

## Co-deposition and Tuned Blue Emission Color from New Tetraphenylethylene Derivatives

Soo-Kang Kim and Jong-Wook Park\*

Department of Chemistry, The Catholic University of Korea, Pucheon, 420-743, Korea

TEL:82-2-2164-4821, e-mail: [hahapark@catholic.ac.kr](mailto:hahapark@catholic.ac.kr)

Keywords : OLED, Blue EML, Co-deposition, Tetraphenylethylene

### Abstract

By combining tetraphenylethylene and anthracene, we synthesized 9,10-bis(4-(1,2,2-triphenylvinyl)phenyl)anthracene [BTPPA] and 1,2-di(4'-tert-butylphenyl)-1,2-bis(4'-(anthracene-9-yl)phenyl)ethene [BPBAPE]; both BTPPA and BPBAPE have similar band-gaps, however their PL spectra were shifted by about 30 nm with respect to each other. The fabricated multilayered non-doped OLED devices based on pure BTPPA or BPBAPE exhibited luminance efficiencies of 3.93 cd/A at 6.8 V and 10.33 cd/A at 8.1 V, respectively, at 10 mA/cm<sup>2</sup>. As the BPBAPE content of the emitting layer increased, the luminance efficiency of the device increased; in addition, the CIE coordinates of the fabricated devices shifted gradually from deep-blue for pure BTPPA to sky-blue for pure BPBAPE.

### 1. Introduction

Organic light emitting diodes (OLEDs) have been the subject of intensive research, and are of great current interest in the area of full-color large displays<sup>[1-5]</sup>. Many conjugated organic molecules have been developed that show red, green or blue electroluminescence (EL). To develop a full-color display with excellent performance based on OLEDs, red<sup>[6]</sup>, green<sup>[7]</sup> and blue<sup>[8]</sup> materials with high EL efficiencies are essential. These materials should have good thermal properties, long life-times and pure color coordinates (Commission Internationale de l'Eclairage (CIE) characteristics). In efforts to achieve such properties, materials comprised of a host and dopant have been widely studied to improve efficiency. The host/dopant approach has been adopted in fluorescence and phosphorescence systems, and, in particular, red or green emitters have successfully reached a commercial level.

Recently, red emitting materials with CIE coordinates of (0.67, 0.23) and long life-times (>100,000 hours) at 11 cd/A and green emitting materials with CIE coordinates of (0.29, 0.64) and life-times of 100,000 hours at 21 cd/A have been developed<sup>[9]</sup>. However, the best blue material

developed to date has a lifespan of only 12,000 hours at 7 cd/A and CIE coordinates of (0.14, 0.16)<sup>[9]</sup>. In addition, performance further deteriorates if the hole injection layer (HIL) and hole transporting layer (HTL) used for green and red are applied as a shared hole carrier layer, causing problems for commercialization.

To date, the development of blue materials with high efficiencies and long life-times has proved very difficult. For blue light emission, the band gap should be wider than that of red or green light. As a result, if a blue light emitting substance is used, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the material become distant from the levels of the other OLED layers (e.g., the HTL and electron transporting layer (ETL)). This situation results in a mismatch between electrons and holes, which inevitably leads to low EL efficiency.

In a recent paper<sup>[10]</sup>, we have reported new high performance blue-light emitters based on compounds with tetraphenylethylene or anthracene groups at their cores. Of these synthesized compounds, BTPPA contains a mixture of anthracene and tetraphenylethylene units, which are non-alkylated bulky side groups. This compound has better thermal properties, a lower operating voltage, and deeper blue CIE<sub>x,y</sub> coordinates (0.159, 0.135) than other tetraphenylethylene derivatives. In particular, the BPBAPE device exhibits a luminance efficiency in excess of 10 cd/A even without using a doping method.

In the present study, we produced and characterized seven OLED devices in which the emitting layer was a co-deposited mixture of BTPPA and BPBAPE. We demonstrate that these co-deposited devices show a tunable EL spectrum without a doping effect.

