

Electroluminescent Fluorene-Based Alternating Polymers Bearing Triarylamine or Carbazole Moieties in the Main Chain: Synthesis and Properties

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ABSTRACT: Two soluble conjugated polyfluorenes, poly{9,9-dioctylfluorene-2,7-diyl-co-4,4'-bis[2-(4-phenyl)-2-cyanovinyl]triphenylamine}(PF-BCT) and poly{9,9-dioctylfluorene-2,7-diyl-co-3,6-bis[2-(4-phenyl)-2-cyanovinyl]-9-octyl carbazole}(PF-BCC), have been synthesized from 2,7-dibromo-9,9-dioctylfluorene and 4,4'-bis[2-(4-bromophenyl)-2-cyanovinyl]triphenylamine or 3,6-bis[2-(4-bromophenyl)-2-cyanovinyl]-9-octyl carbazole comonomers through a Suzuki polymerization reaction. The copolymers are characterized by gel permeation chromatography, elemental analysis, thermogravimetric analysis. The polymers have good thermal stability with 5 wt % loss temperatures of more than 380°C. Cyclic voltammetry measurements show that the polymers present good electron and hole-injection abilities. PF-BCC possesses higher oxidization potential than that of PF-BCT, which indicates that PF-BCT has better hole injection ability. The photophysical properties of the polymers are investi-

gated in both solutions and spinning-coated films. Compared to that of PF-BCC, the absorption and emission peaks of PF-BCT bathochromic shift in the solid film or solution states. Single layer light-emitting devices have been fabricated in the ITO/PEDOT: PSS/polymer/Ca/Al configuration. The electroluminescence (EL) device based on PF-BCT shows yellow emission with the current efficiency of 0.21 cd/A, while PF-BCC shows greenish yellow emission with the current efficiency of 0.08 cd/A. In addition, to improve the electroluminescence of PF-BCC, a PVK layer is introduced, the brightness and efficiency get improved to 700 cd/m² and 0.12 cd/A, respectively. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 978–987, 2009

Key words: triphenylamine; carbazole; Suzuki polymerization reaction; photophysical properties; electroluminescence

INTRODUCTION

Great research interests on electroluminescent (EL) polymers include tailoring of their spectral characteristics and the improvement of their processability and long-term stability,^{1–4} but one of the most challenging problems is to optimize the carrier transport characteristics and recombination efficiency of the EL materials to achieve high photoluminescence quantum yield and high efficiency EL devices. It is well established that good quantum efficiency of EL devices can be obtained by achieving efficient injection and balanced transport of both charge carriers from the electrodes and inside the EL materials.^{5–7} Therefore, the synthesis of light-emitting polymers containing carrier transporting unit is necessary for

fabricating high-efficient and stable polymer light emitting devices (PLEDs).

Poly(fluorene) derivatives (PFs) show interesting chemical and physical properties because they contain a rigid planar biphenyl unit, and the facile substitution at the remote C9 position can improve the solubility and processability of the polymers without significantly increasing the steric interactions in the polymer backbone.^{8–11} But its low electron affinity potential (EA) and high ionization potential (IP) usually lead to large injection barrier of electrons and holes. It is established that high quantum efficiency of PLEDs can be obtained by achieving both efficient charge injection and balanced mobility of both charge carriers inside the emitting materials. In general, many light-emitting polymers inject and transport holes more efficiently than electrons due to their inherent richness of δ -electrons. So it is a very challenging task to develop bipolar emitters which combine both electron and hole transport units on a molecule and it can offer good recombination sites for hole and electron carriers.

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Triphenylamine (TPA) seems to be a promising candidate as the electron-rich moieties, polymers containing TPA unit have presented high PL efficiency, good hole-transporting ability and outstanding photoconductivity.^{12,13} A carbazole derivative also, is a typical organic molecule that has shown potential for technological applications. Polymers based on this molecule have good electro- and photo-active properties due to their high hole transporting mobility, strong absorption in the ultraviolet spectral region and blue-light emission.^{14,15} The hole transporting units such as carbazole or triphenylamine introduced into the polymer backbone can raise the highest occupied molecular orbital (HOMO) energy level of the polymer. The introduction of cyano groups onto poly(fluorene) backbone has been proved an effective way of lowering the lowest unoccupied molecular orbital (LUMO) energy level of the polymer, but it has relatively little effect on the HOMO energy level.^{16,17} Furthermore, electrochemical stability of the polymers could be enhanced by introducing cyano groups, which is also desirable for optoelectronic devices. In this presentation, we synthesized two copolymers which incorporated hole and electron transporting units into PF backbone through a Suzuki coupling reaction. The optical and electrochemical properties of two PFs are also investigated in this contribution. Furthermore, their electroluminescence was examined.

EXPERIMENTAL

Materials

Tetrakis(triphenylphosphine) palladium [Pd(PPh₃)₄] was purchased from Alfa Asia Chemical (Tianjin, China). Toluene and THF was distilled over sodium and benzophenone. DMF was dried by reduced distillation over CaH₂. Methylene chloride was dried by distillation over CaH₂. Acetonitrile was spectroscopic grade from Beijing Chemical Co. Analytical-grade solvents were used throughout the experiments, and all chemicals were analytical grade and used without further purification. 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**8**) was prepared according to the literature procedure.¹⁸

