

Novel red and white PLED devices consisting of PVK blended with blue-emitting fluorene derivatives and carbazole dopants

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Abstract

Highly fluorescent polymeric LEDs (PLEDs) utilizing blue-emitting FB fluorene derivatives (FBF14 and FBPh4) blended with PVK are demonstrated. Significant red shift of the emission from blue to red can be achieved by increasing the concentration of FB in the blend. The origin of emission was attributed to electromer (or electroplex) formation. Addition of Carb9 in the blend enhanced the electromer (or electroplex) formation, and red- or white-emission device with high brightness (3440 cd/m² for red; and 17368 cd/m² for white) was obtained.

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1. Introduction

Recently, organic light-emitting diodes (OLEDs) and polymeric light-emitting diodes (PLEDs) have been applied to display technologies. They can also be combined with color filters to provide red, green, and blue light-emitting pixels. Small-molecule organic LEDs have shown quite high efficiency and brightness in white light LEDs [1]. In order to achieve this goal, numerous approaches have been explored, such as dye-dispersed matrixes of poly (*N*-vinylcarbazole) (PVK) [2–4], polyfluorene [5–8], and other polymers [9,10]. Metal-containing complexes also received considerable attention since the seminal work by Thompson and co-workers [11]. These crystalline materials normally have to be doped into some small molecule [12] or polymer [13] hosts. There have been some reports using Ir [14–20] and Ru [21–25] derivatives doped into polymer matrixes for red-emitting devices. It is interesting to note that a single blue-emitting phosphor [26] dopant in combination with its excimer emission generated white light efficiently. This may avoid complex device structure using multiple dopants. Heeger and co-workers [27] and List and co-workers [28]

reported some other polymer devices applied in white light also.

In this work, we found that 9-ethyl-*N,N'*-diphenyl-*N,N'*-dipyren-1-yl-9*H*-carbazole-3,6-diamine (Carb9) [29a] doped into fluorescent FB fluorene derivatives (FBPh4 or FBF14) [29b] and blended with PVK to induce the shift of the emission color, which eventually leads to red and white light. By increasing the concentration of the FB molecule in the presence of Carb9 dopant, the red electroplex (or electromer) emission was enhanced at the expense of the blue emission from the FB molecule. Furthermore, white light emission can also be achieved in these devices.

2. Experimental

The molecular structures of materials used are shown in Fig. 1. The synthesis and characterization of Carb9 has been published before [29a] and FB derivatives (FBPh4 and FBF14) will be reported elsewhere [29b]. The synthetic procedures of BCP (hole-blocking layer) and Alq (electron-transporting layer) were reported in the literature [30].

Glass slides precoated with indium tin oxide (ITO) with sheet resistances of $\sim 20 \Omega/\text{square}$ and with an effective individual device area of 3.14 mm² were used for fabrication of devices. The ITO glasses were routinely cleaned by ultrasonic treatment

