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고효율 청색 유기발광다이오드의 DPVBi와 BCzVBi 사이에서 발생하는 흡열 페르스터 에너지전이

김유현 · 이상연 · 송 욱 · 신성식 · 류대현† · Richard Wood‡ · Jay Yatulis§ · 김우영*
호서대학교 공과대학 디스플레이공학과
†한세대학교 IT학부 정보통신공학과
‡Department of Engineering Physics, McMaster University, Hamilton, Ontario, Canada
§Department of Photonics, Niagara College, Welland, Ontario, Canada
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Endothermic Förster Energy Transfer from DPVBi to BCzVBi in High Efficient Blue Organic Light-Emitting Diodes

You Hyun Kim, Sang Youn Lee, Wook Song, Sung Sik Shin, Dae-Hyun Ryu†, Richard Wood‡, Jay Yatulis§, and Woo Young Kim*
School of Display Engineering, Hoseo University, 29-1 Sechul-ri, Baebang-myun, Asan 336-795, Korea
**E-mail: wykim@hoseo.edu*
†*Department of IT, Hansei University 604-5, Dangjung-Dong, Gunpo-si, Gyunggi-Do 435-742, Korea*
‡*Department of Engineering Physics, McMaster University, Hamilton, Ontario, Canada*
§*Department of Photonics, Niagara College, Welland, Ontario, Canada*
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요약. 본 연구에서는 다양한 농도의 BCzVBi를 청색 형광도판트, DPVBi를 청색 호스트 물질로 적용한 청색OLED 소자를 제작하였다. 최적화된 고효율 청색 OLED 소자의 적층 구조는 NPB (500 Å)/DPVBi:BCzVBi-6%(150 Å)/Alq_3(300 Å)/Liq(20 Å)/Al (1000 Å)으로 구성되었다. 청색 OLED의 최대휘도는 구동전압 13.8V에서13200 cd/m^{2}이고 전류밀도 및 최대효율은 각각 1000 cd/m^{2}의 휘도에서 26.4 mA/cm^2, 구동전압 3.9 V에서 4.24 cd/A 이었다. 도핑된 청색 OLED 소자의 발광효율은 도핑되지 않은 소자의 2배에 이른 반면 색좌표는 (0.16, 0.19)로 서로 비슷하였다. BCzVBi가 6% 도핑된 청색 OLED 445 nm와 470 nm에 2개의 EL 스펙트럼의 Peak이 존재하는 반면 도핑되지 않은 순수한 DPVBi 청색OLED 소자는 456 nm에서의 유일한 Peak만을 보여주고 있다. 이는 호스트 물질인 DPVBi의 LUMO와 도판트 물질인 BCzVBI의 LUMO 사이에 분자 진동에 의한 페르스터 에너지 전이에 기인한 것이다.

주제어: 유기발광디이오드, BCzVBi, DPVBi, 청색발광, 페르스터 에너지전이, 고효율

ABSTRACT. In this study, we demonstrated high-efficiency blue organic light-emitting diodes (OLEDs) employing BCzVBi as a blue fluorescent dye doped into blue host material, DPVBi with various concentration. The optimized blue OLED device having high-efficiency was constructed with structure of NPB (500 Å) / DPVBi:BCzVBi-6% (150 Å) / Alq_3 (300 Å) / Liq (20 Å) / Al (1000 Å). The maximum luminescence of blue OLED was 13200 cd/m^2 at 13.8 V and current density and maximum efficiency were 26.4 mA/cm^2 at 1000 cd/m^2 and 4.24 cd/A at 3.9 V, respectively. Luminous efficiency shows two times higher than comparing with non-doped BCzVBi blue OLED whereas $CIE_{x,y}$ coordinate was similar with bare DPVBi blue OLED such as (0.16, 0.19). Electroluminescence of BCzVBi-6% doped blue OLED has two major peaks at 445 nm and 470 nm whereas pure DPVBi's blue peak appears at 456 nm and it is happened through endothermic Förster energy transfer by molecule's vibration between LUMO of DPVBi as host material and LUMO of BCzVBi as dopant in device.