Measurements

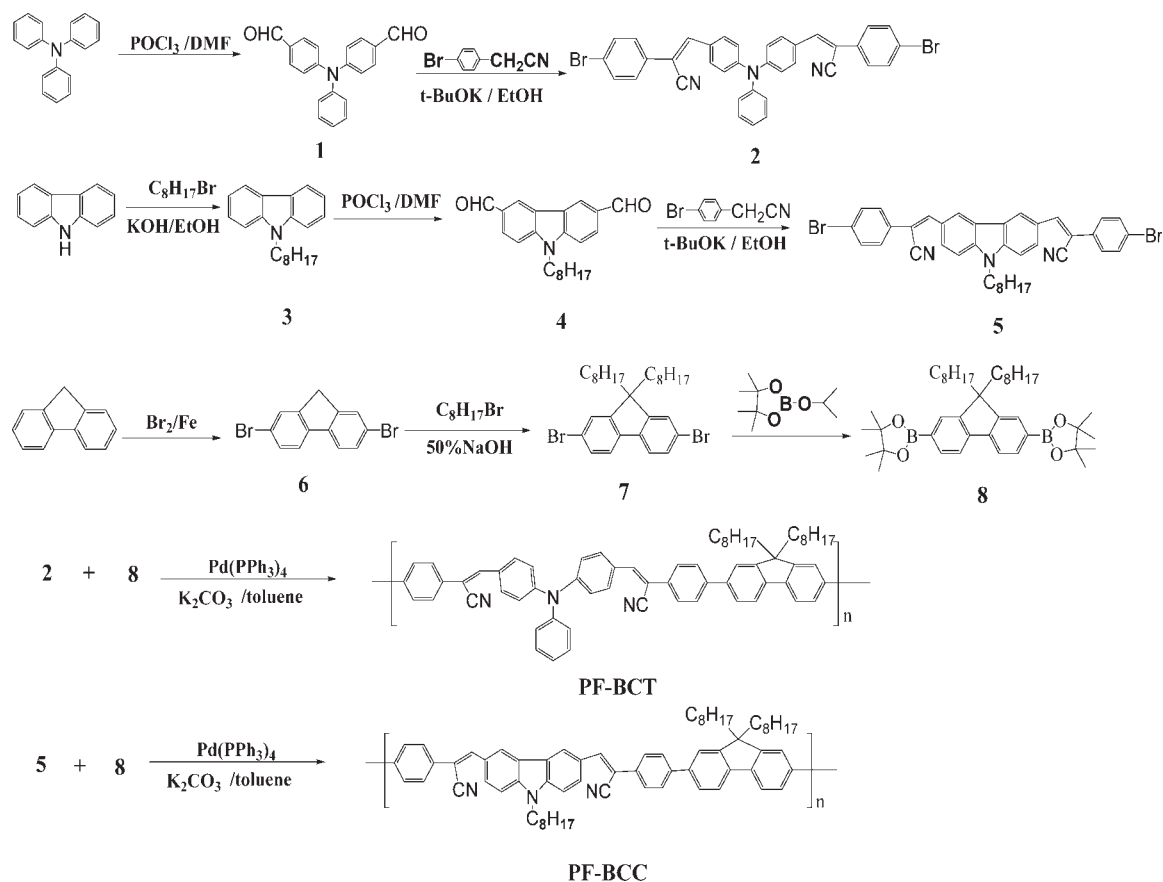
¹H-NMR spectra were recorded using a Bruker DMX-300 or Bruker AV-400 spectrometer, and chemical shifts were recorded in ppm with tetramethylsilane as an internal standard. Deuterated chloroform (CDCl₃) was used as the solvent for recording NMR spectra. Mass spectra were obtained with an

AEI-MS50-MS spectrometer. Elemental analysis was measured on a Flash EA 1112 elemental analyzer. Fourier transforms infrared (FTIR) spectra were recorded on a BIO FTS-135 spectrometer by dispersing samples in KBr disks. Melting point measurement was done by XT4-100x melting-point apparatus. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis relative to polystyrene calibration [Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4)] using THF as eluent at a flow rate of 1.0 mL/min at 35°C. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer 7 thermogravimetric analyzer with a heating rate of 10°C/min under a nitrogen atmosphere. The Ultraviolet-visible (UV) absorption spectra were recorded on a Hitachi UV-3010 spectrometer. The photoluminescence (PL) spectra were obtained with a Hitachi F-4500 Fluorescence spectrophotometer. The quantum yields of fluorescence were determined in deoxygenated chloroform against quinine sulfate in 0.5 mol/L H₂SO₄ assuming a quantum yield of 0.546 according to the Ref. 19.

The electrochemical cyclic voltammetry (CV) was conducted on a Zahner IM6e Electrochemical Workstation. The CV was performed in an acetonitrile solution of 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) at a scanning rate of 50 mV/s at room temperature under the protection of argon. A Pt plate coated with a thin polymer film was used as the working electrode. A Pt wire and a Ag/Ag⁺ (0.01M in acetonitrile) electrode were used as the counter electrode and reference electrode respectively. The experiments were calibrated with the standard ferrocene/ferrocenium (FOC) redox system and assumption that the energy level of FOC is 4.8 eV below vacuum. The LUMO and HOMO energy levels of the polymers were obtained from the onset reduction and oxidation potentials.

Device fabrication and characterization

The single layer device configuration is ITO (indium-tin-oxide)/PEDOT : PSS (poly-(3,4-ethylene dioxothiophene) : poly(styrene sulfonate)) (30 nm)/polymer (100 nm) /Ca (15 nm)/Al (100 nm). The fabrication process of the device is as follows. First, ITO (indium-tin-oxide)-coated glass (15 Ω/m²) as an anode was patterned by an aqua regia solution (HCl: HNO₃ = 3 : 1). The patterned ITO-coated glass was sonicated in a detergent solution followed by trichloroethylene and isopropyl alcohol, deionized water, and dipped into acetone. After that, ITO-coated glass was dried by high purity N₂ and exposed to UV-ozone for 10 min. PEDOT: PSS (Baytron-P, Bayer AG) was spin-coated on a precleaned



Scheme 1 Synthetic routes of the monomers and polymers.

and UV-ozone-treated ITO substrate and dried in vacuum oven. Second, we dissolved polymer in toluene solution (10 mg/mL) and spin-coated on the top of the PEDOT: PSS as emitting layer, the polymer film was treated by thermal annealing at 80°C for 30 min. The thickness of the active layer was determined to be 100 nm by an Ambios Tech. XP-2 profilometer. At last, a layer of Ca capped with Al was thermally deposited through a shade mask at a pressure of $\sim 5 \times 10^{-5}$ Pa. The deposition rates and the thickness of the evaporation layers were monitored by a ZMK-II film thick/rate meter. The deposition rates were usually 0.5–1 nm/s. With the exception of spin-casting a PEDOT: PSS layer, all the fabrication steps were carried out in a nitrogen glove box. The double layer device configuration is ITO (indium-tin-oxide)/PEDOT: PSS [poly-(3,4-ethylene dioxythiophene) : poly(styrene sulfonate)] (30 nm)/PVK(50 nm)/polymer (90 nm) /Ca (15 nm)/Al (100 nm), the fabrication process is similar to that of the single-layer device.

