

Blue electroluminescent devices made from a naphthyl-substituted benzidine derivative and rare earth metal chelates

W.L. Li^{a,b}, Z.Q. Gao^a, Z.Y. Hong^b, C.S. Lee^a, S.T. Lee^{a,*}

^a Center of Super-Diamond and Advanced Films and Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, People's Republic of China

^b Changchun Institute of Physics, Chinese Academy of Sciences, 130021, Changchun, People's Republic of China

Abstract

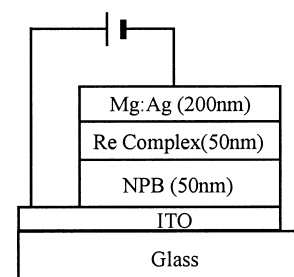
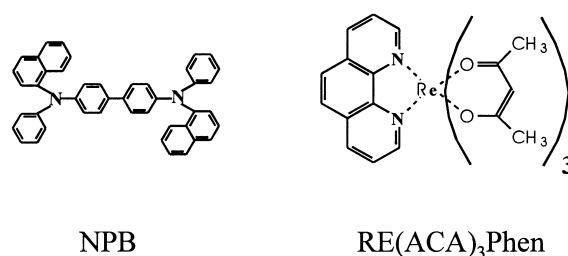
Electroluminescent (EL) devices with a bi-layer structure were fabricated using *N,N'*-bis(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) as a light-emitting and hole-transporting layer and a rare earth (RE) metal chelates (tris(acetylacetonato)-(monophenanthroline) RE(III) (RE(ACA)₃phen; where, RE is Y, La or Gd), as the electron-transporting layer. For the device using the Gd complex, blue EL emission with a maximum luminance of over 1000 cd/m² was achieved at ~22 V. The effects of using the yttrium and lanthanide complexes instead of the Gd complex on the EL emission spectra were discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Electroluminescence; Blue light; Organic film; Rare earth

1. Introduction

Blue organic electroluminescent devices (OELDs) are of considerable interest in full color OELDs. Many polymers [1–3] and small molecules [4,5] have been used to make blue OELDs. It has recently been reported that a device with a structure of Indium Tin Oxide (ITO)-coated glass/*N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)(1,1'-biphenyl)4,4'-diamine (TPD)/terbium chelate (Tb(ACA)₃phen)/Al gives EL emission around 400–430 nm [7], but the EL emission also includes the sharp green emission originating from the Tb complex. *N,N'*-bis(1-naphthyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) (see Fig. 1 for its structure) is another commonly used hole-transporting material with a chemical structure very similar to that of the TPD [6]. In fact, NPB has a higher glass transition temperature ($T_g = 98^\circ\text{C}$) than that of TPD ($T_g = 65^\circ\text{C}$) and thus, a better thermal stability. As NPB is also known to have a strong blue photoluminescence (PL), it is the intention of the present work to use NPB as a blue emitter and hole-transporting material in EL devices. This was achieved by matching NPB with different electron-transporting materials that have no PL emission in the

visible range so that the narrow blue emission from NPB will not be interfered. (Tris(acetylacetonato)-(monophenanthroline) RE(III) (RE(ACA)₃phen) complexes (with RE = Y, La, or Gd) have been considered to be good



Basic EL structure of the present work

* Corresponding author. Tel.: +852-2788-9606; fax: +852-2784-4696. E-mail address: apannale@cityu.edu.hk (S.T. Lee).

Fig. 1. Configuration of the EL device and the molecular structure of materials used.

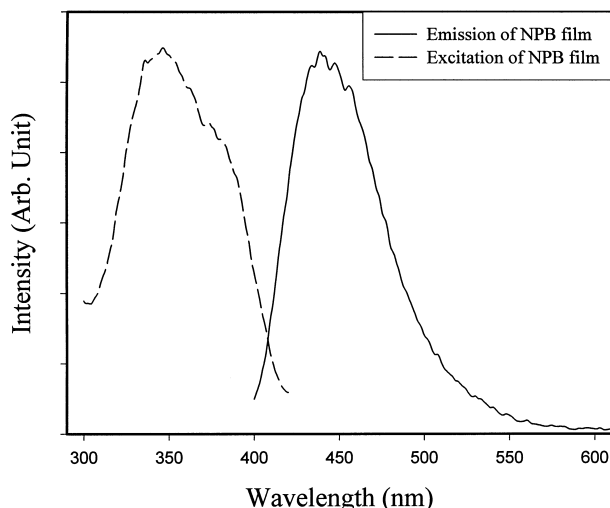


Fig. 2. The PL excitation and emission spectra of an NPB film.

electron-transporting materials because of the phenanthroline ligand [7]. As these complexes do not have visible emission, they were chosen for use in the present study. Furthermore, the RE^{3+} ions in the complexes have eight coordination sites, which are filled with six oxygen atoms and two nitrogen atoms. In other words, the chelates are “molecular inner complex salts” [8]. This kind of chelate can be evaporated and deposited to form smooth films.

