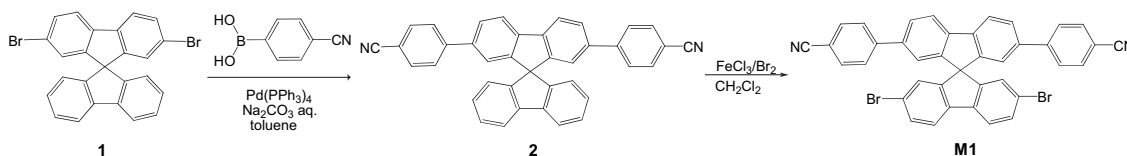
Scheme 1. Synthetic route for **M1**.
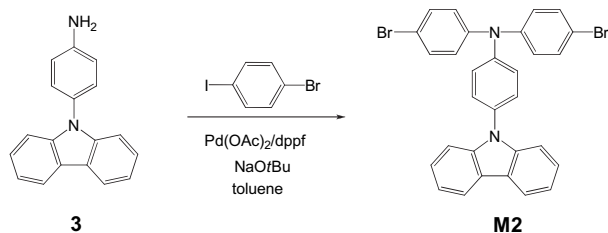
Scheme 2. Synthetic route for **M2**.

polystyrene standards eluting with THF ranged from 4600 to 17 600 with a polydispersity index from 1.28 to 2.56 (Table 1). All the copolymers showed good solubility in toluene, dichloromethane, chloroform, and tetrahydrofuran and could be processed into high quality films by spin-coating for device fabrication. **PSF**, which was copolymerized only with **M1** and **M3**, precipitated from solution during the polymerization propagation. Owing to its poor solubility, **PSF** had the lowest molecular weight ($M_n = 4600$) compared with other polymers. The chemical structures of the monomers were verified by ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectra of the copolymers were consistent with their statistic chemical structures. The actual molar ratios of the monomers in each polymer calculated from ^{1}H NMR are in good agreement with the corresponding feed molar ratios. The NMR spectra of the polymers are shown in the Supplementary Content. The elemental analysis results showed good purities of these polymers.

3.2. Physical properties

The thermal properties of the copolymers were evaluated by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA and DSC spectra of these polymers are shown in Fig. 1 and Fig. 2, respectively. The decomposed temperature (T_d, 5 wt.% loss) and glass-transition temperature (T_g) of the polymers are shown in Table 1. T_ds and T_gs of the polymers are higher than 400 °C and 200 °C, respectively. The first stage of weight loss ($\sim 20\%$) below 480 °C is due to the decomposition of alkyl groups. Even at 800 °C, there is only about 30% weight loss. The TGA results indicate that the polymers possess extremely good thermal stability. It is worthwhile to note that the T_gs of the polymers are increasing steadily with the composition of spirobifluorene moiety in the copolymers, from 213 °C for **PCF** to 260 °C for **PSF**. This indicates that the incorporation of the rigid spirobifluorene linkage in the polymer backbone results in significant reduction of the segmental mobility [23].

The normalized UV–vis and PL spectra of the polymers in dilute (10^{-6} M) toluene solution are shown in Fig. 3a. The absorption maxima are in the range of 359–378 nm corresponding to the π–π^* transition of the polymer backbone. The absorption maxima are in the range of 359–378 nm corresponding to the π–π^* transition of the polymer backbone. The absorption spectra of copolymers **PCC-1**, **PCC-2**, and **PCC-3** peak at 360–371 nm, lying between those of **PSF** (359 nm) and **PCF** (378 nm). The absorption bands of the polymers are red-shifted steadily with increasing the content of carbazole-triphenylamines. This might be due to the elevated HOMO energy levels of the polymers. In the emission spectra, **PSF** has the shortest emission peak at 414 nm with a vibronic shoulder at around 436 nm. **PCF** has an emission peak at 425 nm with a shoulder at 449 nm; while **PCC-1** and **PCC-3** have similar but slightly red-shifted emission maxima at 428 and 429 nm, respectively. It should be noted that **PCC-2**, whose molar ratio of **M1** and **M2** is 1:1, has the most red-shifted emission peak at 449 nm and the largest Stokes shift of 83 nm among the polymers. The large Stokes shift may result from structural differences between the ground and excited states [24,25] as well as migrated excitons in the segments of the chain where ring rotates more flexibly [26].