Electroluminescence (EL) spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer. The current-voltage (I - V) and luminance-voltage (L - V) characteristics of the light-emitting devices were recorded with a computer-controlled Keithley

236 source measure unit and a Keithley 2000 Multimeter coupled with a Si photomultiplier tube. All the measurements were performed under ambient atmosphere at room temperature.

Synthesis of the monomers

The synthetic routes of the monomers and polymers are shown in Scheme 1.

4,4'-Diformaltriphenylamine (1)

4,4'-Diformaltriphenylamine was synthesized by Vilsmeier reaction. To the mechanically stirred mixture of triphenylamine (5 g, 0.02 mol) and *N,N*-dimethylformamide (80 mL, 1.03 mol) was dropwisely added to phosphorus oxychloride (150 mL, 1.58 mol) under ice bath under the protection of N_2 for an hour, the reaction solution turned from the colorless transparent to the red viscous liquid. Then the mixture was heated to 60°C slowly in the oil bath and the reaction proceeded for 30 h, a brown-dark solution formed. After cooling down to room temperature, the mixture was poured into large amount of ice and neutralized with 0.1N NaOH, the yellow solid was suction filtered and purified by column

chromatography using CHCl_3 as the eluent to obtain 0.8 g triformyl-triphenylamine (yield: 12.2%) and 3.5 g 4, 4'-diformaltriphenylamine (yield: 57%). mp: 142–144°C. IR(KBr, cm^{-1}): 1694, 1588, 1505, 1332, 832, 822, 762.

Ms: $m/z = 301$ [M^+]. $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 9.90 (s, 2H), 7.76 (d, 4H), 7.40 (t, 2H), 7.24 (t, 1H), 7.18 (m, 6H).

4,4'-Bis[2-(4-bromophenyl)-2-cyanovinyl]triphenylamine (2)

A mixture of 0.301 g (1 mmol) of compound 1 and 0.392 g (2 mmol) 4-bromophenyl acetonitrile was stirred in 30 mL of ethanol at room temperature. A catalytic amount of potassium *tert*-butoxide in ethanol was added to this mixture. After 1 day, yellow solid was filtered and washed by water and methanol alternatively. The resulting solid was purified by column chromatography using petroleum ether as the eluent, and then the solid was dried *in vacuo*. The resulting product yield was 87% (0.571 g). MS: $m/z = 657$ [M^+]. $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 7.83(d, 4H), 7.51(m, 9H), 7.4(s, 2H), 7.17(m, 8H).

Anal. calcd. For $\text{C}_{36}\text{H}_{23}\text{N}_3\text{Br}_2$: C, 65.75%; H, 3.50%. Found: C, 65.52%; H, 3.46%.

9-Octyl carbazole (3)

1-octylbromide (11.6 g) was added dropwise to a stirring mixture of carbazole (10 g, 60 mmol), potassium hydroxide (5 g, 89 mmol) and DMSO (60 mL) under argon atmosphere. The reaction mixture was under reflux for 5 h. After being cooled to room temperature, poured into the cracked ice, the white solid was obtained by filtration, and was recrystallized from ethanol twice to give a pure white solid, 15.4 g with 91.6% yield. $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 8.10(d, 2H), 7.45(m, 4H), 7.21(t, 2H), 4.26(t, 3H), 1.84(t, 2H), 1.32(m, 10H), 0.86(t, 3H).

3,6-Diformyl-9-octyl carbazole (4)

To a flask containing DMF (60 mL) was added dropwise POCl_3 (40 mL) over 1 h at 0°C, and the obtained deep-red solution was stirred at room temperature for 2 h. A solution of 3 (7 g, 25 mmol) in 1, 2-dichloroethane(40 mL) was added dropwise to the mixture, and the mixture was allowed to be heated to 90°C and be kept at this temperature for 36 h. The dark reaction mixture was poured into ice water, stirred at room temperature overnight; the reaction mixture was neutralized carefully with the powder of sodium bicarbonate, and extracted with methylene chloride. The organic layer was washed with water, dried over Na_2SO_4 , and concentrated *in vacuo*. The crude product was purified by column

chromatography on silica by using a mixture of solvents [a 10 : 1 mixture of petroleum ether and ethyl acetate (v/v)] to give four as a white solid with 73% yield. MS: $m/z = 335$ [M^+]. $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 10.13(s, 2H, CHO), 8.67(s, 2H), 8.10 (dd, 2H), 7.56 (d, 2H), 4.38 (t, 2H), 1.93(t, 2H), 1.60-1.32 (m, 10H), 0.85 (t, 3H).

3,6-Bis[2-(4-bromophenyl)-2-cyanovinyl]-9-octyl carbazole (5)

A mixture of 0.335 g (1 mmol) of compound 1 and 0.588 g (3 mmol) 4-bromophenyl acetonitrile was stirred in 30 mL of ethanol at room temperature. A catalytic amount of potassium *tert*-butoxide (50 mg) in 20 mL ethanol was added to this mixture. After 1 day, yellow-greenish solid was filtered and washed by water and methanol alternatively. The resulting solid was purified by column chromatography using petroleum ether as the eluent, and then the solid was dried under vacuum to give 5 (0.591 g, yield: 86%) as yellow solid. MS: $m/z = 691$ [M^+]. $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 8.66(s, 2H), 8.19 (d, 2H), 7.60 (s, 2H), 7.56 (m, 8H), 7.50 (d, 2H), 4.36 (m, 2H), 1.92 (m, 2H), 1.38 (m, 10H), 0.87 (t, 3H). Anal. Calcd for $\text{C}_{38}\text{H}_{33}\text{Br}_2\text{N}_3$: C, 66.00; H, 4.78; N, 6.08. Found: C, 65.53; H, 4.72; N, 5.92.

