

Interlayer Engineering with Different Host Material Properties in Blue Phosphorescent Organic Light-Emitting Diodes

Jonghee Lee, Jeong-Ik Lee, Joo-Won Lee, and Hye Yong Chu

We investigated the light-emitting performances of blue phosphorescent organic light-emitting diodes, known as PHOLEDs, by incorporating an *N,N'*-dicarbazolyl-3,5-benzen interlayer between the hole transporting layer and emitting layer (EML). We found that the effects of the introduced interlayer for triplet exciton confinement and hole/electron balance in the EML were exceptionally dependent on the host materials: 9-(4-*tert*-butylphenyl)-3,6-bis(triphenylsilyl)-9H-carbazole, 9-(4-*tert*-butylphenyl)-3,6-ditriptyl-9H-carbazole, and 4,4'-bis-triphenylsilyl-biphenyl. When an appropriate interlayer and host material were combined, the peak external quantum efficiency was greatly enhanced by over 21 times from 0.79% to 17.1%. Studies on the recombination zone using a series of host materials were also conducted.

Keywords: Organic light-emitting diodes (OLED), blue, phosphorescent, interlayer.

I. Introduction

Organic light-emitting devices (OLEDs) are promising and efficient solid-state lighting sources for lighting applications [1]-[5]. In particular, the development of efficient phosphorescent OLEDs (PHOLEDs) in recent years allows for harvesting of both triplet and singlet excitons, thus providing a nearly 100% realization of internal quantum efficiency [6]. While green and red PHOLEDs have already reached a theoretical maximum internal quantum efficiency of 100%, one of the remaining challenges for OLED technology is the blue emission of white OLEDs with both long-term stability and high efficiency. Since blue electro-phosphorescent dopants have high triplet-energy (T_1) levels, wide band gap host materials with high T_1 levels are required [7]-[11]. Therefore, a proper choice of host materials to achieve highly efficient blue PHOLEDs is essential. In pursuing highly efficient blue PHOLEDs, a variety of efforts have been demonstrated through the development of host materials and device structures [7]-[19].

Many carbazole, trizine, pridine, or phenylsilane-type wide band-gap host materials [7]-[12] have been reported for blue PHOLEDs. Enhanced blue PHOLED performances have also been reported through device engineering, such as a mixed host, stepwise doping, or double emissive layer structure [13]-[18]. Previously, we reported on highly-efficient blue PHOLEDs in which the peak external quantum efficiency is over 20% when using a blue light emitting iridium(III)bis(4,6-difluorophenyl)-pyridinato-*N,C*²⁻ picolinate (FIrpic) doped m-bis-(triphenylsilyl) benzene (UGH3) host material and an adequate interlayer [19].

Manuscript received Mar. 22, 2010; revised May 27, 2010; accepted June 10, 2010.

This work was supported by IT R&D program of MKE/KEIT, Rep. of Korea (2009-F-016-01, Development of Eco-Emotional OLED Flat-Panel Lighting) and the future technology development program of MKE/KEIT (2006-10028439, OLED Lighting).

Jonghee Lee (email: clrpaper@gmail.com) was with the Convergence Components & Materials Research Laboratory, ETRI, Daejeon, Rep. of Korea, and is now with Institut für Angewandte Photophysik, Technische Universität Dresden, Dresden, Germany

Jeong-Ik Lee (email: jiklee@etri.re.kr), Joo-Won Lee (email: wo2@etri.re.kr), and Hye Yong Chu (email: hchu@etri.re.kr) are with the Convergence Components & Materials Research Laboratory, ETRI, Daejeon, Rep. of Korea.

doi:10.4218/etrij.11.0110.0172

Incorporation of an mCP interlayer at the hole transport layer/emitting layer (HTL/EML) interface dramatically enhanced the OLED performances by blocking triplet exciton quenching and reducing the charge overflow.

In this work, we developed blue PHOLEDs with improved efficiency by incorporating an mCP interlayer at the HTL/EML interface, and we also found that the advantage of the interlayer was influenced by the properties of the host materials which were 9-(4-tert-butylphenyl)-3,6-bis(triphenylsilyl)-9H-carbazole (CzSi), 9-(4-tert-butylphenyl)-3,6-ditrityl-9H-carbazole (CzC), and bis-triphenylsilylanyl-biphenyl (BSB). In addition, we investigated the location of the recombination zone in blue PHOLEDs depending on the host materials by fabricating the blue PHOLEDs with a partially doped EML.

