

Synthesis and Electroluminescent Properties of Carbazolyl Vinylene Derivatives

H.J. Seo

Display Institute, Vistorm, D503-2 Bundang Techno-Park, Seongnam, 463-816

E-mail : chem92@ivistorm.com

Tel: +82-31-709-8385, Fax: +82-31-609-8387

H.C. Park¹

Display Institute, Vistorm, D503-2 Bundang Techno-Park, Seongnam, 463-816

S.E.Lee², J.W.Park^{2*}

Dept. of Chemistry/Center for Nanotech. Res., Catholic Univ., Pucheon, 420-734

Abstract

We report the photo-(PL) and electroluminescence (EL) properties of new conjugated compounds based on carbazolyl vinylene moiety, 3,3'-(1,4-phenylene di-2,1-ethenediyl) bis[9-ethyl-(E,E)-9H-carbazole](PEEC) and 3,3'-([1,1'-biphenyl]-4,4'-diyldi-2,1-ethenediyl)bis[9-ethyl-9H-carbazole](BPEEC), as emitting materials.

The ITO/m-MTDATA/NPB/BPEEC/Alq3/LiF/Al device shows bluish-green EL spectrum at 490nm and turn-on voltage at 8V. PEEC shows bluish-green EL around $\lambda_{max}=496nm$ and turn-on voltage at 6V and 2.4 Cd/A efficiency in ITO/m-MTDATA/NPB/PEEC/Alq3/LiF/Al device.

1. Introduction

Impressive scientific progress in electroluminescence(EL) materials has been made to obtain high performance EL devices [1], [2]. We have also investigated electroluminescent properties of hole injection or emitting materials [3]-[5].

Recently, there has been considerable interest of EL devices using materials with high Tg [6]-[7].

In this paper, we report the synthesis and electroluminescent properties of carbazole derivatives, 3,3'-(1,4-phenylene di-2,1-ethenediyl)bis[9-ethyl-(E,E)-9H-carbazole](PEEC) and 3,3'-([1,1'-biphenyl]-4,4'-diyldi-2,1-ethenediyl)bis[9-ethyl-9H-carbazole](BPEEC) which are conjugated molecules.

2. Experimental

2.1. Materials and characterization

p-xylylenebis(triphenylphosphoniumbromide), 4,4'-Bis-(methyldiethoxyphosphate)-[4,4']biphenyl, 9-Ethyl-3-carbazolecarboxaldehyde were synthesized and used.

All chemicals were purchased from Aldrich and used without further purification unless otherwise noted.

Solvents were purified by normal procedures and handled under moisture free atmosphere.

¹H-NMR spectra were recorded with Bruker AM-360 spectrometer in CDCl₃ and chemical shifts were recorded in ppm units with the residual proton solvent resonance.

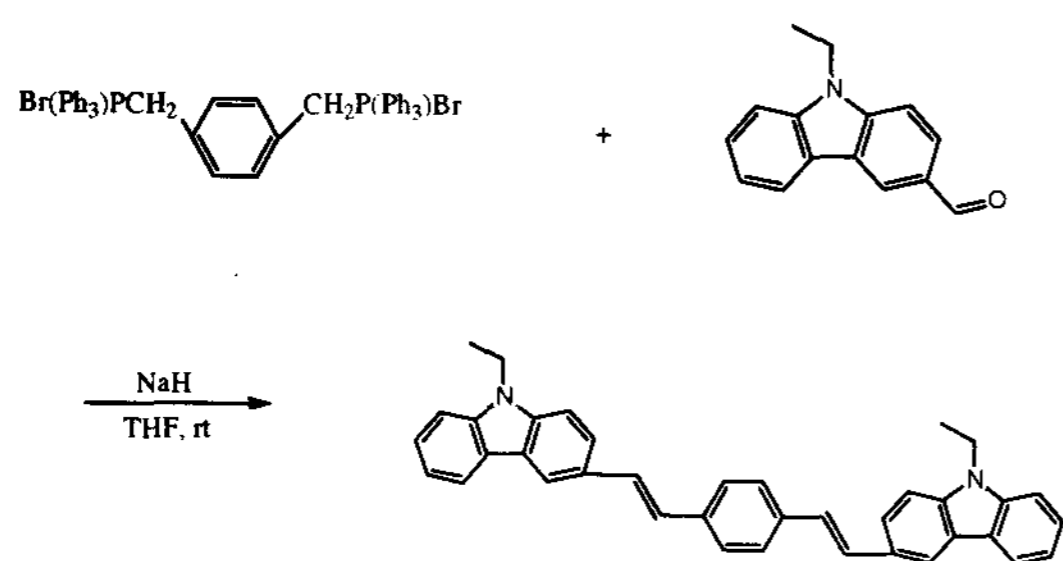
The optical absorption spectra were measured by a Shimadzu UV-3100 UV-VIS-NIR Spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo- and electroluminescence spectroscopy.

