Mol. Cryst. Liq. Cryst., Vol. 531: pp. 55/[355]–64/[364], 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.499317

Taylor & Francis
Taylor & Francis Group

Highly Efficient Blue Light-Emitting Diodes Using New Fluorescent Host Materials Based on Naphthalenes

JEONG KEUN PARK,[1] KUM HEE LEE,[1]
JUNG SUN PARK,[2] JI HOON SEO,[2]
YOUNG KWAN KIM,[2] AND SEUNG SOO YOON[1]

[1]Department of Chemistry, Sungkyunkwan University, Suwon, Gyeonggi-do, Korea
[2]Department of Information Display, Hongik University, Seoul, Korea

The naphthalene-based blue materials 4,4′-(Dinaphthalen-2-yl)-1,1′-binaphthyl (DNBN) and 1,4-(Dinaphthalen-2-yl)-naphthalene (DNN) were designed and synthesized for OLEDs. A device (non-doped) employing DNN as the emitter exhibited a maximum luminance, luminous efficiency, and external quantum efficiency of 1120 cd/m^2, 1.40 cd/A, and 3.83%, respectively. Moreover, its CIE coordinates (0.152, 0.069) are very close to the NTSC blue standard of (0.14, 0.08). In order to improve EL efficiencies, these materials were used as the blue host materials for the blue dopants PFVtPh and PCVtPh. A device 1b (PFVtPh-doped) showed high EL efficiencies of 5.24 cd/A, 2.75 lm/W, and 3.82% at 20 mA/cm^2.

Keywords Blue OLEDs; dopant; fluorescence; host; naphthalene; suzuki cross-coupling reaction

Introduction

Organic π-conjugated materials continue to attract considerable interest because of their potential applications in various optoelectronic devices, especially in organic light-emitting diodes (OLEDs) [1,2]. Blue emitters exhibit relatively poor performance compared with red and green emitters, many studies have been recently undertaken toward making blue emitters with high efficiency, color purity, and long operation. Blue emitters with excellent Commission Internationale d'Énclairage (CIE) coordinates (0.14, 0.08) for the National Television Standards Committee (NTSC) standard blue need to have wide energy band-gaps near 3.0 eV [3]. Such blue emitters have high HOMO (highest occupied molecular orbital) levels and low LUMO (lowest unoccupied molecular orbital) levels. Accordingly, the performance of blue OLEDs is usually inferior to that of green and red OLEDs due to poor efficiency [4,5]. Blue-emitting materials based on small molecules with various

Address correspondence to Prof. Seung Soo Yoon, Department of Chemistry, Sungkyunkwan University, Cheoncheon-dong, Jangan-gu, Suwon, Gyeonggi-do 440-746, Korea (ROK). Tel.: (+82)31-290-7071; Fax: (+82)31-290-5971; E-mail: ssyoon@skku.edu

chromophore structures such as distrylarylene [6], spiro [7], biaryls [8], fluorine [9], and silicon [10] have been reported and developed.

In this article, novel blue fluorescent materials based on naphthalenes; 4′-(Dinaphthalen-2-yl)-1,1′-binaphthyl (DNBN), and 1,4-(Dinaphthalen-2-yl)-naphthalene (DNN) were synthesized, and their electroluminescent properties were investigated (Scheme 1). These non-planar molecules based on naphthalenes have a large dihedral angle and twisted conformation [11] to mitigate unfavorable intermolecular interactions, and thus can decrease self-quenching between the host materials. Furthermore, it can form a good amorphous pinhole-free thin film in the solid state. Therefore, high efficiencies can be expected for blue OLEDs using naphthalenes molecules.

Experimental

General Procedure for the Suzuki Cross-Coupling Reaction

2-Naphthalene boronic acid (2.5 mol) and the corresponding aryl halide derivatives (1.0 mol), $Pd(PPh_3)_4$ (0.04 mol), aqueous 2.0 M Na_2CO_3 (10.0 mol), ethanol, and toluene were mixed in a flask. The mixture was refluxed for 4 h. After the reaction finished, the reaction mixture was extracted with toluene and washed with water. The organic layer was dried with anhydrous $MgSO_4$ and filtered with silica gel. The solution was then evaporated. The crude product was recrystallized from CH_2Cl_2/EtOH.

