Pure Deep Blue Light-Emitting Diodes from Alternating Fluorene/ Carbazole Copolymers by Using Suitable Hole-Blocking Materials

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Received October 22, 2003; Revised Manuscript Received January 14, 2004

ABSTRACT: The influences of the carbazole content on the photophysical, electrochemical, and electroluminescent properties of alternating fluorene/carbazole copolymers PFnCz (n = 1, 2, 3) with well-defined chemical structures have been systematically investigated. The incorporation of carbazole units into the polyfluorene (PF) backbone resulted in a blue shift of both the absorption and photoluminescence (PL) emission peaks, improved PL thermal stability, raised HOMO energy levels, and thus facilitated hole injection into the copolymers. Pure deep blue electroluminescence (EL) with narrow fwhms (full width at the half-maximum) (39–52 nm) and negligible low-energy emission bands was successfully achieved from the PFnCz copolymers by using 1,3,5-tris(4'-fluorobiphenyl-4-yl)benzene (F-TBB) as a hole-blocking layer and Alq<sub>3</sub> as an electron injection/transporting layer. This device configuration stabilized the blue emission from the PF derivatives. An efficiency of 0.72 cd/A at a luminance of 100 cd/m<sup>2</sup> was obtained even with aluminum metal as the cathode.

# Introduction

The first report in 1990 on the electroluminescence (EL) from poly(*p*-phenylenevinylene)<sup>1</sup> triggered a large amount of interest in polymeric light-emitting diodes (PLEDs). Since their initial appearance, many improvements have been made in polymer-based devices, including emission across the entire visible spectrum, low drive voltage, good efficiency, and high brightness.<sup>2</sup> However, the development of blue-light-emitting polymers remains the subject of intense research in both academia and industry due to their potential application in full-color flat panel displays. They can be used either as the active layer in PLEDs or as the host material for internal color conversion techniques.<sup>3</sup>

In the past decade, fluorene-based conjugated polymers (PFs) have emerged as a very promising class of blue-light emitting materials for use in PLEDs because of their high photoluminescence (PL) and electroluminescence quantum efficiencies, thermal stability, good solubility, and facile functionalization at the C-9 position of fluorene.<sup>4</sup> However, the application of polyfluorenes in PLEDs has been hampered because of the troublesome formation of a tailed emission band at long wavelengths (> 500 nm) during device fabrication and operation, leading to both a color instability and reduced efficiency. Some researchers attributed this instability to the undesired interchain aggregation and/or excimer formation and demonstrated that the introduction of bulky groups at the C-9 position of the fluorene or introduction of cross-linkable moieties such as styryl groups tended to suppress the excimer emission and to improve the thermal stability of PL spectra.<sup>5</sup> However, recent results indicated that keto defects in the polymer backbone, originating probably from photo- and/or electrooxidative degradation of 9,9,-dialkylated PFs, were

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mainly responsible for this strong low-energy emission.<sup>6</sup> Scherf and co-workers have shown that the end-capping of polyfluorenes with bis(4-methylphenyl)phenylamine can almost completely suppress the keto defect emission band.<sup>7</sup> Another serious problem associated with polyfluorene homopolymer is the significant energy barrier for hole injection from the ITO anode since its HOMO energy level is as low as 5.8 eV.8 As a result, an additional hole transport layer (HTL) is necessary in polyfluorene-based PLED structures to achieve acceptable device performance. Poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT-PSS)<sup>9</sup> and camphorsulfonic acid-doped polyaniline<sup>10</sup> are widely used as the hole injection/transport layer in blue PLED devices. Although these conducting polymers have been shown to increase hole injection, none of them is perfect because of their significant absorption in the visible region and the unstable interface they form with ITO.<sup>11</sup> Another approach to address the deficiency in hole injection is the modification of chemical structures of PFs through the incorporation of electron-donating moieties, such as thiophene,12 triphenylamine,13 and carbazole,<sup>4b</sup> into the polymer backbone.

In this study, we prepared a series of alternating fluorene/carbazole copolymers PFnCz (n = 1, 2, 3) with well-defined chemical structures and systematically investigated the influences of the carbazole content on photophysical, electrochemical, and electroluminescent properties of the resulting polymers. Cyclic voltammetric studies have shown that the HOMO energy levels of copolymers PFnCz can be raised by increasing the carbazole content. Consequently, the hole injection was greatly improved, as proven by the current densityelectric field strength characteristics of the hole-only devices consisting of the PFnCz film sandwiched between ITO and Au electrodes. As the main-chain conjugation is interrupted by the presence of the 3.6carbazole units, the absorption and PL emission peaks of the alternating copolymers were blue-shifted with an increase in the carbazole content. Compared to PF

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homopolymer, all of the PFnCz copolymers examined in this study exhibited much more stable emission spectra with very little change after annealing at 150 °C under vacuum for 24 h. This is probably due to the interruption of the linearity of the polymer backbones by the 3,6-carbazole units. A pure deep blue PLED with negligible emission in the 500-600 nm region has been achieved from the PFnCz copolymers by using 1,3,5-tris-(4'-fluorobiphenyl-4-yl)benzene (F-TBB) as a hole-blocking layer and Alq<sub>3</sub> as an electron injection/transporting layer. An efficiency of 0.72 cd/A at a luminance of 100 cd/m<sup>2</sup> was obtained even with aluminum metal as the cathode. However, when the F-TBB was replaced by 1,3,5-tris(4'-cyanobiphenyl-4-yl)benzene (CN-TBB), device performance degraded, leading to the broadening of the emission peak and a much lower efficiency. This means that the choice of hole-blocking material has a large impact on the device performance.