Keywords: OLED, DPVBi, BCzVBi, Blue emission, Föster energy transfer, High efficiency

INTRODUCTION

Since the efficient small molecule organic light-emitting diode (OLED) was reported by Tang and VanSlyke in 1987[1] enormous interests have been shown in developing the emitting materials to realize high-resolution full-color flat panel displays with long lifetime. However, the performances of blue emitting materials are still not sufficient for their

applications. There are few reports of OLEDs with deep blue color, high efficiency, and long operational lifetime.[2-5]

Among red, green and blue of the three principal colors necessary for display applications, blue-emitting materials and devices are particularly in need of improvement in terms of efficiency and color purity than those of the green and red emitters. In recent years, developing deep blue electroluminescence (EL) color with a CIEy coordinate value of 0.15 has been considered essential[6] as such emitters can effectively reduce the power consumption of a full-color OLED panel and can also be utilized to generate emission of other colors by energy transfer to a matching emissive dopant.[7,8]

While high-efficiency green and red emitting colors could be obtained readily by doping in the commonly used guest materials such as tris(8-ydroxyquinolinato) aluminum(Alq_3). A wider band gap host is essential for the efficient generation of blue gap host to obtain efficient emission of blue dopant. Therefore, key for developing deep blue OLEDs is not only finding the highly fluorescent deep blue dopant but also appropriately matching host material in order to enhance the probability of carrier recombination as well as the efficiency of Förster energy transfer from the host to the dopant molecule. There were a number of reports on the design and synthesis of dopants that can produce deep blue photoluminescence.[9] However, because of the considerably blue shifted absorption of these deep blue dopants, better matching host materials with sufficient spectral overlap for reasonable high Förster energy transfer are needed to facilitate the generation of blue dopant emission with high efficiency as well as deep blue color.[10]

Blue emission is undoubtedly the basic element to achieve perfect white emission. Therefore, there have been many efforts toward exploring blue-emitting materials and improving color purity as well as efficiency of blue OLEDs.[11-13] despite the fact that great progress has been achieved, many efforts are still required to further improve the performance of blue OLEDs, especially the efficiency, to meet the demands of display application.

In this work, we demonstrated high efficient blue OLEDs using a blue organic materials, 4,4′-bis(9-ethyl-3-carbazovinylene)-1,1′-biphenyl (BCzVBi) doped in 4,4′-bis(2,2′-diphenylyinyl)-1,1′-biphenyl (DPVBi) as a blue emissive layer and its energy transfer.

EXPERIMENTAL DETAILS

ITO coated glass was cleaned in ultrasonic bath by regular sequence: in acetone, methanol, diluted water and isopropyl alcohol. Hereafter, pre-cleaned ITO was treated by O_2 plasma