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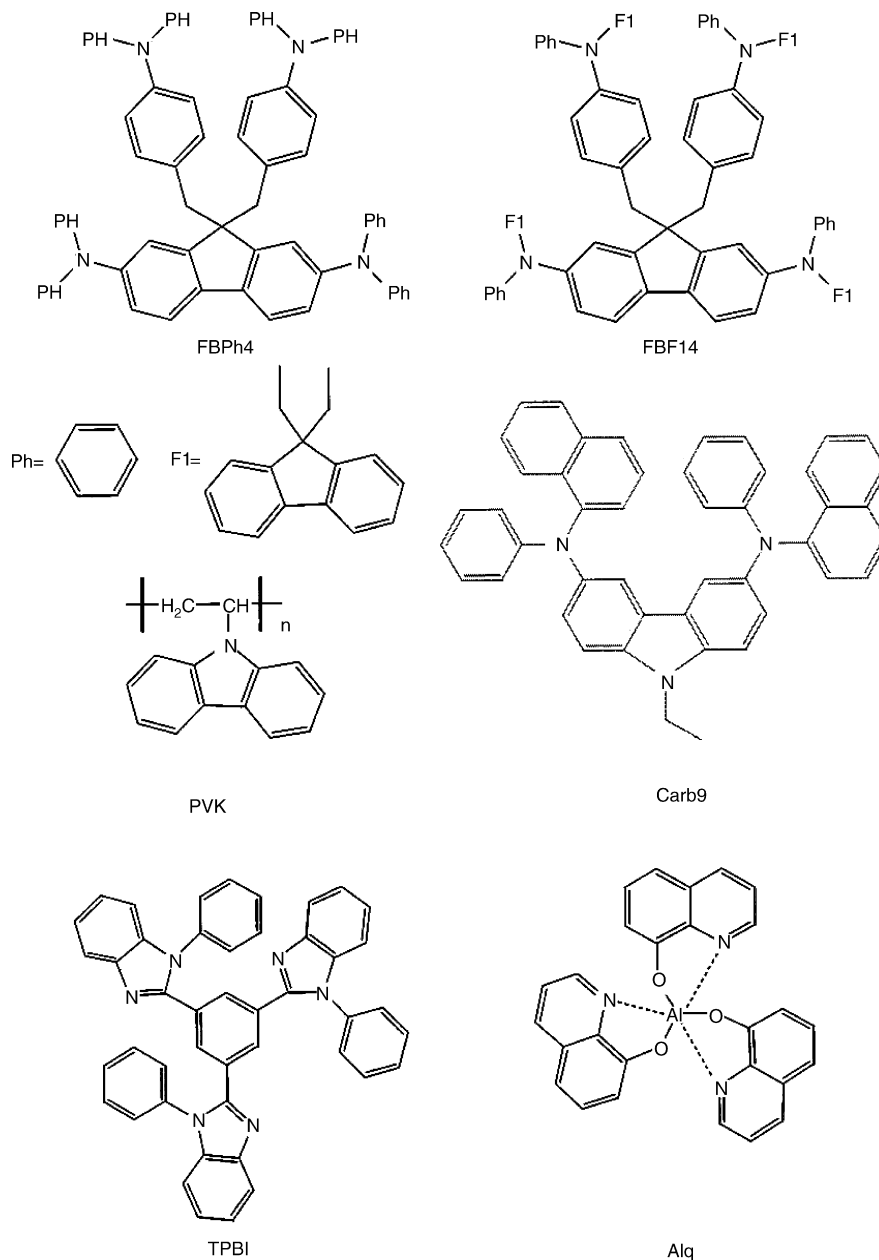


Fig. 1. Molecular structures of materials used in this study.

in detergent solution, followed by through rinsing in acetone and then ethanol, and dried in oxygen plasma for 3 min before being loaded into the vacuum chamber. The Carb9 dopant and FB derivatives blended in PVK are dissolve in 1,2-dichloroethane with a concentration of 30 mg/ml and the spin coating rate was 3000 rpm for 40 s. The hole-blocking and electron-transporting layers were deposited thermally at a rate of 0.1–0.3 Å/s under a pressure of $\sim 2 \times 10^{-5}$ Torr in an Ulvac Cryogenic deposition system. An alloy of magnesium and silver (ca. 10:1, 50 nm) was deposited as a cathode, which was then capped with 100 nm of silver. The device configuration is shown in Fig. 2.

The HOMO and LUMO values shown in Fig. 2 were calculated from cyclic voltammetry (vide supra) using ferrocene (4.8 eV) as the reference. The current–voltage–luminescence (*I–V–L*) spectra were measured in ambient conditions with

Keithley 2400 Source meter and a Newport 1835C optical meter equipped with 818ST silicon photodiode and emission spectra of photoluminescence (PL) and electroluminescence (EL) were recorded on a Hitachi spectrofluorometer.

