Ultrahigh Efficiency from Novel Blue Emitters Using a Rational Molecular Design

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Abstract

We investigated new deep blue emitting materials including a novel side group such as CB-203. CB-203 shows relatively 40% increased PL quantum efficiency and higher Tg of 30℃ compared to MADN. It exhibits high External Quantum Efficiency (EQE) of 7.18% that is two times bigger than MADN's, which is the best efficiency in case of non-doped blue fluorescence OLED device to our knowledge. And deep blue emitting materials with a new core structure (CB-301) have been synthesized. CB-301 exhibit excellent blue fluorescence properties. Undoped OLED devices using CB-301 as blue emitters was found to deep blue CIE value (0.154, 0.078) and exhibit high luminance efficiencies of 2.01cd/A at 10 mA/cm^2.

1. Introduction

Organic light-emitting diodes (OLEDs) based on organic molecules are currently the subject of intense research efforts due to their promise as devices for full-color large display applications[1-5]. To date, numerous conjugated organic molecules have been synthesized and reported to exhibit electroluminescence (EL) ranging from red to green and blue. In order to fabricate full color OLED displays, we need high performance red[6], green[2,7], and blue[8] materials with high EL efficiencies, good thermal properties and long lifetimes as well as pure color coordinates (Commission Internationale de l'Eclairage (CIE)). Both host and dopant methods have been used in fluorescence and phosphorescence systems to produce high efficiency OLEDs, and red and green emitters have been developed and improved to the standard required for commercializing full color OLEDs.

In recent times, red materials with CIE coordinates (0.67, 0.23) and long lifetimes of more than 100,000 h at 11 cd/A have been produced. Green emitting materials with CIE coordinates (0.29, 0.64) and lifetimes of 100,000 h at 21 cd/A have also been developed. However, the best blue materials have lifetimes of only 12,000 h at 7 cd/A and CIE coordinates (0.14, 0.16)[9].

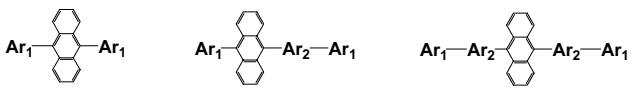
It is not easy to produce highly efficient blue materials with long device lifetimes. The electronic levels of blue materials with a wide band gap are generally mismatched with the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the other OLED layers, such as the hole transporting layer (HTL) and the electron transporting layer (ETL). These differences between the electronic levels result in a mismatched carrier balance of electrons and holes and a low EL efficiency.

In previous study, we have synthesized new blue categorized materials with tetra-substituted ethylene moiety[10] and we concluded and agreed with the general rule; the first one is that the chromophore having the high PL efficiency leads the higher EL efficiency. The second one is that the emitting compound including an alkyl group of electron donating property causes red-shifted spectrum and the increased operating voltage as well as longer conjugation length makes the more red-shifted PL and EL spectrum.

In this study, we have synthesized new kinds of blue material such as CB-201, 202, 203 and CB-301, etc.

2. Experimental

For EL device, blue-emiting materials were vacuum-deposited on top of NPB(150Å)/2-TNATA (600Å)/ITO(1200Å/30ohm) under 10^{-6} torr, the rate of deposition being 1Å/sec to give an emitting area of 4mm^2 and other organic layer and aluminum layer were continuously deposited under the same vacuum condition. Current-voltage (I-V) characteristics of the fabricated OLEDs were measured by using Keithley 2400 electrometer. Light intensity was obtained by Minolta CS-1000.



CB-201 CB-202 CB-203

Scheme 1. Chemical structures of the new blue materials.

3. Result and Discussion

We synthesized new kinds of blue material and described three chemical structures in here such as CB-201, 202, and 203. (scheme 1) In this series of compounds, we did not introduce alkyl group which can make relatively red-shift in PL and EL and increase operating voltage. Also we put anthracene moiety in core site like BTPPA[CB-105B][10] chemical structure, and attached bulky aromatic ring with #9 and #10 position of anthracene. We believe that it causes longer distance between molecules and twisted chemical structure compared to naphthalene group of MADN. Table 1 shows optical data of the synthesized compounds and MADN.

Table 1. Optical properties of synthesized materials.