# **Experimental Section**

Materials. Reagent grade solvents and chemicals were used as received unless otherwise noted. Aluminum chloride, 4-bromobiphenyl, acetyl chloride, copper(I) cyanide, and trifluoromethanesulfonic acid were purchased from Aldrich. 4-Fluorobiphenyl was obtained from Fluorochem USA. Acetonitrile used in the electrochemical measurements was refluxed in the presence of calcium hydride under argon and distilled prior to use. Alternating 9,9-dioctylfluorene/9-octylcarbazole copolymers PFnCz (n = 1, 2, 3) were synthesized using the Suzuki coupling reaction of 9-octylcarbazole-3,6-bis(ethyleneboronate) and the corresponding fluorene oligomer dibromo compounds in refluxing toluene in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.5% equiv), 2 M NaCO<sub>3</sub> (3.3 equiv), and a phase-transfer catalyst, tricaprylylmethylammonium chloride (Aliquat 336). The chemical structures of the resulting copolymers PFnCz are shown in Chart 1, and the detailed synthetic procedures were published elsewhere.14

Characterization. <sup>1</sup>H NMR spectra were obtained in CDCl<sub>3</sub> on a 400 MHz Varian Unity Inova spectrometer. Thinlayer chromatography (TLC) was carried out on Silica gel 60 F (254) precoated sheets (Aldrich). The molecular weights of fluorene/carbazole copolymers were determined using gel permeation chromatography (GPC) on a Waters model 515 HPLC equipped with  $\mu$ -Styragel columns (10<sup>3</sup>, 10<sup>4</sup>, and 10<sup>5</sup>) using THF as an eluent with polystyrene standards. UV-vis absorption spectra were recorded on a Varian Cary 50 spectrophotometer. Fluorescence measurements were carried out on a Spex Fluorolog 3 spectrometer. The absorption  $\lambda_{max}$  of samples were used as the excitation wavelengths ( $\lambda_{exc}$ ) for the measurement. The differential scanning calorimetry (DSC) analysis of small molecules and fluorene/carbazole copolymers was performed under a nitrogen atmosphere on a TA Instruments DSC 2920 at heating rates of 10 °C/min. High-resolution mass spectrometry was carried out by the mass spectroscopy facility in the Chemistry Department, University of Ottawa. Cyclic voltammetry (CV) measurements were conducted in a 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution using a Solartron SI 1287 potentiostat at a scan rate of 50 mV s<sup>-1</sup> at room temperature under nitrogen. A silver wire (2 mm diameter), a platinum wire (0.5 mm diameter), and a platinum disk (1 mm diameter)

sealed in a soft glass rod were used as the quasi-reference electrode, counter electrode, and working electrode, respectively. The Ag quasi-reference electrode was calibrated using a ferrocene/ferrocenium redox couple as an external standard prior to measurements.

EL Device Fabrication and Testing. ITO-glass substrates (15  $\Omega/\Box$ ) were patterned by the conventional photolithography using an acid mixture of HCl and HNO<sub>3</sub> as the etchant. After patterning, the samples were rinsed in deionized water and then ultrasonicated sequentially in acetone and 2-propanol. The active area of each EL device was  $5 \times 6 \text{ mm}^2$ . A thin layer of PFnCz copolymer was spin-coated onto the ITO substrate from its chloroform solution (ca. 12 mg/mL) at 2000 rpm for 60 s. The thickness of the resulting film was measured using a Dektak<sup>3</sup> surface profilometer and found to be around 100 nm. A hole-blocking layer (20 nm) was then vacuumdeposited on top of the polymer film at  $2 \times 10^{-7}$  Torr, followed by the deposition of  $\hat{Alq_3}$  thin film (10 nm). The device fabrication was completed by the evaporation of LiF and aluminum cathode. The devices were tested in air under ambient conditions with no protective encapsulation. EL spectra, device luminances, and current-voltage characteristics were recorded using a combination of a Photo Research PR-650 SpectraScan and a Keithley 238 source meter.

