Synthesis and Electroluminescent Properties of Diphenyl Benzeneamine Derivatives as Dopant Material

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. Park[1], T.G.Chung[1]

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

S.E.Lee[2], J.W.Park[2*]

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

Abstract

We report the photo-(PL) and electro-luminescence (EL) properties of new conjugated compounds based on diphenyl benzeneamine moiety, 4,4'-[1,4-phenylenedi-(1E)-2,1-ethenediyl]bis[N,N-diphenyl-benzenamine](PEDB) and 4,4'-([1,1`-biphenyl]-4,4`-diyldi-2,1-ethenediyl)bis[N,N-diphenyl-benzenamine](BPEDB), as emitting materials and dopant materials.

The ITO/m-MTDATA/NPB/DPVBi + BPEDB(1%) /Alq3/LiF/Al device shows blue EL spectrum at 458nm and high efficiency(5.3 cd/A). PEDB as dopant shows also blue EL spectrum around λ max=463nm and 4.1 cd/A high efficiency in ITO/m-MTDATA/NPB/DPVBi + PEDB(1%)/Alq3/ LiF/Al device.

1. Introduction

The low molecular-type organic light emitting diode(OLED) has been shown to have a high efficiency and a long lifetime as a practical OLED display[1]-[3]. Many organic materials have been synthesized and extended efforts have been made to obtain high performance OLED. We have also investigated electroluminescent properties of bipolar organic materials such as a bis(3-N-ethylcarbazolyl)cyanoterephtalidene(BECCP) [4]-[6].

In this study, we report the synthesis and electroluminescent properties of new blue dopant materials, 4,4'-[1,4-phenylenedi-(1E)-2,1-ethenediyl]bis[N,N-diphenyl-benzenamine](PEDB) and 4,4'-([1,1`-biphenyl]-4,4`-diyldi-2,1-ethenediyl)bis[N,N-diphenyl-benzenamine](BPEDB) which are aromatic *tert*-amine derivatives. We applied these molecules as dopant materials to host material, DPVBi(4,4'-Bis-(2,2-diphenyl-vinyl)-biphenyl).

2. Experimental

2.1. Materials and characterization

4-diphenyl benzaldehyde (98%), *p*-xylylenbis (triphenyl phosphonium bromide) (98%) and Sodium hydride (95%) were purchased from Aldrich and used without further purification unless otherwise noted. Solvents were purified by normal procedures and handled under moisture free atmosphere.

^{1}H-NMR spectra were recorded with Bruker AM-360 spectrometer in $CDCl_3$ 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 were vacuum deposited on top of ITO under 10^{-6}torr, the rate of deposition being 1Å per second to give an emitting area of 6mm^2 and aluminum layer was continuously deposited with same vacuum condition.

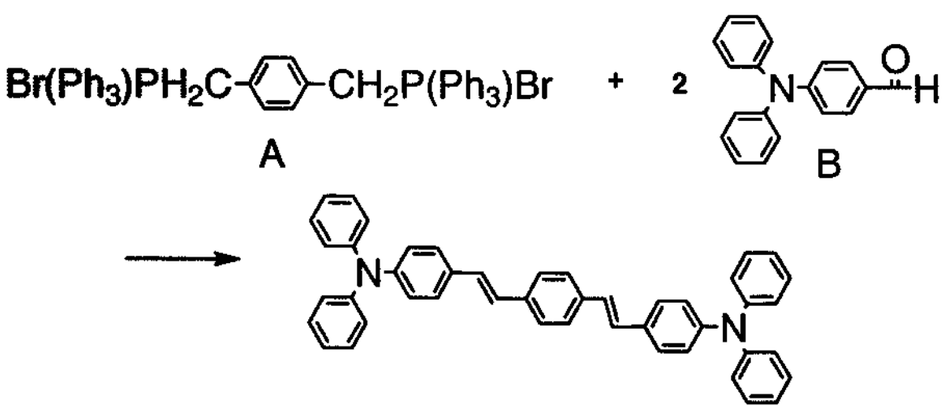
Current-voltage(I-V) characteristics of the film in plane was measured using Keithley 2400 electrometer. Light intensity is obtained by Minolta CS-1000.