4′-(Dinaphthalen-2-yl)-1,1′-binaphthyl (DNBN): Yield: 90.6%. ^{1}H-NMR (300 MHz, $CDCl_3$) [δ ppm]: 8.07 (d, $J = 9.6$ Hz, 4H), 8.01 (d, $J = 8.4$ Hz, 2H), 7.98–7.93 (m, 4H), 7.76 (dd, $J = 1.5$, 8.4 Hz, 2H), 7.68–7.55 (m, 10H), 7.40 (td, $J = 1.5$, 7.7 Hz, 2H), 7.34 (td, $J = 1.2$, 7.5 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) [δ ppm]: 140.4, 138.6, 138.5, 133.7, 133.5, 132.9, 132.1, 129.2, 128.9, 128.4, 128.1, 128.0, 127.8, 127.4, 127.1, 126.7, 126.6, 126.4, 126.3, 126.2. FT-IR [ATR]: $\nu = 3050$, 1598, 1502, 843, 822, 769, 745 cm^{-1}. MS(EI$^+$) m/z 506 (M^+). Anal. calcd for $C_{40}H_{26}$: C 94.83, H 5.17; found: C 93.30, H 5.15.

1,4-(Dinaphthalen-2-yl)-naphthalene (DNN): Yield: 81.3%. ^{1}H-NMR (300 MHz, $CDCl_3$) [δ ppm]: 8.04–8.00 (m, 4H), 7.96–7.90 (m, 6H), 7.70 (dd, $J = 1.5$, 8.4 Hz, 2H), 7.60 (s, 2H), 7.55 (dd, $J = 3.3$, 6.2 Hz, 4H), 7.44 (dd, $J = 3.3$, 6.5 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) [δ ppm]: 140.0, 138.5, 133.6, 132.8, 132.3, 129.0, 128.7, 128.3, 127.9, 127.8, 127.0, 126.7, 126.5, 126.2, 126.1. FT-IR [ATR]: $\nu = 3051$, 1738, 1598, 1502, 846, 826, 766, 745 cm^{-1}. MS(EI$^+$) m/z 380 (M^+). Anal. calcd for $C_{40}H_{26}$: C 94.70, H 5.30; found: C 93.95, H 5.44.

Materials and Measurements

1-Bromonaphthalene, 1-Naphthalene boronic acid, 2-Naphthalene boronic acid, and 1,4-Dibromonaphthalene were used as received from Alfa Asear or TCI. 1,1′-Binaphthyl (A), 4,4′-Dibromo-1,1′-binaphthyl (B) [12], 4′-[2-(2-Diphenylamino-9,9-diethyl-9H-fluoren-7-yl)vinyl]-*p*-terphenyl (PFVtPh) [13], and 3-(N-phenyl-carbazol)vinyl-*p*-terphenyl (PCVtPh) [14] were synthesized as previously reported. The solvents were dried using standard procedures. All reagents were used as received from commercial sources, unless otherwise stated. All reactions were performed under N_2 atmosphere.

^{1}H and ^{13}C NMR were recorded on a Varian Unity Inova 300Nb spectrometer. FT-IR spectra were recorded using a Bruker VERTEX70 FT-IR spectrometer.

Elemental analysis (EA) was measured using a EA 1108 spectrometer. Low resolution mass spectra were measured using a Jeol JMS-600 spectrometer in EI mode. The UV-Vis absorption and photoluminescence spectra of these newly designed host materials were measured in CH_2Cl_2 (10^{-5} M) using a Shimadzu UV-1650PC and an Amincobrowman series 2 luminescence spectrometer. The fluorescent quantum yields were determined in the CH_2Cl_2 solution at 293 K against the host ($\Phi_{DPA} = 0.90$) as a standard. Energy levels were measured with a low-energy photo-electron spectrometer (Riken-Keiki, AC-2). Thermal property was measured using thermogravimetric analysis (TGA) (DTA-TGA, TA-4000) under nitrogen at a heating rate of 10°C/min.