4-Acetyl-4'-bromobiphenyl (1). 4-Bromobiphenyl (10.0 g, 42.9 mmol) was dissolved in 60 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C under a blanket of nitrogen. In a separate 150 mL three-necked flask equipped with an addition funnel, a condenser, and a nitrogen inlet, AlCl<sub>3</sub> (10.00 g, 74.9 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (80 mL) were added. Acetyl chloride (3.80 mL, 53.4 mmol) was added to the AlCl<sub>3</sub> suspension. The pale greenish mixture of the AlCl<sub>3</sub>/CH<sub>3</sub>-COCl complex with uncomplexed AlCl<sub>3</sub> was then added dropwise to the 4-bromobiphenyl solution over a period of 1 h. Upon the addition of the AlCl<sub>3</sub>/CH<sub>3</sub>COCl complex, the reaction solution turned dark yellow immediately. After the completion of the addition, the reaction mixture was further stirred at 0 °C for another 5 h. The reaction mixture was then poured into ice-HCl (300 mL of broken ice/30 mL of concentrated HCl). The organic layer was separated, washed with water, and dried with MgSO<sub>4</sub>. The crude product was isolated as a pale yellow powder by distilling the solvent out under reduced pressure and purified by silica gel column chromatography using CH2-Cl<sub>2</sub> as the eluent. After drying at 45 °C in vacuo overnight, 8.21 g (69.6% yield) of a white crystalline powder was obtained.

Mp: 129.7 °C. TLC (silica, CH<sub>2</sub>Cl<sub>2</sub>): one spot,  $R_f = 0.32$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 8.02 (d, 2H, J = 8.4 Hz), 7.64 (d, 2H, J = 8.4 Hz), 7.59 (d, 2H, J = 8.4 Hz), 7.48 (d, 2H, J = 8.4 Hz), 2.63 (s, 3H).

**1,3,5-Tris(4'-bromobiphenyl-4-yl)benzene (Br-TBB), 3.** To a 100 mL three-necked round-bottom flask fitted with a magnetic stirrer, a condenser, and a nitrogen inlet was added 4-acetyl-4'-bromobiphenyl, **1** (4.40 g, 0.016 mol), trifluo-romethanesulfonic acid (0.8 mL), and toluene (35 mL). The reaction solution was stirred at reflux under nitrogen for about 14 h. After cooling, the crude product was collected by filtration, washed with methanol, and purified by recrystalizing twice from chloroform. After drying at 90 °C in vacuo overnight, 1.60 g (38.9%) of a white crystalline powder was obtained.

Mp: 280.7 °C. TLC (silica, CH<sub>2</sub>Cl<sub>2</sub>): one spot,  $R_f = 0.92$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 7.86 (s, 3H), 7.79 (d, 6H, J = 8.4 Hz), 7.69 (d, 6H, J = 8.4 Hz), 7.59 (d, 6H, J = 8.4 Hz), 7.53 (d, 6H, J = 8.4 Hz). MS: found M<sup>+</sup> 768; calcd M<sup>+</sup> 768.

**1,3,5-Tris(4'-cyanobiphenyl-4-yl)benzene (CN-TBB), 5.** A 100 mL three-necked round-bottom flask fitted with a magnetic stirrer, a condenser, and a nitrogen inlet was charged with Br-TBB **3** (1.60 g, 2.08 mmol), CuCN (1.12 g, 12.5 mmol), and *N*-methyl-2-pyrrolidinone (15 mL). The reaction mixture was heated to reflux under nitrogen. Upon heating, both compound **3** and CuCN dissolved into NMP to form a greenish yellow solution. The reaction solution was stirred at reflux for about 4 h. During stirring, a brown solid precipitated out of the solution. The hot reaction mixture was poured into a solution of FeCl<sub>3</sub> (8.0 g), concentrated HCl (4 mL), and H<sub>2</sub>O (24 mL), and stirred at 50 °C for 20 min. The crude product





was collected by filtration and washed sequentially with a queous HCl solution,  $H_2O$ , and methanol. Purification by column chromatography using  $CH_2Cl_2$  as an eluent afforded 1.05 g (83.1% yield) of a white powder.

Mp1: 265.5 °C; Mp2: 333.6 °C (major peak).  $T_g$ : 116.0 °C. TLC (silica, CH<sub>2</sub>Cl<sub>2</sub>): one spot,  $R_f = 0.33$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 7.90 (s, 3H), 7.85 (d, 6H, J = 8.8 Hz), 7.77 (s, 12H), 7.75 (d, 6H, J = 8.8 Hz). High-resolution MS: found M<sup>+</sup> 609.2216; calcd M<sup>+</sup> 609.2205.

**4-Acetyl-4'-fluorobiphenyl (2).** With the same procedure as described for the synthesis of the compound **1**, 4-fluorobiphenyl (10.00 g, 58.1 mmol) was reacted with acetyl chloride (5.20 mL, 73.1 mmol) in the presence of  $AlCl_3$  as catalyst. Purification by column chromatography afforded 10.36 g of a white powder in 83.3% yield.

Mp: 104.3 °C. TLC (silica, CH<sub>2</sub>Cl<sub>2</sub>): one spot,  $R_f = 0.43$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 8.03 (d, 2H, J = 8.4 Hz), 7.64 (d, 2H, J = 8.4 Hz), 7.59 (dd, 2H,  $J_1 = 8.8$  Hz,  $J_2 = 5.2$  Hz), 7.16 (t, 2H, J = 8.8 Hz), 2.63 (s, 3H).