2.2. Synthesis

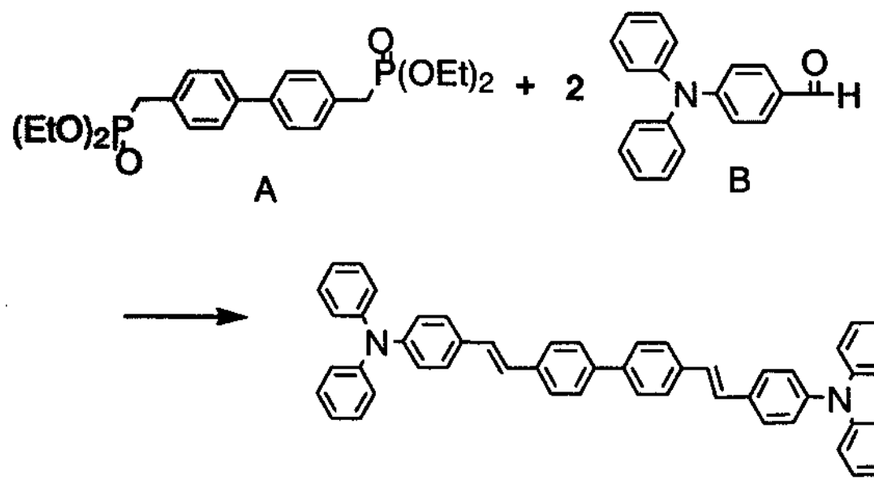
PEDB was synthesized by Wittig Honor reaction(see Scheme I).

The reaction mixture of p-xylylenbis(triphenylphosphonium bromide) (5g, 6 mmol), 4-diphenyl benzaldehyde (3.7 g, 13 mmol), and NaH (0.9 g, 38 mmol) was stirred in THF (150

ml) at room temperature for 24 h under N_2 condition. After methanol (50 ~ 100ml) was added to the reaction mixture, the precipitate was filtered and washed with methanol to afford pure PEDB (3.2 g, 83% yield). BPEDB was also synthesized by same Wittig Honor reaction with similar process (see scheme II).



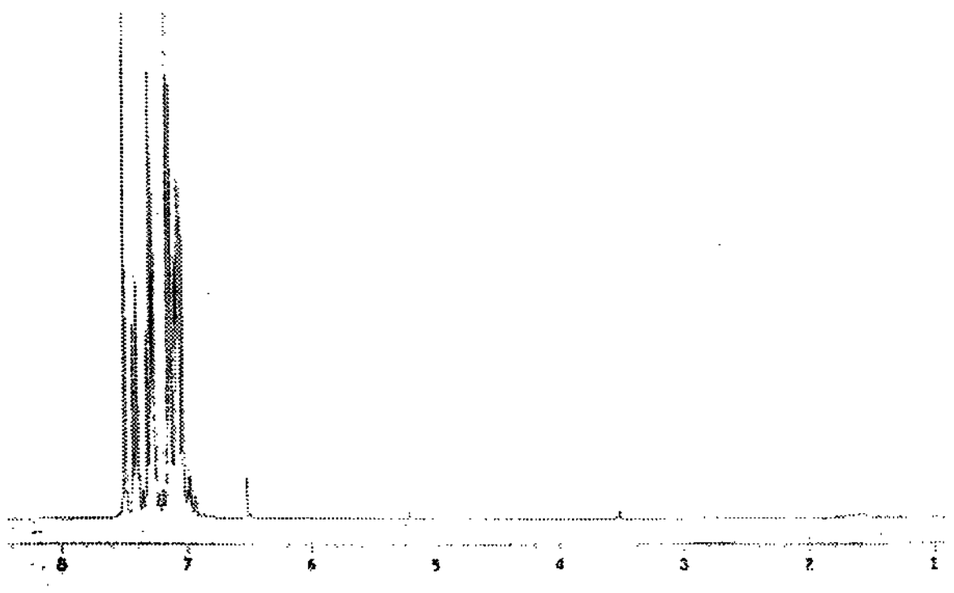
(Scheme I)



