

White Electroluminescence from Bicarbazyl-containing Conjugated Polymers as Single-Emitting Component

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Two bicarbazyl-containing fluorene copolymers, PFEB Cz (95/5) and PFEB Cz (75/25), were synthesized for white light electroluminescence from a single emitting polymer. All synthesized polymers were soluble in common organic solvents such as chloroform and toluene. The weight-average molecular weights (M_w) of the PFEB Cz (95/5) and PFEB Cz (75/25) copolymers were found to be 11,000 and 5,700 with polydispersity indices 1.4 and 1.8. The EL spectrum of the PFEB Cz (75/25) device showed bright white-light emission with CIE coordinates of (0.32, 0.34) at 1000 cd/m², which is very close to that for pure white (0.33, 0.33). This white emission may have been due to strong excimer formation between the bicarbazyl and fluorene polymer backbone. The device exhibited a maximum brightness of 3400 cd/m² with a maximum efficiency of 0.2 cd/A.

Key Words : White emitting, Bicarbazyl, Excimer, Single-emitting

Introduction

The potential for making large-area multicolor displays from easily processible polymers has driven much of the recent research in the area of polymer light-emitting diodes (PLEDs). Recently, white PLEDs (WPLEDs) have received particular attention because of their potential applications in backlight and full color displays with color filters.¹⁻¹² One of main approaches to producing WPLEDs is to use a polymer blend system, such as three-polymer blends containing red, green and blue polymers,¹³ and blends consisting of two or three kinds of fluorescent dyes in an efficient blue-emitting polymer matrix.^{14,15} However, it is difficult to obtain highly efficient and color stable WPLEDs using polymer blend systems due to undesirable Forster-type energy transfer between chromophores. Another approach is to use single layer devices made from homopolymers^{16,17} or copolymers.¹⁸⁻²⁰ However, the devices constructed to date according to this approach have not shown ideal CIE (Commission International de l'Eclairage) coordinates for white light emission (0.33, 0.33) and color stability. Therefore, new polymer materials are needed that are better suited to these single-layer devices. Here we report on efficient single emitting component WPLEDs with a single-layer structure fabricated from poly[9,9'-bis(2'-ethylhexyl)fluorene-2,7-diyl-co-*N,N'*-diethyl-3,3'-bicarbazyl-6,6'-diyl], copolymers (PFEB Cz).

Experimental Section

Synthesis of Monomers

Synthesis of *N,N'*-Diethyl-3,3'-bicarbazyl (1): To a solution of *N*-ethylcarbazole (20 g, 99.35 mmol) in chloroform (150 mL), FeCl₃ (64.46 g 0.397 mol) was added dropwise. At this point, the reaction mixture gradually turned to dark green color due to the formation of carbazole cation radicals. After 24 hours, the reaction mixture was poured into an excess of methanol. The precipitated solids were isolated by filtration and continuously washed with excess methanol and three times with water. After dried, the title compound was obtained at 95% yield. ¹H-NMR (300 MHz, CDCl₃): δ 1.50 (t, 6H, 2-CH₃), 4.45 (quartet, 4H, 2-NCH₂), 7.26-8.5 (m, 14H, aromatic protons).

Synthesis of *N,N'*-Diethyl-6,6'-dibromo-3,3'-bicarbazyl (2): Compound (1) (4 g, 10 mmol) was put into a 100 mL Schlenk flask and 50 mL of chloroform was added to dissolve the contents. Separately, bromine (5.0 g, 31 mmol) was dissolved in 10 mL of chloroform. The resulting solution was added to the flask dropwise. The reaction temperature was kept at 0 °C using an ice bath. After 40 minutes, the reaction mixture was poured into an excess of water and washed with 1.0 N NaOH (aq). The reaction mixture was dissolved in chloroform (250 mL) and again poured into an excess of methanol. The precipitated solids were isolated by filtration and washed repeatedly with excess methanol and water. After drying, the crude product was purified by column chromatography using a cosolvent (*n*-hexane/chloroform = 3/1) as the eluent. Finally, the title compound was obtained at 90% yield (4.92 g). ¹H-NMR (300 MHz, CDCl₃): δ 1.46 (t, 6H, 2-CH₃), 4.34 (quartet, 4H, 2-NCH₂), 7.26-8.33 (m, 12H, aromatic protons); ¹³C-NMR

(75 MHz, CDCl_3): δ 139.3, 139.0, 133.5, 128.36, 126.2, 124.8, 123.3, 122.5, 119.1, 111.6, 110.0, 109.0, 37.8, 13.8; Fab^+ -Mass m/e 546.3.

