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Sun-Hee Lee [a], Man Su Kim [a], Yong-Bum Cha [b], Kwang-Hyun Ahn [b] & Young Chul Kim [a]

[a] Department of Chemical Engineering and MRCID, Kyung Hee University, Yongin-si, Gyeonggi-do, Korea

[b] Department of Applied Chemistry and MRCID, Kyung Hee University, Yongin-si, Gyeonggi-do, Korea

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Electroluminescence Characteristics of a New Green-Emitting Phenothiazine Derivative with Biphenyl Benzimidazole Substituent

SUN-HEE LEE,[1] MAN SU KIM,[1] YONG-BUM CHA,[2]
KWANG-HYUN AHN,[2] AND YOUNG CHUL KIM[1]

[1]Department of Chemical Engineering and MRCID, Kyung Hee University, Yongin-si, Gyeonggi-do, Korea
[2]Department of Applied Chemistry and MRCID, Kyung Hee University, Yongin-si, Gyeonggi-do, Korea

We report on the synthesis and electroluminescence characteristics of a new green-emitting material, 3,7-bis(1-(biphenyl-4-yl)benzimidazol-2-yl)10-methylphenothiazine (PhBBMP) containing the electron-donating phenothiazine core and the electron-accepting biphenyl benzimidazole substituent. An optimized OLED device with the structure of [ITO/NPB (40 nm)/PhBBMP (30 nm)/BCP (10 nm)/TPBI (30 nm)/LiF (1 nm)/Al (100 nm)] exhibited a luminous efficiency of 4.5 cd/A and an external quantum efficiency of 0.9% at 100 mA/cm^2, and the maximum luminance of 12,000 cd/m^2 with the CIE 1931 chromaticity coordinates of (0.21, 0.54). A more balanced charge carrier injection and the charge confinement in the emitting layer cooperatively contributed to improve the performance of the device prepared with the PhBBMP emitting layer.

Keywords Biphenyl benzimidazole; green OLED; phenothiazine

Introduction

Organic light-emitting diode (OLED) [1] is attracting increasing interest due to its potential applicability to large area displays and two-dimensional light sources, and small full-color display products are already on the market. Accordingly, tremendous efforts have been made over the recent two decades to improve the emission efficiency of OLEDs by developing either high efficiency materials or efficient device structures. In order to fabricate full-color displays or white light sources, it is also of essential importance to have blue-, green-, and red-emitting materials with high color purity and long-term stability as well as high luminous quantum yield.

π-conjugated donor-acceptor (D-A) molecules have been successfully employed in OLEDs as high efficiency emitting materials [2–6] because energy transfer and charge carrier recombination can easily occur within the molecular structure to give

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Address correspondence to Prof. Young Chul Kim, Department of Chemical Engineering, Kyung Hee University, Yongin-si, Gyeonggi-do 446-701, Korea. E-mail: kimyc@khu.ac.kr a high emission efficiency. In this work, we synthesized a new green-emitting D-A molecule with a phenothiazine core and two biphenylbenzimidazole substituents. Phenothiazine is a well known electron donor with electron-rich sulfur and nitrogen heteroatoms [7] and its unique non-planar geometry can make the molecule have an amorphous nature with decreased crystallinity, resulting in an enhanced device performance [8,9]. Benzimidazole group was introduced to the material as an electron acceptor due to its high electron affinity [10,11]. We also prepared the OLED devices with three different multilayer structures using the new material as the emitting layer, and characterized their performance to optimize the device structure.