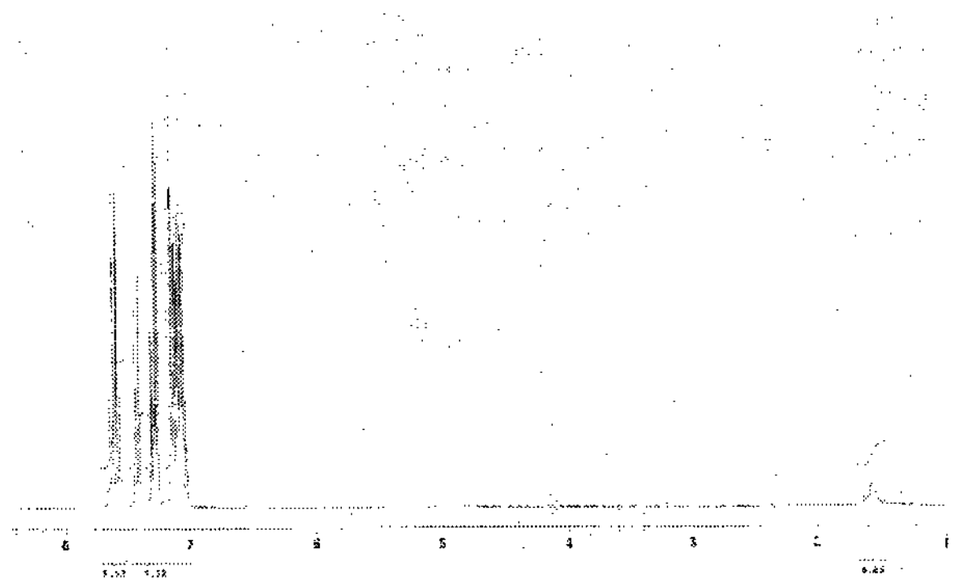
(Scheme II)

3. Results and Discussions

PEDB and BPEDB were identified and characterized by NMR (see Figure 1), EA, UV-Vis. spectroscopies and Photoluminescence(PL) spectroscopies(see Figure 2). The resulting products are soluble in common solvents such as chloroform or THF.



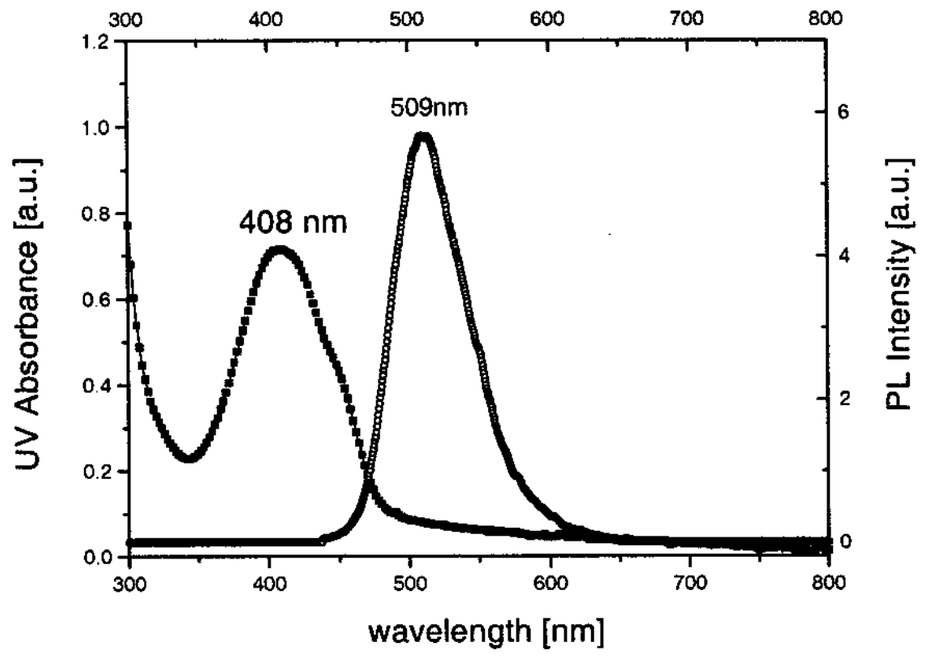
(a)