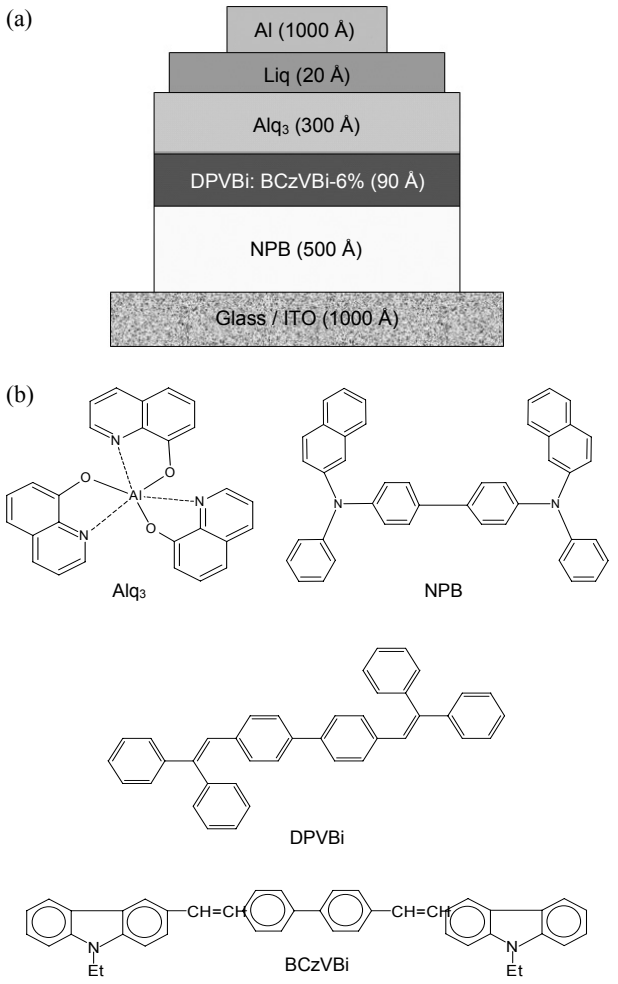

***Fig.* 1.** (a) Schematic device configuration. (b) Molecular structures.

under condition of 2×10^{-2} Torr, 125 W during 2 minites.[14] blue OLEDs were fabricated using the high vacuum (1.0×10^{-6} Torr) thermal evaporation and NPB, DPVBi, Alq3 and BCzVBi and Liq and Al were deposited by evaporation rate of 1.0, 0.1, 0.1, 5.0 Å/s, respectively.

Fig. 1(a) shows the schematic configuration of the blue OLEDs construction in this study, and *Fig*. 1(b) does the molecular structures of the chromophores in the devices as emitting layer materials. The host-guest multilayered blue OLED device structures using blue fluorescence dopant BCzVBi with fluorescence host DPVBi were as follows: ITO/N,N′-bis-(1-naphyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) as a hole transport layer / 4,4′-bis(9-ethyl-3-carbazovinylene)-1,1′-biphenyl (BCzVBi) doped in 4,4′-bis (2,2′-diphenylyinyl)-1,1′-biphenyl (DPVBi) as a blue emissive layer / 8-hydroxyquinolino!aluminum (Alq_3) as an electron transport layer / lithium quinolate (Liq) as an electron injection layer / aluminum (Al) as a cathode. Three kinds of the devices were fabricated using doped BCzVBi 3%, 6%,