2. Experimental

The $\text{RE}(\text{ACA})_3\text{phen}$ ($\text{RE} = \text{Y}, \text{La}, \text{or Gd}$) chelates were prepared by reacting ethanol solutions of RECl_3 and 1,10-

phenanthroline with acetylacetone solution at pH of 6–7. The precipitates were filtered, washed and then dried in vacuum at 80–100°C. Fig. 1 shows the configuration of the present electroluminescent (EL) devices and the molecular structures of the organic materials used. The ITO-coated glass has a sheet resistance of about $100 \Omega/\square$. The first organic layer (50 nm thick) on top of the ITO substrate is NPB and the second organic layer is the RE-chelate ($\text{RE} = \text{Y}, \text{La}$ or Gd) (50 nm thick). The top electrode (200 nm thick) is an alloy of Mg and Ag with a mass ratio of 10:1. The organic and metal layers were all deposited by vacuum evaporation at a vacuum 1×10^{-5} Torr in one pump-down. The emitting area of the devices was about $3 \times 3 \text{ mm}^2$.

The EL luminance spectra and CIE color coordinates of the devices were measured with a Photo Research PR650 spectrophotometer. A computer controlled dc power source was used to trace the current–voltage characteristics. The fluorescent excitation and emission spectra of the NPB film were determined with a Perkin Elmer LS-50B luminescence spectrometer. All measurements were conducted in ambient atmosphere.

3. Results and discussions

Fig. 2 shows the PL excitation and emission spectra of an NPB film deposited on a quartz substrate. The emission peak is situated at 440 nm with a full width at half maximum (FWHM) of 69 nm. The excitation peak is located at 345 nm.

Although blue EL emission was observed in all three devices made with different rare earth (RE) metal chelates,

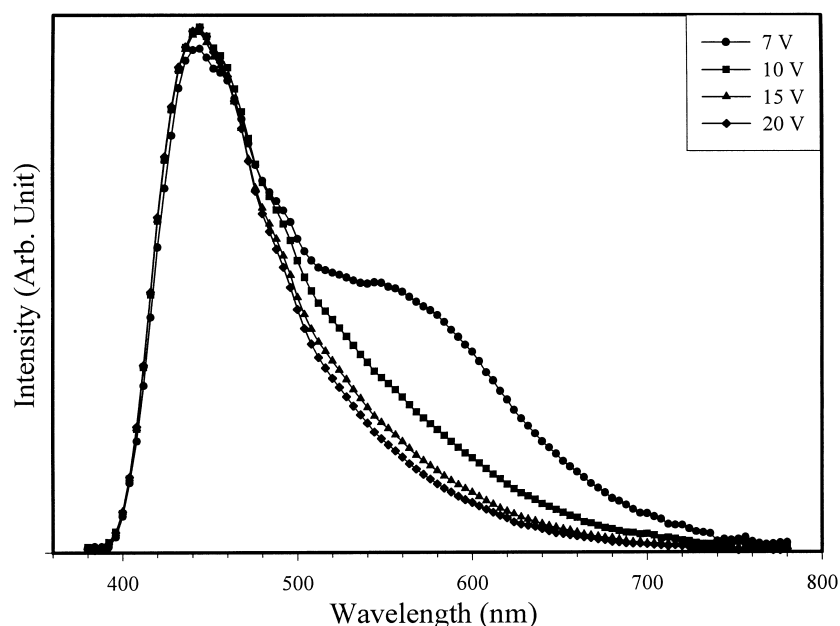


Fig. 3. Dependence of the EL spectra of the ITO/NPB/Gd chelate/Mg:Ag device on the driving voltage.

Table 1

CIE color coordinates of the present EL devices with different electron-transporting layer

Driving voltage [V]	Gd complex	Y complex	La complex
7	0.206, 0.194	0.261, 0.264	0.284, 0.292
10	0.204, 0.194	0.222, 0.229	0.241, 0.248
15	0.199, 0.196	0.204, 0.216	0.229, 0.235
20	0.182, 0.145	0.204, 0.219	0.241, 0.255

only the device with the Gd complex gave reasonably good color purity. The EL spectra of this device at various driving voltages are shown in Fig. 3. It can be seen that EL spectra at voltages higher than 7 V are almost the same as the PL spectrum of the NPB thin film (Fig. 2). When the driving voltage is 7 V or lower, another peak at around 560 nm was observed. This peak might be due to the exciplexes that were formed at the interface of the two organic layers [9]. This will be further discussed later. The CIE color coordinates at different driving voltages are shown in Table 1. The luminance–voltage and the luminance–current density characteristics for the device using Gd complex are shown in Fig. 4. A maximum luminance of about 1200 cd/m² was observed at a current density of 400 mA/cm² and a driving voltage of 25 V.

For the devices made with the Y and La complexes, blue emission can only be obtained at high driving voltages (> 20 V). The color purity is poor at low voltages. The EL spectra of the three devices at a driving voltage of 5 V are shown in Fig. 5. It is also obvious that the color purity at low driving voltages depends on the metal ion. The difference was presumably attributed to the different number of 4f electrons in the RE ions [8]. The chelate of the paramagnetic heavy Gd³⁺ seems to differ from the chelates of the diamagnetic ions of Y and La. The underlying physics are still under investigation.