3. Results and discussion

The PL spectra of FBPh4 in dichloroethane solution (10^{-6} M), and blend films (with various concentrations in PVK) are shown in Fig. 3. The energy transfer from PVK to FBPh4 is evident from the PL spectra of PVK:FBPh4 blend. The emission of FBPh4 is red shifted as the relative concentration of FBPh4 increases in the blend up to $x=150$, where PVK:FBPh4=100: x by weight. This could be attributed to the aggregation of FBPh4. The EL spectra of FBPh4 in blend films

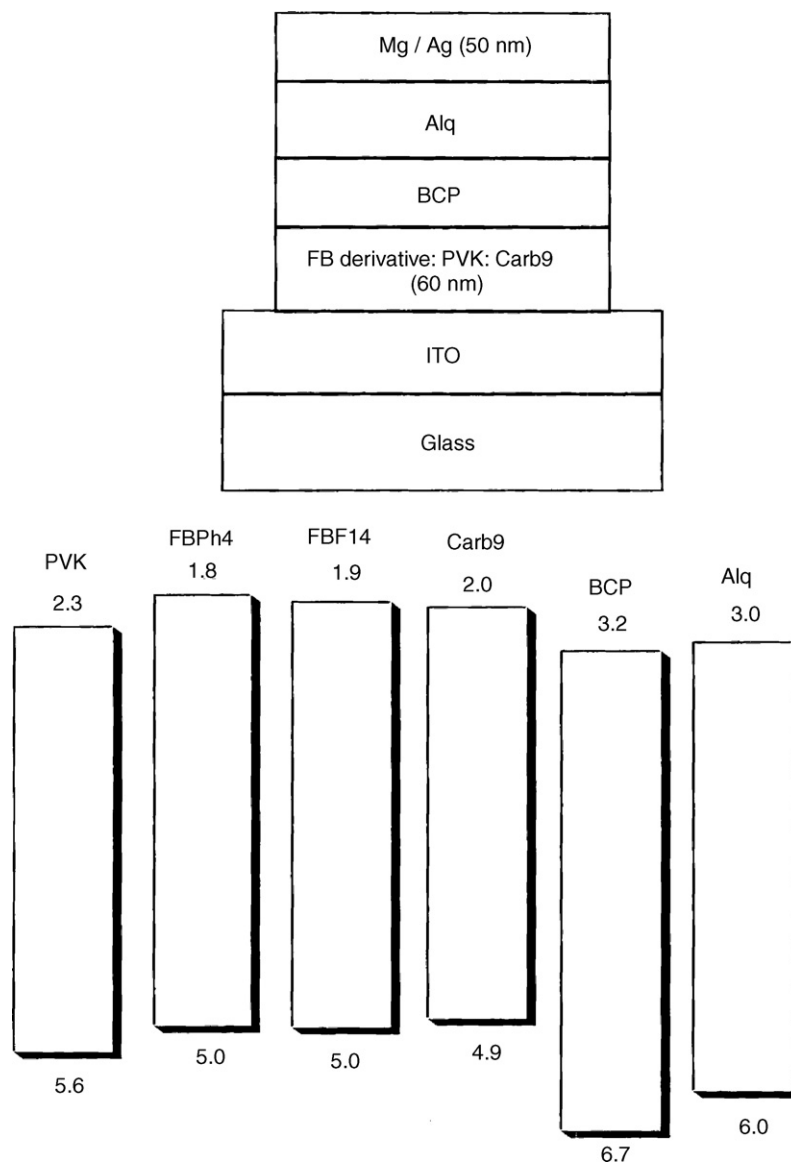


Fig. 2. The device configuration and the HOMO, LUMO values of PVK, FB derivatives, Carb9, hole-blocking BCP, and electron-transporting Alq.

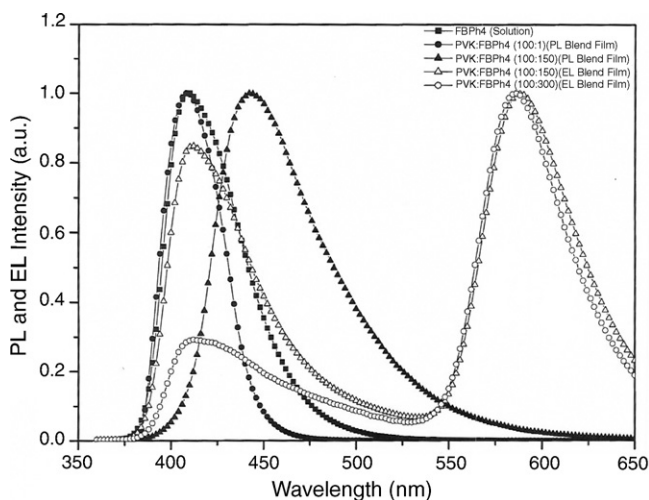


Fig. 3. PL and EL spectra of FBPh4 in solution (10^{-6} M in dichloroethane) and blend films (with various concentrations in PVK).