Fabrication of OLEDs

To fabricate OLEDs, indium-tin-oxide (ITO) thin films coated on glass substrates were used, which had 30 Ω resistivity per square of sheets with 100 nm of thickness. The ITO-coated glass was cleaned in an ultrasonic bath by the following sequence: acetone, methyl alcohol, and distilled water; it was then stored in isopropyl alcohol for 48 h and dried by a N_2 gas gun. The substrates were treated by O_2 plasma under 2.0×10^{-2} torr at 125 W for 2 min [15]. All organic materials and metals were deposited under high vacuum (5×10^{-7} torr). The OLEDs were fabricated in the following sequence: ITO/4,4′-bis(N-(1-naphthyl)-N-phenylamino)biphenyl (NPB) (50 nm)/Blue emitting materials (DNBN and DNN) (30 nm)/4,7-diphenyl-1,10-phenanthroline (Bphen) (30 nm)/lithium quinolate (Liq) (2 nm)/Al (100 nm), with NPB as the hole-transporting layer, Bphen as the electron-transporting layer, and Liq: Al as the composite cathode. The current density (J), luminance (L), luminous efficiency (LE), and CIE chromaticity coordinates of the OLEDs were measured with a Keithley 2400 Chroma meter CS-1000A. Electroluminance was measured using a Roper Scientific Pro 300i.

Results and Discussion

The optical properties of the blue materials (DNBN and DNN) are presented in Table 1. The decomposition temperature (T_d; corresponding to 5% weight loss)

Table 1. Optical properties of Compounds

Compound	T_d[a] [°C]	UV_{max}[b] [nm]	PL_{max}[b] [nm]	FWHM[b] [nm]	PL_{max}[c] [nm]	HOMO/LUMO[d] [eV]	E_g	Φ[e]
MADN	397[f]	377	425	54	447[f]	−5.50[f]/−2.50[f]	3.00[f]	0.54
DNBN	398	305	412	62	403	−6.01/−2.58	3.43	0.45
DNN	329	304	404	59	383	−6.00/−2.52	3.48	0.32

[a]The decomposition temperature.
[b]In CH_2Cl_2 solution.
[c]In film state.
[d]Obtained from AC-2 and UV-vis absorption measurements.
[e]Using 9,10-Diphenylanthracene as a standard; $\lambda_{ex} = 360$ nm ($\Phi = 0.90$ in CH_2Cl_2).
[f]Ref. 18.

was measured with by a thermogravimetric analysis (TGA). The T_d for DNBN and DNN were 398 and 329°C, respectively. The HOMO energy levels were measured by a low-energy photo-electron spectrometer (Riken-Keiki AC-2). The HOMO/LUMO energy levels of DNBN and DNN were −6.01/−2.58, and −6.00/−2.52, respectively. Both the HOMO and LUMO energy level of the blue host materials (DNBN and DNN) reveal the similar values. Their optical energy band gaps (E_g) were 3.43 and 3.48 eV, respectively, as determined from the absorption spectra. These materials have higher energy band gaps than those of PFVtPh (2.82 eV) and PCVtPh (3.10 eV). It is possible that efficient Förster energy transfer occurs from the host to the dopant.

Figure 1(a) shows the absorption of the dopant materials (PFVtPh and PCVtPh) and emission of the blue host materials (DNN and DNBN). The PL spectra of DNN and DNBN were 412 and 404 nm, respectively. There is a slight red-shift in the PL spectrum of DNBN as compared to DNN, due to the lengthening π-conjugation