**1,3,5-Tris(4'-fluorobiphenyl-4-yl)benzene (F-TBB), 4.** With the same procedure as described for the synthesis of the compound **3**, 4-acetyl-4'-fluorobiphenyl, **2** (4.40 g, 0.021 mol), was stirred in refluxing toluene in the presence of trifluoromethanesulfonic acid. The crude product was purified by silica gel column chromatography using  $CH_2Cl_2$  as the eluent, followed by recrystallization from toluene/hexanes. Yield: 1.55 g (38.5%). This was further purified by train sublimation at  $10^{-5}$  Torr.

Mp: 237.0 °C (lit.<sup>15</sup> 236 °C).  $T_g$ : 89.4 °C. TLC (silica, CH<sub>2</sub>-Cl<sub>2</sub>): one spot,  $R_f = 0.92$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 7.88 (s, 3H), 7.80 (d, 6H, J = 8.4 Hz), 7.69 (d, 6H, J = 8.4 Hz), 7.63 (dd, 6H,  $J_1 = 9.2$  Hz,  $J_2 = 5.2$  Hz), 7.17 (dd, 6H,  $J_1 = 9.2$  Hz,  $J_2 = 8.0$  Hz).

## **Results and Discussion**

Synthesis and Physical Properties of Hole-Blocking Materials F-TBB and CN-TBB. As a holeblocking material, the compound should have a high oxidation potential and large HOMO-LUMO energy band gap. 1,3,5-Tris(4'-fluorobiphenyl-4-yl)benzene (F- TBB) was first synthesized by Shirota via the Suzuki coupling reaction of 1,3,5-tris(4-iodophenyl)benzene with 4-fluorophenylboronic acid.<sup>15</sup> The energy gap of F-TBB was reported to be about 3.85 eV. In this study, we synthesized this compound by another approach, namely a condensation reaction. The synthetic route is outlined in Scheme 1. Besides F-TBB, we also synthesized CN-TBB with an intension to improve the electron injection/ transport property by replacing the fluorine in F-TBB with the stronger electron-withdrawing cyano group. The powder sample of CN-TBB obtained from column chromatography showed two crystallization temperatures at 172.3 and 211.8 °C, respectively, and one melting point at 333.6 °C in the first DSC analytical scan. Meanwhile, the second DSC scan following slow cooling in nitrogen exhibited a glass transition temperature at 116.0 °C, a broad crystallization peak around 250 °C, and a double melting exotherm at 265.5 and 333.6 °C. The third DSC scan was identical to the second scan. This thermal behavior associated with polymorphism has been observed for a number of amorphous molecular materials.<sup>15</sup> Both F-TBB and CN-TBB can form stable amorphous thin films by vacuum deposition and exhibit glass transition temperatures at 89.4 and 116.0 °C, respectively. The UV-vis absorption and fluorescence spectra of the vacuum-deposited 20 nm thick films of F-TBB and CN-TBB are shown in Figure 1. As can be seen from Figure 1, the replacement of fluorine with the cyano group causes a red shift in both absorption and PL emission peaks, indicating that CN-TBB has a longer effective conjugation length and lower energy gap. The physical properties of the F-TBB and CN-TBB are summarized in Table 1.

Thermal and Optical Properties of Alternating Copolymers PFnCz. DSC curves of the PFnCz copolymers show no crystallization and melting peaks but only glass transition temperatures ( $T_{g}$ s) ranging from 98 to



**Figure 1.** UV-vis absorption and fluorescence spectra of vacuum-deposited 20 nm thick films of F-TBB (solid line) and CN-TBB (dashed line).

Table 1. Physical Properties of Hole-Blocking Materials F-TBB and CN-TBB

compound	$T_{\rm g}$ (°C) <sup>a</sup>	$\lambda_{\max}^{abs}$ (nm) <sup>b</sup>	$\lambda_{\mathrm{em}}$ (nm) <sup>b</sup>
F-TBB	89.4	294	379
CN-TBB	116.0	314	396

 $^a$  Determined by DSC.  $^b$  Measured on vacuum-deposited 20 nm thick films.

113 °C. The  $T_{\rm gs}$  of PFnCz increase with the amount of carbazole in the copolymer. On the contrary, poly(9,9-dioctylfluorene) (POF) had a crystallization temperature of 113 °C and a melting point at 159 °C. This clearly indicates that the presence of the carbazole units in these copolymers effectively suppresses the crystallizability (or chain aggregation) of the polymer chains. Table 2 summarizes the physical properties of copolymers PFnCz.