(with various concentrations in PVK) are also demonstrated in Fig. 3. Surprisingly, in addition to the characteristic band of FBPh4 at ~ 410 nm, the EL spectra of PVK:FBPh4 (100:150) and PVK:FBPh4 (100:300) blend films have a prominent band at ~ 583 nm (Fig. 3), which was not observed in the PL spectra of the previous PVK:FBPh4 blends. This strongly implies that the EL emission peak at ~ 583 nm is owing to the formation of electromers [31] from FB or electroplexes [32–37] from PVK/FB. The ratio of electromer (or electroplex) emission (ca. 583 nm) to intrinsic emission (ca. 410 nm) increases as the relative concentration of FBPh4 in the PVK:FBPh4 blend increases. However, the intrinsic emission of FBPh4 still remains up to a weight ratio of 100:300 (PVK:FBPh4).

When Carb9 was added to the PVK:FBPh4 blend, emission of FBPh4 (ca. 410 nm) was completely suppressed (Fig. 4), possibly due to the efficient energy transfer from FBPh4 and PVK to Carb9 which emits at ~ 460 nm. It is interesting to note that the higher concentration of FBPh4 versus Carb9 or

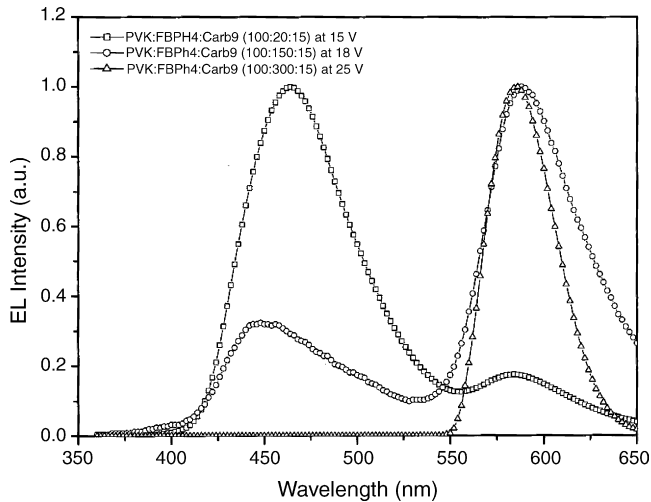
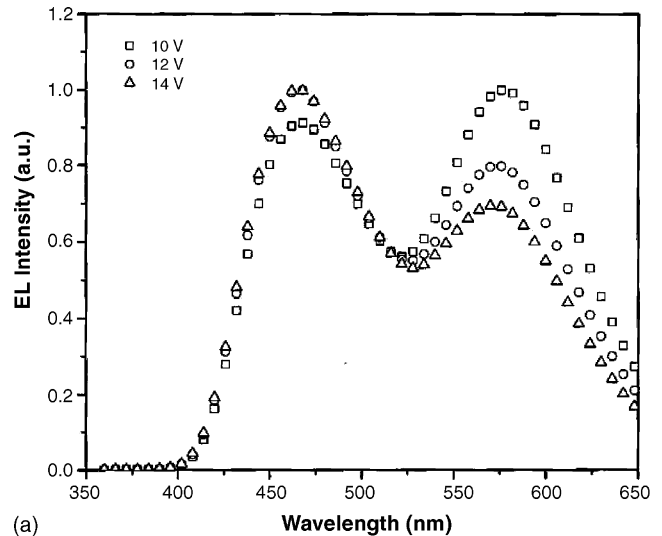


Fig. 4. EL spectra of blend films with various concentrations of FBPh4.