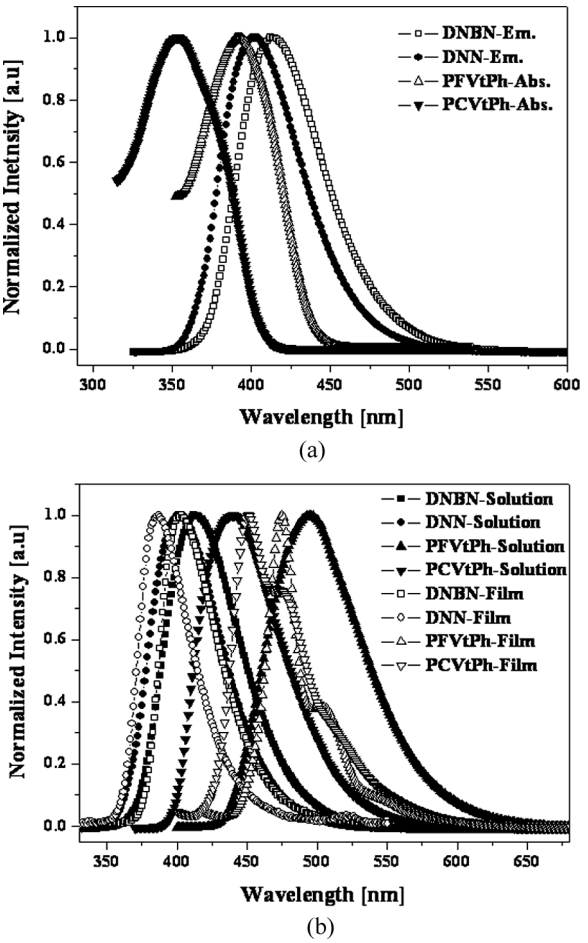


Figure 1. (a) the emission spectra of the host materials and absorption spectra of dopant materials in solution and (b) the emission spectra of host and dopant materials in solution and film state.

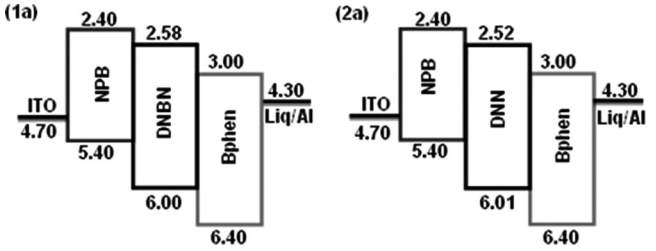


Figure 2. Energy diagrams of non-doped devices **1a-2c**.

length. Figure 1(b) shows the PL spectra of the dopant materials (PFVtPh and PCVtPh) and host materials (DNN and DNBN) in solid film state. Interestingly, compared to PL spectra of DNBN and DNN in solution state, the PL spectra of those in film state are blue-shifted due to the differences in solvation.

Figure 2 shows the energy band diagrams of the non-doped devices. The EL performance characteristics of the non-doped devices are summarized in Table 2. As shown in Figure 3, devices 1a–2a emitted at 440 nm with (0.153, 0.064), and 442 nm with (0.152, 0.069) at 8.0 V, respectively, all in the deep-blue region. These devices with naphthalenes generate a *y*-CIE coordinate value of less 0.07 in comparison to a common host MADN ($y = 0.08$). Interestingly, the EL spectra of devices 1a–2a are red-shifted about 30 nm as compared to PL spectra of DNN and DNBN in solution. Presumably, these results are originated from the differences in solvation states between solution and solid-state devices. The luminance-voltage-current density (L-V-J), luminous efficiencies (LE), and external quantum efficiency (EQE) of the devices 1a–2a are shown in Figures 3–4. Among non-doped devices with the similar EL performances within 10%, the luminous efficiency (LE), and external quantum efficiency (EQE) of device 2a reach 1.40 cd/A, and 2.15% (1.26 cd/A, and 1.93% at 20 mA/cm^2), respectively. Although the efficiencies of two devices were higher than that of 2-methyl-9,10-di(naphthalen-2-yl)anthracene (MADN), they had low EL performances. It is conjectured that the hole-injection from HTL (NPB) to EML is difficult due to a high energy barrier (ca. 0.60 eV). Thus, the two devices have overall low EL properties.

In order to enhance EL efficiencies, we doped these host materials (DNBN and DNN) with blue dopant materials (PFVtPh and PCVtPh) with a concentration of

Table 2. EL performance characteristic of the non-doped devices

Device (compound)	V_{on}[a] [V]	λ_{max}^{EL} [nm]	L[b] [cd/m^2]	J[b] [mA/cm^2]	LE[c/d] [cd/A]	PE[c/d] [lm/W]	EQE[c/d] [%]	CIE[e] (*x*,*y*)
MADN	4.0	442	954	154	1.35/1.08	1.01/0.48	1.45/0.98	(0.153,0.080)
1a (DNBN)	3.7	440	994	151	1.30/1.07	1.04/0.54	2.14/1.81	(0.153,0.064)
2a (DNN)	3.4	442	1120	139	1.40/1.26	1.12/0.70	2.15/1.93	(0.152,0.069)

[a]Turn-on voltage at 1 cd/m^2.
[b]Maximum luminance and current density.
[c]Maximum value.
[d]At 20 mA/cm^2.
[e]Commission Internationale d'Énclairage (CIE) coordinates at a 8.0 V.