Fig. 3b shows the normalized UV–vis and PL spectra of the copolymers in thin films. The absorption maxima are in the range of 367–381 nm, which are red-shifted by 1–12 nm from the respective spectra in dilute solution. At the same time, the emission maxima of the polymers are red-shifted by 6–23 nm. The emission peak of **PCC-2** in thin film is only red-shifted by 6 nm with respect to that in dilute toluene solution. This phenomenon could be ascribed to the weak inter-molecular interaction and the suppressed aggregation [24a,27]. The Stokes shifts of **PSF**, **PCC-1**, **PCC-2**, **PCC-3**, and **PCF** in solid states are 59, 79, 88, 77, and 54 nm, respectively. The largest Stokes shift of **PCC-2** in thin film is consistent with the observation of **PCC-2** in solution. All the physical properties of the polymers are summarized in Table 1. The optical band gaps of these polymers calculated from their respective onset wavelengths of absorption spectra in thin films gave similar values of 2.77–2.88 eV.

3.3. Electrochemical properties

The electrochemical properties of the polymers were investigated by cyclic voltammetry (CV). The CV measurement on drop-cast polymer film on Pt foil electrode was conducted in a solution of tetra-n-butylammonium hexafluorophosphate (nBu$_4$NPF$_6$, 0.1 M) in acetonitrile at room temperature. An Ag/Ag$^+$ electrode was used as the reference electrode, and a gold electrode was used as the counter electrode. The highest occupied molecular orbital (HOMO) levels of the polymers were calculated from their respective onset oxidation potentials according to the equation HOMO $= -(E^{ox}_{onset} + 4.4)$ eV with the ferrocene oxidation potential as the standard [28]; the lowest unoccupied molecular orbital energy (LUMO) levels could only be estimated from the corresponding HOMO energy levels and optical band gaps (E_g). In Fig. 4, the polymers showed reversible or
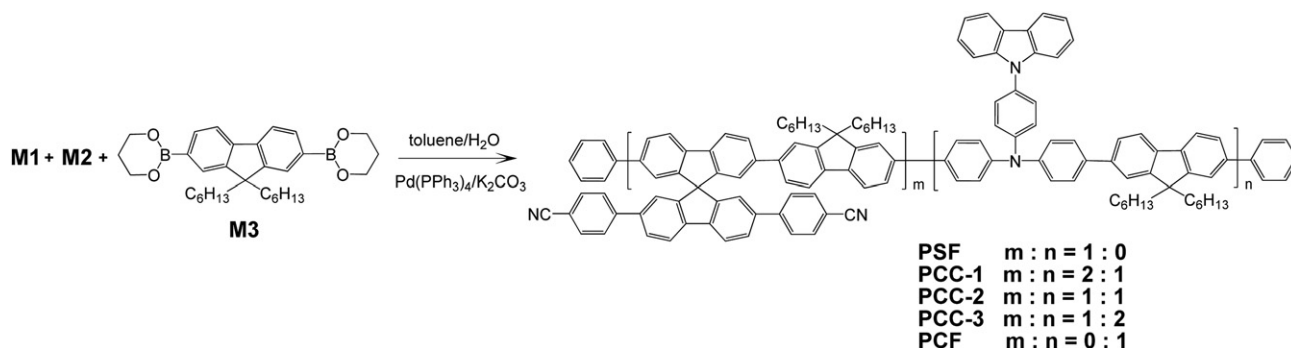
Scheme 3. Synthetic route for the copolymers.

Table 1
Physical Properties of the Polymers.