Compounds	UV_{onset} (nm)	UV_{max} (nm)	PL_{max} (nm)	Eg (eV)
CB-201	419	402	439	2.96
CB-202	420	403	445	2.95
CB-203	422	403	445	2.94
MADN	424	405	447	2.92

All CB-20X compounds exhibited slightly blue-shifted UV and PL maximum values compared to MADN. It can be explained by bulky effect of aromatic ring.

The relative PL quantum efficiency (PLQE) was measured for the correlation of EL efficiency [11]. When the PLQE of MADN was fixed to 1.00 as a reference, the PLQE values of CB-201, 202 and 203 were 1.22, 1.25 and 1.39, which showed very high levels.

In order to measure the HOMO values of the synthesized compounds, CV analyses were carried out. According to the CV data, all the compounds have an electrochemical stability of greater than 50 cycles.

TGA and DSC to examine the thermal properties of the synthesized molecules were carried out. We believe that thermal properties in the film state are deeply associated with lifetimes of OLED devices because of Joule heating during device operation.[12] All synthesized materials, CB-201, CB-202 and CB-203 showed over 120℃ of Tg. CB-203 exhibited especially Tg of 150℃, which means the highest thermally stable. This value is two times higher than DPVBi's (T_g = 64℃) and also much higher than MADN's. Besides, it was found that these three materials have more than 300℃ of T_m and 400℃ of T_d and thermally very stable property.

The band gaps of CB-201, CB-202 and CB-203 were found to be 2.96, 2.95 and 2.94 eV respectively. The band gaps and the HOMO and LUMO levels are summarized in Table 1. The HOMO levels of CB-201, CB-202 and CB-203, which all contain anthracene groups, are all near 5.5~5.6 eV. The presence of anthracene moieties is thought to be the principal factor determining the HOMO levels of these materials. It has been reported that the HOMO levels of 9,10-di(2-naphthyl)anthracene (ADN) and 2-methyl-9,10-di(2-napthyl)anthracene (MADN) as well as of many other compounds that have an anthracene group are also near 5.5~5.6 eV[13].

We fabricated EL devices with new blue materials and MADN in the following configuration: ITO/2-TNATA (60 nm)/NPB (15 nm)/EML [CB-20X or MADN] (30 nm)/Alq_3 (30 nm)/LiF (1 nm)/ Al (200 nm).

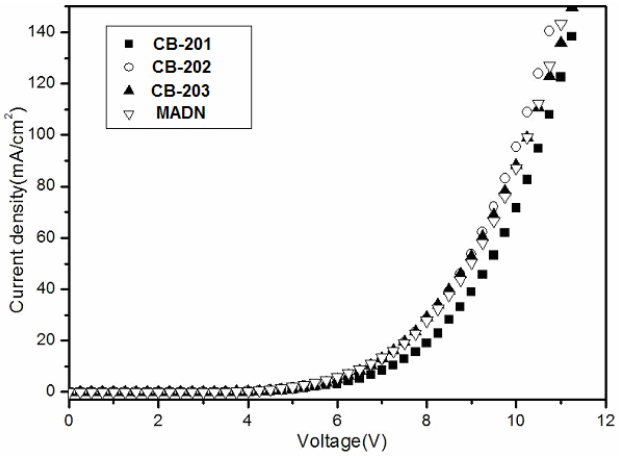


Figure 1. Current density-voltage characteristics of ITO/ 2-TNATA(60 nm)/ NPB(15 nm)/ CB-201(■) or CB-202(○) or CB-203(▲) or MADN(▽) (30 nm)/ Alq_3(30 nm)/ LiF(1 nm)/ Al(200nm) device.

Table 2. EL performance of multi-layered devices with the structure; ITO /2-TNATA(60 nm) /NPB(15 nm) /CB-201 or CB-202 or CB-203 or MADN(30 nm) /Alq_3(30 nm) /LiF(1 nm) /Al(200 nm) at 10 mA/cm^2.

	EL_{max} (nm)	Voltage (V)	Brightness (cd/m^2)	C.I.E. (x,y)	L.E. (cd/A)	P.E (lm/W)	E.Q.E (%)
CB-201	444	7.99	294.4	0.163, 0.124	2.94	1.28	3.90
CB-202	438	6.81	297.3	0.156, 0.085	2.97	1.52	6.14
CB-203	444	6.75	363.7	0.156, 0.088	3.64	1.87	7.18
MADN	454	6.71	285.5	0.171, 0.138	2.86	1.48	3.18

Figure 1 shows I-V characteristics of four fabricated devices and they exhibit the typical rectifying diode characteristics. I-V curves show the similar curve shapes

since four compounds have almost same values of HOMO and LUMO levels. According to these I-V curves, we expect that the conductivity value as well as hole and electron mobility of the synthesized materials have similar order range with MADN's.