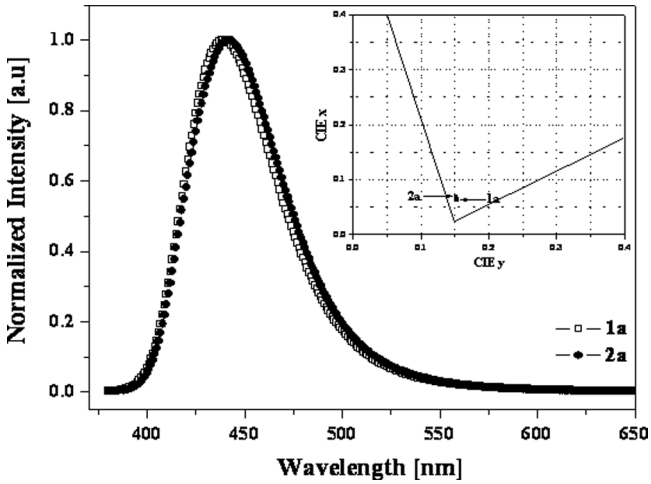


Figure 3. EL spectra and the CIE coordinates at 8.0 V of the non-doped devices.

8% in each device structure. The EL performances of the doped-OLEDs are summarized in Table 3. The normalized EL spectra of the doped devices revealed an emission peak around 444–457 nm in Figure 5. The luminance-voltage (L-V), luminous efficiencies (LE), and external quantum efficiency (EQE) of each of the

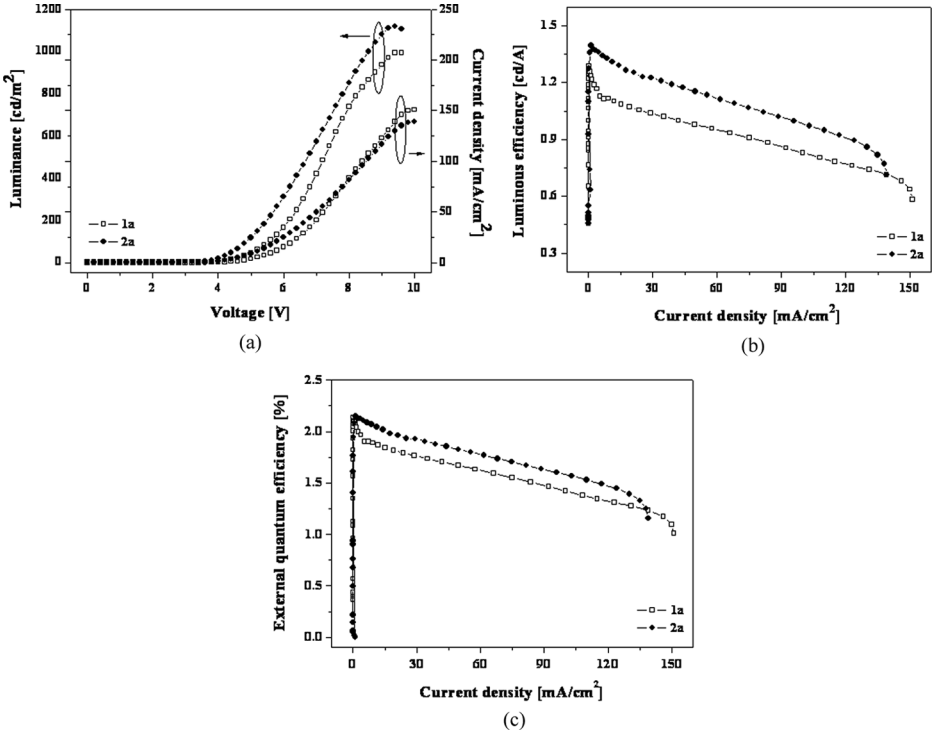


Figure 4. (a) L-V-J characteristics, (b) the luminous efficiencies, and (c) external quantum efficiencies as a function of current density for the non-doped devices.