The variation of the EL color with the driving voltage has been reported by Wang et al. [10] and was considered to be due to the variation in the location of the carrier

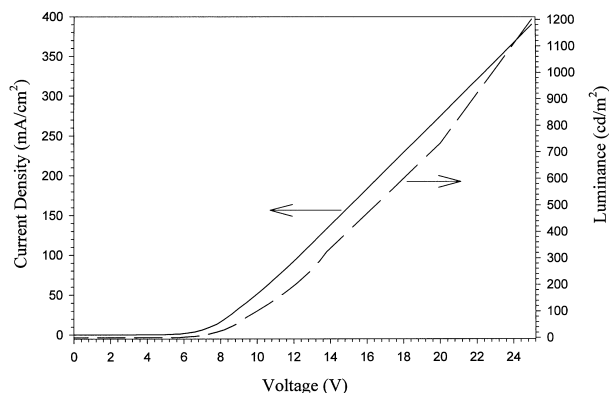


Fig. 4. Luminance–current–voltage characteristics of the ITO/NPB/Gd chelate/Mg:Ag device.

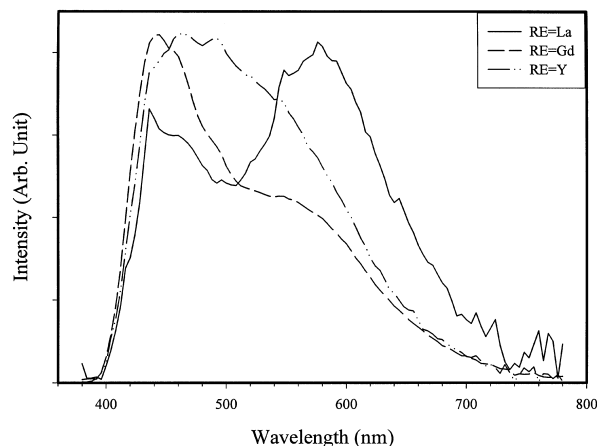


Fig. 5. The EL spectra of the devices at a driving voltage of 5 V.

recombination zone. In the present work, it is considered that as the driving voltage increases, the carrier recombination zone gradually moves away from the NPB/metal chelate interface towards the interior of the NPB layer. Hence, the high-voltage EL spectra are similar to the PL spectrum of NPB while the low-voltage EL spectra are considered to be a mixture of the emissions from NPB and the exciplexes formed at the organic interface. The detailed mechanisms of the exciplexes formation need more investigation.

In summary, the present work demonstrates how blue EL emission is achieved by using NPB as the emitter and hole-transporting layer and a non-emitting RE metal chelate as the electron transporting layer. For the device using the Gd chelate, a bright and pure blue emission can be obtained at driving voltages higher than 7 V. A maximum luminance of 1000 cd/m² was obtained at 20 V.

Acknowledgements

This work was supported by the Research Grant Council of HongKong (project #8730009 and 9040293) and Strategic Research Grant (project #7000771) of the City University of Hong Kong.

References

- [1] F. Garten, A. Hilberer, F. Cacialli, E. Esselink, Y. van Dam, B. Schlattman, R.H. Friend, T.M. Klapwijk, G. Hadziioannou, *Adv. Mater.* 9 (1997) 127.
- [2] J.G. Lee, B. Park, H.S. Woo, Y. Kim, C.H. Ha, C.M. Lee, K. Jeong, J.H. Ha, Y.R. Kim, *Solid State Commun.* 102 (1997) 895.
- [3] J. Kido, K. Honggawa, K. Okuyama, K. Nagai, *Appl. Phys. Lett.* 63 (1993) 2627.
- [4] C. Hosokawa, H. Tokailin, H. Higashi, H. Nakamura, T. Ksumoto, *Appl. Phys. Lett.* 78 (1995) 1441.
- [5] W.S. Bacsa, M. Schaer, Zuppiroli, *J. Appl. Phys.* 84 (1998) 5733.

- [6] S.A. Van Slyke, C.H. Chen, C.W. Tang, *Appl. Phys. Lett.* 79 (1996) 2160.
- [7] J. Kido, W. Ikeda, M. Kimura, K. Nagai, *Jpn. J. Appl. Phys.* 35 (1996) L394.
- [8] Y. Hamada, T. Sano, H. Fujii, Y. Nishio, H. Takahashi, K. Shibata, *Jpn. J. Appl. Phys.* 35 (1996) L1339.
- [9] G. Blass, B.C. Grabmaier, *Luminescent Materials*, Springer Verlag, Berlin, 1994, pp. 25–27, 41–50.
- [10] Y.Z. Wang, R.G. Sun, D.K. Wang, T.M. Swager, A.J. Epstein, *Appl. Phys. Lett.* 74 (1999) 2593.