II. Experiment

The chemical structures of the materials used in this study and their energy level diagrams are shown in Fig 1. Indium tin oxide (ITO) was cleaned using a standard oxygen plasma treatment. OLED-grade materials were purchased and used without further purification. All organic layers were deposited in a high vacuum chamber below 5×10^{-7} torr, and thin films of LiF and Al were deposited as a cathode electrode. The OLEDs were transferred directly from the vacuum into an inert environment glove-box, where they were encapsulated using a UV-curable epoxy and a glass cap with a moisture getter. The electroluminescence spectrum was measured using a Minolta CS-1000. The current-voltage (J-V) and luminescence-voltage (L-V) characteristics were measured with current/voltage source/measure unit Keithley 238 and a Minolta CS-100, respectively.

Three blue PHOLEDs of type Device A were used as standard devices in the current study. They were fabricated using a configuration of ITO / *N,N'*-di(naphthalene-1-yl)*N,N'*-diphenyl-benzidine (NPB) (40 nm) / Host:Flrpic 5% (30 nm) / Bphen (50 nm) / LiF (1 nm) / Al (120 nm) with CzSi, CzC, or BSB host materials, as shown in Fig 2. Three devices of type Device B with an mCP interlayer (10 nm) between an NPB-HTL (30 nm) and the EML were fabricated. Also, 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl (NPB), and bathocuproine(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) (Bphen) were used as an HTL and an electron transporting layer (ETL), respectively. A blue-light-emitting dopant Flrpic was doped in the host materials (CzSi, CzC, or BSB), which have a large triplet energy of 3.02 eV, 2.97 eV, or 2.76 eV, respectively [11], [12], and the doping concentration of Flrpic was fixed at 5%.

Additionally, recombination zone studies in blue PHOLEDs with different host materials were also demonstrated by

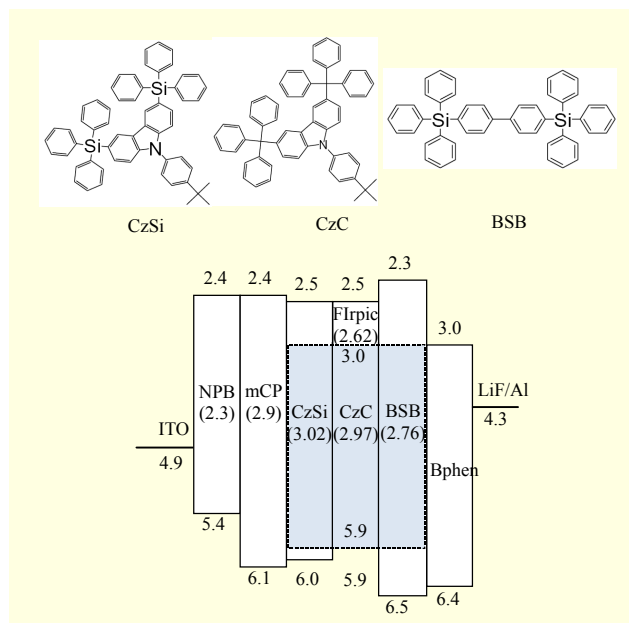


Fig. 1. Chemical structures and energy level diagrams for the materials tested in this study.