Table 3. EL performance characteristic of the doped-devices

Device (compound)	V_{on}[a] [V]	λ_{max}^{EL} [nm]	L[b] [cd/m^2]	J[b] [mA/cm^2]	LE[c/d] [cd/A]	PE[c/d] [lm/W]	EQE[c/d] [%]	CIE[e] (*x*,*y*)
1b (DNBN: PFVtPh)	3.5	457	6128	202	8.43/5.24	6.89/2.75	5.98/3.82	(0.153,0.167)
2b (DNN: PFVtPh)	2.9	453	2342	254	5.13/3.88	5.17/2.26	3.61/2.79	(0.159,0.168)
1c (DNBN: PCVtPh)	4.0	449	1960	169	2.37/1.69	1.86/0.77	3.16/2.29	(0.152,0.081)
2c (DNN: PCVtPh)	3.8	444	791	109	1.13/1.11	0.68/0.53	1.50/1.47	(0.154,0.084)
PCVtPh (non-doped)	2.5	452	798	397	1.20/1.16	1.06/0.87	1.15/1.12	(0.163,0.124)

[a]Turn-on voltage at 1 cd/m^2.
[b]Maximum luminance and current density.
[c]Maximum value.
[d]At 20 mA/cm^2.
[e]Commission Internationale d'Énclairage (CIE) coordinates at a 8.0 V.

four doped devices (1b–2c) are shown in Figure 6. Devices 1b and 2b, using doped PFVtPh, had more effective energy transfer (Förster-type energy transfer from host to dopant) [16] because of good overlap between the absorption of PFVtPh and the emission of DNBN and DNN in Figure 1. As well, the direct charge trapping in the dopant [17] could effectively occurred in devices 1b and 2b, because both the HOMO energy difference (0.03 eV) between levels of PFVtPh (−5.43 eV) and NPB (−5.40 eV), and the LUMO energy difference (0.39 eV) between PFVtPh (−2.61 eV) and Bphen (−3.00 eV) is small. Therefore, devices 1b and 2b had lower turn-on voltage and higher EL efficiencies than that of the devices 1c and 2c, respectively.

The EL efficiencies of the doped devices were opposite to those of the non-doped devices. Thus, the doped-devices employing DNBN as host have higher efficiencies

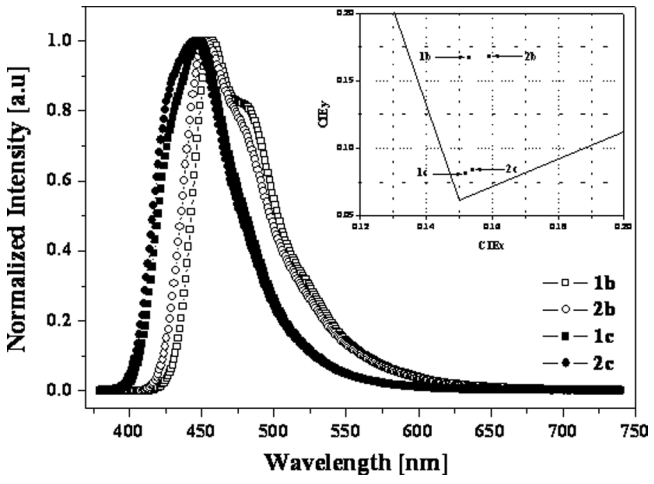


Figure 5. EL spectra and the CIE coordinates at 8.0 V of the doped devices.

