Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

A New Blue Light-Emitting Material with Phenylbenzimidazole Moiety and Its Electroluminescence Properties

Yoo Sung Lee [a], Man Su Kim [a], Young Chul Kim [a], Hanil Lee [b], Chunji Gao [b] & Kwang-Hyun Ahn [b]

[a] Department of Chemical Engineering and RIC-CAMID, Kyunghee University, Yongin-si, Gyeonggi-do, Korea

[b] Department of Applied Chemistry, Kyunghee University, Yongin-si, Gyeonggi-do, Korea

Version of record first published: 10 Nov 2009

To cite this article: Yoo Sung Lee, Man Su Kim, Young Chul Kim, Hanil Lee, Chunji Gao & Kwang-Hyun Ahn (2009): A New Blue Light-Emitting Material with Phenylbenzimidazole Moiety and Its Electroluminescence Properties, Molecular Crystals and Liquid Crystals, 513:1, 311-319

To link to this article: http://dx.doi.org/10.1080/15421400903217157

Mol. Cryst. Liq. Cryst., Vol. 513, pp. 311–319, 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903217157

A New Blue Light-Emitting Material with Phenylbenzimidazole Moiety and Its Electroluminescence Properties

Yoo Sung Lee[1], Man Su Kim[1], Young Chul Kim[1], Hanil Lee[2], Chunji Gao[2], and Kwang-Hyun Ahn[2]
[1]Department of Chemical Engineering and RIC-CAMID, Kyunghee University, Yongin-si, Gyeonggi-do, Korea
[2]Department of Applied Chemistry, Kyunghee University, Yongin-si, Gyeonggi-do, Korea

1,3,5-tris[4′-(1″-phenylbenzimidazol-2″-yl)phenyl]benzene (BTPBB), was synthesized and its electroluminescence (EL) properties were investigated. In order to enhance the emission efficiency, the device structure was optimized by balancing the charge carrier injection and reducing the barrier height for electron transport to the emitting layer. The OLED device with a structure of [ITO/α-NPB (50 nm)/BTPBB (30 nm)/TPBI (10 nm)/Alq3 (20 nm)/LiF (1 nm)/Al (120 nm)] exhibited the luminous efficiency of 2.2 cd/A and the external quantum efficiency of 0.9% at 120 mA/cm^2 with the CIE 1931 color coordinates of (0.15, 0.08), which was pure blue and almost invariant within the operating voltage range of 12∼19.5 V.

Keywords: 1,3,5-tris[4′-(1″-phenylbenzimidazol-2″-yl)phenyl]benzene; balanced charge carrier injection; blue-emitting organic material; hole blocking layer

INTRODUCTION

Intense research on organic light-emitting diodes (OLEDs) has made a significant progress in the last decade, and commercial full-color, flat panel display products are now available [1]. A variety of blue-emitting materials have been synthesized and evaluated, [2–5] however,

This research was supported by the "GRRC" Project of Gyeonggi Provincial Government, Republic of Korea.

Address correspondence to Prof. Young Chul Kim, Department of Chemical Engineering and RIC-CAMID, Kyunghee University, Yongin-si, Gyeonggi-do 446-701, Korea (ROK). E-mail: kimyc@khu.ac.kr or Kwang-Hyun Ahn, Department of Applied Chemistry, Kyunghee University, Yongin-si, Gyeonggi-do 446-701, Korea (ROK). E-mail: khahn@khu.ac.kr

compared with green- or red-emitting organic materials, blue materials still have much to be improved in terms of efficiency, lifetime, and color purity, which are essential for the realization of full color display and two-dimensional lighting applications based on OLEDs.

In view of color stability, when an OLED is configured with an electron transport layer (ETL) that can also act as an emissive layer (EML), the device tends to give an EL with rather significant driving voltage-dependent variations in the emission peak wavelength and the CIE color coordinates ($\geq$0.15, $\geq$0.30) due to the driving voltage-dependent contribution of ETL emission [6]. The injected holes are generally more mobile than the electrons under the same electric field and therefore some of the holes may recombine with the electrons at the ETL, which give rise to the driving voltage-dependent emission characteristics. A larger energy barrier for electron injection than that for hole injection to EML also shifts the emission zone from EML to ETL. Many attempts have been made to confine the charge carriers in EML only. By inserting a hole blocking layer (HBL) between ETL and EML, both the EL peak wavelength and color chromaticity of the device has been successfully stabilized over a certain range of operating voltage [7,8].