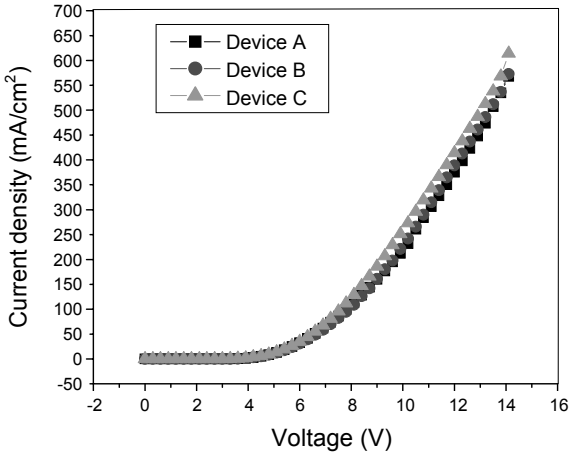

***Fig*. 2.** Current density of blue OLED devices. (a) BCzVBi-non doped (b) BCzVBi-3% doped (c) BCzVBi-6% doped.

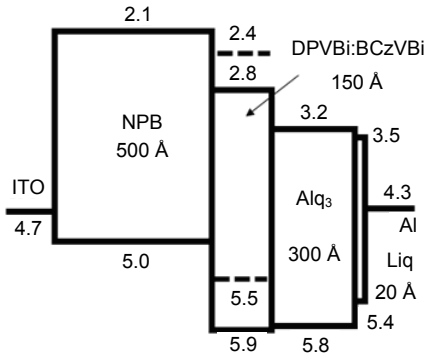

***Fig*. 3.** Energy diagrams of BCzVBi doped blue OLED devices.

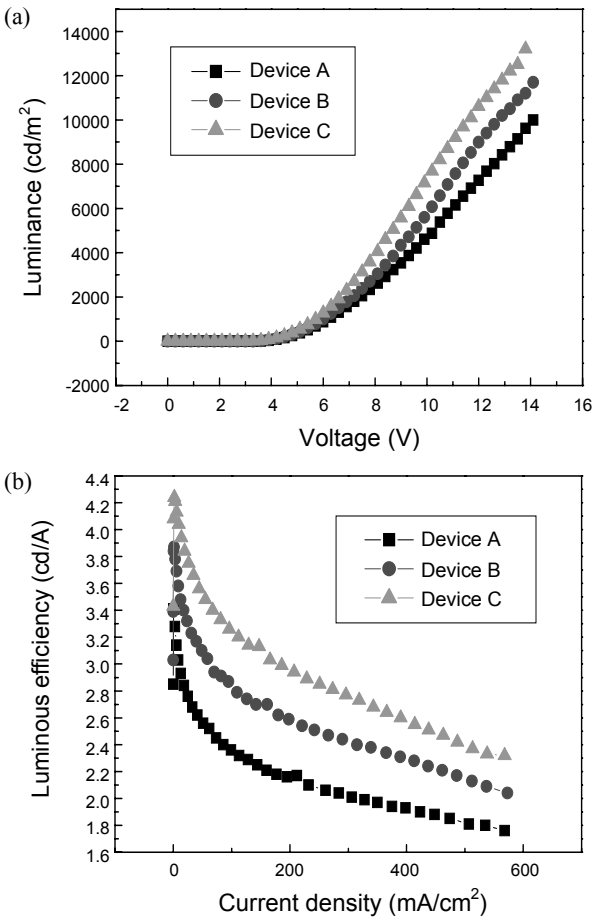

***Fig*. 4.** Optical characteristics of blue OLED devices (a) Luminance (b) Luminous efficiency.

and, non-doped BCzVBi to DPVBi in blue OLED devices. With various DC voltage bias, the optical and electrical properties of blue OLEDs such as the current density, luminance, luminous efficiency, Commission Internationale de L'eclairage (CIExy) coordinates and electroluminescence characteristics were measured with Keithley 236, CHROMA METER CS-100A and JBS OLED analysis system IVL-200.

RESULTS AND DISCUSSION

Current density of blue OLEDs with driving voltage was as shown in *Fig*. 2. Device A, B, and C was constructed NPB (500 Å) / DPVBi:BCzVBi-x% (150 Å) / Alq_3 (300 Å) / Liq (20 Å) as varying BCzVBi concentration with non-doped, 3%, and 6%, respectively. As shown *Fig*. 2, Current density characteristics of blue device A, B, and C was 375, 384, and 414 mA/cm^2 at 12 V each. Device C doping BCzVBi 6% into DPVBi had higher current density than Device A and device B. HOMO levels of NPB and DPVBi in device A were 5.0 and 5.9 eV. DPVBi blocked holes due to its high HOMO levels, therefore, blue OLED device using pure DPVBi showd low current density. In *Fig*. 3, BCzVBi in doped blue device acts as a hole carrier and mitigates the hole blocking effect by DPVBi because of its 0.4 eV higher HOMO energy level than DPVBi. Thus, as increasing BCzVBi concentration increase into DPVBi generates increase of current density in blue OLED device.

In *Fig*. 3, BCzVBi doped device was blocked electrons transported from Alq_3 because BCzVBi's LUMO levels are lower than that of DPVBi. Electron trapping effect due to BCzVBi's LUMO levels and hole carrying effect according to BCzVBi's HOMO levels resulted in increase of BCzVBi concentration and high luminous efficiency eventually in the blue emitting layer.