Polymer	$M_n(\times 10^3)$	M_w/M_n	$T_d{}^a(°C)$	$T_g{}^b(°C)$	$\lambda_{Abs}{}^c(nm)$	$\lambda_{em}{}^c(nm)$	$\lambda_{Abs}{}^d(nm)$	$\lambda_{em}{}^d(nm)$
PSF	4.6	1.28	436	260	359	414 (436)	371	430 (446)
PCC-1	12.9	1.77	431	255	360	429	370	449
PCC-2	16.5	1.57	433	238	366	449	367	455
PCC-3	14.5	2.02	430	235	371	428	374	451
PCF	17.6	2.56	428	213	378	425 (449)	381	435

[a] The temperature at which 5% weight loss of the sample was reached from TGA under nitrogen atmosphere.
[b] Evaluated by DSC during second heating cycle at a rate of 10 °C/min.
[c] Maximum absorption/emission wavelengths in dilute toluene solutions (10^{-6} M).
[d] Maximum absorption/emission wavelengths in thin films.

partially reversible oxidation process. The onset oxidation potential at 1.31 V observed in **PSF** can been assigned to the oxidation of fluorene components [29]. It can be seen that **PCC-1**, **PCC-2**, **PCC-3**, and **PCF** demonstrated one oxidation band in the range from 0.8 to 1.2 V besides the fluorene band (1.2–1.7 V). The first band can be ascribed to the oxidation of carbazole-triphenylamine segments and used to estimate the onset oxidation potentials [30]. The calculated HOMOs and LUMOs of the polymers are summarized in Table 2. As shown in Fig. 4 and Table 2, the onset oxidation potentials of all the polymers were observed in the region of 0.86–1.31 V. The HOMO values of the polymers were estimated to be in the range of −5.26 to −5.71 eV, therefore the LUMO energy levels were calculated to be in the range of −2.38 to −2.94 eV from the optical band gaps and HOMO values. Although all the HOMO values of the polymers except **PSF** are very close to that of **PCF**, it can be clearly seen in Fig. 4 that the first oxidation band assigned to carbazole-triphenylamine becomes weaker when the content of **M2** in the polymer backbone reduced. These results indicate all the copolymers have similar hole injection barriers but different hole transporting properties. In other words, the hole and electron transporting properties of the copolymers could be effectively manipulated through tuning the feed ratios of **M1** and **M2**.

3.4. Electroluminescence properties

The initial electroluminescence (EL) performances of these polymers were investigated by fabricating multilayer devices with the configuration of ITO/PEDOT:PSS (50 nm)/polymers (80 nm)/CsF (1 nm)/Ca (20 nm)/Al (100 nm) (**device 1**). In this device configuration, poly(ethylene dioxy)thiophene mixed with poly(styrene sulfonic acid) (PEDOT:PSS) was used as the hole injection and transport layer, and cesium–fluoride (CsF) (1 nm) was used as the electron-injection layer. 20 nm of Ca and 100 nm of Al were deposited onto CsF layer as the cathode. As summarized in Table 3, the reference polymer **PCF** presented the lowest luminance (1427 cd/m²) and efficiency, which should be ascribed to the poor electron transporting property of the polymer. Another reference polymer **PSF** showed high current efficiency but low brightness; thereby this structure was not the best one. Yang et al. [31] reported

Table 2
Electrochemical Properties of the Polymers.

Polymer	$E_g{}^a$ (eV)	$E^{ox}{}_{onset}{}^b$ (V)	HOMO^c (eV)	LUMO^d (eV)
PSF	2.77	1.31	−5.71	−2.94
PCC-1	2.87	0.87	−5.27	−2.40
PCC-2	2.86	0.86	−5.26	−2.40
PCC-3	2.87	0.86	−5.26	−2.39
PCF	2.88	0.86	−5.26	−2.38

[a] Determined from UV–vis absorption spectra.
[b] $E^{ox}{}_{onset}$: onset oxidation potential.
[c] HOMO $= -(E^{ox}{}_{onset} + 4.4)$ eV.
[d] Estimated from HOMO levels and the optical band gaps. LUMO $=$ HOMO $+ E_g$.