### 2. Experimental

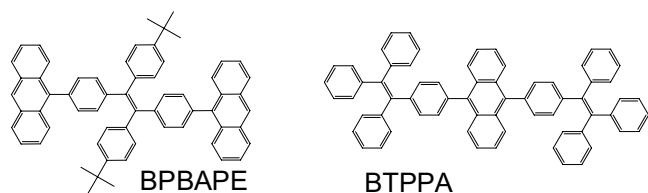
EL devices were fabricated using 2-TNATA as a hole injection layer, NPB as a hole transporting layer, BTPPA and BPBAPE as an emitting layer, Alq<sub>3</sub> as electron

transporting layer, LiF as electron injection layer, ITO (1200 Å, 30ohm) as the anode and Al as the cathode; ITO/2-TNATA(60nm)/NPB(15nm)/EML (30nm)/ Alq<sub>3</sub>(30 nm)/LiF (1 nm)/Al (200 nm). The organic layer was vacuum-deposited using thermal evaporation at a vacuum base pressure of 10<sup>-6</sup> torr, the rate of deposition being 1 Å/s to give an emitting area of 4mm<sup>2</sup> and aluminum layer was continuously deposited with same vacuum condition.

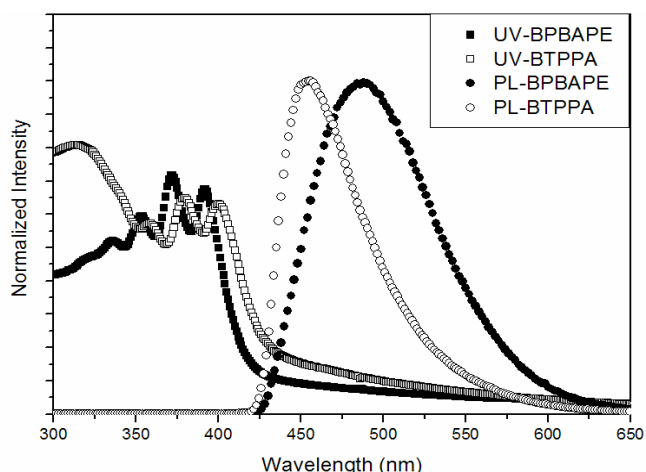
The current-voltage (I-V) characteristics of the fabricated EL devices were obtained with a Keithley 2400 electrometer. Light intensity was obtained with a Minolta CS-100A.

### 3. Result and Discussion

Scheme 1 shows the structures of the blue emitting materials containing a combination of tetraphenylethylene and anthracene moieties. In these materials, BPBAPE has a tetraphenylethylene group at its core with anthracene connected on the side, whereas BTPPA has anthracene at the core with tetraphenylethylene connected on the side. Both materials were synthesized through the McMurry reaction and Suzuki coupling<sup>[10]</sup>.



**Scheme 1.** Chemical structures of the blue-emitting materials.

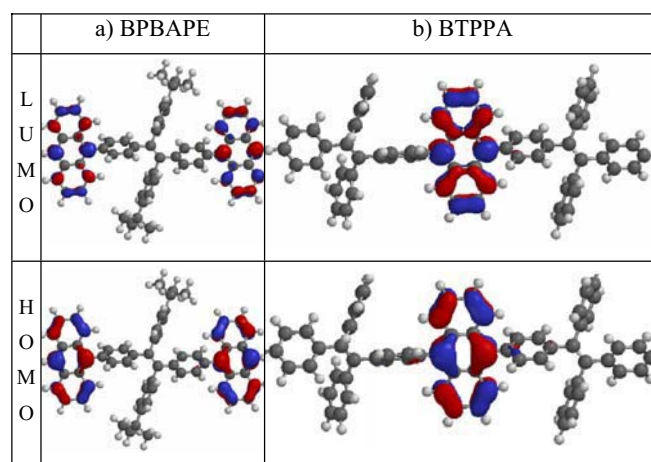


**Figure 1.** Normalized UV-Visible (Square) and PL (Circle) spectra of BPBAPE(solid) and BTPPA(open) film on glass.

Figure 1 shows the UV-Visible (UV-Vis) and PL spectra of BPBAPE and BTPPA in the thin-film state. The UV-Vis spectra of both materials showed a UV peak corresponding to the anthracene moiety in the range of 350-402 nm; this

feature is red-shifted by about 10 nm for BTPPA compared to BPBAPE, indicating that BTPPA has a longer conjugation length. In the PL spectra, the BTPPA spectrum was blue-shifted by more than 30 nm with respect to the BPBAPE spectrum, and the full width at half maximum (FWHM) was reduced to 60 nm.

To determine the factors giving rise to the above findings, we used molecular modeling to determine the ground-state structure and HOMO and LUMO of each molecule. Figure 2 shows the electron distribution of HOMO and LUMO in BPBAPE and BTPPA, calculated using the AM-1 method of Spartan'04<sup>[11,12]</sup>.