Synthesis of the polymers

A general procedure of polymerization is proceeded through the Suzuki coupling reaction with an equivalent molar ratio of the diboronic ester monomer to the dibromo monomers under the protection of argon atmosphere. The purifications of the polymers were conducted in air with yields of 50–70%.

PF-BCT

A mixture of 2,7-Bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (8) (128 mg, 0.2 mmol), 4, 4'-Bis[2-(4-bromophenyl)-2-cyanovinyl]triphenylamine (2)(131.4 mg, 0.2 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (10 mg) were added into a degassed mixture of toluene(10 mL) and aqueous 2M potassium carbonate (2 mL). The mixture was vigorously stirred at 110°C for 48 h. At the end of the polymerization, a small amount of 8 was added to remove the bromine end group, and bromobenzene was added as a monofunctional end capping reagent to remove the boronic ester end group because boron and bromine units could quench emission and contribute to excimer formation in LED application. After the mixture was cooled to room temperature, it was poured into vigorously stirred methanol. A solid was obtained by filtration. The solid was purified sequentially with methanol, acetone for 1 day respectively, by Soxhlet

extraction to remove the oligomers and catalyst residues. The solid was extracted from CHCl_3 , the CHCl_3 solution was evaporated under reduced pressure and precipitated from methanol solution, then centrifugation and dried *in vacuo*, a brown-yellowish polymer was obtained. Yield: 65%. $M_w = 2.28 \times 10^4$, $M_w/M_n = 1.76$.

ELEM. ANAL. Calcd. For $(\text{C}_{65}\text{H}_{63}\text{N}_3)_n$: C, 88.09%; H, 7.17%; N, 4.74%. Found: C, 86.82%; H, 6.89%; N, 4.35%; Br, 1.5%.

PF-BCC was polymerized in the same manner to the PF-BCT. Yield: 52%. $M_w = 1.68 \times 10^4$, $M_w/M_n = 1.90$. ELEM. ANAL. Calcd. for $(\text{C}_{67}\text{H}_{73}\text{N}_3)_n$: C, 87.48%; H, 7.94%; N, 4.57%. Found: C, 82.62%; H, 7.24%; N, 4.31%; Br, 2.2%.

RESULTS AND DISCUSSION

Synthesis and characterization

The general synthetic route to the monomers and polymers is outlined in Scheme 1. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (8) can be prepared from fluorene according to the literature procedure.¹⁸ Polymers were prepared by a Suzuki polycondensation reaction in a biphasic system (toluene/aqueous K_2CO_3) using $\text{Pd}(\text{PPh}_3)_4$ as a catalyst. All of the polymers were end-capped with bromobenzene. The molecular weights of polymers were determined by GPC using THF as the eluent and polystyrene as the standard. The polymerization results are summarized in Table I. The copolymers are found to be soluble in common solvents, such as chloroform, tetrahydrofuran, and toluene.

Thermal stability

The thermal stability of the copolymers was evaluated in a nitrogen atmosphere by TGA. Figure 1 shows the TGA diagram of copolymers. PF-BCT starts to lose weight at 162°C and is 200°C at 2% weight loss, which is similar to the reported some PFs.^{20–22} PF-BCT and PF-BCC is 343°C and 427°C, respectively, at 5% weight loss, which indicates two polymers possess good thermal stability. In two copolymers, PF-BCC has better thermal property than that of PF-BCT, which may be concerned with the rigidity structure of carbazol group. Obviously, the thermal stability of the polymers is adequate for the fabrication processes of optoelectronic device

TABLE I
Polymerization and Molecular Weights of Polymers

Polymer	M_w	M_w/M_n	DP	Yield (%)
PF-BCT	2.28×10^4	1.76	15	65
PF-BCC	1.68×10^4	1.90	10	52

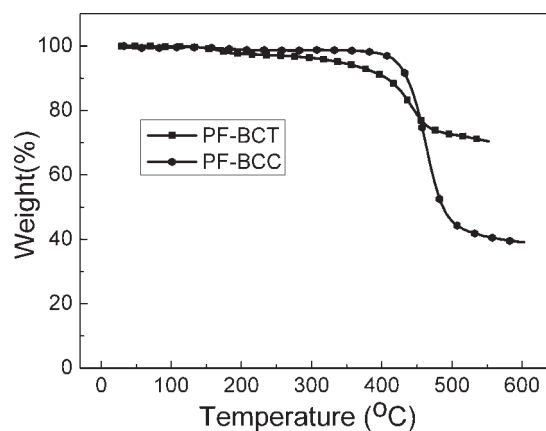


Figure 1 TGA of PF-BCT and PF-BCC with a heating rate of 10°C/min.