the comparison of the current efficiencies of fuorene-based copolymers with hole- or electron-transporting segments: PF-Carbazole (0.02 cd/A), PF-Spirobifluorene (0.23 cd/A), PF-Oxadiazole (0.40 cd/A). The efficiencies of **PSF** and **PCF** are higher than those of PF-Oxadiazole and PF-Carbazole reported [31], respectively. The polymers we prepared also exhibited higher brightness than the polyfluorenene with quinoline substituents [32]. Thereby, the cyano groups and carbazole-triphenylamine units functioned well as the electron-withdrawing and electron-donating moieties, respectively. When the copolymers containing both **M1** and **M2** building blocks were used as the active layers, the devices demonstrated higher efficiencies than **PCF**. The efficiencies are sustained over a wide range of current density. Among the three copolymers incorporated with **M1** and **M2**, **PCC-2** showed the lowest turn-on voltage (3.7 V), highest luminance (3024 cd/m²) and current efficiency (0.64 cd/A). All these polymers exhibit good spectral stability during device operated at different voltages. Fig. 5d shows the EL spectra of these polymers at the applied voltage of 8 V. It can be observed that the EL spectra of the polymers are all dissimilar to their PL spectra in thin films. **PSF** showed a broad emission band with the maximum emission wavelength at 488 nm and two shoulders at 432 and 460 nm corresponding to the CIE color coordinates of (0.21, 0.28) at 8 V; whilst its PL spectrum peaked at 430 nm with one shoulder at 446 nm. Its EL emission bands at 432, 460, and 488 nm could be assigned to the vibronic 0-0, 0-1, and 0-2 transitions, respectively. Similar phenomenon was also observed for the **PCF**-based device: its EL peaked at 436 nm with two shoulders at 460 and 488 nm with the CIE coordinates of (0.19, 0.22), but its PL spectrum showed the maximum emission at 435 nm without an obvious shoulder. The EL spectra of the other three copolymers are all broader and red-shifted by 30–55 nm compared with their corresponding PL spectra. The difference between the PL and EL spectra may be 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. [33,34] Moreover, the recombination of electron-hole in EL increases the formation of excimers, which may be another reason.

To further optimize the device, the devices with doped emitting layers were fabricated (**device 2**). 5-Biphenyl-2-(4-tert-butyl)-phenyl-1,3,4-oxadiazole (PBD) was chosen to mix with each polymer with a weight ratio of 3:7 to raise the color purity, brightness and EL efficiency because PBD can block the holes from migrating to cathode side thus can enhance the recombination probability with electrons. Fig. 6a–d show the EL performances of these polymers in doped devices. As can be seen in Table 4, all the doped devices showed higher brightness, lower turn-on voltages and much better efficiencies. Actually, the maximum luminances have been improved ranging from 68% to 152% for the five doped devices, compared to the pure polymer-based devices. The improvements for **PCC-1**, **PCC-2**, and **PCC-3** are even more obvious than **PSF** and **PCF**. The turn-on voltages were reduced by 0.6–1.5 V. The

Table 3
EL performance of the polymers in devices with the configuration of ITO/PEDOT:PSS/polymers/CsF/Ca/Al.

Emissive Layer	$V_{turn-on}$[a] (V)	L_{max}[b] (cd/m^2)	$V_{L,max}$[c] (V)	η@100 cd/m^2[d] (cd/A)	η@1000 cd/m^2[e] (cd/A)	$η_{max}$[f] (cd/A)	$η_{max}$[g] (lm/w)	$λ_{EL}$[h] (nm)	CIE1931[i] (x, y)
PSF	4.5	1505	8.7	0.68	0.57	0.70	0.44	488 (432, 460)	(0.21, 0.28)
PCC-1	4.7	2108	10.5	0.57	0.57	0.61	0.34	504	(0.24, 0.38)
PCC-2	3.7	3024	9.5	0.54	0.64	0.64	0.38	492	(0.20, 0.34)
PCC-3	4.7	1717	11.7	0.55	0.52	0.58	0.35	481	(0.17, 0.26)
PCF	5.5	1427	12.1	0.38	0.33	0.38	0.23	436 (460, 488)	(0.19, 0.22)

[a] Turn-on voltage corresponding to 1 cd/m^2 of lumiance.
[b] Maximum luminance.
[c] Driving voltage corresponding to maximum luminance.
[d] Current efficiency at the luminance of 100 cd/m^2.
[e] Current efficiency at the luminance of 1000 cd/m^2.
[f] Maximum current efficiency.
[g] Maximum power efficiency.
[h] Maximum EL wavelength.
[i] Measured at 8 V.