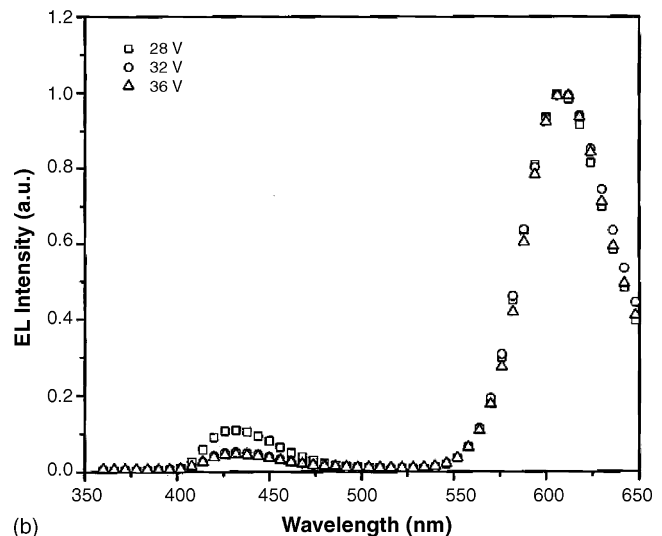
PVK will lead to a decrease of the emission from Carb9 (ca. 460 nm). The emission of Carb9 was completely suppressed, and only the electromer (or electroplex) emission was detected at a blend concentration of 100:300:15 (PVK:FBPh4:Carb9) (as shown in Fig. 4). The enhancement of the electromer (or electroplex) emission with increasing ratio of FBPh4 versus PVK in the PVK:FBPh4:Carb9 blend is consistent with that observed for the PVK:FBPh4 blend. However, the complete suppression of FBPh4 and Carb9 emission (ca. 410 and 460 nm, respectively) occurs only in the PVK:FBPh4:Carb9 blend at a ratio of 100:300:15. Possibly FBPh4 can transfer the electron to the excited Carb9, and the process is deemed favorable based on the relative HOMO and LUMO energy levels between the two (Fig. 2). Alternately, the higher concentration of FBPh4 not only competes favorably with Carb9 for carriers, but may also facilitate the aggregation of Carb9. It appears to be interesting that the orange-emitting devices (with blend concentrations of PVK:FBPh4:Carb9 = 100:150:15 and 100:300:15) can be obtained from three purple/blue-emitting components. The performance parameters of the orange-emitting device with PVK:FBPh4:Carb9 ratio of 100:150:15 are listed in Table 1. It is interesting that appropriate combination of Carb9 emission and the electromer (or electroplex) emission can lead to white-light in the PVK:FBPh4:Carb9 blend. Since all three components in this blend are hole carriers, hole blocker (BCP) and electron transporter (Alq) were inserted between the blend film and the cathode. The multi-layered device,

Table 1
EL characteristics of PLED devices

	PVK:FBPh4:Carb9	PVK:FBPh4:Carb9/BCP/Alq	PVK:FBPh4:Carb9/BCP/Alq
	100:150:15	100:200:15/5 nm/20 nm	100:200:15/10 nm/10 nm
Turn-on voltage (V)	8.8	10.1	28.7
Maximum brightness (cd/m ²)	747	17368	3440
Maximum external quantum efficiency (%)	0.18	1.84	0.42
Maximum power efficiency (lm/W)	0.06	1.36	0.06
λ_{em} (FWHM) (nm)	446,586 (186)	470,586(190)	614,448 (70)
CIE, x, y	0.40, 0.31	0.33, 0.35	0.56, 0.32



(a)



(b)

Fig. 5. EL spectra of the devices (a) PVK:FBPh4:Carb9(100:200:15)/BCP(5 nm)/Alq(20 nm) and (b) PVK:FBPh4:Carb9(100:200:15)/BCP(10 nm)/Alq(10 nm) with different driving voltages.