The EL efficiency of four EL devices at 10mA/cm^2 which is the representative current density is summarized in Table 2. It is found that the order of the luminance efficiency and External Quantum Efficiency (EQE) is CB-203 > CB-202 > CB-201 > MADN. This tendency is matched with the PLQE of side groups and it means that it is useful to change the chemical structure of the side group for improving remarkably emitting performance. CB-203 shows especially two times higher EQE than MADN's. Besides, 7% value of EQE in real blue color has been achieved by using non-doped device structure and it is the best data among the non-doped blue devices to our knowledge. We believe that it is attributed to the deep-blue EL shift of (0.156, 0.088) as well as the PLQE increase of 40% compared to MADN.

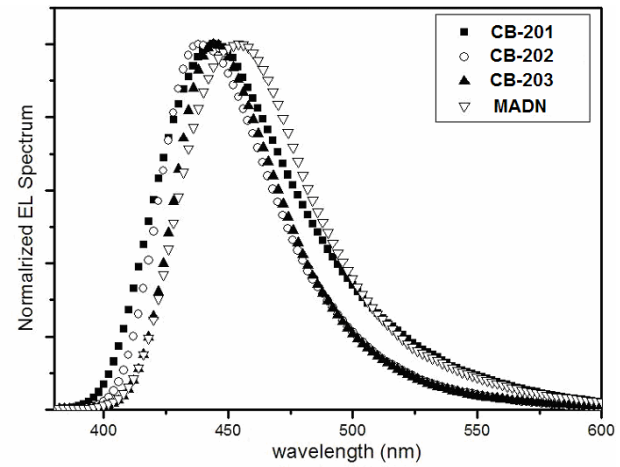


Figure 2. Normalized EL Spectrum of ITO/ 2-TNATA(60 nm)/ NPB(15 nm)/ CB-201(■) or CB-202(○) or CB-203(▲) or MADN(▽) (30 nm)/ Alq_3(30 nm)/ LiF(1 nm)/ Al(200nm) device at 10mA/cm^2.

Next, we new blue emitting material with good color purity was synthesized for the first time and used as the core component of new blue OLED material (CB-301).

The UV maximum absorption wavelengths of CB-301 in solution is 398 nm and the maximum wavelengths of the PL spectrum is in the blue region 450 nm. Further, the PL maximum wavelength is 450 nm for both solution and film. The FWHM (full width at half maximum) values are 47 nm for the solution state and 54 nm for the solid state; these widths are narrower than those of other blue emitting materials. The narrowness of these FWHM values indicates that the transition states of CB-301's luminescence processes are relatively simple.

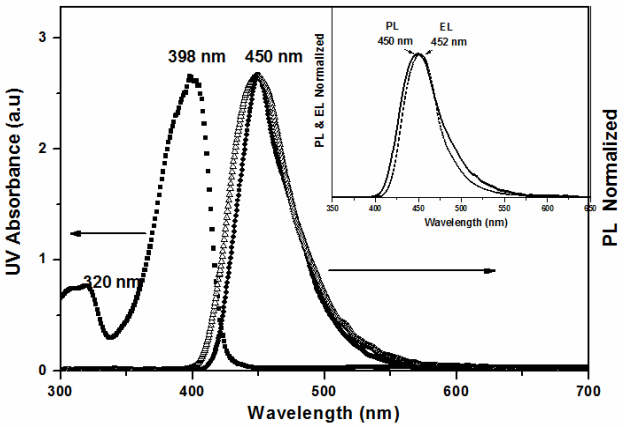


Figure 3. UV-Visible (■) and PL spectra (solution: ●, film: △) of CB-301 (UV: 6.06 x 10^{-5} M, PL: 4.85 x 10^{-4} M in THF). The inset shows the EL (dash) and PL film (line) spectra.