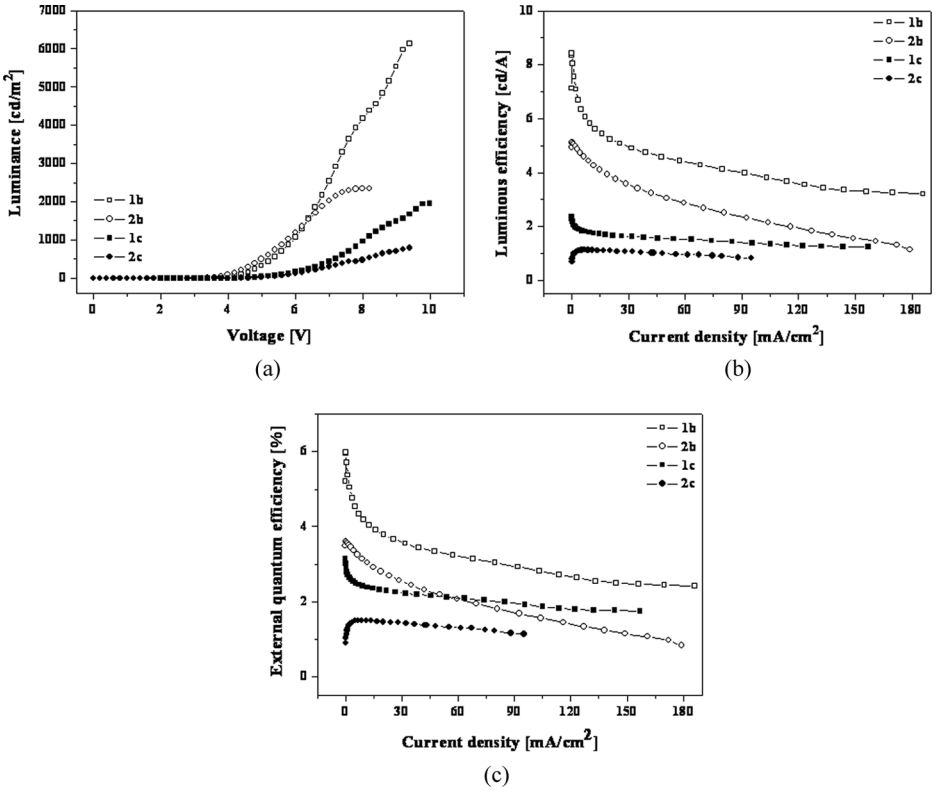
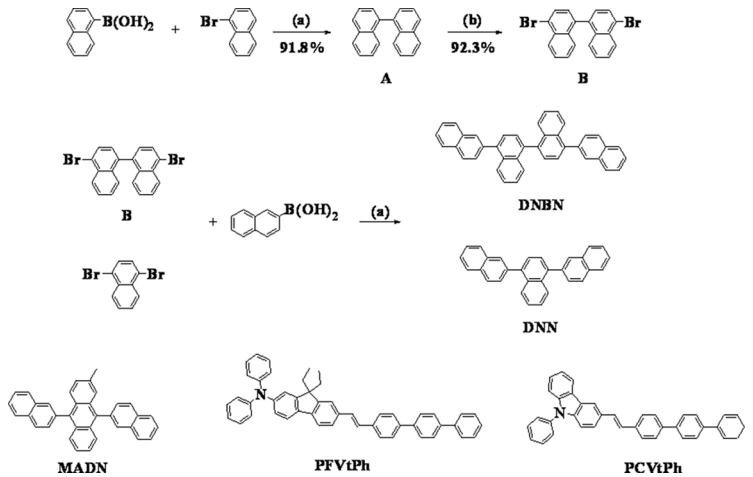


Figure 6. (a) L-V-J characteristics, (b) the luminous efficiencies, and (c) external quantum efficiencies as a function of current density for the doped devices.



Scheme 1. Synthetic route for new host materials and the structures of the dopant materials. (a) toluene/ethanol, Na_2CO_3 (2M), $Pd(PPh_3)_4$, reflux, 4h. (b) Br_2/CH_2Cl_2, rt, 2 h.

than those of DNN. This observation implies that the energy transfer of dopant with DNBN is more effective than that with DNN. Among those doped devices, device 1b had an excellent EL performances; its a maximum luminance (L), luminous efficiency (LE), and external quantum efficiency (EQE) reach 6128 cd/m^2, 8.43 cd/A, and 5.98%, respectively. It is conjectured that DNBN would be a suitable host for PFVtPh blue dopant material. In case of device 2c, employing DNN as a host for PCVtPh dopant, the EL performances were remarkably lower than the others. As shown in Table 3, the efficiencies of device 2c are similar to that of the non-doped device as a PCVtPh emitter. Presumably, this is an indication that the energy transfer from DNN (host) to PCVtPh (dopant) is difficult.