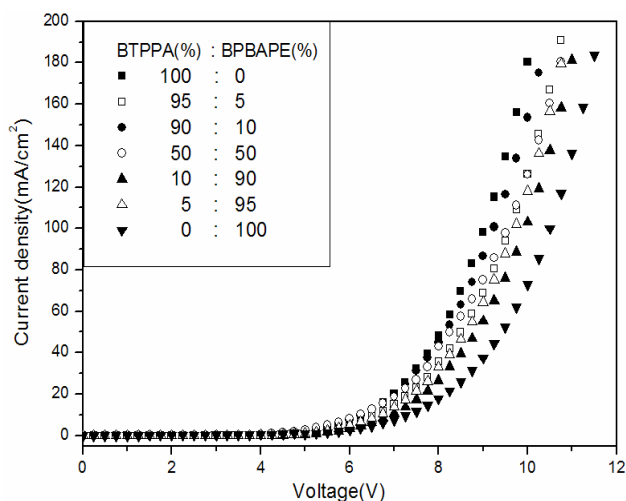


**Figure 2.** HOMOs and LUMOs of a) BPBAPE and b) BTPPA calculated at semi-empirical with a AM-1 basis set using Spartan'04.

For both the HOMO and LUMO, the electron densities of both BPBAPE and BTPPA were found to be high at the anthracene moiety. This indicates that if these compounds are reduced or oxidized, electrons will move in or out through the anthracene, respectively. There is, however, a significant difference between the two materials: BTPPA has anthracene at the core with the bulky tetraphenylethylene unit on the side, and hence the anthracene chromophore interaction between molecules is anticipated to be relatively difficult. In BPBAPE, by contrast, the anthracene is located on the side of the molecule; hence various types of overlap between molecules probably occur through the anthracene, resulting in various intermolecular exciton transitions. These anticipated findings coincide with the features of the PL spectra in Figure 1. Specifically, compared to the spectrum of BTPPA, the PL spectrum of BPBAPE is red-shifted and shows a larger FWHM of 88 nm.

Cyclic voltammetry (CV) was used to identify the HOMO values of the synthesized materials. The LUMO level of each material was then determined from the band-gap identified with UV<sub>onset</sub> and the HOMO value measured through CV. The HOMO levels of BPBAPE and BTPPA

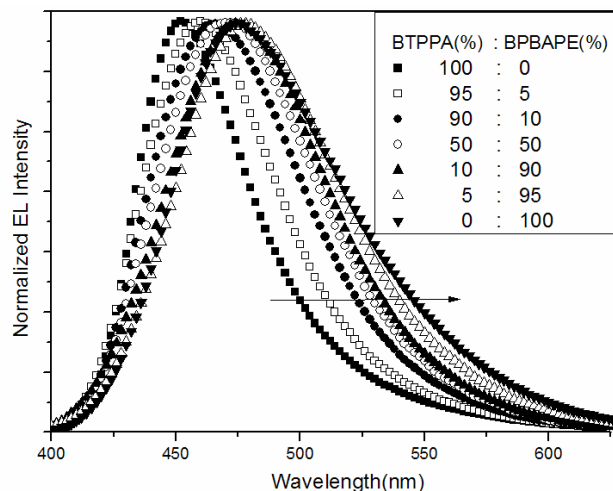
are near 5.6 eV, which is similar to the HOMO levels of 9,10-di(2-naphthyl)anthracene (ADN) and 2-methyl-9,10-di(2'-naphthyl)anthracene (MADN) as well as many other compounds containing an anthracene group as a core [13]. As shown in Figure 1, BPBAPE does not absorb in the wavelength range of the PL from BTTPA, suggesting that if both materials are jointly vapor-deposited, the doping effect that acts through Förster energy transfer will be negligible. Such behavior could potentially be applied to produce three-color white OLEDs that take advantage of three wavelengths in a way that produces maximum efficiency. To test these effects, we examined seven devices in which BPBAPE and BTTPA were co-deposited at various ratios as an EML. These EL devices had the following structure: ITO/2-TNATA (60 nm)/ NPB (15 nm)/BTTPA(100-x%) and BPBAPE(x%) (30 nm)/ Alq<sub>3</sub> (30 nm)/LiF (1 nm)/Al (200 nm).



**Figure 3.** Current density-voltage characteristics of ITO/ 2-TNATA(60nm) / NPB(15nm) / EML(30nm)/ Alq<sub>3</sub>(30nm) / LiF(1nm) / Al (200nm) devices.