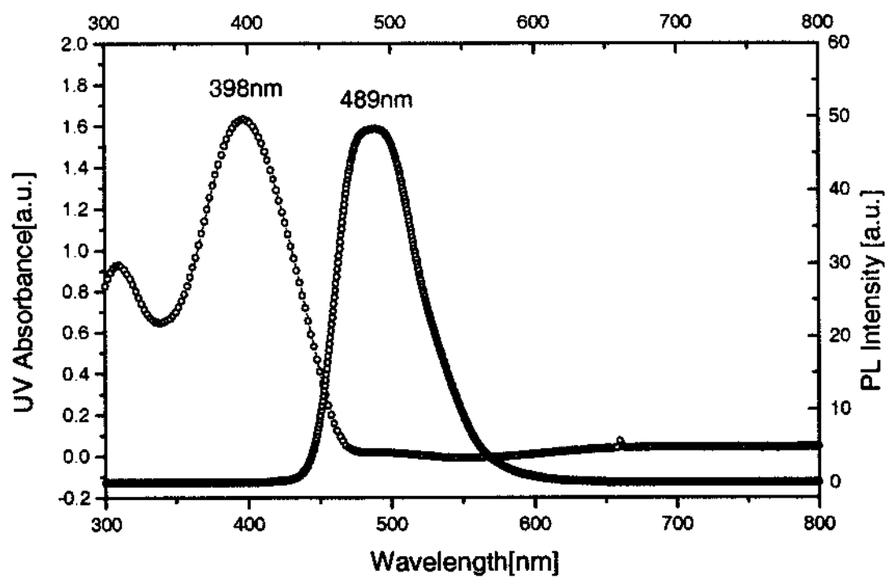
(b)

Figure 1. ^{1}H NMR spectrum of PEDB(a), BPEDB(b)

PEDB film(thickness 600 Å) on glass substrate did not show particle on surface and exhibited clear surface property by microscope, and also showed characteristic UV-Visible absorption band at 408nm and PL spectrum at 509nm corresponding to the photon energy of 2.48 eV.



(a)



(b)

Fig 2. UV-visible spectra and Photoluminescence spectra of PEDB (a) and BPEDB (b)

The typical EL devices were fabricated by using vacuum(10^{-6} torr) deposited PEDB and BPEDB film layer(see Figure 3). In here, PEDB and BPEDB was used as emitting layer or dopant materials(1%) for common blue emitting material, DPVBi(see scheme III).