ITO/PVK:FBPh4:Carb9(100:200:15)/BCP(5 nm)/Alq(20 nm)/Mg:Ag, was fabricated. The EL spectra (at different voltages) and pertinent data of the device are demonstrated in Fig. 5(a) and Table 1, respectively. Interestingly, the device emits white light by the insertion of hole blocking (BCP) and electron transporting (Alq) layers to enhance the emission peak of Carb9

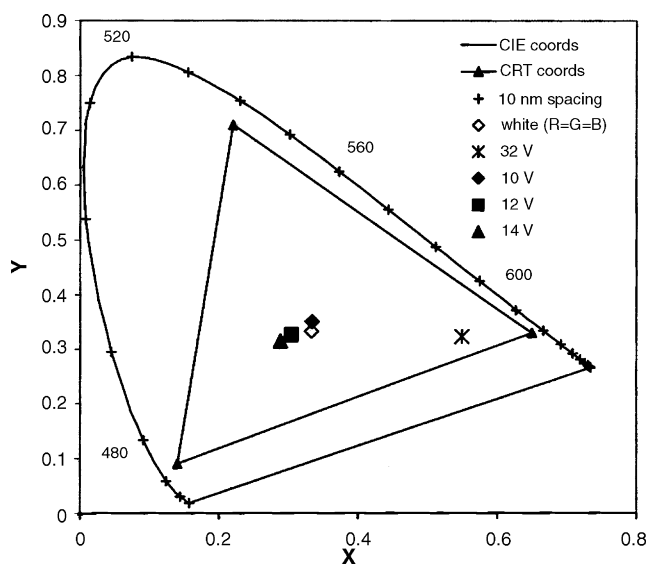


Fig. 6. CIE coordinate of PVK:FBF14:Carb9(100:200:15)/BCP(10 nm)/Alq(10 nm) at 32 V and PVK:FBPh4:Carb9(100:200:15)/BCP(5 nm)/Alq(20 nm) at 10, 12, and 14 V.

(~460 nm), which has relatively constant chroma at applied voltages ranging from 10 to 14 V: CIE coordinate (0.33, 0.35) at 10 V, (0.30, 0.33) at 12 V, and (0.27, 0.30) at 14 V (Fig. 6). The performance of the device appears to be good with brightness reaching 17368 cd/m^2 at 13 V. The CIE diagram is shown in Fig. 6, and the I - V - L plot of the device is illustrated in Fig. 7. Table 1 compiles the important performance parameters of the devices from the PVK:FBPh4:Carb9 blend.

Though energy transfer from PVK to FBF14 is also evident, the formation of the electromers (or electroplexes) in the EL devices of PVK:FBF14 blend does not appear to be as significant as the PVK:FBPh4 congener (Fig. 8). In contrast to

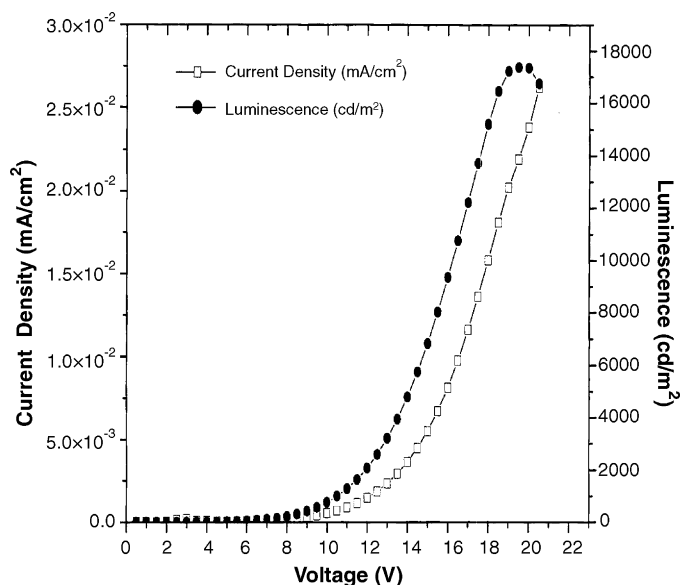


Fig. 7. I - V - L spectra of device PVK:FBPh4:Carb9(100:200:15)/BCP(5 nm)/Alq(20 nm).