Synthesis of 2,7-Dibromo-9,9'-dioctylfluorene (3). was prepared according to a previously reported method.²¹

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 0.60 (m, 4H), 0.83 (t, 6H, 2- CH_3), 1.29-1.07 (m, 20H), 1.96 (m, 4H) 7.28-7.55 (m, 6H, aromatic protons).

General Procedure for Polymerization. Two bicarbazyl-containing copolymers PFEBcZ (95/5) and PFEBcZ (75/25) were synthesized by nickel(0)-mediated polymerization. The feed ratio of bicarbazyl monomer was 5 and 25 mol % of total amount of polymer, and the total amount of reactants was ranged from 1.6 to 1.8 mmol. Each 100 mL Schlenk flask containing anhydrous DMF (5 mL), bis(1,5-cyclooctadienyl) nickel(0), 2,2'-dipyridyl and 1,5-cyclooctadiene (the last three in a molar ratio of 1:1:1) was kept under nitrogen atmosphere at 78 °C for 15 min. Reactants dissolved in anhydrous toluene (15 mL) were added to the mixture. The polymerization was maintained at 78 °C for 36 h, and then 0.5 mL of bromopentafluorobenzene was added to reaction mixture for end-capping reaction. When the reaction had finished, each polymer was precipitated from an equi-volume mixture of HCl, methanol and acetone. The polymers were dissolved in small amount of toluene and precipitated in methanol. The resulting polymers were purified with column chromatography using toluene as the eluent. Finally, the resulting polymers were further purified by Soxhlet extraction using methanol and then dried in vacuum. The polymer yields ranged from 30 to 40% after purification.

PFEBcZ (95/5): $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 0.73 (m, N- $\text{CH}_2\text{-CH}_3$), 0.86 (m, $-\text{CH}_2-$ of dioctylfluorene), 1.56-1.13 (m, $-\text{CH}_2-$ of dioctylfluorene), 2.17 (m, $-\text{CH}_2-$ of dioctylfluorene), 4.48 (m, N- CH_2-), 7.56-7.99 and 8.55 (aromatic protons). FT-IR (KBr, cm^{-1}): 3055 (aromatic C-H), 2955-2855 (aliphatic C-H), 2000-1670 (multi-substituted combination), 1605, 1459 (aromatic C=C), 1230 (C-N), 877, 814 (1,2,4-substituted out-of-plane C-H bending).