Optical properties

The photophysical properties of the copolymers were measured by UV-vis and PL spectroscopy in chloroform solution and thin films on quartz plates, and shown in Figure 2. As can be seen from Figure

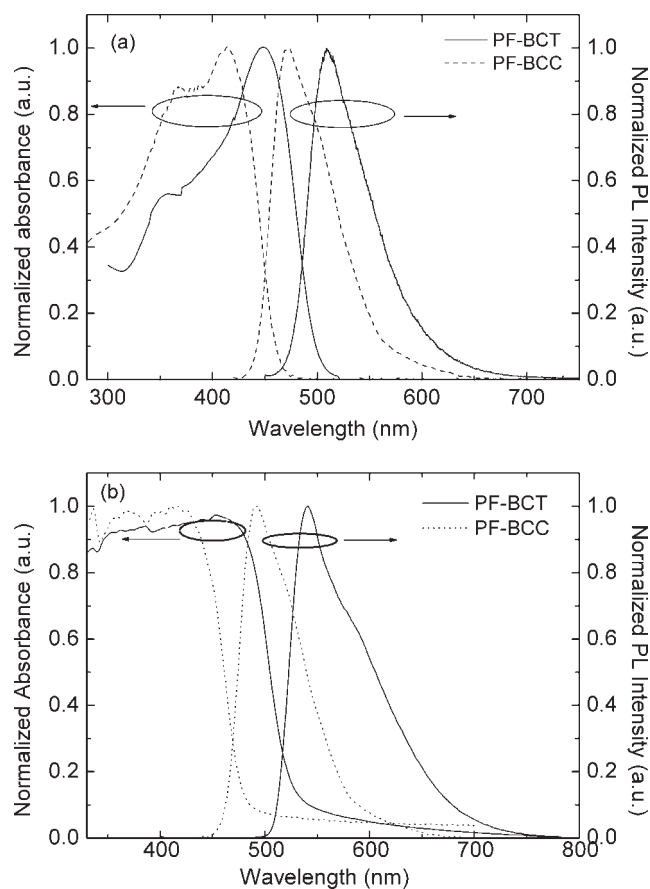


Figure 2 (a) Absorption and Emission spectra of PF-BCT (line) and PF-BCC (dashed) in diluted chloroform solution. (b) Absorption and Emission spectra of PF-BCT (line) and PF-BCC (dashed) films spinning coated from chloroform solution on a quartz plate.

TABLE II
Optical and Photoluminescence Properties of the Polymers

Polymer	Soln λ_{\max} (nm) ^a		Film λ_{\max} (nm) ^b		E_g (eV) ^c
	Abs	PL	Abs	PL	
PF-BCT	435, 450	508	458	541	2.31
PF-BCC	368, 414	470	415	491	2.56

^a Measured in chloroform solution.

^b Polymer cast from chloroform solution.

^c Band gap estimated from the onset wavelength of the optical absorption of the solid thin films.

2(a), PF-BCT shows a UV-vis absorption peak in chloroform solution at about 450 nm, there exists a shoulder peak at 435 nm, which greatly redshifts compared with the absorption peak of poly(triphenylamine)s (300 nm) and PFO.²³ For PF-BCC, its UV-vis absorption peak in chloroform solution is at about 414 nm, a shoulder peak at 368 nm is also shown, which shifts to the longer wavelength compared with these of poly(carbazole)s (308 nm in chloroform solution)²⁴ and PFO,²³ the above phenomena suggest the presence of a charge-transferred (CT) electronic state in PF-BCT and PF-BCC; such CT behavior is attributed to the formation of a conjugation system between electron-withdrawing cyano unit and electron-donating triphenylamine unit or carbazole unit. Peak at about 368 nm, which is near to that of poly(carbazole-co-fluorene)s (ca. 380 nm, solution).^{25,26}

As can be seen from Figure 2(a), the polymers are excited at the wavelength corresponding to the maximum absorption of the π - π^* transition. PF-BCT and PF-BCC emit blue-green and blue light in dilute chloroform solution, respectively. As shown in Figure 2(a), the PL spectra of the polymers are regular and symmetrical. PF-BCT in chloroform solution shows emission peak at 508 nm with quantum yield of near 67%, estimated by using a quinine sulfate, as a reference.¹⁹ For PF-BCC, with quantum yield of near 43%, its solution in diluted chloroform (10^{-6} mol/L) shows the emission peak at 470 nm.

Figure 2(b) shows the optical absorption and PL spectra of PF-BCT and PF-BCC in solid state. In the solid state, the onset positions of the UV-vis absorption band of polymers appear at longer wavelength position than these of the polymers in solutions, indicating that there are certain *p*-stacking structures in the polymers. Optical band gaps (E_g^{EC}) determined from the absorption edge of the solid-state spectra of PF-BCT and PF-BCC are found to be 2.28 and 2.55 eV. The shapes of PL spectra of PF-BCT and PF-BCC in solid state are almost identical to those in dilute chloroform solution, and the maximum emission peaks of PF-BCT and PF-BCC are observed at about

541 and 493 nm, respectively. Compared to the solution, PL spectra, PF-BCT, and PF-BCC red-shifts for 23 and 33 nm, respectively. In the solid film, the interchain interactions make the main chains extended and the conjugation degree increased, which makes the emission red-shifted. With introduction of the narrower band-gap comonomers, the PL emissions around 420 and 440 nm, which are assigned to the emission of poly(dioctylfluorene) (PFO),²³ disappeared, whereas new emissions from the low energy band-gap comonomer units of the copolymer appeared with the peak positions at 541 and 493 nm for PF-BCT and PF-BCC in the film state, respectively, [Fig. 2(b)]. This appears to indicate that the energy transfer from the fluorene segment to the narrow band-gap comonomer occurred mainly along the polymer chain. In other words, the intramolecular energy transfer via efficient Foster energy transfer or a trapping mechanism along the polymer chain must be very efficient. The same phenomena can be observed in the copolymerization of fluorene and other narrow band gap unit.²⁷⁻²⁹ The optical and photoluminescence properties of the polymers are summarized in Table II.