Table 4
EL performance of the polymers in devices with the configuration of ITO/PEDOT:PSS/polymers:PBD/CsF/Ca/Al.

Emissive Layer	$V_{turn-on}$[a] (V)	L_{max}[b] (cd/m^2)	$V_{L,max}$[c] (V)	η@100 cd/m^2[d] (cd/A)	η@1000 cd/m^2[e] (cd/A)	$η_{max}$[f] (cd/A)	$η_{max}$[g] (lm/w)	$λ_{EL}$[h](nm)	CIE1931[i] (x, y)
PSF/PBD	3.5	2530	8.7	0.91	0.96	0.98	0.67	456 (432, 484)	(0.16, 0.16)
PCC-1/PBD	3.2	5306	10.3	1.52	1.61	1.64	1.12	484	(0.16, 0.27)
PCC-2/PBD	3.1	6369	10.9	1.86	1.91	1.97	1.40	484	(0.16, 0.27)
PCC-3/PBD	3.2	4072	10.3	1.10	1.12	1.16	0.81	472	(0.16, 0.21)
PCF/PBD	4.7	2466	10.9	0.39	0.55	0.56	0.22	444, 464	(0.16, 0.17)

[a] Turn-on voltage corresponding to 1 cd/m^2 of luminance.
[b] Maximum luminance.
[c] Driving voltage corresponding to maximum luminance.
[d] Current efficiency at the luminance of 100 cd/m^2.
[e] Current efficiency at the luminance of 1000 cd/m^2.
[f] Maximum current efficiency.
[g] Maximum power efficiency.
[h] Maximum EL wavelength.
[i] Measured at 7 V.

maximum efficiencies for the three copolymers were improved by one to two folds. The device fabricated with **PCC-2**/PBD showed the best performance: 3.1 V of turn-on voltage, 6368 cd/m^2 of maximum brightness, 1.97 cd/A of current efficiency and 1.40 lm/W of power efficiency. The EL spectra of the polymers/PBD devices driven at 7 V are shown in Fig. 6d. The emission peaks are blue-shifted and narrower compared with their EL spectra in **device 1**. The device performances of the polymers with the configuration of **device 2** are summarized in Table 4. All the results suggest that the best ratio of **M1**:**M2** is 1:1 to achieve the best device performance among these devices based on the copolymers.

4. Conclusion

We have designed and successfully synthesized a new series of blue light emitting polymers **PSF**, **PCC-1**, **PCC-2**, **PCC-3**, and **PCF** containing cyano-spirobifluorenes and/or carbazole-triphenyl-amines. The feed ratios of two monomers (**M1** and **M2**) in **PSF**, **PCC-1**, **PCC-2**, **PCC-3**, and **PCF** were varied from 1:0, 2:1, 1:1, 1:2, to 0:1, respectively. TGA and DSC analyses indicated that the thermal properties of the polymers were enhanced by incorporation of the rigid spirobifluorene units into the polymer backbone. Investigation of the cyclic voltammetric behavior of the polymer films revealed that all the polymers except **PSF** have similar HOMO energy levels, which are mainly determined by the carbazole-tri-phenylamine units. Although the copolymers **PCC-1**, **PCC-2**, **PCC-3** and **PCF** have similar barriers for hole injection, their hole trans-porting abilities are different and it can be effectively tuned by changing the feed ratios between **M1** and **M2**. 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 1**) and ITO/PEDOT:PSS/polymers:PBD (30%)/CsF/Ca/Al (**device 2**). Doping the polymers with 30 wt.% of PBD as the active layers can dramatically improve the device performance. Among the copolymers, **PCC-2** demonstrated the best performance with the lowest turn-on voltage of 3.1 V, the highest luminance of 6369 cd/m^2, the highest current efficiency of 1.97 cd/A, and the best power efficiency of 1.40 lm/w. All the EL results suggest that the best ratio of **M1**:**M2** is 1:1 to achieve the best device performance. The monomer **M1** and **M2** are good electron-transporting and hole-transporting segments, respectively, therefore might be useful in further study of PLEDs.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2010.01.024