Figure 3 shows the I-V properties of the seven devices. All devices show similar I-V curves that are typical of diodes; this is because the HOMO levels, LUMO levels, and carrier mobilities of the emitting materials are similar. Figure 4 shows the EL spectra of the seven fabricated devices. For the systems with 100% BTTPA and 100% BPBAPE, the maximum wavelength of EL was 452 nm and 475 nm, respectively. In general in OLED devices, when a doping agent is introduced into the EML at a doping ratio such as 5%, the EL spectrum becomes asymmetrical or exhibits features of the doping agent's EL spectrum due to Förster energy transfer. In the system considered here, however, no doping effects were observed when BPBAPE was co-deposited with BTTPA, regardless of the doping ratio. As the BPBAPE content of the sample increases, the EL spectrum is gradually red-shifted and broadened. This change in wavelength with varying the ratio of BTTPA to

BPBAPE should prove useful in tuning the blue color.

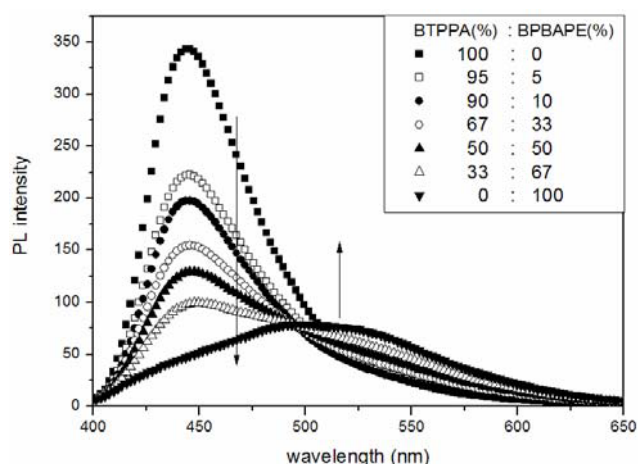


**Figure 4.** EL spectra of ITO/ 2-TNATA(60nm) / NPB(15nm) / EML(30nm)/ Alq<sub>3</sub>(30nm) / LiF(1nm) / Al (200nm) devices at 10 mA/cm<sup>2</sup>.

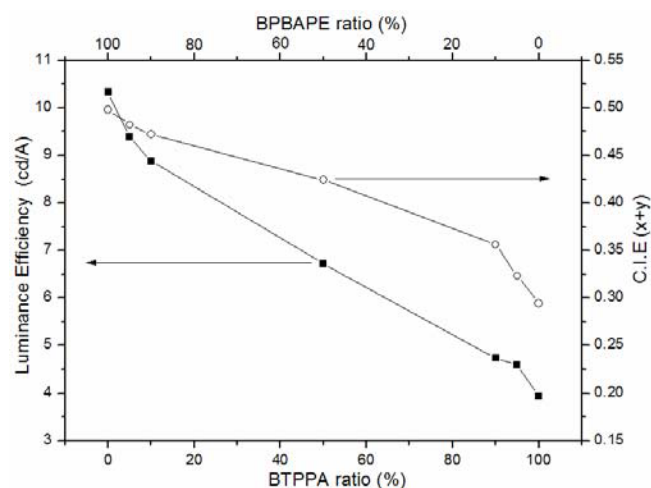
The EL results for the BTTPA/BPBAPE co-deposited samples coincide with the behavior of the PL spectra recorded for solutions mixed with various ratios. Figure 5 shows the PL spectra for toluene solutions of BTTPA and BPBAPE with various ratios measured at 4.5 x 10<sup>-5</sup> M. As the BPBAPE content of the solution is increased, the PL intensity of BTTPA decreases and that of BPBAPE increases. As for the EMLs in the devices, no general doping effect was observed for the solutions; the respective luminescent characteristics of the two materials occurred separately. This behavior can be attributed to the similar band-gaps and UV spectra of BTTPA and BPBAPE.

**Table 1.** EL performance of multi-layered devices with the structure ITO /2-TNATA(60 nm) /NPB(15 nm) /EML(30 nm) /Alq<sub>3</sub>(30 nm) /LiF(1 nm) /Al(200 nm) at 10 mA/cm<sup>2</sup>.