Electrochemical properties

The HOMO and LUMO energy levels of the materials are very crucial parameters for LED configuration. To gain information on the charge injection, cyclic voltammogram (CV) was employed to estimate the HOMO and LUMO energy levels of the polymers.³⁰ The CV curves of the two polymers are shown in Figure 3 in the potential range of 0–1.4 V versus Ag/Ag⁺. Electrochemical *p*-doping (oxidation) of PF-BCT and PF-BCC starts at about 0.7 and 0.9 V versus Ag/Ag⁺ and shows *p*-doping peaks at 0.85 and 1.15 V versus Ag/Ag⁺, respectively. The

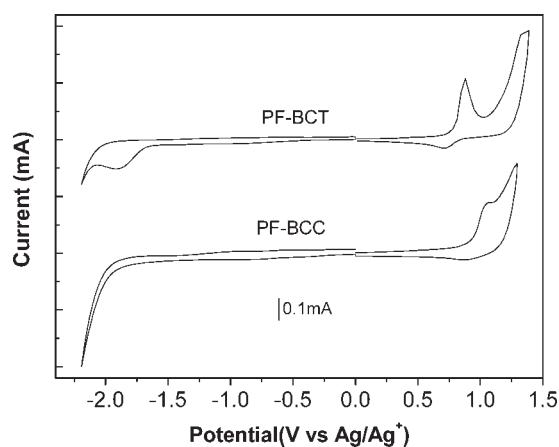


Figure 3 Cyclic voltammograms of PF-BCT and PF-BCC films on platinum plates in an acetonitrile solution of 0.1 mol/L $[\text{Bu}_4\text{N}]\text{PF}_6$ (Bu = butyl) with a sweep rate of 50 mV/s.

electrochemical *n*-doping (reduction) of PF-BCT and PF-BCC starts at about -1.69 V versus Ag/Ag⁺ and -1.90 V versus Ag/Ag⁺. It is well known that the onset potentials of the *p*- and *n*-doping are corresponding to the HOMO and LUMO energy levels of the conjugated polymers.^{30,31} By assuming the energy level of ferrocene/ferrocenium (Fc/Fc⁺) to be -4.8 eV below the vacuum level,³² the formal potential of Fc/Fc⁺ was measured as 0.09 V against Ag/Ag⁺. So, we can get the HOMO and LUMO energy levels of PF-BCT and PF-BCC according to the equations³¹: HOMO = $-e(E_{\text{on}}^{\text{ox}} + 4.71)$ (eV); LUMO = $-e(E_{\text{on}}^{\text{red}} + 4.71)$ (eV). The HOMO and LUMO energy levels of PF-BCT are calculated to be -5.41 eV and -3.02 eV, and The HOMO and LUMO energy levels of PF-BCC is -5.61 eV and -2.81 eV, respectively. As well known, carbazol and triphenylamine units have little effect on the LUMO energy of the copolymers such as poly(carbazole-*co*-fluorene)s.²⁴ From this, we can conclude that CN units reduced LUMO energy level and the hole transporting units such as triphenylamine and carbazole group raised HOMO energy level of the copolymers compared to that of PFO without cyano units and hole transporting units in the backbone (LUMO: -2.12 eV, HOMO: -5.80 eV).³³ The increased HOMO energy level can decrease the barrier of the polymer and PEDOT : PSS layer, which made hole injection improved. On the other hand, decreased LUMO energy level can facilitate electron injection. Therefore, we can get relatively balanced energy level through the introduction of the electron-withdrawing units and hole transporting units in the copolymers compared to PF homopolymers such as PFO.

For comparing expediently, electrochemical data are listed in Table III. From Table III, we can see that the HOMO energy level decreased and LUMO energy level raised from PF-BCT to PF-BCC, so the electrochemical bandgap (E_g^{EC}), calculated from CV data ($E_{\text{on}}^{\text{ox}} - E_{\text{on}}^{\text{red}}$) got increased. The optical bandgap (E_g^{opt}), estimated from the absorption band edge of the film ($1240/\lambda_{\text{onset}}$) increased from PF-BCT to PF-BCC, which is in agreement with that the electro-

TABLE III
Electrochemical Properties of Polymers

Polymer	Cyclic voltammograms				E_g^{EC} (eV)
	<i>p</i> -doping		<i>n</i> -doping		
	$E_{\text{on}}^{\text{ox}}$ (V)	HOMO (eV)	$E_{\text{on}}^{\text{red}}$ (V)	LUMO (eV)	
PF-BCT	0.70	-5.41	-1.69	-3.02	2.39
PF-BCC	0.90	-5.61	-1.90	-2.81	2.80

^a Band gap calculated according to the equation: $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{gap}}$.

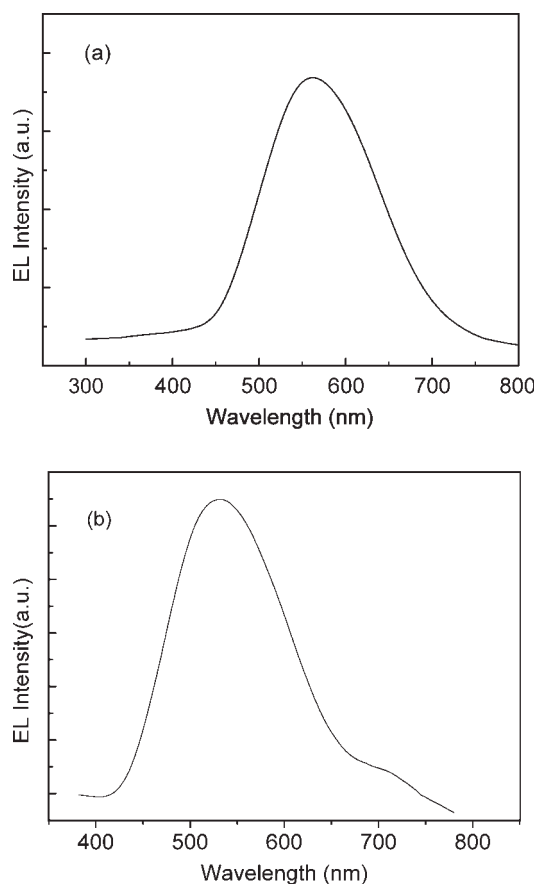


Figure 4 EL spectra of the ITO/PEDOT: PSS/polymer/Ca/Al devices (a) PF-BCT (b) PF-BCC.

chemical bandgap. The E_g^{opt} is somewhat lower than corresponding E_g^{EC} .