References

[1] Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, et al. Nature 1990;347:539.
[2] (a) Kraft A, Grimsdale AC, Holmes AB. Angew Chem Int Ed 1998;37:402;
(b) Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, et al. Nature 1999;397:121;
(c) Bernius MT, Inbasekaran M, O'Brien J, Wu W. Adv Mater 2000;12:1737;
(d) Wang P, Chai CP, Chuai YT, Wang FZ, Chen XF, Fan XH, et al. Polymer 2007;48:5889.
[3] de Gans BJ, Duineveld PC, Schubert US. Adv Mater 2004;16:203.

[4] (a) Chen CT. Chem Mater 2004;16:4389;
    (b) Lyu YY, Kwak J, Jeon WS, Byun Y, Lee HS, Kim D, et al. Adv Funct Mater 2009;19:420.
[5] (a) Liu MS, Luo JD, Jen AKY. Chem Mater 2003;15:3496;
    (b) Liu J, Tu GL, Zhou QG, Cheng YX, Geng YH, Wang LX, et al. J Mater Chem 2006;16:1431. (c) Liu J, Bu LJ, Dong JP, Zhou QG, Geng YH, Ma DG, et al. J Mater Chem 2007;17:2832.
[6] (a) Woudenbergh TV, Wildeman J, Blom PWM, Bastiaansen JJAM, Langeveld-Voss BMW. Adv Funct Mater 2004;14:677;
    (b) Lu H, Liu C, Chang C, Chen S. Adv Mater 2007;19:2574.
[7] (a) Neher D. Macromol Rapid Comm 2001;22:1365;
    (b) Scherf U, List EJW. Adv Mater 2002;14:477;
    (c) Babel A, Jenekhe SA. Macromolecules 2003;36:7759.
[8] (a) Yu WL, Pei J, Huang W, Heeger AJ. Adv Mater 2000;12:828;
    (b) Tang S, Liu MR, Gu C, Zhao Y, Lu P, Lu D, et al. J Org Chem 2008;73:4212.
[9] Huang B, Li J, Shao P, Qin J, Yu G, Liu YQ, et al. Synth Met 2005;153:261.
[10] Natera J, Otero L, Sereno L, Fungo F, Wang NS, Tsai YM, et al. Macromolecules 2007;40:4456.
[11] Sanchez JC, Trogler WC. J Mater Chem 2008;18:3143.
[12] Fu Y, Sun M, Wu Y, Bo Z, Ma D. J Polym Sci Part A Polym Chem 2008;46:1349.
[13] Wang P, Chai CP, Yang Q, Wang FZ, Shen ZH, Guo HQ, et al. J Polym Sci Part A Polym Chem 2008;46:5452.
[14] (a) Chen YC, Huang GS, Hsiao CC, Chen SA. J Am Chem Soc 2006;128:8549;
    (b) Tang R, Tan Z, Li Y, Xi F. Chem Mater 2006;18:1053;
    (c) Bernius MT, Inbasekaran M, O'Brien J, Wu WS. Adv Mater 2000;12:1737;
    (d) Zhao Z, Li JH, Lu P, Yang Y. Adv Funct Mater 2007;17:2203;
    (e) Park JH, Cho NS, Jung YK, Cho HJ, Shim HK, Kim H, et al. Org Electron 2007;8:272.
[15] (a) Jiang HJ, Wang HY, Zhu R, Wan JH, Liu F, Feng JC, et al. J Polym Sci Part A Polym Chem 2008;46:1548;
    (b) Su SJ, Chiba T, Takeda T, Kido J. Adv Mater 2008;20:2125;
    (c) Wang LH, Chen ZK, Xiao Y, Kang ET, Huang W. Macromol Rapid Comm 2000;21:897.
[16] (a) Oyston S, Wang C, Hughes G, Batsanov AS, Perepichka IF, Bryce MR, et al. J Mater Chem 2005;15:194;