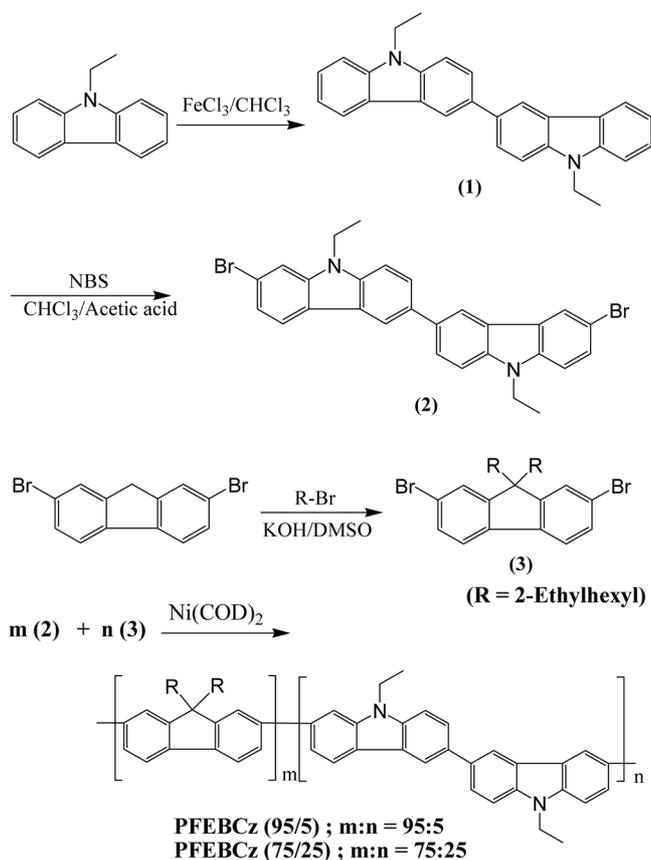
Instruments. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance-400 spectrometer. The absorption spectra were measured using a Hitachi spectrophotometer model U-3501 and the steady-state PL spectra were recorded on a Spex FL3-11. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) analysis relative to a polystyrene standard using a Waters high-pressure GPC assembly Model M590. Thermal analyses were carried out on a DuPont TGA 9900 thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 10 °C/min. Cyclic voltammograms (CV) of the polymer films (dip-coated onto Pt wire) were recorded on an AUTOLAB/PGSTAT12 at room temperature in a solution of tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) (0.1 M) in acetonitrile under nitrogen gas protection at a scan rate of 100 mV/s. For the measurement of EL device characteristics, current-voltage (I-V) changes were obtained using a current/voltage source (Keithley 238) and an optical power meter (Newport 818-SL). The brightness and 1931

CIE chromaticity of each EL device were recorded with a PR-650 SpectraScan colorimeter.

Fabrication of the Light-Emitting Diodes. Each polymer film was prepared by spin casting a blend solution containing 1% of the polymer by weight in toluene. Uniform and pinhole free films with a thickness around 100 nm were easily obtained from the polymer solutions. For the double layer device, a modified water dispersion of PEDOT [poly(3,4-ethylenedioxy-thiophene)] doped with poly(styrene sulfonate) (PSS) (Bayer AG, Germany) was used as the hole-injection/transport layer. A metal contact (Ca) was deposited on top of the polymer film through a mask by vacuum evaporation at a pressure below 4×10^{-6} torr., yielding active areas of 4 mm^2 . In the case of the Ca cathode (~ 50 nm), an additional encapsulating layer of Al (~ 200 nm) was thermally evaporated onto it. All processes and measurements mentioned above were carried out in nitrogen atmosphere with glass encapsulation at room temperature.

Results and Discussion

Scheme 1 shows an overview of the synthesis of the monomer and polymers. The copolymers were synthesized using the Ni(0)-mediated coupling reaction. All synthesized polymers were soluble in common organic solvents such as chloroform and toluene without evidence of gel formation. The weight-average molecular weights (M_w) of the PFEBcZ (95/5) and PFEBcZ (75/25) copolymers were found to be