For EL device, PEEC and BPEEC was vacuum deposited on top of ITO under 10⁻⁶ torr, the rate of deposition being 1Å per second to give an emitting area of 6mm² and aluminum layer was continuously deposited with same vacuum condition.

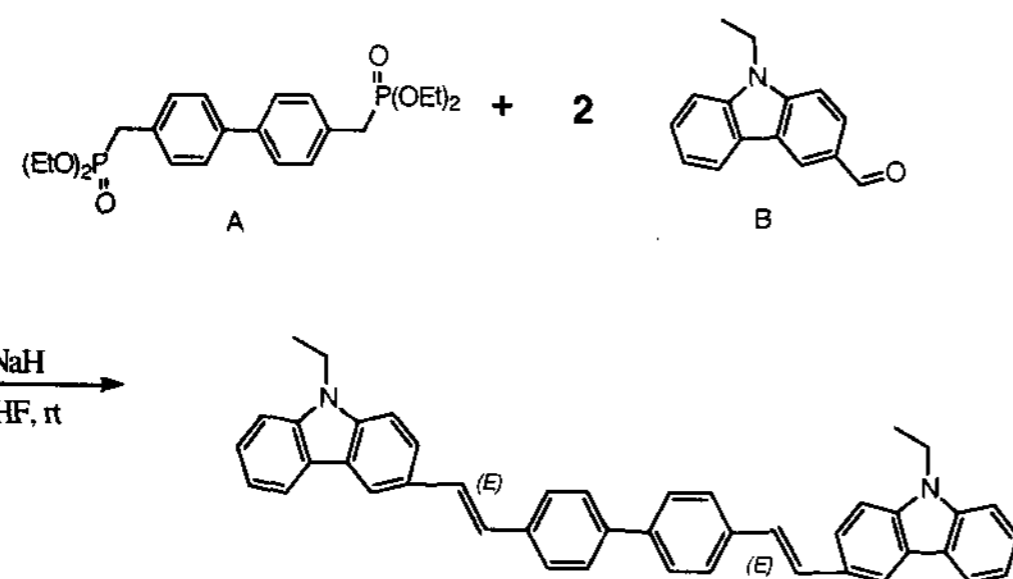
Current-voltage(I-V) characteristics of the film in plane were measured using Keithley 2400 electrometer. Light intensity is obtained by Minolta CS-1000.

2.2. Synthesis of 3,3'-(1,4-phenylene di-2,1-ethenediyl) bis[9-ethyl-(E,E)-9H-carbazole](PEEC) and 3,3'-([1,1'-biphenyl]-4,4'-diyldi-2,1-ethenediyl)bis[9-ethyl-9H-carbazole](BPEEC)

3,3'-(1,4-phenylene di-2,1-ethenediyl) bis[9-ethyl-(E,E)-9H-carbazole](PEEC)(see Scheme I) and 3,3'-([1,1'-biphenyl]-4,4'-diyldi-2,1-ethenediyl)bis[9-ethyl-9H-carbazole](BPEEC) were synthesized by Wittig-Honor reaction(see Scheme II).