UV-vis absorption and PL spectra of PFnCz films spin-coated on quartz slides are shown in Figures 2 and 3, respectively. These two spectra indicate that the absorption and emission peaks are gradually blueshifted to shorter wavelengths with an increase in the carbazole content in the copolymer. This is due to the interruption of the main-chain conjugation by the presence of the 3,6-carbazole units. The PL efficiencies ( $\Phi_{\rm fl}$ ) of these copolymers were measured in dilute THF solution by comparing emission with that of a standard solution of 9,10-diphenylanthracene in cyclohexane ( $\Phi_{\rm fl}$  = 0.95) at room temperature.<sup>16</sup> In general, these copolymers showed slightly decreased PL efficiencies ( $\Phi_{\rm fl}$  = 0.68–0.76) compared with POF ( $\Phi_{\rm fl}$  = 0.84) because of their shorter fluorene sequences. One striking prop-



**Figure 2.** UV–vis absorption spectra of PF*n*Cz films (normalized to 100 nm) spin-coated on quartz slides.



**Figure 3.** PL spectra of PF*n*Cz films spin-coated on quartz slides.

erty of these copolymers was that their PL spectra showed remarkable stability having very little change on annealing in a vacuum oven at 150 °C (a temperature well above their glass transition temperatures) for 24 h. In contrast, the emission spectrum of the annealed POF film red-shifted  ${\sim}10$  nm, and a featureless broad

Table 2. Physical Properties of Alternating PFnCz Copolymers and POF Homopolymer

polymer	$M_{ m n}$ ( $ imes 10^3$ )	PDI	<i>T</i> <sub>g</sub> (°C)	$\lambda_{ m max}^{ m abs}( m nm)^{a}$	$\lambda_{\mathrm{em}}^{\mathrm{fl}}$ (nm) As-sp <sup>a</sup>	$\lambda_{\mathrm{em}}^{\mathrm{fl}}$ (nm) Ann <sup>b</sup>	$\Phi_{\mathrm{fl}}$ $^c$
PF <sub>1</sub> Cz	26.0	2.29	113	348	412	413	0.68
PF <sub>2</sub> Cz	35.9	2.51	108	364	415, 439	416, 439	0.76
PF <sub>3</sub> Cz	31.0	2.65	98	370	419, 443,471	421, 445, 474	0.76
POF	47.2	3.45	$\mathbf{nd}^d$	385	422, 447, 481	430, 455, 485, 512	0.84

<sup>*a*</sup> Obtained from the pristine films spin-coated on quartz slides. <sup>*b*</sup> Films annealed at 150 °C under vacuum for 24 h. <sup>*c*</sup> Measured in THF solution relative to 9,10-diphenylanthracene ( $\Phi_{fl} = 0.95$  in cyclohexane) as a reference. <sup>*d*</sup> No noticeable  $T_g$  was observed; instead, a crystallization peak at 113 °C and a melting peak at 159 °C were noted.

Table 3. Electrochemical Properties and Energy Levels of F-TBB, CN-TBB, and PFnCz

sample	$E^{\mathrm{ox}}_{\mathrm{1/2}}$ or $E^{\mathrm{ox}}_{\mathrm{p/2}}$ , $\mathrm{V}^a$	$E^{ m red}_{ m 1/2}$ or $E^{ m red}_{ m p/2}$ , V $^a$	$E_{\rm HOMO}$ , <sup>b</sup> eV	$E_{\rm LUMO}$ , <sup>b</sup> eV	$E_{\rm g}$ , eV (Echem) <sup>c</sup>	$E_{\rm g}$ , eV (UV) <sup>d</sup>
F-TBB	1.91	-2.01	6.34	2.42	3.92	3.63
CN-TBB	1.78	-1.83	6.21	2.60	3.61	3.33
$PF_1Cz$	0.95	-2.36	5.38	2.07	3.31	3.06
$PF_2Cz$	0.96	-2.34	5.39	2.09	3.30	2.98
PF <sub>3</sub> Cz	1.01	-2.21	5.43	2.22	3.22	2.95
POF	1.25	-1.95	5.68	2.48	3.20	2.91

 $^{a}E_{1/2}^{\text{ox}}$  and  $E_{1/2}^{\text{red}}$  stand for half-wave oxidation (p-doping) and reduction (n-doping) potentials vs an Ag quasi-reference, respectively.  $^{b}$  Estimated from  $E_{1/2}$  by using empirical equations:  $E_{\text{HOMO}} = E_{1/2}^{\text{ox}} + 4.43 \text{ eV}$  and  $E_{\text{LUMO}} = E_{1/2}^{\text{red}} + 4.43 \text{ eV}$ .  $^{c}$  Electrochemical band gaps determined using  $E_{\text{g}} = E_{\text{HOMO}} - E_{\text{LUMO}}$ .  $^{d}$  Optical energy gap calculated from the edge of the electronic absorption band.

peak centered at 512 nm appeared. These spectral changes were observed previously for fluorene homopolymers and were believed to be due to the formation of interchain aggregates at high temperatures.<sup>17</sup> We think the interruption of the linearity of the polymer backbone by the 3,6-carbazole units can hamper close chain packing.<sup>18</sup>