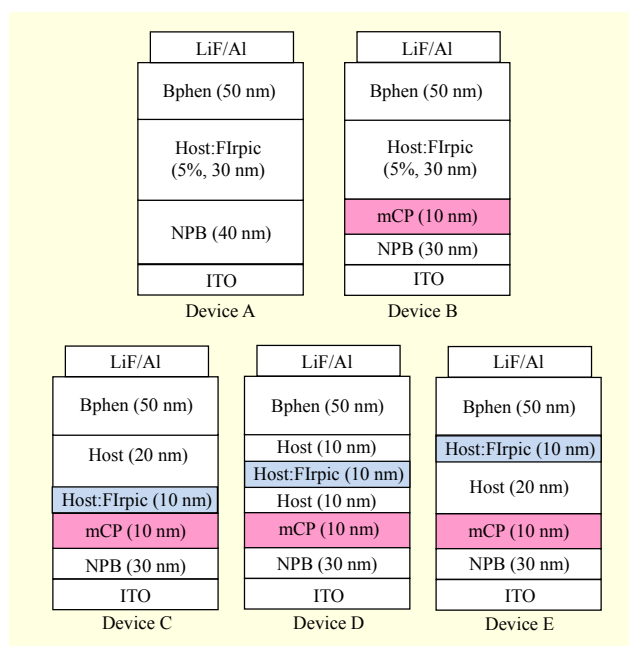


Fig. 2. Device structures of blue PHOLEDs tested in this study.

analyzing partially doped devices (Devices C to E), as shown in Fig 2. A detailed description of these partially doped devices will be discussed in the next section.

III. Results and Discussion

The current density-voltage-luminance curves of blue PHOLEDs without an mCP interlayer (Device A) are shown in

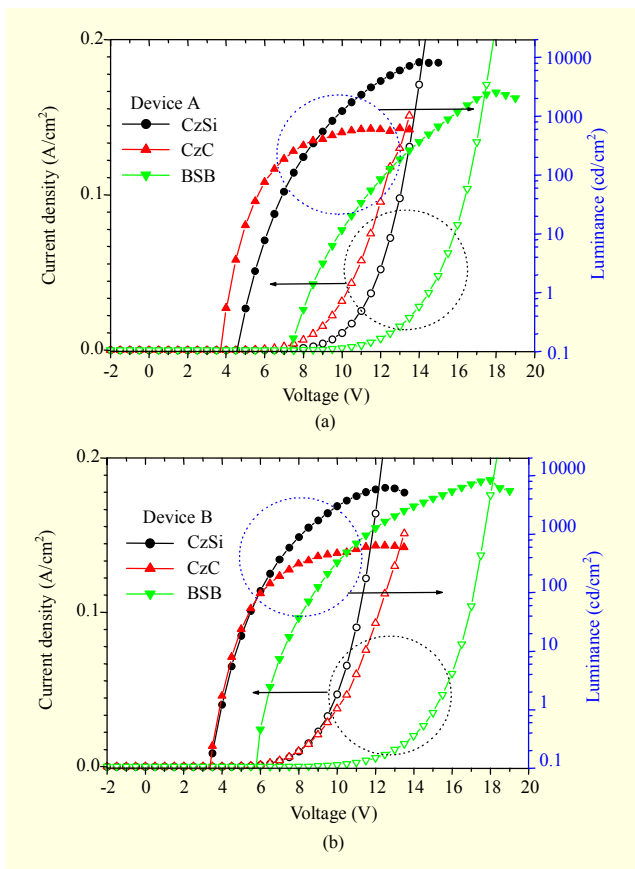


Fig. 3. Current density-voltage-luminescence (J-V-L) characteristics of (a) Device A and (b) Device B.

Fig. 3(a) according to the host materials. The lowest current density was observed in Device A with the BSB host in the EML, and there was little difference in current density in Device A with CzC and CzSi. The low current density of Device A (BSB) can be explained by the inefficient hole injection from NPB-HTL and the electron injection from Bphen-ETL to the EML. As shown in Fig. 1, the highest occupied molecular orbital (HOMO) level of NPB and BSB are 5.4 eV and 6.5 eV, respectively, and therefore the hole injection from NPB to BSB was greatly restricted due to the HOMO level difference of 1.1 eV between NPB and BSB. Similarly, there was also poor electron injection from Bphen-ETL to EML in Device A (BSB) due to a large electron injection barrier (0.7 eV) between Bphen and BSB. However, in the case of Device A (CzC), the HOMO level of CzC (5.9 eV) is higher than that of BSB (6.5 eV), and the lowest unoccupied molecular orbital (LUMO) level of CzC (2.5 eV) is lower than that of BSB (2.3 eV), which led to a lower energy barrier for both hole and electron injection.