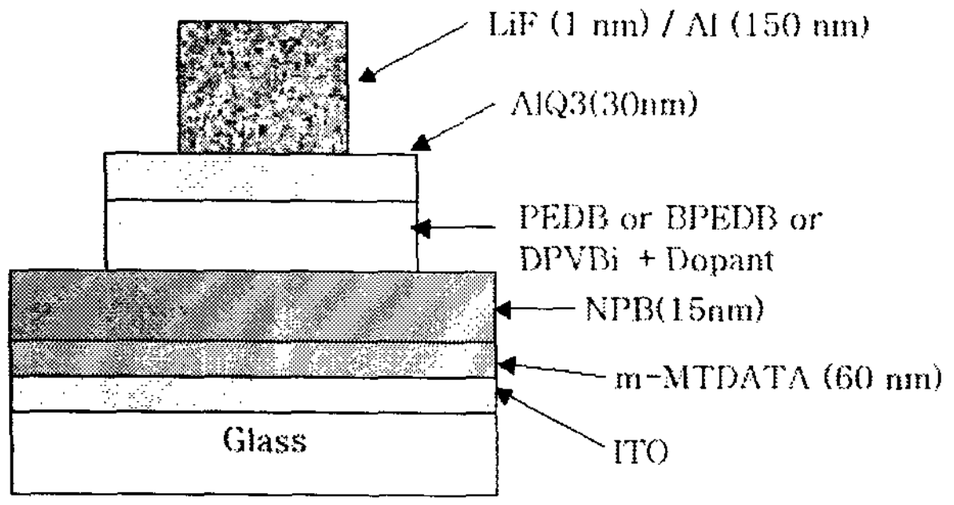
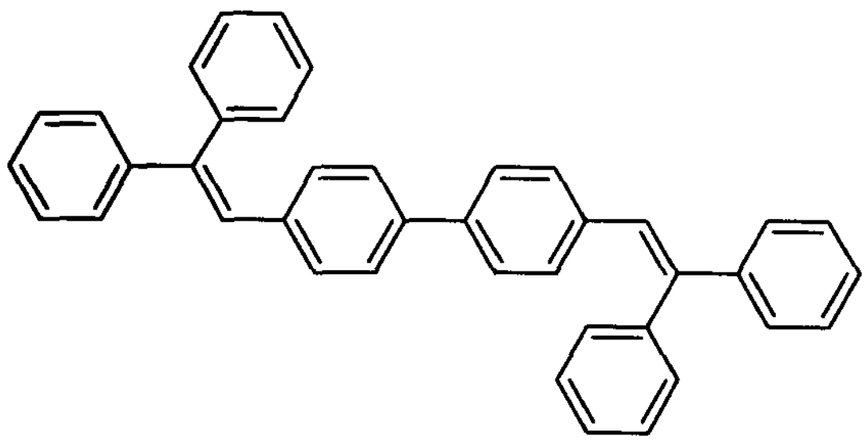


Figure 3. Schematic diagram of typical OLED structure



Scheme III. The structure of DPVBi

In Figure 4a and Table 1, PEDB device used as emitting material shows bluish-green EL spectrum at around 478 and 501nm and 1.8 ~ 2.3 cd/A efficency. Color coordinate values and EL maximum values lied in the range x : 0.19 ~ 0.21, y : 0.41 ~ 0.45 and 478nm ~ 506nm, respectively, which maybe due to the different ITO thickness and surface resistance.

BPEDB also shows greenish-blue or bluish-green EL spectrum at around 471nm or 496nm with similar device structure in Figure 4b and Table 2. BPEDB device exhibited relatively much higher efficiency(5.0 cd/A) and higher CIE value than PEDB's as host material. We believe biphenyl moiety might be contributed to the increased EL efficiency in this host derivatives