Electrochemical Study. To investigate the electrochemical properties of CN-TBB, F-TBB, and copolymers PFnCz and estimate their HOMO and LUMO energy levels, cyclic voltammetry (CV) was carried out using a platinum disk (1 mm diameter), a platinum wire (0.5 mm diameter), and a silver wire (2 mm diameter) as the working electrode, counter electrode, and quasireference electrode, respectively. CV measurements were conducted in a 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution at room temperature under nitrogen with a scan rate of 50 mV s<sup>-1</sup>. PFnCz copolymers were coated on the working electrode, while small molecules F-TBB and CN-TBB were directly dissolved in acetonitrile. The Ag quasi-reference electrode was calibrated using ferrocene/ ferrocenium (Fc/Fc<sup>+</sup>) redox couple (4.8 eV below the vacuum level)<sup>17</sup> as an external standard, and the  $E_{1/2}$ of the Fc/Fc<sup>+</sup> redox couple was found to be 0.37 V vs the Ag quasi-reference electrode. Therefore, the LUMO and HOMO energy levels of the materials can be estimated using the empirical equations  $E_{LUMO} = E_{1/2}^{ox}$ + 4.43 eV and  $E_{HOMO} = E_{1/2}^{red}$  + 4.43 eV, respectively, where  $E_{1/2}^{ox}$  and  $E_{1/2}^{red}$  are the half-wave potentials for oxidation and reduction relative to the Ag quasi-reference electrode, respectively. Table 3 summarizes the electrochemical properties of the materials used in this study. Both CN-TBB and F-TBB underwent reversible cathodic reduction. However, the anodic oxidation process of F-TBB was only partially reversible. This partial reversibility does not prevent it from acting as a hole blocker because it serves to pass on electrons from the electron-transport layer to the emitting layer.<sup>15</sup> As compared with F-TBB, CN-TBB has a lower LUMO level and relatively smaller energy gap due to its longer effective conjugation length and the electron-withdrawing nature of the cyano groups.

The POF thin films showed typical CV curves similar to those reported previously for this polymer.<sup>19</sup> Both the cathode and anode sweeps were reversible. As can be seen from Table 3, the incorporation of the carbazole units raises the HOMO energy levels from 5.68 to 5.38 eV and also slightly increases the energy band gaps of the copolymers. HOMO levels rise up with increasing the carbazole content.

The electrochemical band gaps are higher than the optically measured ones probably due to the interfacial energy barrier for charge injection.<sup>20</sup> It should be noted that the alternating copolymer  $PF_1Cz$  had an irreversible CV curve in the n-doping process, although  $PF_2Cz$  and  $PF_3Cz$  underwent reversible cathodic reduction.



**Figure 4.** Electric field strength—hole current density characteristics of the hole-only devices ITO/PF*n*Cz/Au.

This implies that the electron-charged state (reductive state) of  $PF_1Cz$  is rather unstable.

The hole injection/transporting properties of these copolymers were further investigated using "hole-only" devices with a configuration of ITO/PFnCz/Au. The thickness of the spin-coated polymer films ranged from 90 to 110 nm, depending on the molecular weights of the copolymers. The concentration of POF solution was reduced to 10 mg/mL in order to give similar thickness. As shown in Figure 4, the hole current densities of the devices at the same electric field strength increase with increased carbazole contents. This result is analogous to their HOMO levels as determined by cyclic voltammetry and confirms the improved hole injection and/or transporting by the incorporation of the carbazole units.

The Role of Hole-Blocking Layers. Although the incorporation of the carbazole units can raise the HOMO energy levels, the LUMO levels of the copolymers are also raised, leading to larger energy barriers for electron injection. As anticipated, the single layer device of ITO/ PF<sub>2</sub>Cz/LiF(1 nm)/Al gave a very weak emission (1.9 cd/ m<sup>2</sup>) even at a current density of 63 mA/cm<sup>2</sup>. A very possible reason for this extremely low EL efficiency is that a major fraction of holes just passed through the device and did not combine with electrons to form excitons; i.e., holes are the majority carrier in these devices. To improve the device performance, a holeblocking layer has to be used to balance the charge carriers in the emissive layer. The hole-blocking material should have a high oxidation potential and large HOMO-LUMO energy band gap. Shirota first demonstrated that F-TBB can be used as a hole-blocking



**Figure 5.** Voltage–luminance (a) and voltage–efficiency (b) curves of  $PF_2Cz$  for devices A, B and C. A:  $ITO/PF_2Cz/F$ -TBB (20 nm)/Alq<sub>3</sub> (10 nm)/LiF/Al; B:  $ITO/PF_2Cz/CN$ -TBB (20 nm)/Alq<sub>3</sub> (10 nm)/LiF/Al; and C:  $ITO/PF_2Cz/CN$ -TBB (30 nm)/LiF/Al.