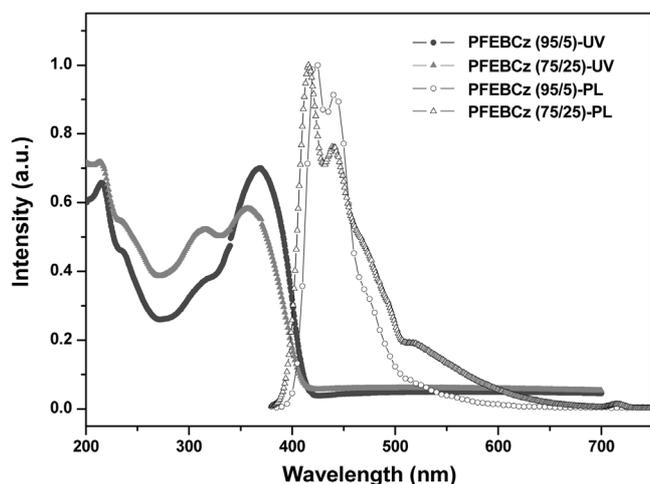
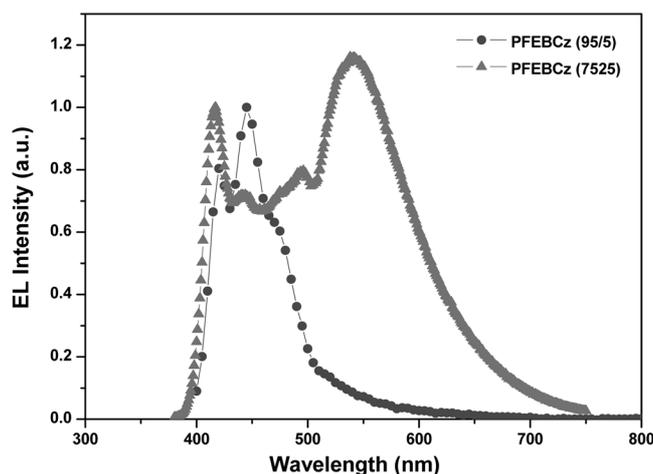


Scheme 1. Synthetic routes for PFEBcZ copolymers.

Table 1. Summary of the characteristics of the synthesized polymers

	Feed ratios of BCz (mole %)	Actual ratios of BCz (mole %) ^a	M _n	M _w	PDI	Polymer yield (%)
PFEBzCz (95/5)	5	4.5	8,000	11,000	1.4	40
PFEBzCz (75/25)	25	23.9	3,100	5,700	1.8	35

^aDetermined by ¹H-NMR integration of -NCH₂ protons of BCz vs. methylene (-CH₂-) protons of the fluorene moiety.

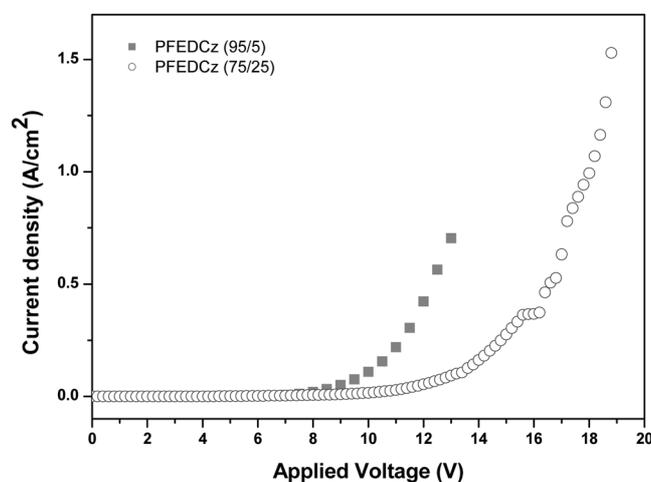
**Figure 1.** UV-visible absorption and PL emission spectra of the polymer films.**Figure 2.** EL spectra of the EL devices with ITO/PEDOT/polymer/Ca/Al configuration.

11,000 and 5,700 with polydispersity indices 1.4 and 1.8, using gel permeation chromatography (GPC) with a polystyrene standard. The polymer yields were around 40% after purification. The actual ratios of the monomers within the copolymers were determined using the ¹H-NMR method. The results for the synthesized polymers are summarized in Table 1.

Figure 1 shows the normalized UV-visible absorption and photoluminescence (PL) spectra of thin films of the polymers coated onto fused quartz plates. Both films exhibit absorption maxima at around 360 nm and a weak absorption peak at 310 nm. The main peak is consistent with that reported for the fluorene homopolymer.⁶ The relative ratio of the absorbances, 310/360 nm, was found to increase as the fraction of bicarbazyl units (BCz) in the polymer increased, indicating that the weak absorptions at 310 nm result from the BCz unit.²² When the PFEBzCz (75/25) and PFEBzCz (95/5) polymers are excited at their absorption maximum, their PL emission peaks appear at round 420 nm with shoulder peaks at round 470 and 530 nm, respectively. The PL intensity of the longer wavelength emission at around 530 nm of the PFEBzCz (75/25) film is slightly greater than that of the PFEBzCz (95/5) film, indicating that excimer formation is enhanced by increasing the proportion of BCz units in the copolymer.