Experimental

Synthesis of PhBBMP

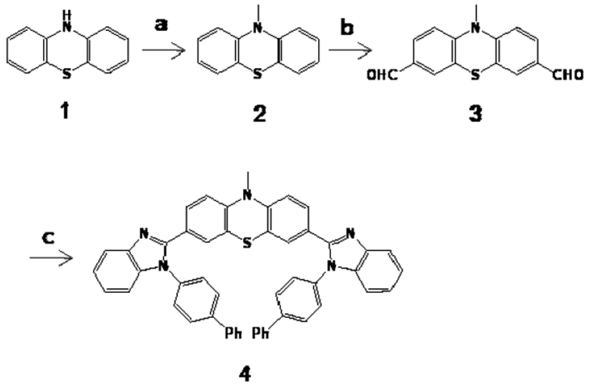
3,7-Bis(1-(biphenyl-4-yl)benzimidazol-2-yl)10-methylphenothiazine (PhBBMP) **4** was prepared according to Scheme 1. 10H-Phenothiazine **1** was alkylated to give 10-methylphenothiazine **2** in an excellent yield (99%). Vilsmeier-Haak reaction of 10-methylphenothiazine **2** by phosphorus(III) oxychloride and DMF in 1,2-dichloroethane afforded 10-methylphenothiazine-3,7-dicarbaldehyde **3** (53%). 3,7-Bis(1-(biphenyl-4-yl)benzimidazol-2-yl)10-methylphenothiazine **4** was obtained by the oxidative coupling of N-(biphenyl-4-yl)benzene-1,2-diamine with **3** under the treatment of sodium metabisulfite. The compound was purified by column chromatography using hexane and ethyl acetate (78%).

10-Methylphenothiazine (2)*, Mp: 101°C.* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15–7.20(m, 4H), 6.87–6.98(m, 4H), 3.41(s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 145.74, 127.37, 127.08, 123.29, 122.38, 114.01, 35.22.

10-Methylphenothiazine-3,7-dicarbaldehyde (3)*, Mp: 153°C.* ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.83(s, 2H), 7.69(dd, $J = 8.40$, $J = 1.80$ Hz, 2H), 7.16(d, $J = 1.80$ Hz, 2H), 6.92(d, $J = 8.40$ Hz, 2H), 3.49(s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 189.85, 149.22, 131.88, 130.48, 127.78, 123.27, 114.47, 36.20.



Scheme 1. Reagent and conditions: (a) NaH, CH_3I, THF, 0°C; (b) $POCl_3$, DMF, $ClCH_2CH_2Cl$, 90°C; (c) N-(biphenyl-4-yl)benzene-1,2-diamine, $Na_2S_2O_5$, DMF, 150°C.

***3,7-Bis(1-(biphenyl-4-yl)benzimidazol-2-yl)10-methylphenothiazine (4)**, Mp: 300°C.* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80(d, 2H), 7.56–7.66(dd, 8H), 7.18–7.41(m, 20H), 6.55(d, 2H), 3.20(s, 3H).

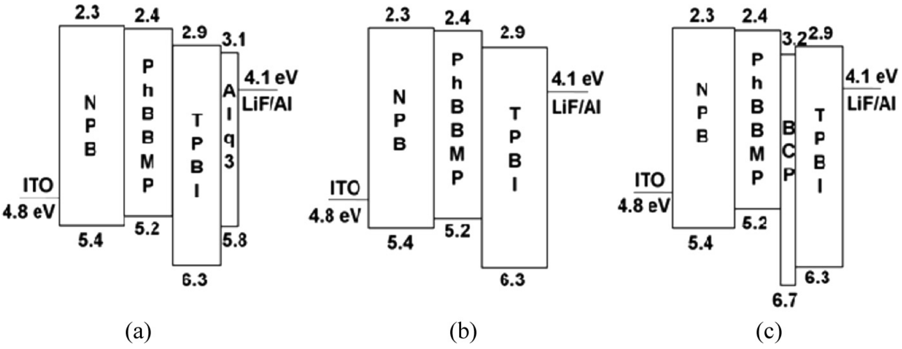
^{13}C NMR (75 MHz, $CDCl_3$): δ 151.16, 145.88, 141.55, 139.56, 137.02, 135.73, 128.98, 128.73, 128.49, 127.94, 127.90, 127.62, 127.10, 123.95, 123.93, 123.35, 123.16, 123.08, 119.40, 113.72, 110.40, 35.45.