In this work, we synthesized a new blue-emitting material with phenylbenzimidazole moiety and investigated its OLED device structures containing one or two electron transporting layers to obtain a stable blue emission over a wide range of driving voltage.

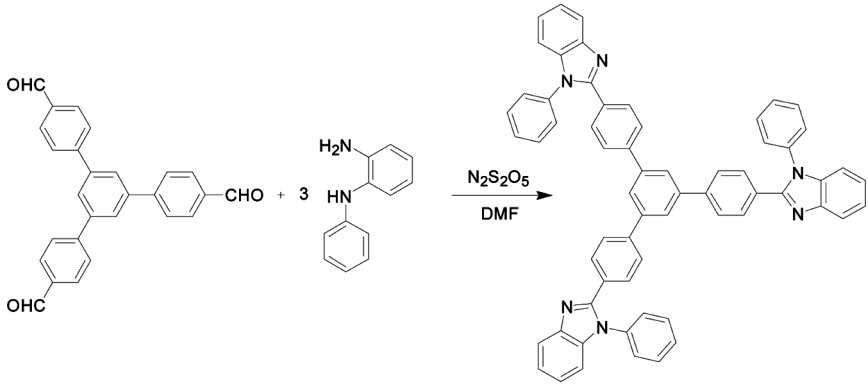
EXPERIMENTAL

Synthesis of BTPBB

As presented in Scheme 1, 1,3,5-tris[4′-(1″-phenylbenzimidazol-2″-yl) phenyl]benzene (BTPBB) was prepared from the reaction between 1,3,5-tris[4′-(1″-phenylbenzimidazol-2″-yl)phenyl]benzene and 2-aminodiphenylamine in the presence of $Na_2S_2O_5$ according to the procedure that we previously used for the formation of benzimidazole ring [9]. The product was obtained in 95% yield. Spectroscopic analyses including ^{1}H-NMR and high resolution mass spectroscopy were employed to characterize the product.

Fabrication of OLED

We optimized the BTPBB-based OLED device structure in three steps. In the first step, the current density-voltage-luminance (J-V-L) characteristics of the device A-1 with a 100 nm-thick BTPBB emitting



SCHEME 1 Synthetic route of BTPBB.

layer were studied, and then the device A-2 with a 50 nm-thick N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (α-NPB) (hole transport layer) (HTL) and a 50 nm-thick BTPBB EML were examined. In the second step, the devices with a 50 nm-thick α-NPB HTL and a 30 nm-thick BTPBB EML, and three different ETLs of tris-8-hydroxyquinoline) aluminum (Alq3) (device B-1), 1,3,5-tris (N-phenylbenzimidazol-2-yl)benzene (TPBI) (device B-2), and aluminum (III) bis(2-methyl-8-quinolinolato)-4-phenylphenolate (BAlq) (device B-3). In the final step, the same device as in the second step except for employing TPBI as the HBL and Alq3 as the ETL (device C-1) was prepared and their I-V-L characteristics were evaluated. The devices prepared and tested in this work are listed in Table 1.

All the layers were sequentially deposited on an indium-tin oxide (ITO)-coated glass substrate by thermal evaporation under high vacuum (10^{-6} torr). Prior to vacuum deposition, the patterned ITO substrates were sequentially cleaned with trichloroethylene, acetone, deionized water, and isopropyl alcohol in an ultrasonic bath, followed

TABLE 1 Device Structures Studied in this Work

Device (thickness)	HTL (nm)	EML (nm)	HBL (nm)	ETL (nm)
A-1	–	BTPBB (100)	–	–
A-2	α-NPB (50)	BTPBB (50)	–	–
B-1	α-NPB (50)	BTPBB (30)	–	Alq3 (30)
B-2	α-NPB (50)	BTPBB (30)	–	TPBI (30)
B-3	α-NPB (50)	BTPBB (30)	–	BAlq (30)
C-1	α-NPB (50)	BTPBB (30)	TPBI (10)	Alq3 (20)

by rinsing in deionized water. After the lithium fluoride (LiF)/ aluminum (Al) bilayer was deposited as the cathode, the device was encapsulated with a glass cap in a nitrogen atmosphere. The emitting area of the devices was defined to be $3 \times 3\,mm^2$ by using a shadow mask.