(Scheme I)



(Scheme II)

3. Results and Discussion

3.1. Characterization of PEEC and BPEEC

PEEC and BPEEC were synthesized and identified by NMR (see Figure 1) and UV-Vis. Spectroscopies (See Figure 2). The resulting product is soluble in chloroform or THF. As the reaction proceeds, the aldehyde proton peaks disappeared and a new vinylic proton peaks appeared around 7.5 ppm in NMR and the color of PEEC and BPEEC were yellow and yellow green. The TGA thermograms of PEEC and BPEEC were tested under nitrogen atmosphere for EML thermal stability. PEEC and BPEEC showed thermally stable property and retained 100% of its original weight by 350°C.

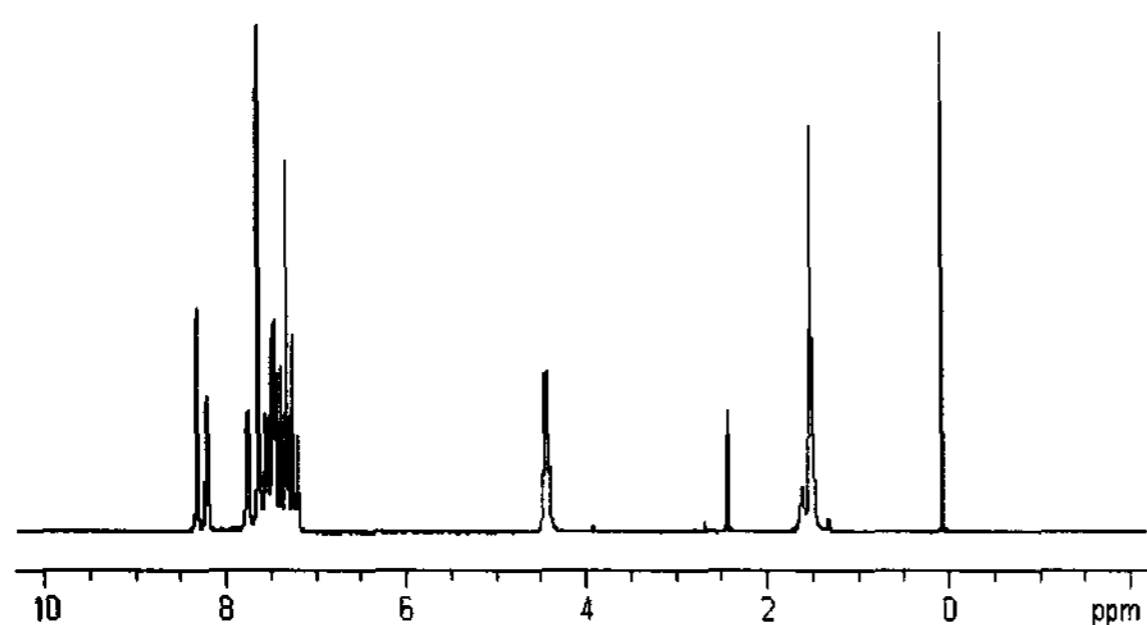


Figure 1. ¹H NMR spectrum of PEEC

3.2. Optical and electroluminescent properties of PEEC and BPEEC

Figure 2 shows the UV-visible spectra and photoluminescence spectra of PEEC film (thickness 600 Å) on glass substrate. PEEC film did not show particle on surface and exhibited clear surface property by microscope, and also showed characteristic UV-Visible absorption band at 378 nm and bluish-green PL spectrum at 493 nm corresponding to the photon energy of 2.52 eV. The band gap energy of PEEC was estimated to be 2.67 eV from the analysis of the absorption edge with a plot of $(h\nu)$ vs. $(\alpha h\nu)^2$, where α , h , and ν are the absorbance, Planck's constant, and the frequency of light, respectively. BPEEC film also showed similar characteristics, which has blue PL spectrum at around 477 nm.