Conclusion

Two fluorescent blue-emitting materials based on naphthalenes, DNBN and DNN, have been synthesized *via* the Suzuki Cross-Coupling reaction. In non-doped device using DNBN and DNN in the emitting layer, both devices (1a and 2a) showed efficient blue electroluminescence (1.30 cd/A, 1.04 lm/W and 2.14% for device 1a; 1.40 cd/A, 1.12 lm/W and 2.15% for device 2a) which were higher than that of MADN. Furthermore, their CIE coordinates (0.153, 0.064) and (0.152, 0.069) were very close to the NTSC blue standard of (0.14, 0.08). Using DNBN as host material for PFVtPh blue dopant material, device 1b shows excellent efficiencies of 8.43 cd/A, 6.89 lm/W, and 5.98% (5.24 cd/A, 2.75 lm/W, and 3.82% at 20 mA/cm^2). This study demonstrates that fluorescent blue materials based on naphthalenes have sufficient potential for display or lighting applications.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (20090073679).

References

[1] Tang, C. W., & Slyke, Van. (1987). *Appl. Phys. Lett.*, *51*, 913.
[2] Baldo, M. A., Thompson, M. E., & Forrest, S. R. (2000). *Nature*, *403*, 750.
[3] Tonzola, C. J., Kulkarni, A. P., Gifford, A. P., Kaminsky, W., & Jenekhe, S. A. (2007). *Adv. Funct. Mater.*, *17*, 863.
[4] Hosokawa, C., Higashi, H., Nakamura, H., & Kusumoto, T. (1997). *Synth. Met.*, *3*, 91.
[5] Matsuura, M., Edia, M., Funahashi, M., Fukuoka, K., Tokailin, H., Hosokawa, C., & Kusumoto, T. (1997). *Proc. IDW'97*, 581.
[6] Hosokawa, C., Hiroaki, N., Higashi, H., & Kusumoto, T. (1995). *Appl. Phys. Lett.*, *67*, 3853.
[7] Okumoto, K., & Shirota, Y. (2003). *Chem. Mater.*, *15*, 699.
[8] Shin, H.-T., Lin, C.-H., & Cheng, C.-H. (2002). *Adv. Mater.*, *14*, 1409.
[9] Wang, K., Chien, Y., Chen, R., Wang, C., Lin, Y., Chiang, H., Hiseh, P., Wu, C., Chou, C., Su, Y. O., Lee, G., & Peng, S. (2002). *J. Am. Chem. Soc.*, *124*, 11576.
[10] Chan, L., Lee, R., Hiseh, H., & Chen, C. (2002). *J. Am. Chem. Soc.*, *124*, 6469.
[11] Zheng, L., Urian, R. C., Liu, Y., Jen, A. K.-Y., & Pu, L. (2000). *Chem. Mater.*, *12*, 13.
[12] Lee, J. Y., Park, J.-Y., Min, S.-H., Lee, K.-W., & Baek, Y. G. (2007). *Thin Solid Films*, *515*, 7726.

[13] Kwon, Y. S., Lee, K. H., Kim, G. Y., Seo, J. H., Kim, Y. K., & Yoon, S. S. (2009). *J. Namosci. Nanotechnol. 9*, 7056.
[14] Lee, K. H., Kwon, Y. S., Kang, L. K., Kim, G. Y., Seo, J. H., Kim, Y. K., & Yoon, S. S. (2009). *Synth. Met. 159*, 2603.
[15] Li, C. L., Shieh, S. J., Lin, S. C., & Liu, R. S. (2003). *Org. Lett.*, *5*, 1131.
[16] Lee, S. J., Park, J. S., Yoon, K. J., Kim, Y. I., Jin, S. H., Kang, S. K., Gal, Y. S., Kang, S. W., Lee, J. Y., Kang, J. W., Lee, S. H., Park, H. D., & Kim, J. (2008). *J. Adv. Funct. Mater.*, *18*, 3922.
[17] Littman, J., & Martic, P. (1992). *J. Appl. Phys. Lett.*, *72*, 3610.
[18] Wen, S. W., Lee, M. T., & Chen, C. H. (2005). *J. Display Technol.*, *1*, 90.