Measurements

UV-Vis absorption and photoluminescence (PL) data were recorded on an Agilent 8453 UV-Vis spectrometer and a PTI QuantaMaster™ spectrofluorometer, respectively. EL characteristics of the devices were measured using a JBS I-V-L 300 EL characterization system equipped with a Keithley 2400 sourcemeter. The highest occupied molecular orbital (HOMO) energy level was measured by ultraviolet photoemission spectroscopy (UPS) and the optical band gap energy was added to the HOMO level to estimate the lowest unoccupied molecular orbital (LUMO) level.

RESULT AND DISCUSSION

Figure 1 shows the UV-Vis absorption and photoluminescence (PL) spectra of BTPBB, where the absorption maximum ($\lambda_{max,\ UV}$) and the PL maximum ($\lambda_{max,\ PL}$) were observed at 320 and 412 nm, respectively.

In the first step, the EL characteristics of BTPBB were investigated with the single layer device A-1 and the device A-2 with the α-NPB HTL incorporated to reduce the barrier height for hole transport to

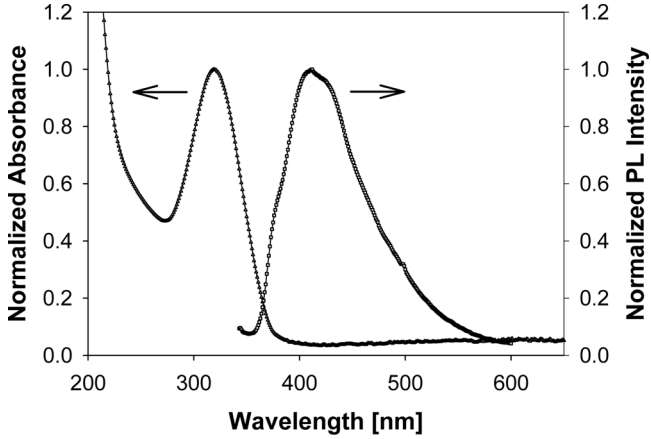


FIGURE 1 UV-Vis absorption and photoluminescence (PL) spectra of BTPBB.

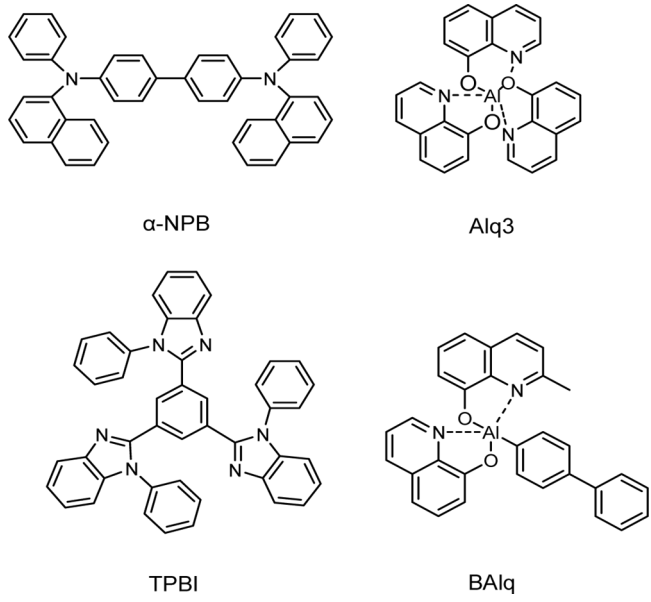


FIGURE 2 Chemical structures of the HTL and ETL materials.

the BTPBB EML. Although the device A-1 exhibited no emission, the device A-2 showed blue emission with a luminous efficiency of 0.8 cd/A and an external quantum efficiency (E.Q.E.) of 0.8% at around 15 mA/cm^2. The performance of the device A-2, however, was not high due to the high energy barrier for electron injection (~2.0 eV) and poor charge carrier injection balance.