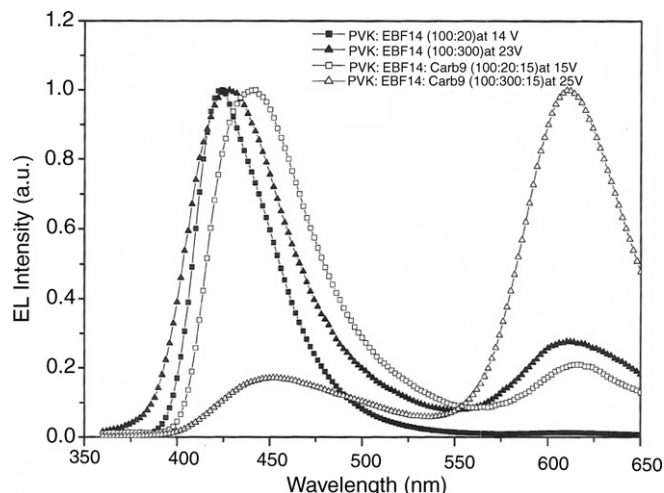


Fig. 8. EL spectra of blend films with various concentrations of FBF14 and Carb9.

the device of PVK:FBPh4:Carb9 blend, we found no complete suppression of the Carb9 emission in the EL devices of PVK:FBF14:Carb9 blend. Nevertheless, device of the structure ITO/PVK:FBF14:Carb9(100:200:15)/BCP(10 nm)/Alq(10 nm)/Mg:Ag has orange-red emission (EL spectra with different voltages shown in Fig. 5(b)) and the maximum brightness reaches 3440 cd/m^2 (CIE coordinate = 0.56, 0.32 in Fig. 6) at 32 V. The I - V - L plots of this device are shown in Fig. 9, and device of structure ITO/PVK:FBF14:Carb9(100:200:15)/BCP(10 nm)/Alq(10 nm)/Mg:Ag has red emission when the applied voltage is higher than 40 V. No white light-emitting devices can be obtained from PVK:FBF14:Carb9 blend; however, their EL characteristics of FB derivatives are also listed in Table 1.

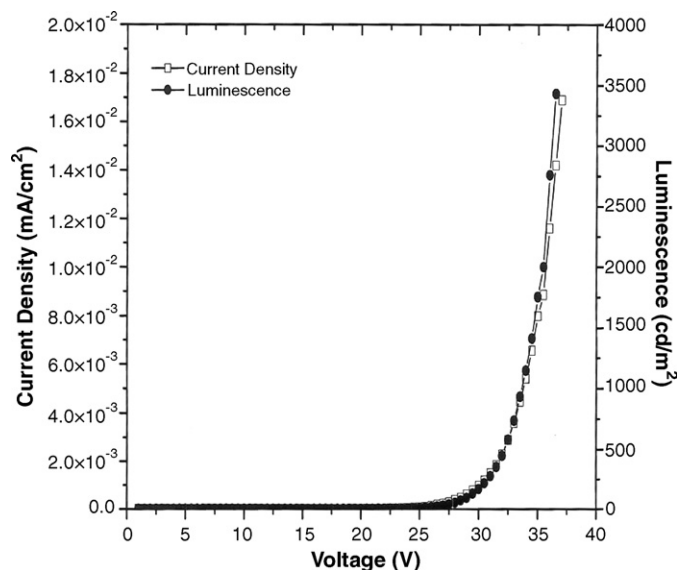


Fig. 9. I - V - L spectra of device PVK:FBF14:Carb9(100:200:15)/BCP(10 nm)/Alq(10 nm).

4. Conclusion

Under applied voltages, blends of PVK and blue-emitting FB derivatives emit orange or red colors due to the formation of electromers from FB or electroplexes from PVK/FB. Orange- or red-emitting electroluminescent devices can be achieved if a carbazole derivative, Carb9, is added to the blends at an appropriate ratio. White-light emission is also possible from the device of PVK/FB/Carb9 blend.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [10.1016/j.synthmet.2006.05.015](https://doi.org/10.1016/j.synthmet.2006.05.015).

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