Fabrication of OLEDs

ITO-coated glass substrates with a surface resistance of 10 Ω/sq were patterned by photholithography and cleaned with trichloroethylene, acetone, deionized water, and isopropyl alcohol in an ultrasonic bath. The cleaned ITO surface was oxygen plasma-treated to improve adhesion with organic materials. OLED devices with three different structures were prepared by using PhBBMP as the emitting layer, as depicted in Figure 1. In the devices, N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) was used as a hole transport layer (HTL), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a hole blocking layer (HBL), 1,3,5-tris (N-phenylbenzimidazol-2-yl)benzene (TPBI) and tris-(8-hydroxyquinoline) aluminum (Alq_3) as an electron transport layer (ETL), and the bilayer of lithium fluoride (LiF) and aluminum (Al) as a cathode. All organic and metal layers were deposited by thermal evaporation under $\sim 10^{-6}$ torr on the ITO substrate and the deposition rates were 1.0, 0.1, 3 ~ 4 Å/s for the organic, LiF, and Al layers, respectively. Active emitting area of the devices was defined to be $3 \times 3\,mm^2$.

Measurements

UV-vis absorption and photoluminescence (PL) spectra were obtained using an Agilent 8453 UV-visible spectrophotometer and a PTI QuantaMaster^{TM} spectrofluorometer, respectively. The current-voltage-luminance (J-V-L) characteristics of the devices were measured with a JBS IVL-300 EL characterization system and a Keithley 2400 sourcemeter. The highest occupied molecular orbital (HOMO) energy level of PhBBMP was measured by cyclic voltammetry (CV) and the lowest unoccupied molecular orbital (LUMO) energy level was obtained by adding the optical absorption band gap to the HOMO level.



(a) (b) (c)

Figure 1. Structures and energy level diagrams of the OLED devices; (a) device 1, (b) device 2, (c) device 3.

Results and Discussion

Thermal and Optical Properties

The thermal properties of PhBBMP were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) as shown in Figure 2. The TGA thermogram of PhBBMP measured at a rate of 5°C/min showed that the material has a fairly high thermal decomposition temperature (T_d) of 394°C. In the DSC thermograms, both melting and recrystallization behavior were not observed when heated up to 300°C and then cooled to room temperature at a scan rate of 5°C/min. On the second heating, however, the thermogram showed a relatively high glass transition temperature (T_g) of 162°C, which is far above the normal operating temperature of OLED. It is considered that the non-planar structure of PhBBMP with biphenyl benzimidazole group prevents close packing of the molecules. Accordingly, the PhBBMP layer can remain homogeneous and amorphous under the joule heating during the device operation.

Figure 3 presents the normalized UV-vis absorption and PL spectra of PhBBMP in dilute toluene solution (10^{-5} M). When the PhBBMP solution was excited at the two absorption peak wavelengths of 294 and 382 nm, the solution exhibited almost the same PL spectrum centered at 502 nm but the PL intensity was much stronger when excited at 294 nm. This implies that there is a large Stokes shift between absorption and emission. It has been reported that the two biphenyl rings in the benzimidazole substituent have different geometric structures between the ground and the excited states because the twisted phenyl rings transform into planar structure when excited, leading to a large Stokes shift [12–14]. A large Stokes shift sometimes enhances the emission efficiency by preventing the self-absorption of the emitted light.