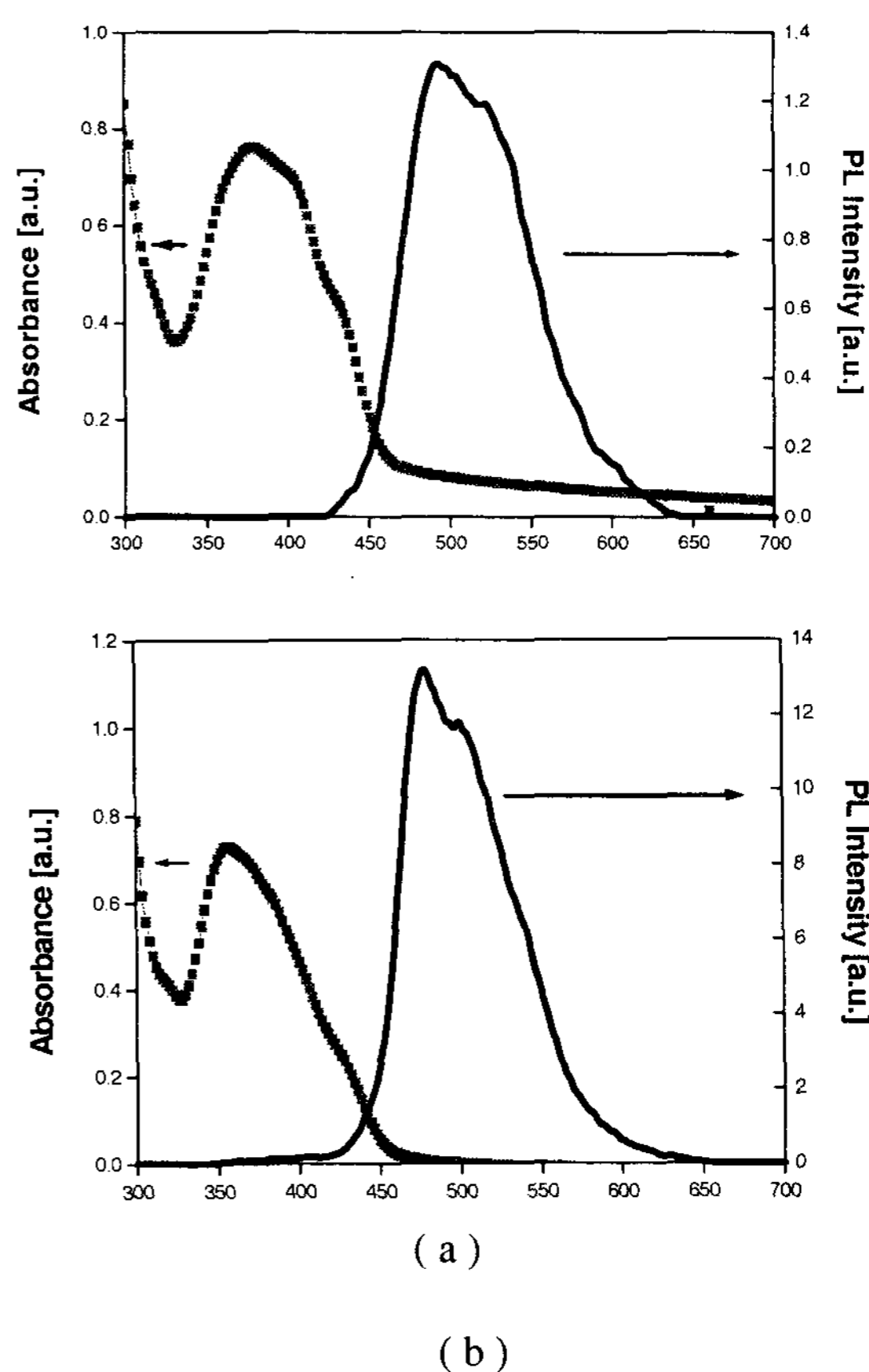