material in small molecular blue-violet emitting diodes. In our study, we investigated the effects of F-TBB and CN-TBB on the device performance with PF<sub>2</sub>Cz as the emitting layer. Three types of devices were designed and fabricated: ITO/PF2Cz/F-TBB(20 nm)/Alq3 (10 nm)/LiF/ Al (device A), ITO/PF<sub>2</sub>Cz/CN-TBB(20 nm)/Alq<sub>3</sub> (10 nm)/ LiF/Al (device B), and ITO/PF<sub>2</sub>Cz/CN-TBB(30 nm)/LiF/ Al (device C). As can be seen from Figure 5, the choice of the blocking layer has a strong impact on device performance. To our surprise, the F-TBB was much superior to CN-TBB, giving higher luminance and EL efficiency. The turn-on voltages, corresponding to a luminance of 1 cd/m<sup>2</sup>, increased from 10 to 14 V when F-TBB was replaced by CN-TBB. Figure 6 displays the EL spectra of devices A, B, and C. No emission from Alq<sub>3</sub> was observed from devices A and B, indicating both CN-TBB and F-TBB can function as hole-blocking materials. The fwhms (full width at the half-maximum) of the EL spectra, however, increased from 52 nm (device A) to 69 nm (device B). The CIE 1931 chromaticity coordinates of the emission of devices A, B, and C are (0.172, 0.087), (0.194, 0.162), and (0.188, 0.144), respectively. It is clear that from device A to device B the emission colors changed from deep blue to blue. In



Figure 6. EL spectra of PF<sub>2</sub>Cz for devices A, B, and C.



**Figure 7.** EL spectra of PF<sub>2</sub>Cz (solid line), PF<sub>3</sub>Cz (dashed line), and POF (dotted line) from devices ITO/PF*n*Cz/F-TBB/Alq<sub>3</sub>/LiF/Al.

device C, no Alq<sub>3</sub> was used; however, its EL spectrum, I-V curve, and luminance efficiency are quite similar to those of device B. Therefore, we think that although CN-TBB can function as a hole-blocking and electron-transporting layer, it may form exciplexes with PF<sub>2</sub>Cz at the interface, leading to the broadening of the EL emission and poor luminance efficiency.

**EL Properties of PFnCz.** In this paper, we also studied the effect of carbazole contents on the EL performance by fabricating double-layer devices with a configuration of ITO/PFnCz/F-TBB/Alq<sub>3</sub>/LiF/Al. The copolymer PF<sub>1</sub>Cz was not studied here due to its too short a conjugation length and low PL efficiency. As can be seen from Figure 7, a pure deep blue EL with negligible emission in the 500–600 nm region can be achieved from the PFnCz copolymers by using F-TBB as a hole-blocking layer and Alq<sub>3</sub> as an electron injec-



**Figure 8.** Electric field strength–luminance (a) and electric field strength–efficiency (b) characteristics of  $PF_2Cz$ ,  $PF_3Cz$ , and POF.

tion/transporting layer. This device structure can provide stable blue emission, and no voltage dependence of the EL spectra was observed. The CIE 1931 chromaticity coordinates of the emission of  $PF_2Cz$ ,  $PF_3Cz$  and POF in Figure 7 are (0.172, 0.087), (0.165, 0.070), and (0.166, 0.069), respectively. The fwhm of the EL spectrum of POF is surprisingly narrow (39 nm). Recently, Heeger's group reported a similar result with the insertion of a thin layer of oxadiazole small molecules between the emissive PF and the Ca cathode which resulted in improved blue emission stability.<sup>21</sup> Compared with their data, it is safe to claim that the combination of F-TBB with Alq<sub>3</sub> is superior to the oxadiazole compounds as the hole-blocking/electrontransporting layer in PF-based PLEDs.

Figure 8 shows the electric field strength–luminance (E-L) characteristics of PF<sub>2</sub>Cz, PF<sub>3</sub>Cz, and POF. As anticipated, the PF<sub>2</sub>Cz gave the brightest emission at the same electric field strength due to its improved hole injection and transporting properties. The maximum luminance was 530 cd/m<sup>2</sup> at a voltage of 33 V. The high

driving voltage was probably due to the aluminum cathode used in the devices and nonoptimized layer thicknesses, while the efficiencies at a practical luminance of 100 cd/m<sup>2</sup> (0.54 cd/A for PF<sub>2</sub>Cz and 0.72 cd/A for PF<sub>3</sub>Cz) are comparable to the literature data, <sup>4d,21,22</sup> considering the use of the air stable aluminum cathode, which provided less ideal electron injection into the devices as compared to the commonly used calcium electrode. In addition, our device configuration provides stable deep blue EL with negligible emission in the 500–600 nm region.

# Conclusions

In a summary, we have systematically studied the photophysical, electrochemical, and electroluminescent properties of a series of alternating fluorene/carbazole copolymers. Both absorption and PL emission peaks of the alternating copolymers were blue-shifted with an increase in the carbazole content due to the interruption of the main-chain conjugation by the presence of the 3,6carbazole units. Meanwhile, the HOMO energy levels were also raised, and thus the hole affinity was improved. Pure deep blue emission with narrow fwhms (39–52 nm) and negligible low-energy emission bands was successfully achieved from the PFnCz copolymers by using F-TBB as a hole-blocking layer and Alq<sub>3</sub> as an electron injection/transporting layer. It seems that this kind of device structure can stabilize the blue emission from PF derivatives. In future work, we intend to focus on the device optimization to further improve the EL efficiency and luminance, such as treating ITO substrates with Ar/O<sub>2</sub> plasma, optimizing the emissive layer thickness, and using a better cathode material to replace the aluminum.