EML ratio (%)		EL <sub>max</sub> (nm)	Voltage (V)	Luminance Efficiency (cd/A)	Power Efficiency (lm/W)	CIE (x,y)
BTTPA	BPBAPE					
100	0	452	6.8	3.93	1.82	(0.159, 0.135)
95	5	460	6.9	4.59	2.09	(0.158, 0.165)
90	10	466	6.9	4.74	2.16	(0.163, 0.193)
50	50	473	6.8	6.72	3.10	(0.170, 0.254)
10	90	475	7.0	8.88	3.99	(0.182, 0.290)
5	95	477	7.0	9.39	4.21	(0.184, 0.298)
0	100	475	8.1	10.33	4.00	(0.195, 0.303)



**Figure 5.** PL spectra of various BTTPA and BPBAPE ratio. ( $4.5 \times 10^{-5}$  M in Toluene solution)



**Figure 6.** Luminance efficiency (cd/A) and CIE (x+y) value of various EML ratio.

The EL performances of the devices at a current density of  $10 \text{ mA/cm}^2$  are summarized in Table 1 and Figure 6. Multilayered non-doped OLED devices based on pure BTTPA or BPBAPE yielded luminance efficiencies of  $3.93 \text{ cd/A}$  at  $6.8 \text{ V}$  and  $10.33 \text{ cd/A}$  at  $8.1 \text{ V}$ , respectively, at  $10 \text{ mA/cm}^2$ . Figure 6 shows the luminance efficiency and the sum of the values of the CIE x and y coordinates for each device. As the CIE values in the blue region shift toward a deeper blue, the values of x and y become smaller. Thus, a smaller value of  $x + y$  indicates a deeper blue color. As shown in Figure 6, as the BPBAPE content of the device increases, the luminance efficiency increased up to a maximum of  $10.33 \text{ cd/A}$  in the device with 100% BPBAPE. The CIE coordinates were found to move from the deep-blue area for the device with 100% BTTPA to the sky-blue area for the device with 100% BPBAPE. These findings demonstrate that the EL efficiency and CIE values can be tuned by varying the co-deposition ratio of BPBAPE to BTTPA.

## 4. Conclusion

We fabricated and characterized seven OLED devices of BTTPA and BPBAPE with co-deposition method. In the cases of 100% BTTPA and 100% BPBAPE, the maximum wavelength of EL was  $452 \text{ nm}$  and  $475 \text{ nm}$ , respectively. As said above, there was no doping effect in various cases of co-deposition as well as in the composition for doping. And the more increased the ratio of BPBAPE, the more red-shifted and broader the EL spectrum became. Those results will be helpful in the color tuning of blue wavelength. When the ratio of BPBAPE increased, the luminance efficiency also became increased. And CIE coordinates were found to move from the deep-blue areas of BTTPA to the sky-blue areas of BPBAPE. We found that EL efficiency and CIE values are gradually tunable according to the co-deposition ratio of BPBAPE and BTTPA.

## 5. Reference

- [1] C. W. Tang, S. A. Van Slyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
- [2] M. A. Baldo, M. E. Thompson, S. R. Forrest, *Nature*, 2000, **403**, 750.
- [3] S. K. Kim, C. J. Lee, I. N. Kang, J. H. Lee and J. W. Park, *Thin Solid Films*, **2006**, **509**, 132.
- [4] P. L. Burn, S. C. Lo, I. D.W. Samuel, *Adv. Mater.*, 2007, **19**, 1675.
- [5] Y. S. Yao, Q. X. Zhou, X. S. Wang, Y. Wang, B. W. Zhang, *J. Mater. Chem.*, 2006, **16**, 3512.
- [6] B. J. Jung, J. I. Lee, H. Y. Chu, L. M. Do, J. M. Lee, H. K. Shim, *J. Mater. Chem.*, 2005, **15**, 2470.
- [7] K. T. Kamtekar, C. Wang, S. Bettington, A. S. Batsanov, I. F. Perepichka, M. R. Bryce, J. H. Ahn, M. Rabinal, M. C. Petty, *J. Mater. Chem.*, 2006, **16**, 3823.
- [8] S. K. Kim, B. Yang, Y. Ma, J. H. Lee, J. W. Park, *J. Mater. Chem.*, 2008, DOI : 10.1039/B805062G
- [9] T. Arakane, M. Funahashi, H. Kuma, K. Fukuoka, K. Ikeda, H. Yamamoto, F. Moriwaki, C. Hosokawa, C., *SID Dig.*, 2006, 37.
- [10] S. K. Kim, Y. I. Park, I. N. Kang, J. W. Park, *J. Mater. Chem.*, 2007, **17**, 4670
- [11] *Spartan'04 for Windows*; Wavefunction, Inc.: Irvine, CA, 2003.
- [12] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
- [13] a) S. W. Wen, M. T. Lee, C. H. Chen, *J. Display Tech.*, 2005, **1**, 90; b) M. X. Yu, J. P. Duan, C. H. Lin, C. H. Chung, Y. T. Tao., *Chem. Mater.*, 2002, **14**, 3958.