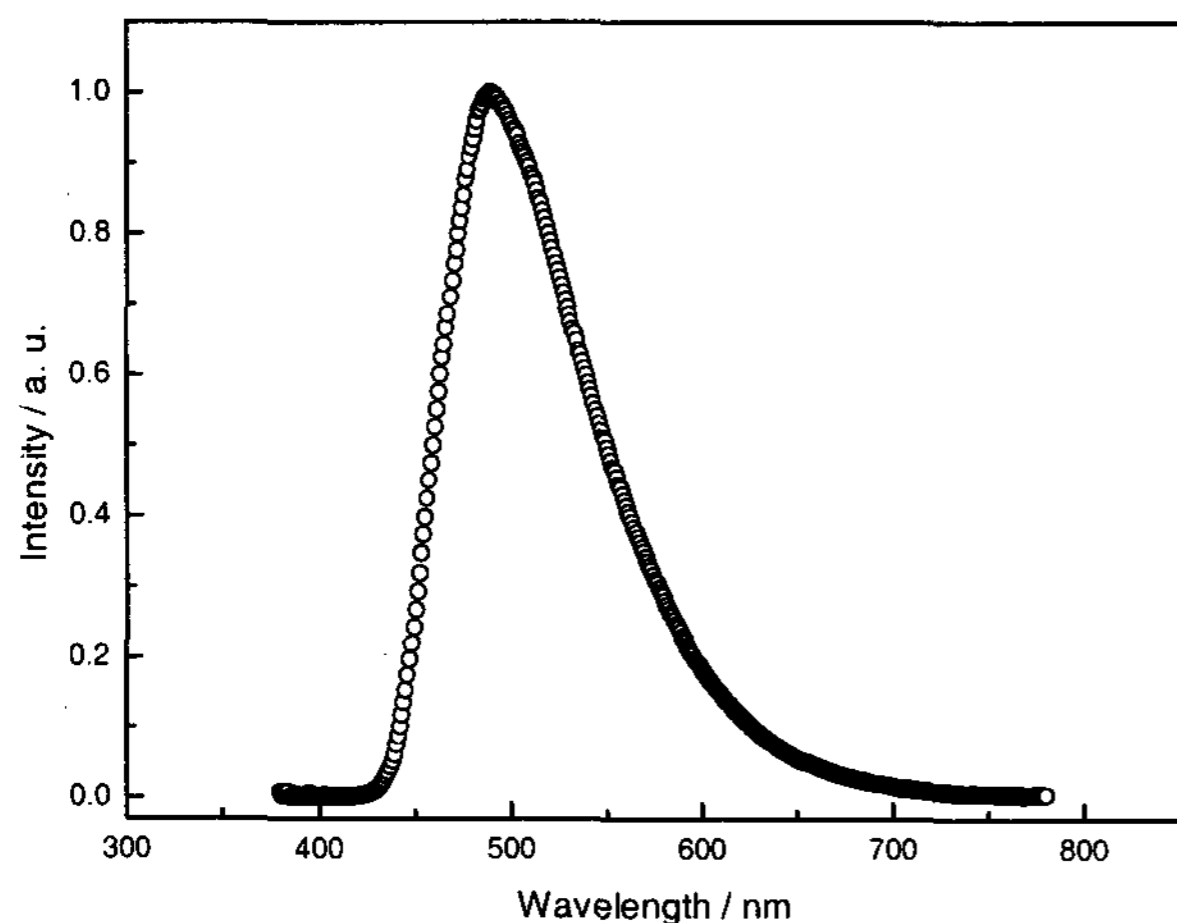