Electroluminescence properties

Initial investigation of the EL properties of PF-BCT and PF-BCC were made by fabricating single-layer PLEDs of the type ITO/PEDOT: PSS(30 nm)/polymer(100 nm)/Ca (15 nm)/Al(150 nm). It was observed that PF-BCT and PF-BCC emitted yellow and greenish yellow light, respectively.

The EL spectra of PF-BCT and PF-BCC were shown in Figure 4, yellow electroluminescence with an emission peak at 561 nm was observed from PF-BCT in diodes of the type ITO/PEDOT: PSS/PF-BCT/Ca/Al [Fig. 4(a)]. PF-BCC exhibited a greenish yellow emission at 528 nm, there was increased peak at about 700 nm due to the electroplex emission caused by the interactions of a polymer segment at the excited state with its neighboring segment at the ground state of the same polymer and a different polymer, respectively,³⁴ which is similar to the reported PFCAR10 in the literature.³⁵ All the EL spectra of the copolymers are red shifted to the corresponding PL spectra of their films. Similar results

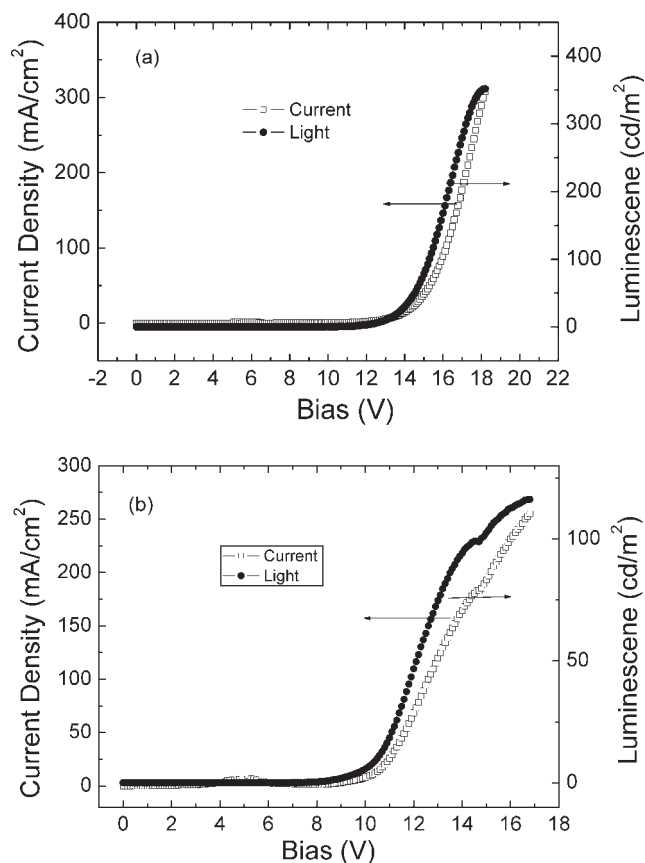


Figure 5 Current density-voltage ($I - V$) and luminance-voltage ($L - V$) characteristics of the ITO/PEDOT:PSS/polymer/Ca/Al devices of (a) PF-BCT (b) PF-BCC.

were reported before,^{36,37} which indicates that the molecules may be partially oriented, the molecules can be arrayed more orderly, therefore, increases the interactions between molecules under the electric field.³⁸

Figure 5 shows current density-voltage ($I - V$) and luminance-voltage ($L - V$) characteristics of the single-layer PLED devices. The current density increased exponentially with the increasing forward bias voltage, which was a typical diode characteristic. The turn-on voltage of the PLEDs based on PF-BCT and PF-BCC was ~ 12 and 9 V, respectively. The maximum luminance of the single-layer PLEDs based on PF-BCT and PF-BCC was about 375 cd/m^2 at 17.2 V, and 120 cd/m^2 at 16.8 V, respectively.

The luminescence-efficiency/current-density curves of the single devices are shown in Figure 6. As shown in Figure 6, a maximum luminescence efficiency of PF-BCT was about 0.21 cd/A . Although the maximum luminescence efficiency of PF-BCC was about 0.08 cd/A , in comparison of PF-BCC, the EL efficiency of PF-BCT is $\sim 170\%$ higher than that of PF-BCC. The lower EL efficiency of PF-BCC is probably due to the larger hole injection barrier because of higher ionization potential than that of

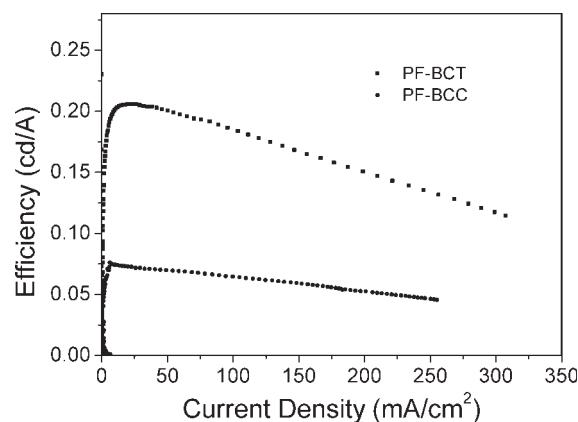


Figure 6 EL current efficiency curves of the ITO/PEDOT:PSS/polymer/Ca/Al devices.