Luminance and luminous efficiency of blue OLED devices were shown in *Fig*. 4. Luminances of device A, B, and C were 7270, 8990, and 10600 cd/m^2 at 12 V, respectively. Maximum luminance of device C using BCzVBi 6% was 13200 cd/m^2, at 13.8 V. Luminance is also increased by BCzVBi concentration increase with DPVBi due to Förster

***Table* 1.** CIE(x,y) coordinates of blue OLED devices with different bias voltages

	Device A	Device B	Device C
6 V	(0.166 , 0.206)	(0.162 , 0.196)	(0.160, 0.191)
9 V	(0.166 , 0.203)	(0.162 , 0.195)	(0.160, 0.189)
12 V	(0.167 , 0.201)	(0.164 , 0.196)	(0.161, 0.190)

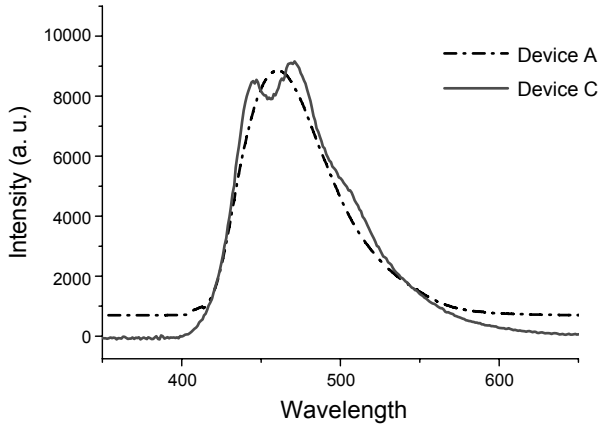

***Fig*. 5.** Electroluminescence spectra of BCzVBi 6 % doped and bare DPVBi device

energy transfer from LUMO of DPVBi to LUMO of BCzVBi. Luminous efficiency of blue OLED device A, B, and C was 3.41, 3.87, and, 4.24 cd/A, at 3.9 V, respectively. Device C using doped BCzVBi 6% was compared with non-doped device A and it has two times higher efficiency than device A.

Table 1 shows CIE(x,y) coordinates of blue OLED devices with various voltages. BCzVBi doped and non-doped blue OLED devices were independent on bias voltage with different concentration of BCzVBi. It also shows that blue OLED devices with doped BCzVBi were significantly improved luminous efficiency by blue fluorescent dopant without change of CIE(x,y) coordinates.

Electroluminescence spectra of blue OLED device A and C were shown in *Fig*. 5. The blue EL spectra of device A using bare DPVBi had the highest intensity at 456 nm but BCzVBi 6% doped device C was two major peaks, at 445 and 470 nm. These two peaks in the blue emission region suggest the presence of exciplex through energy transfer between LUMO and HOMO levels of DPVBi and BCzVBi, which is considered as endothermic Förster energy transfer from DPVBi to BCzVBi by molecule's vibration. Considering energy level of HOMO/LUMO of DPVBi and BCzVBi, holes injected from NPB layer would stay more favorably on HOMO of BCzVBi than DPVBi while electrons injected from Alq_3 would be accumulated on LUMO of DPVBi than BCzVBi. Then electrons transition is happened from LUMO of DPVBi to that of BCzVBi *via* endothermic Förster energy transfer followed by recombination between holes on HOMO of BCzVBi and electrons on LUMO of BCzVBi to achieve blue emission, which results in only appearing two peaks from BCzVBi in electroluminescence spectrum.

CONCLUSION

In summary, we fabricated highly efficient blue OLED devices using doped BCzVBi into DPVBi with different dopant concentrations. Blue fluorescence dopant BCzVBi enhances the current density, luminance and luminous efficiency of blue OLED devices as improving carrier injection into the emitting layer according to forming complex at BCzVBi's HOMO and LUMO level with DPVBi. The luminous efficiency of BCzVBi doped OLED is 4.24 cd/A and it has two times higher than pure DPVBi blue OLED device with no change of CIEx,y coordinates. However electroluminescence spectrum of BCzVBi-6% doped blue OLED has two major peaks at 445 nm and 470 nm whereas DPVBi does 456 nm peak only because of endothermic and endothermic Föster energy transfer from DPVBi to BCzVBi by molecule's vibration.

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