Electroluminescence Properties of OLED Devices

The current density-voltage-luminance characteristics of the OLED devices are shown in Figure 4. As shown in Figure 4(a), device 1 with the TPBI (30 nm) and

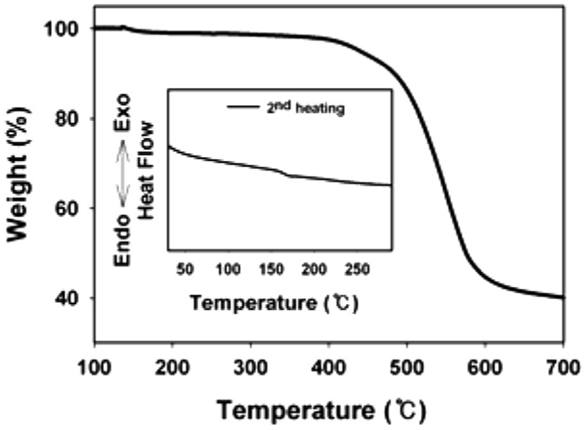


Figure 2. TGA and DSC thermograms of PhBBMP measured at a scan rate of 5°C/min in nitrogen.

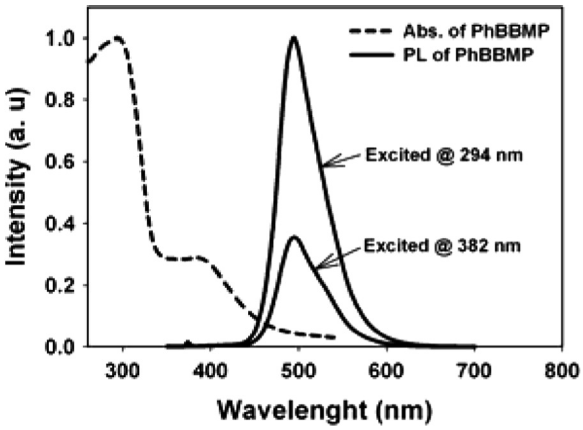
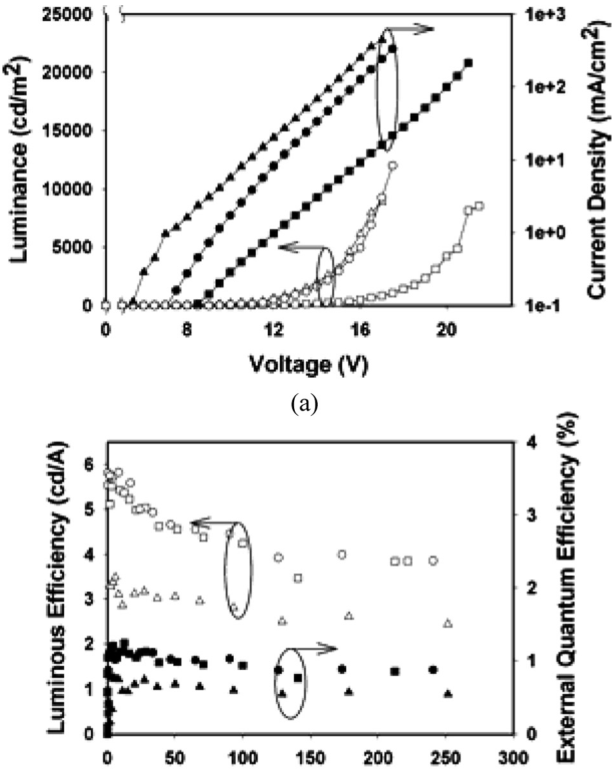


Figure 3. UV-vis absorption and photoluminescence spectra of PhBBMP in dilute toluene solution.



(b)

Figure 4. (a) Luminance and current density vs. voltage, and (b) luminous efficiency and external quantum efficiency vs. current density characteristics of device 1 (□,■), device 2 (△,▲), and device 3 (○,●).

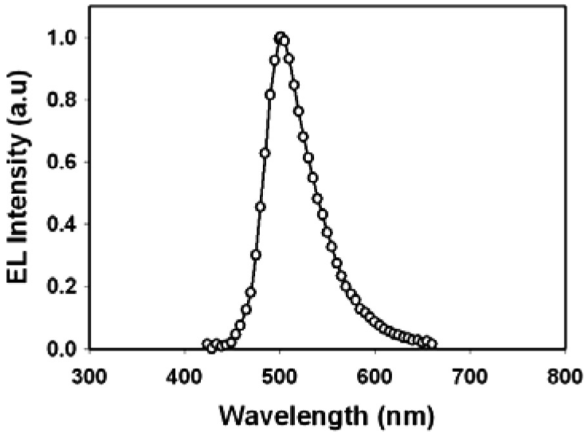


Figure 5. Electroluminescence spectrum of device 3.