The CB-301 was used as the emitting layers (EMLs) in OLEDs with the following structure: ITO/2-TNATA (60 nm)/NPB (15 nm)/CB-301 (30 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al (200 nm). The EL spectrum of CB-301 device was found to be almost identical to the PL spectra. The CB-301 device was found to exhibit luminescence efficiencies of 2.01cd/A. Further, the EL maximum wavelength of CB-301 device is 452 nm, in the deep blue region, with CIE coordinates (0.150, 0.078). As shown in Figure 3, CB-301 in particular has an EL maximum wavelength that is almost the same as its PL maximum wavelength at 452 nm in the deep blue region, with an EL FWHM of 47 nm, i.e., the band is very narrow; thus this material produces a very pure deep blue.

4. Conclusion

New deep blue emitting materials, CB-20x series including a novel side group were synthesized and characterized. CB-203 especially showed higher PLQE increase of 40% and the Tg increase of 30℃ than MADN's. Moreover, it exhibits two times bigger EQE of 7.18% compared to MADN and it is the best data in the non-doped blue devices to our knowledge. Also deep blue emitting materials with a new core structure (CB-301) have been synthesized. CB-301 exhibits excellent blue fluorescence properties. Undoped OLED devices using CB-301 as blue emitters was found to deep blue CIE value (0.154, 0.078) and exhibit high luminance efficiencies of 2.01cd/A at 10 mA/cm^2.

5. Acknowledgment

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6. Reference

[1] C. W. Tang, S. A. Van Slyke, Appl. Phys. Lett., 1987, 51, 913.

[2] C. W. Tang, S. A. Van Slyke, C. H. Chen, J. Appl. Phys., 1989, 65, 3610.

[3] M.A. Baldo, M.E. Thompson, S.R. Forrest, Nature, 2000, 403, 750.

[4] C.C. Wu, Y.T. Lin, K.T. Wong, R.T. Chen, Y.Y. Chien, Adv. Mater., 2004, 16, 61.

[5] C. Adachi, T. Tsutsui, S. Saito, Appl. Phys, Lett., 1989, 55, 1489.

[6] a) L. C. Picciolo, H. Murata, Z. H. Kafafi., Appl. Phys. Lett., 2001, 78, 2378. b) M. Ikai, F. Ishikawa, N. Aratani, A. Osuka, S. Kawabata, T. Kajioka, H. Takeuchi, H. Fujikawa, Y. Taga, Adv. Funct. Mater., 2006, 16, 515.

[7] J. Ding, J. Gao, Y. Cheng, Z. Xie, L. Wang, D. Ma, X. Jing, F. Wang, Adv. Funct. Mater., 2006, 16, 575.

[8] a) Y.H. Kim, H.C. Jeong, S.H. Kim, K. Yang, S.K. Kwon, Adv. Funct. Mater., 2005, 15, 1799. b) J.W. Park, J.H. Lee, H.S. Lee, D.Y. Kang, T.W. Kim, Thin Solid Films, 2006, 363, 90.

[9] T. Arakane, M. Funahashi, H. Kuma, K. Fukuoka, K. Ikeda, H. Yamamoto, F. Moriwaki, C. Hosokawa, SID Dig., 2006, 37.

[10] a)S. K. Kim, Y. I. Park, J. W. Park, Mol. Cryst. Liq. Cryst., 2007, 470, 215.; b)S. K. Kim, Y. I. Park, I. N. Kang, J. W. Park, J. Mater. Chem., 2007, 17, 4670.; c)S. K. Kim, J. W. Park, S. Y. Oh, Mol. Cryst. Liq. Cryst., 2007, 471, 89

[11] H. S. Joshi, R. Jamshidi, Y. Tor, Angew. Chem. Int. Ed., 1999, 18, 38.

[12] H. Aziz, Z. D. Popovic, Chem. Mater. 2004, 16, 4522.

[13] a) Y. H. Kim, S. K. Kwon, D. S. Yoo, M. F. Rubner, M. S. Wrington, Chem. Mater, 1997, 9, 2699; b) T. H. Liu, W. J. Shen, B. Balaganesan, C. K. Yen, C. Y. Iou, H. H. Chen, C. H. Chen, Synth. Met., 2003, 137, 1033; c) M. X. Yu, J. P. Duan, C. H. Lin, C. H. Chung, Y. T. Tao., Chem. Mater., 2002, 14, 3958.