**Supporting Information Available:** General procedure for the preparation of alternating 9,9-dioctylfluorene/9-octyl-carbazole copolymers PF*n*Cz (n = 1, 2, 3) and their <sup>1</sup>H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **References and Notes**

- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539.
- (2) (a) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradlay, D. D. C.; Dos Santo, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (c) Shim, H. K.; Jin, J. I. *Adv. Polym. Sci.* **2002**, *158*, 194.
- (3) (a) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. Appl. Phys. Lett. **1994**, 64, 815. (b) McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. Adv. Mater. **1999**, 11, 1349. (c) Chen, F. C.; Yang, Y.; Thompson, M. E.; Kido, J. Appl. Phys. Lett. **2002**, 80, 2308. (d) Swanson, S. A.; Wallraff, G. M.; Chen, J. P.; Zhang, W. J.; Bozano, L. D.; Carter, K. R.; Salem, J.; Villa, R.; Scott, J. C. Chem. Mater. **2003**, 15, 2305.
- (4) (a) Pei, Q.; Yang, Y. J. Am. Chem. Soc. 1996, 118, 7416. (b) Leclerc, M. J. Polym. Sci., Part A: Polym. Chem. 2001, 22, 1365. (c) Grice, A. W.; Bradeley, D. D. C.; Bernius, M. T.; Inbasekaran, M.; Wu, W. W.; Woo, E. P. Appl. Phys. Lett. 1998, 73, 629. (d) Shu, C. F.; Dodda, R.; Wu, F. I.; Liu, M. S.; Jen, A. K. Y. Macromolecules 2003, 36, 6698.
- (5) (a) Klärner, G.; Lee, J. I.; Lee, V. Y.; Chan, E.; Chen, J. P.; Nelson, A.; Markiewicz, D.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800. (b) Lee, J. I.; Klärner, G.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1083. (c) Setayesh, S.; Grimsdale,

A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946.

- (6) (a) List, E. J. W.; Guentner, R.; Freitas, P. S.; Scherf, U. Adv. Mater. 2002, 14, 374. (b) Lupton, J. M.; Craig, M. R.; Meijer, E. W. Appl. Phys. Lett. 2002 80, 4489.
- E. W. Appl. Phys. Lett. 2002 80, 4489.
  Miteva, T.; Meisel, A.; Knoll, W.; Nothofer, H. G.; Scherf, U.; Müller, K.; Meerholz, K.; Yasuda, A.; Neher, D. Adv. Mater. 2001, 13, 565.
- (8) Yan, H.; Huang, Q. L.; Cui, J.; Veinot, J. G. C.; Kern, M. M.; Marks, T. *Adv. Mater.* **2003**, *15*, 835.
- (9) Brown, T. M.; Kim, J. S.; Friend, R. H.; Cacialli, F.; Daik, R.; Feast, W. J. Appl. Phys. Lett. 1999, 75, 1679.
- (10) Yang, Y.; Heeger, A. J. Appl. Phys. Lett. **1994**, 64, 1245.
  (11) Jong, M. P.; Ijzendoorn, L. J.; Voigt, M. J. A. Appl. Phys. Lett.
- **2000**, *77*, 2255. (12) Donat-Bouillud, A.; Lévesque, I.; Tao, Y.; D'Iorio, M. *Chem.*
- *Mater.* **2000**, *12*, 1931. (13) Ego, C.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen,
- (15) Ego, C.; Grinsdale, A. C.; Well, T.; Enkelmann, V.; Mullen, K. Adv. Mater. **2002**, *14*, 809.

- (14) Li, Y. N.; Ding, J. F.; Day, D.; Tao, Y.; Lu, J. P.; D'iorio, M. Chem. Mater., submitted for publication.
- (15) Okumoto, K.; Shirota, Y. Chem. Mater. 2003, 15, 699.
- (16) (a) Meech, S. R.; Phillips, D. J. Photochem. 1983, 23, 193. (b) Hamal, S.; Hirayama, F. J. Phys. Chem. 1983, 87, 83.
- (17) Cho, H. J.; Jung, B. J.; Cho, N. S.; Lee, J.; Shim, H. K. Macromolecules 2003, 36, 6704.
- (18) Xia, C.; Advincula, R. C. Macromolecules 2001, 34, 5854.
- Janietz, S.; Bredley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453.
   Chen, Z. K.; Huang, W.; Wang, L. H.; Kang, E. T.; Chen, B.
- (20) Chen, Z. K.; Huang, W.; Wang, L. H.; Kang, E. T.; Chen, B. J.; Lee, C. S.; Lee, S. T. *Macromoleculaes* **2000**, *33*, 9015.
  (21) Gond, X.; Iyer, P. K.; Moses, D.; Bazan, G. C.; Heeger, A. J.;
- Xiao, S. S. Adv. Funct. Mater. 2003, 13, 325. (22) Weinfurther K. H.: Eujikawa, H.: Tokito, S.: Taga, V. Appl.
- (22) Weinfurther, K. H.; Fujikawa, H.; Tokito, S.; Taga, Y. Appl. Phys. Lett. 2000, 76, 2502.

MA030535N