In order to achieve a balanced charge injection by facilitating the electron injection, we employed Alq3, TPBI, and BAlq which are well-known as electron transporting materials (ETMs) in the second step [10–12]. The chemical structures of the materials are shown in Figure 2 and the HOMO and LUMO levels are listed in Table 2.

TABLE 2 The HOMO and LUMO Energy Levels of the HTL or ETL Materials

HTL or ETL	HOMO (eV)	LUMO (eV)
α-NPB	5.21	2.24
Alq3	5.8	3.0
TPBI	6.2	2.9
Balq	5.9	3.0

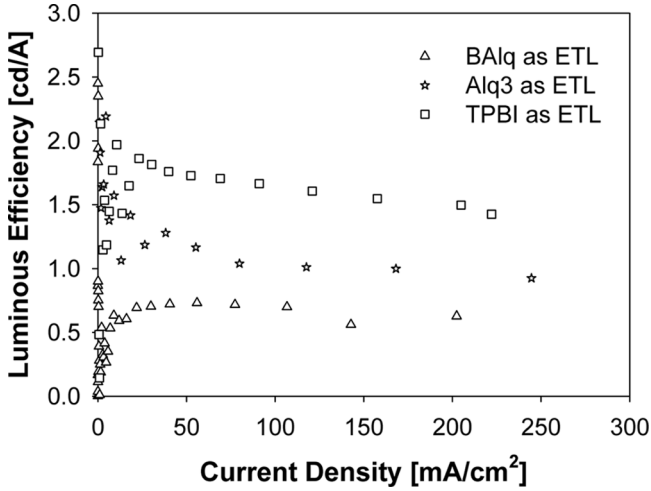


FIGURE 3 Luminous efficiency vs. current density characteristics of the devices with BAlq, Alq3, and TPBI as ETL.

As shown in Figures 3 and 4, the overall J-V-L characteristics of the devices B-1∼B-3 were enhanced by introducing ETMs. The device B-2 with TPBI as ETL gave the highest luminous efficiency, while the device B-1 with Alq3 as ETL exhibited the highest E.Q.E. The highest

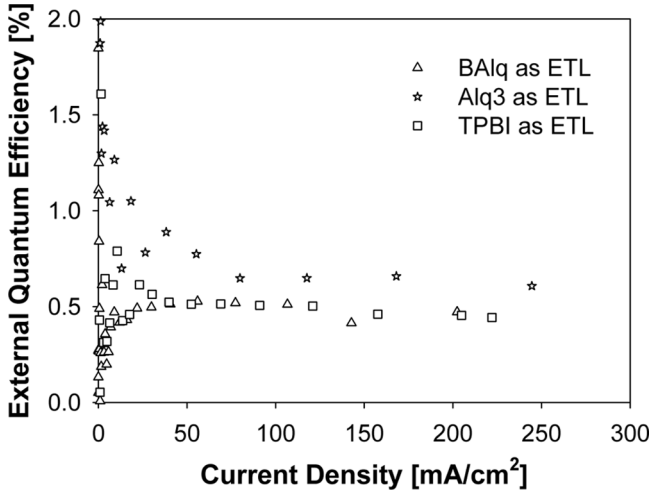


FIGURE 4 External quantum efficiency vs. current density characteristics of the devices with BAlq, Alq3, and TPBI as ETL.