To investigate the EL properties of the polymers, EL devices were fabricated with the configuration ITO/PEDOT (25 nm)/polymer (100 nm)/Ca (50 nm)/Al (200 nm). The EL spectrum of PFEBzCz (75/25) shows white emission consisting of two emission peaks, at 420 and 540 nm, with tailing

of the longer wavelength (see Figure 2). The CIE coordinates of this device were (0.32, 0.34), which is very close to those of standard white emission, (0.33, 0.33). For the PFEBzCz (95/5) device, however, the emission peak was at 440 nm, in the blue region, and the CIE coordinates were (0.17, 0.16) at 1000 cd/m². The blue emission from this device can be attributed to the low bicarbazyl content of the copolymer used. The above results therefore strongly suggest that the main peak and shoulder peak in the PL spectrum, and their corresponding peaks in the EL spectrum, can be assigned to emissions of the lumophore and excimer,

**Figure 3.** Plot of the current density as function of the applied voltage for the EL devices with ITO/PEDOT/polymer/Ca/Al configuration.

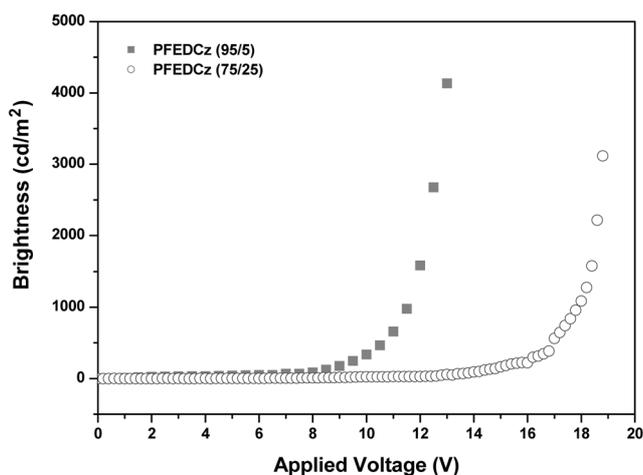


Figure 4. Plot of the luminescence as function of the applied voltage for the EL devices with ITO/PEDOT/polymer/Ca/Al configuration.

respectively. The longer wavelength emission of PFEDCz (75/25) results from excimer formation by the bicarbazyl units, which increased as the fraction of bicarbazyl units in the polymer increased. This excimer emission may be due to enhanced charge separation along the conjugated segment induced by the incorporation of the electron donating bicarbazyl group. The devices made from PFEDCz (95/5) and PFEDCz (75/25) exhibited maximum brightnesses of 6000 and 3400 cd/m^2 with maximum efficiencies of 0.7 and 0.2 cd/A , respectively (see Figure 3 and 4).

To test the color stability of the white light emitted from a single polymer, the EL spectra of the PFEDCz (75/25) device were measured at brightnesses of 100 and 1000 cd/m^2 . The EL spectrum was only slightly different at these brightnesses. The CIE coordinates at the brightnesses of 100 and 1000 cd/m^2 were (0.27, 0.34) and (0.32, 0.34), respectively, corresponding to applied voltages of 13.2 and 18 V, respectively. However, it is worthwhile to note that the bicarbazyl gave strong excimer formation in the fluorene polymer backbone.

Conclusion

In summary, we have successfully developed a white-light emitting device based on a single polymer, the bicarbazyl-containing fluorene copolymer PFEDCz (75/25). The EL spectrum of this device shows white-light emission with CIE coordinates of (0.32, 0.34) at 1000 cd/m^2 . The white-light emission of this device may be due to excimer formation

between the bicarbazyl and fluorene polymer backbone. Further investigation along these lines is in progress.

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