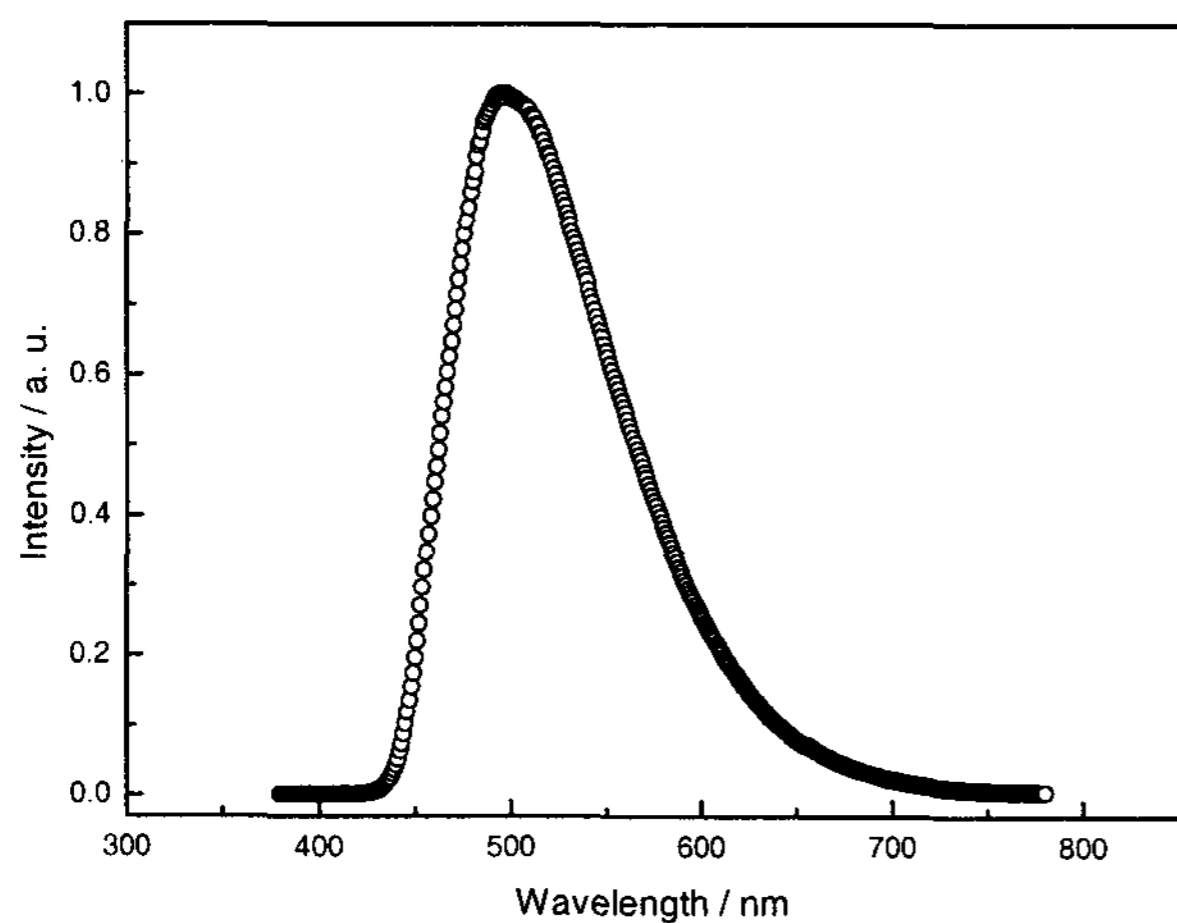
Figure 2. UV-visible spectra and photoluminescence spectra of PEEC (a), BPEEC (b) film (thickness 600 Å) on glass substrate