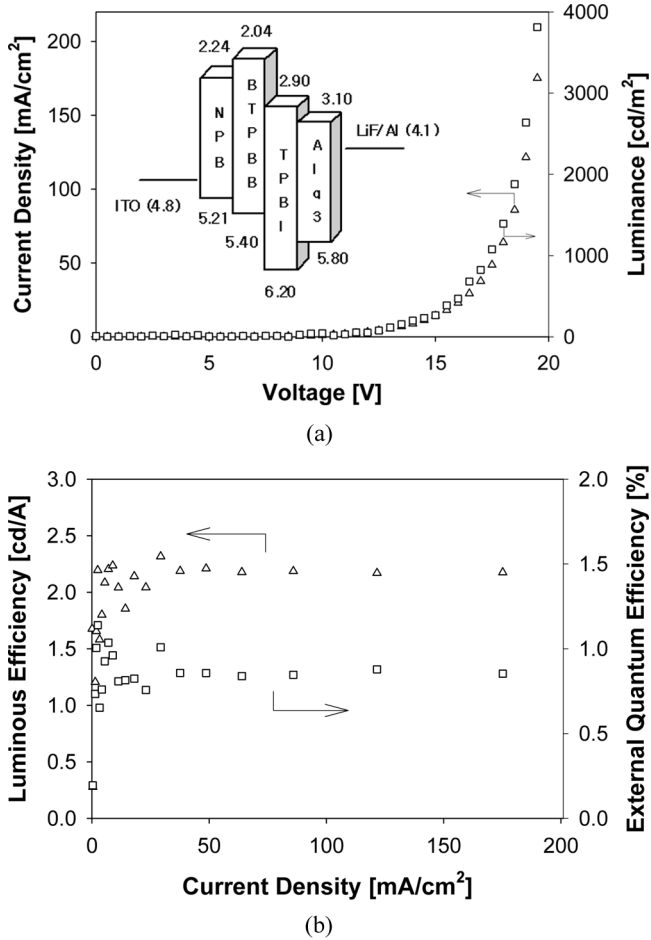


FIGURE 5 (a) Current density (J) and luminance (L) vs. voltage, and (b) luminous efficiency and external quantum efficiency (E.Q.E.) vs. current density (J) characteristics of the device C-1. The inset shows the structure of the device C-1.

E.Q.E. of the device B-1 with Alq3 as ETL, however, is partially contributed by the green-emission from the Alq3 layer because the residual holes after recombination in the EML can further move to the ETL to generate the excitons for green-emission. The device B-1 showed the $\lambda_{max,\ EL}$ at 457 nm and the CIE 1931 coordinates moved from (0.173, 0.155) to (0.154, 0.0134) when the applied voltage increased from 14 to 19.5 V (not shown) because the electron mobility (μ_e) in Alq3 is

dependent on the applied electric field [13,14]. The energy barrier for electron injection from Alq3 to BTPBB is relatively high (0.96 eV) but that for hole injection from α-NPB to BTPBB is low (0.19 eV). Without a HBL, a considerable amount of holes can transport across the BTPBB layer and recombine with electrons in the Alq3 layer that is a better emitter than BTPBB.

For both the high EL efficiency and the color purity, combination of HBL and ETL was the final step. It is possible to confine holes and excitons in EML by introducing HBL such as TPBI and BCP that have the deep HOMO levels of 6.2 and 6.7 eV, respectively. Although the device with BCP as HBL can effectively reduce the green-emission from Alq3, it may increase the operating voltage because it has a lower electron mobility (μ_e) than TPBI. As illustrated in the inset of Figure 5(a), TPBI can also transport electrons from Alq3 to BTPBB because it has the favorable LUMO level of 2.90 eV that can help the electrons inject [15,16]. Thus, we used TPBI not only as ETL but also as HBL of the final device C-1. J-V-L characteristics of the device C-1 and CIE 1931 color coordinates are shown in Figures 5 and 6, respectively. The device C-1 with the configuration of [ITO/α-NPB (50 nm)/BTPBB (30 nm)/TPBI (10 nm)/Alq3 (20 nm)/LiF (1 nm)/Al (120 nm)] exhibited a luminous efficiency of 2.2 cd/A and an E.Q.E of 0.9% at 120 mA/cm^2 with good color stability and purity corresponding

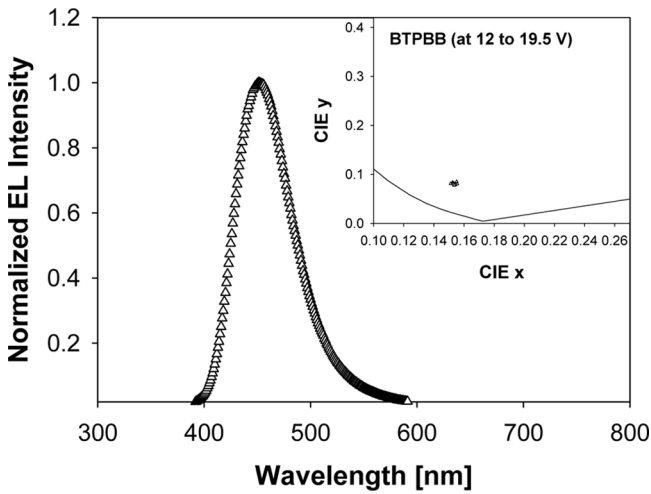


FIGURE 6 The EL spectrum of the optimized device C-1. The inset shows the CIE 1931 color coordinates of the device C-1 measured at the operating voltage of 12∼19.5 V.