    (b) Wu FI, Reddy DS, Shu CF. Chem Mater 2003;15:269;
    (c) Chen ZK, Meng H, Lai YH, Huang W. Macromolecules 1999;32:4351;
    (d) Meng H, Chen ZK, Yu WL, Pei J, Liu XL, Lai YH, et al. Synth Met 1999;100:297;
    (e) Mikroyannidis JA, Gibbons KM, Kulkarni AP, Jenekhe SA. Macromolecules 2008;41:663.
[17] (a) Grisorio R, Piliego C, Fini P, Cosma P, Masterorilli P, Gigli G, et al. J Polym Sci Part A Polym Chem 2008;46:6051;
    (b) Liao HR, Lin YJ, Chou YM, Luo FT, Wang BC. J Lumin 2008;128:1373;
    (c) Jin SH, Kim MY, Koo DS, Kim YI. Chem Mater 2004;16:3299.
[18] (a) Tsai LR, Chen Y. J Polym Sci Part A Polym Chem 2007;45:4465;
    (b) Grice AW, Tajbakhsh A, Burn PL, Bradley DDC. Adv Mater 2004;9:1174.
[19] (a) Pucci A, Biver T, Ruggeri G, Itzel Meza L, Pang Y. Polymer 2005;46:11198;
    (b) Cheylan S, Bolink HJ, Fraleoni-Morgera A, Puigdollers J, Voz C, Mencarelli I, et al. Org Electron 2007;8:641.
[20] Zhen CG, Chen ZK, Liu QD, Dai YF, Shin RYC, Chang SY, et al. Adv Mater 2009; 21:2425.
[21] Lin Y, Chen ZK, Ye TL, Dai YF, Ma DG, Ma Z, et al. J Polym Sci Part A Polym Chem 2010;48:292.
[22] (a) Wang YM, Teng F, Ma CQ, Xu Z, Hou YB, Yang SY, et al. Displays 2004; 25:237;
    (b) Kim BS, Kim CG, Oh JJ, Kim MS, Kim GW, Park DK. Macromol Res 2006; 14:343;
    (c) Cao Y, Parker ID, Yu G, Zhang C, Heeger AJ. Nature 1999;397:414;
    (d) Gürel EE, Pang Y, Karasz FE. Thin Solid Films 2002;417:147.
[23] Chen CH, Wu FL, Shu CH, Chien CH, Tao YT. Mater Chem 2004;14:1585.
[24] Jiang ZQ, Zhang WJ, Yao HQ, Yang CL, Cao Y, Qin JG, et al. J Polym Sci Part A Polym Chem 2009;47:3651.
[25] Wang BC, Liao HR, Yeh HC, Wu WC, Chen CT. J Lumin 2005;113:321.
[26] Feng JC, Li Y, Yang MJ. Eur Polym J 2008;44:3314.
[27] Chen CH, Wu FI, Shu CF, Chien CH, Tao YT. J Mater Chem 2004;14:1585.
[28] Chen ZK, Lee NHS, Huang W. Macromolecules 2003;36:1009.
[29] Lu S, Liu T, Ke L, Ma DG, Chua SJ, Huang W. Macromolecules 2005;38:8494.
[30] (a) Huang F, Zhang Y, Liu MS, Cheng YJ, Jen AKY. Adv Funct Mater 2007; 17:3808;
    (b) Zhang K, Tao YT, Yang CL, You H, Zou Y, Qin JG, et al. Chem Mater 2008; 20:7324;
    (c) Lin HY, Liou GS. J Polym Sci Part A Polym Chem 2009;47:285.
[31] Yang CM, Liao HH, Horng SF, Meng HF, Tseng SR, Hsu CS. Synth Metal 2008;158:25.
[32] Su HJ, Wu FI, Shu CF, Tung YL, Chi Y, Lee GH. J Polym Sci Part A Polym Chem 2005;43:859.
[33] Mal'tsev EI, Brusentseva MA, Berendyaev VI, Kolesnikov VA, Lunina EV, Kotovb BV, et al. Mendeleev Comm 1998;8:31.
[34] Hsieh BY, Chen Y. J Polym Sci Part A Polym Chem 2008;46:3703.