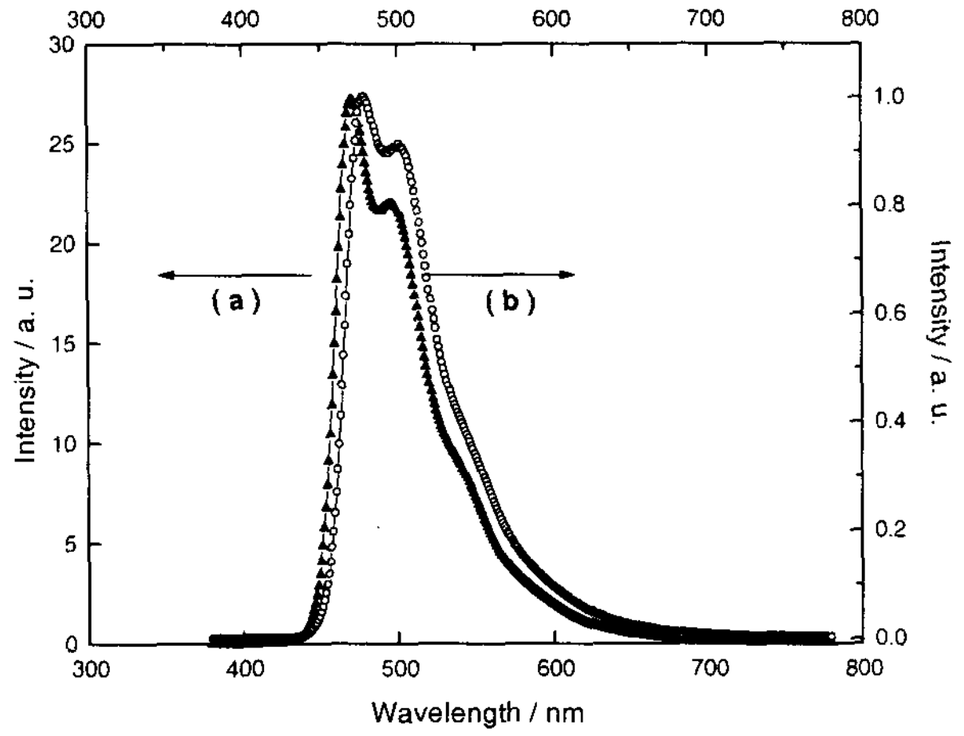


Figure 4. EL spectrum of BPEDB (a) and PEDB(b)

Substrate / ITO	Current Density	10mA/cm^2	25mA/cm^2
1500Å / 10Ohm	Voltage (V)	6.4	7.5
	Luminance (cd)	199	446
	CIE index (x, y)	0.19, 0.41	0.19, 0.41
	Peak ? (nm)	478	478
	Efficiency (cd/A)	2.0	1.8
1200Å / 30Ohm	Voltage (V)	6.5	8.1
	Luminance (cd)	234	474
	CIE index (x, y)	0.21, 0.45	0.21, 0.45
	Peak ? (nm)	506	506
	Efficiency (cd/A)	2.3	1.9

Table 1. EL efficiency data of m-MTDATA 600 / NPB 150 / PEDB 300 / Alq3 300 / LiF 10 / Al 600 device

Substrate / ITO	Current Density	10mA/cm²	25mA/cm²	50mA/cm²	100mA/cm²
1500Å / 10Ohm	Voltage (V)	6.7	7.6	8.5	9.3
	Luminance (cd)	428	1048	1965	3406
	CIE index (x, y)	0.187, 0.361	0.185, 0.358	0.184, 0.355	0.184, 0.351
	Peak ? (nm)	473	473	472	472
	Efficiency (cd/A)	4.2	4.2	4.0	3.4
1200Å / 30Ohm	Voltage (V)	6.7	7.7	8.5	9.4
	Luminance (cd)	493	1188	2184	3590
	CIE index (x, y)	0.209, 0.424	0.207, 0.422	0.206, 0.420	0.207, 0.415
	Peak ? (nm)	502	502	501	501
	Efficiency (cd/A)	5.0	4.8	4.4	3.6

Table 2. EL efficiency data of m-MTDATA 600 / NPB 150 / BPEDB 300 / Alq3 300 / LiF 15 / Al 2000 device

Our motivation for synthesis of these materials was based on doping agent, we fabricated the devices with these materials as dopant for common blue material, DPVBi(EL λmaximum = 453nm, 3.5cd/A), as shown in Figure 5 and 6.