to the CIE 1931 coordinates of (0.15, 0.08), which is close to the National Television System Committee (NTSC) standard of (0.14, 0.08) for blue with the chromatic variation of ($\pm$0.01, $\pm$0.01) when the applied voltage was changed from 12 to 19.5 V.

CONCLUSION

We synthesized a new blue-emitting material, 1,3,5-tris[4′-(1″-phenylbenzimidazole-2″-yl)phenyl] benzene (BTPBB), and investigated its OLED device properties. The device with a configuration of [ITO/ α-NPB (50 nm)/BTPBB (30 nm)/TPBI (10 nm)/Alq3 (20 nm)/LiF (1 nm)/Al (120 nm)] exhibited the best performance. In the optimized device, TPBI acted as HBL as well as ETL to give the enhanced efficiency and fine color purity and stability, showing the CIE 1931 coordinates of (0.15, 0.08) with the chromatic variation of ($\pm$0.01, $\pm$0.01) when the operating voltage was changed from 12 to 19.5 V.

REFERENCES

[1] Forrest, S. R. (2004). *Nature (London)*, *428*, 911.
[2] Noda, T., Ueta, H., Hiita, M., & Yoshiro, K. (1999). *Nonlinear Opt.*, *11*, 283.
[3] Matsuura, M., Kusumoto, T., & Tokailin, H. (1996). US Patent, 5516577.
[4] Hamada, Y., Adachi, C., Tsutsui, T., Saito, S. (1992). *Jpn. J. Appl. Phys.*, *31*, 1812.
[5] Shi, J. M., Chen, C. H., & Klubek, K. P. (2000). US Patent, 5974247.
[6] Tao, S., Lee, C. S., Lee, S.-T., & Zhang, X. (2007). *Appl. Phys. Lett.*, *91*, 013507.
[7] Baldo, M. A., Lamansky, S., Burrows, P. E., Thompson, M. E., & Forrest, S. R. (1999). *Appl. Phys. Lett.*, *75*, 4.
[8] Li, F., Jia, W., Wang, S., Zhao, Y., & Lu, Z.-H. (2008). *J. Appl. Phys.*, *103*, 034509.
[9] Zhang, X. H., Kim, S. H., Lee, I. S., Gao, C. J., Yang, S. I., & Ahn, K.-H. (2007). *Bull. Korean Chem. Soc.*, *28*, 1389.
[10] Wang, L., Lei, G., & Qiu, Y. (2005). *J. Appl. Phys.*, *97*, 114503.
[11] Tokito, S., Iijima, T., Tsuzuki, T., & Sato, F. (2003). *Appl. Phys. Lett.*, *83*, 2459.
[12] Wu, C.-C., Lin, Y.-T., Wong, K.-T., Chen, K.-T., & Chien, Y.-Y. (2004). *Adv. Mater.*, *16*, 61.
[13] Li, Y., Fung, M. K., Xie, Z., Lee, S.-T., Hung, L. S., & Shi, J. (2002). *Adv. Mater.*, *14*, 1317.
[14] Gemmern, P. V., Elsbergen, V. V., Grabowski, S. P., Boerner, H., Löbl, H.-P., Becker, H., Kalisch, H., Heuken, M., & Hanson, R. H. (2006). *J. Appl. Phys.*, *100*, 123707.
[15] Xie, Z. Y., Hung, L. S., & Lee, S. T. (2001). *Appl. Phys. Lett.*, *79*, 1048.
[16] Xie, Z. Y., Wong, T. C., Hung, L. S., Lee, S. T. (2002). *Appl. Phys. Lett.*, *80*, 1477.