PF-BCT as shown in Figure 10. PF-BCT has better hole transporting ability. Since the HOMO for the copolymer PF-BCC is around -5.61 eV , while the work function of PEDOT:PSS is around $5.0\text{--}5.2 \text{ eV}$, it would be possible to expect a better hole injection once a PVK (work function 5.4 eV) is used as the hole injection or electron block layer. So we further fabricated EL devices with a configuration of ITO/PEDOT:PSS/PVK/PF-BCC/Ca/Al. The EL spectra of the devices are shown in Figure 7. The EL speak of PF-BCC is red shifted to 554 nm compared to that of the EL devices without a PVK layer. This might be attributed to different contributions of photon vibration, and also possibly due to a microcavity effect.³⁹ On the other hand, the EL spectrum of the device shows no emission from PVK, implying that efficient energy transfer from PVK to PF-BCC occurs in the double layer device because the emission spectrum of PVK (the maximum emission peak: 400 nm) overlaps with the absorption spectrum of PF-BCC. Figure 8 shows the current-voltage-brightness characteristic of the double layer device of PF-BCC,

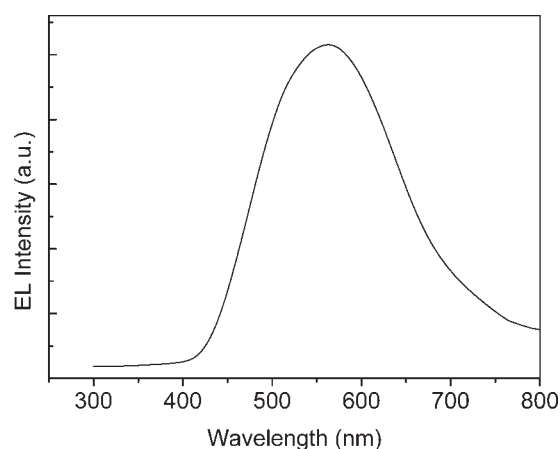


Figure 7 EL spectra of the ITO/PEDOT:PSS/PVK/PF-BCC/Ca/Al devices.

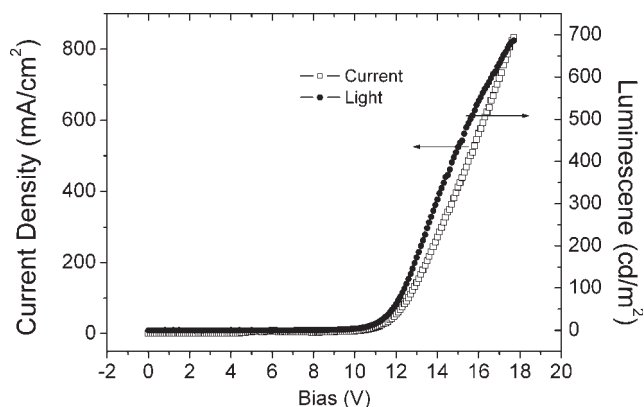


Figure 8 Current density-voltage ($I - V$) and luminance-voltage ($L - V$) characteristics of the ITO/PEDOT : PSS/PVK/PF-BCC/Ca/Al devices.

the performance of the double layer device was greatly improved. The brightness reaches 700 cd/m^2 at a bias voltage of 17.6 V, the maximum luminescence efficiency of PF-BCC was about 0.12 cd/A as shown in Figure 9.

As sketched in Figure 10, for PF-BCC, the energy barrier for hole injection is as high as 0.6 eV , at the cathode, the energy barrier between PF-BCC and Ca electrode is as small as 0.1 eV . Thus, the hole and electron injections are unbalanced in the single device, on the other hand, the PVK is employed as the hole injection and electron blocking layer, the energy barrier for hole injection is reduced from 0.6 to 0.2 eV , therefore, the performance of the double-layer LED got improved because of much more balanced charge transporting ability due to the introduced PVK layer.

CONCLUSIONS

We have successfully synthesized two new polyfluorene derivatives, PF-BCT and PF-BCC according

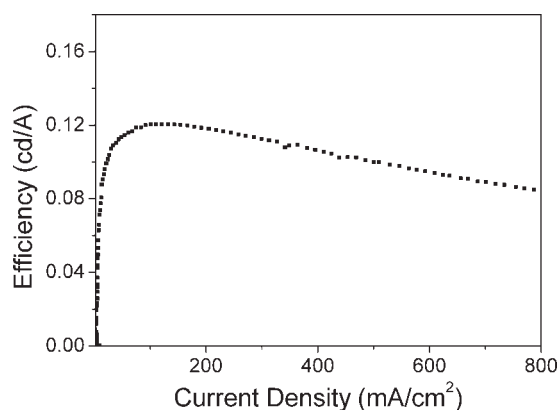


Figure 9 EL current efficiency curve of the ITO/PEDOT: PSS/PVK/PF-BCC/Ca/Al devices.

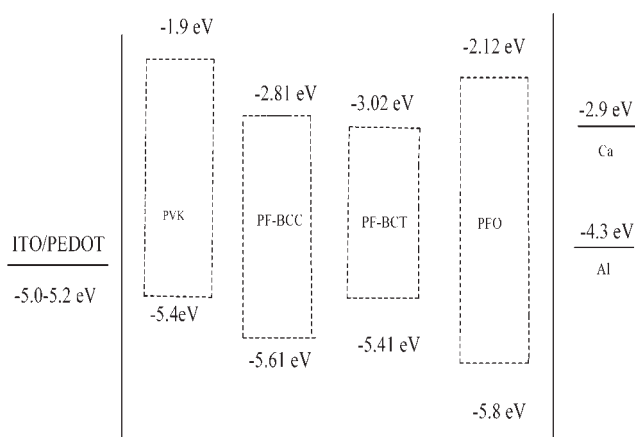


Figure 10 Diagram of the electrochemically determined HOMO and LUMO energy levels relative to the work functions of the electrode materials.

to the Suzuki coupling method. The resulting polymers possess excellent solubility in common organic solvents, good thermal stability, and high molecular weights. The HOMO and LUMO values estimated from CV measurement indicate that the polymers are suitable as bipolar materials. Triphenylamine and carbazole units can facilitate hole injection, and cyano group can facilitate electron transport, therefore the polymers possess more balanced transporting properties than that of PFO. The single layer devices of PF-BCT and PF-BCC exhibit yellow and yellowish green color with the quantum efficiencies of 0.21 cd/A and 0.08 cd/A . The performance got greatly improved in the double layer device of PF-BCC with a maximum brightness of 700 cd/m^2 and quantum efficiency of 0.12 cd/A .

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