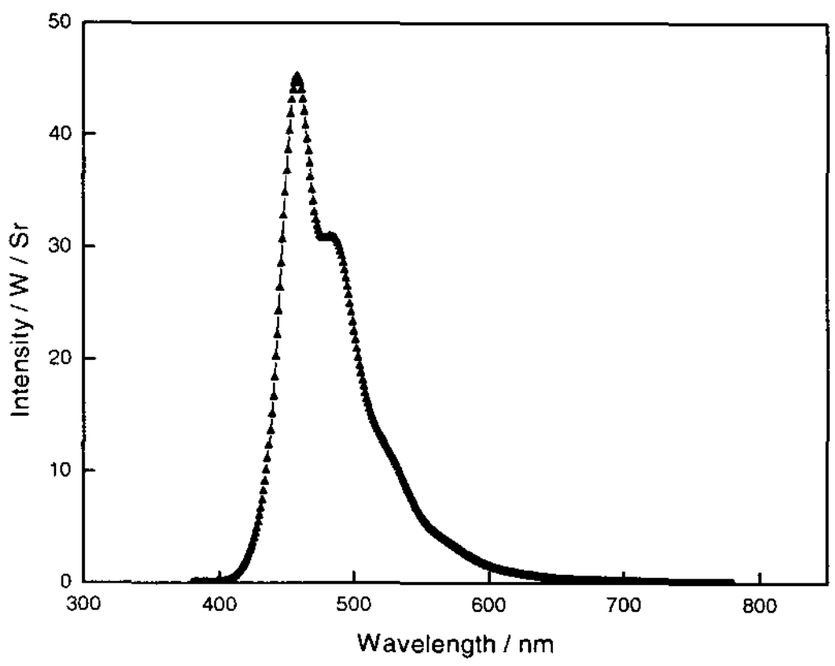


Fig 5. EL spectrum of m-MTDATA 600 / NPB 150 /DPVBi + PEDB(1%) 300 / Alq3 300 / LiF 10 / Al 1500 device

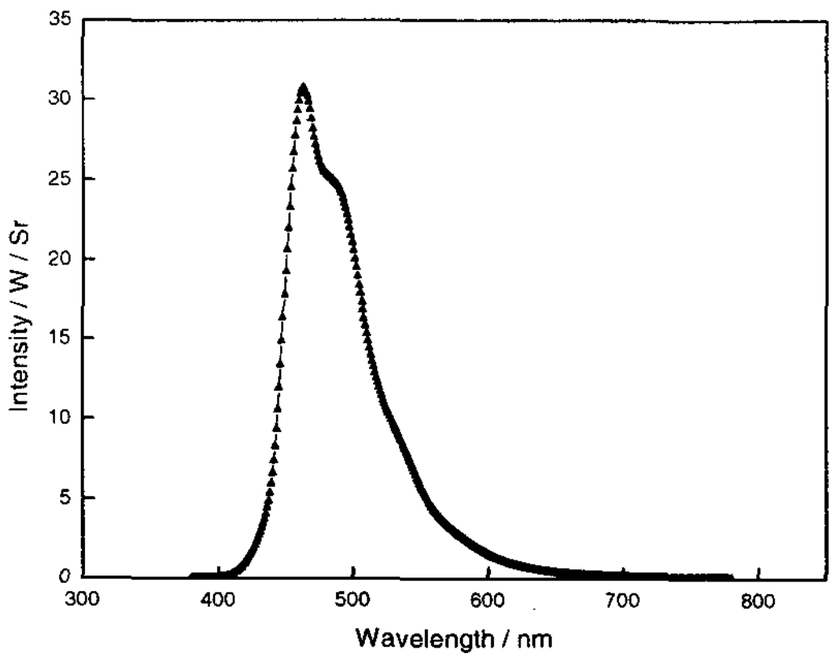


Fig 6. EL spectrum of m-MTDATA 600 / NPB 150 /DPVBi + BPEDB(1%) 300 / Alq3 300 / LiF 10 / Al 1500 device

ITO/m-MTDATA/NPB/DPVBi +PEDB(1%)/Alq3/ LiF/Al device showed EL spectrum at 463nm and EL efficiency was increased to 4.1 cd/A. ITO/m-MTDATA/NPB/DPVBi + BPEDB(1%)/Alq3/LiF/Al device also showed EL maximum value at 458nm and 5.3cd/A. Further studies in these directions are under way.

Acknowledgment

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