The current density as well as luminance behavior of the blue PHOLEDs with mCP interlayer (Device B) are demonstrated in Fig. 3(b) according to the host materials. As

we previously reported, the mCP interlayer was incorporated to block triplet exciton quenching and reduce electron overflow [19]. Note that this mCP interlayer can act as a buffer layer to reduce the HOMO level difference between NPB and host material [5], [19]. In particular, in the case of Device B (BSB), luminance and current density at the same driving voltage were greatly increased. As we mentioned earlier, the HOMO level of mCP is 6.1 eV, and there was a huge hole injection barrier (1.5 eV) from NPB to BSB. This large hole injection barrier was alleviated by employing the mCP interlayer, which resulted in the stepped progression of the HOMO levels (that is, HOMO levels of NPB, mCP, and BSB are 5.4 eV, 6.1 eV, and 6.5 eV, respectively). Accordingly, the driving voltage difference between Device B (BSB, 8.8 V) and Device A (BSB, 12.2 V) at a luminance of 100 cd/m² is 4.0 V, which is over a 30% reduction. This result implies that the proper introduction of an interlayer at the HTL/EML interface can enhance the charge-carrier injection and reduce driving voltage in the EML. However, the driving voltage reduction by introducing this mCP interlayer in the devices with CzSi or CzC host materials was not very effective because there were little HOMO level difference between mCP and CzSi or CzC.

Figure 4 shows the electroluminescence spectra and Commission Internationale de L'Eclairage coordinates of Devices A and B at a current density of 10 mA/m². All the devices exhibit a similar maximum luminescence wavelength, near 470 nm, which originates from the triplet emission of the FIrpic emitter. However, blue PHOLEDs with BSB host material exhibited an increased shoulder emission near 497 nm. In particular, Device A (BSB) emits another broad shoulder near 438 nm. The former broad shoulder emission near 497 nm can be presumed to be an optical effect caused by the recombination zone change in the devices with different host materials [20], [21]. A detailed investigation of this recombination zone shift will be discussed in the recombination zone study, and further described in Figs. 6 and 7. The latter emission near 438 nm is assigned to NPB emission because of electron overflow from BSB to NPB and hole accumulation at the interface between NPB and BSB [12], [19], and [22]. As discussed and shown in Fig. 1, holes can be accumulated between the NPB and BSB interface due to the huge hole injection barrier. These accumulated holes can be recombined with electrons that overflow from the EML to NPB, giving rise to an undesirable NPB emission that can degrade the performance of blue PHOLEDs. Compared to Device A (BSB), no additional emission in Device B (BSB) is observed due to the reduced hole accumulation at the HTL/EML interface. By introducing the mCP interlayer, holes are easily injected from HTL and can be transported through the BSB host materials. Consequently, hole accumulation in

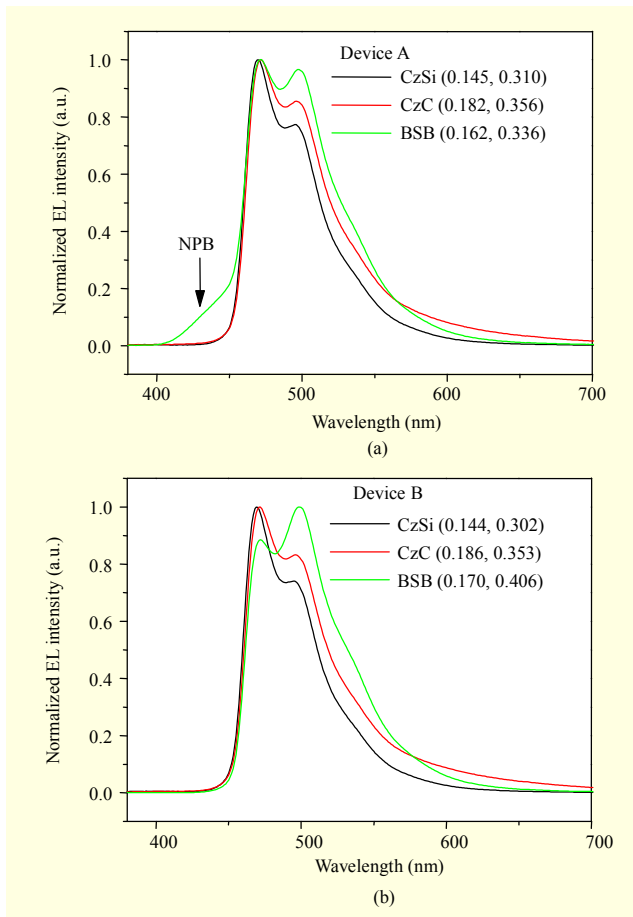


Fig. 4. Normalized electroluminescence spectra of (a) Device A and (b) Device B at a driving current of 10 mA/cm².