The typical EL devices were fabricated with vacuum (10^{-6} torr) deposited PEEC and BPEEC emitting layer (300-600 Å). This ITO/m-MTDATA (60 nm)/NPB (15 nm)/EMLs (30 nm)/Alq3 (30 nm)/LiF (1 nm)/Al devices show bluish-green EL

spectrum at 496nm and 490nm(see Figure 3) and typical rectifying diode characteristics(see Figure 4).



(a)



(b)

Figure 3. The EL spectrum of PEEC(a) and BPEEC(b)

These devices operate in forward bias modes at approximately the same turn-on potential 6V ~ 8V with 300 Å emitting layer thickness. PEEC device showed 2.4cd/A efficiency and (0.27, 0.46) color coordinate value at 6.9V and 10mA/cm² and BPEEC device showed relatively lower efficiency (<1cd/A) than PEEC's.

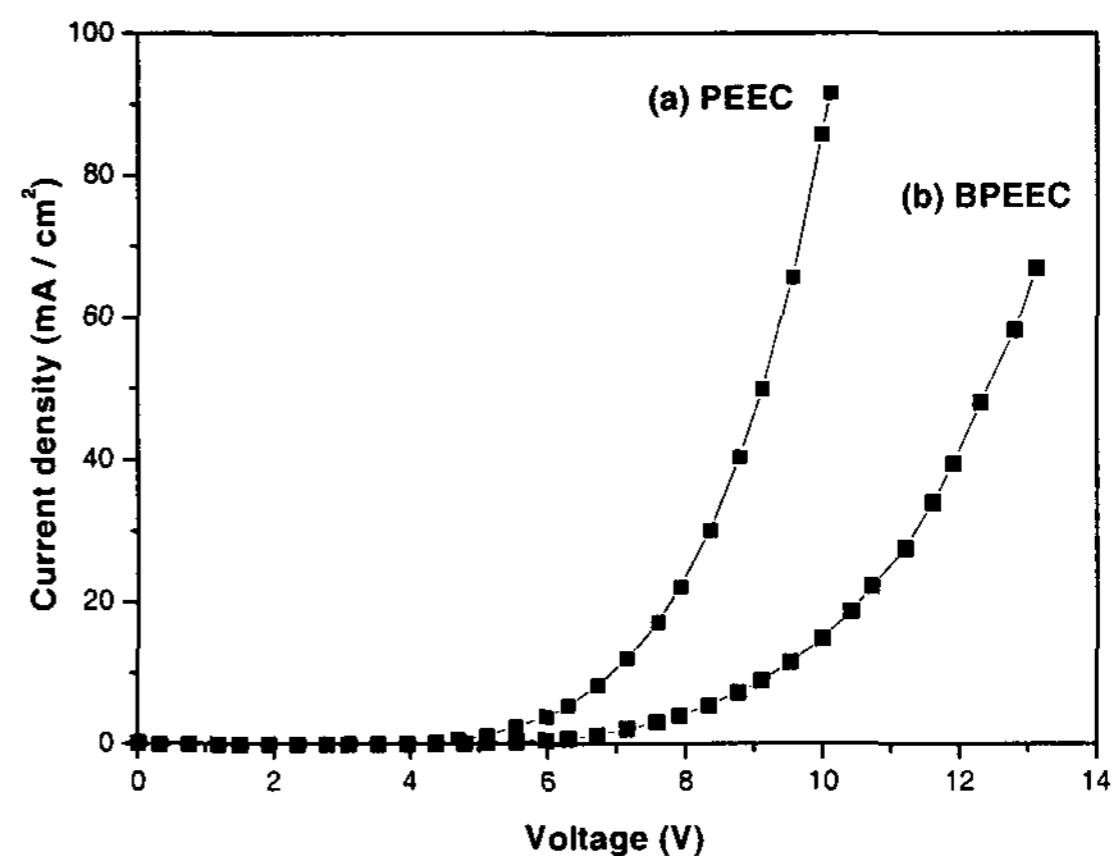


Figure 4. I-V characteristics for ITO/m-MTDATA/NPB/PEEC(a) or BPEEC(b)/AIQ/LiF/Al

Acknowledgment

This study was supported by the Research Fund 2003, The Catholic University of Korea. This work was supported by grant R01-2002-000-00347-0 from the interdisciplinary research program of the KOSEF.

Reference

- [1] C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 51, 913(1987).
- [2] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thomson, and S. R. Forrest, *Nature(London)*, 395, 151(1998).
- [3] H. K. Kim, M. K. Ryu, K. D. Kim, S. M. Lee, S. W. Cho, and J. W. Park, *Macromolecules*, 31, 1114(1998).
- [4] J. W. Park, J. H. Lee, H. S. Lee, D. Y. Kang and T. W. Kim, *Thin Solid Films*, 363, 90(2000).
- [5] J.W. Park, J.H. Lee, S.I. Kho, T.W. Kim, T. Uemura, and Y. Chujo, *Synthetic Metals*, 121, 1689(2001).
- [6] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, and M. E. Thompson, *J. Am. Chem. Soc.*, 123, 4304(2001).
- [7] D. L. Thomsen III, F. Papadimitrakopoulos, *Polymer Preprint*, 38(1), 398(1997).