Alq_3 (10 nm) layers as ETLs required a high driving voltage of 13 V to give a luminance of 100 cd/m^2, however, the driving voltage was reduced to 9 V when the TPBI (40 nm) single layer was employed as ETL (device 2). Although device 2 has a higher energy barrier for electron injection (1.2 eV) from cathode to ETL than that of device 1 (1.0 eV), the higher electron mobility in the TPBI layer than in the Alq_3 layer could reduced the driving voltage [15–19]. On the other hand, device 2 gave a lower luminous efficiency than device 1 as shown in Figure 4(b), which can result from a poorly balanced charge carrier injection.

To obtain an OLED device with a higher luminous efficiency as well as a lower driving voltage, we introduced the BCP (10 nm) layer as a hole blocking layer (HBL) between EML (PhBBMP) and ETL (TPBI) (device 3). Device 3 demonstrated a luminous efficiency of 4.5 cd/A at a current density of 100 mA/cm^2 and a driving voltage of 10 V. The luminous efficiency was increased by 1.7 cd/A compared with device 2 and the driving voltage was reduced by 3 V compared with device 1. As illustrated in Figure 1(b), device 2 has a higher energy barrier for electron injection than that for hole injection therefore, without an HBL, a considerable amount of holes can transport across EML to cause current loss. It is possible to confine the injected holes in EML by introducing an HBL such as BCP that has a deep HOMO level of 6.7 eV, as shown in Figure 1(c), and hole confinement in EML can increase the chance of charge carrier recombination in EML to generate more excitons. Accordingly, device 3 with the optimized device structure exhibited the best performance not

Table 1. Electroluminescence characteristics of the OLED devices

Device	Turn-on voltage [V]	L_{max} [cd/m^2]	η_L [cd/A] at 100 mA/cm^2	η_P [lm/W] at 100 mA/cm^2	η_{ext} [%] at 100 mA/cm^2	CIE coordinates [x, y]
1	13	8500	4.2	0.6	0.9	0.22, 0.55
2	9	8800	2.8	0.6	0.6	0.22, 0.56
3	10	12000	4.5	0.9	1.0	0.21, 0.54

only by the efficient electron injection through TPBI but also by a more effective recombination of injected holes and electrons in EML.

Also, device 3 showed a green emission spectrum peaked at 502 nm (Fig. 6) with the CIE 1931 chromaticity coordinates of (0.20, 0.55) at a current density of 100 mA/cm^2. EL characteristics of devices 1–3 were summarized in Table 1.

Conclusions

We synthesized a new green-emitting material, 3,7-bis(1-(biphenyl-4-yl)-benzimidazol-2-yl)-10-methylphenothiazine (PhBBMP), which contains the electron-donating phenothiazine core and the electron-accepting biphenyl benzimidazole substituent. We also prepared the OLED devices with three different multilayer structures using the new material as the emitting layer, and characterized their performance to optimize the device structure. The optimized device with the configuration of [ITO/NPB (40 nm)/PhBBMP (30 nm)/BCP (10 nm)/TPBI (30 nm)/LiF (1 nm)/Al (100 nm)] exhibited a luminous efficiency of 4.5 cd/A and an external quantum efficiency of 0.9% at 100 mA/cm^2, and the maximum luminance of 12000 cd/m^2 with the CIE 1931 chromaticity coordinates of (0.20, 0.55). The TPBI layer acted as an efficient ETL for the device and the BCP layer employed as an HBL successfully confined holes and excitons in EML to enhance the emission efficiency.

Acknowledgement

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