Device A (BSB) can be reduced, leading to no additional emission near 438 nm. The lack of additional emission in the blue PHOLEDs with CzSi and CzC also supports this explanation. The HOMO levels of CzSi and CzC are only 6.0 eV and 5.9 eV, respectively, and thus holes can be efficiently injected from the NPB to EML.

The external quantum efficiency (EQE) of blue PHOLEDs was plotted against the current density as shown in Fig 5. Among blue PHOLEDs without an mCP interlayer, Device A (CzSi) showed the best peak EQE value of 9.92%, and Device A (CzC) also exhibited a high efficiency of 9.46% compared with only 0.79% of Device A (BSB). Interestingly, Device A (BSB) exhibited very low EQEs, less than 1%. As expected from the electroluminescence study and current density-voltage characteristics in Figs. 3(a) and 4(a), this result can be explained in terms of an ineffective hole injection and electron overflow in the device with BSB host material. Moreover, the triplet energy level of NPB is only 2.3 eV [22], [23], which is not high enough for exciton blocking from the EML because the triplet energy levels of the BSB host and Flrpic-dopant materials are 2.76 eV and 2.62 eV, respectively. However,

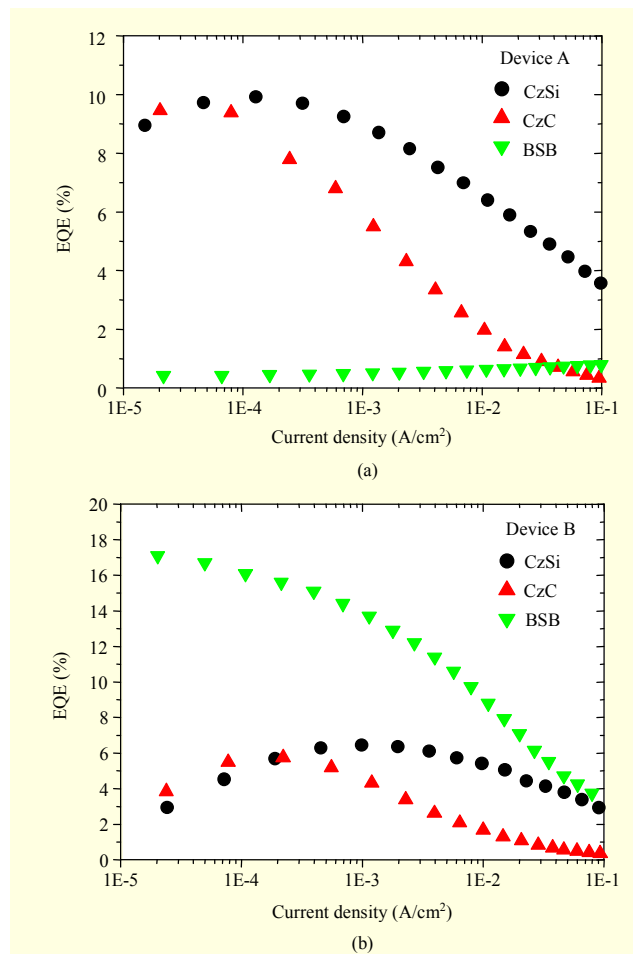


Fig. 5. EQE versus current density characteristics of (a) Device A and (b) Device B.

Device B with an introduced mCP interlayer showed remarkably different results. In the cases of Device B with CzSi and CzC host materials, the EQEs were decreased up to 6.46% and 5.75%, respectively, whereas the peak EQE of Device B (BSB) greatly increased up to 17.1%. This value is more than 21 times higher than that of Device A (BSB) without the mCP interlayer.

Generally, the light-emitting efficiency of OLEDs is determined by the hole/electron balance and confinement in the EML [17], [18], [21], [24]. In the case of Device B (BSB), the mCP interlayer can play an important role of a hole injection buffer layer to reduce the HOMO level difference between NPB and BSB. Furthermore, the mCP interlayer also acts as an excellent exciton blocking layer because mCP has large triplet energies (2.9 eV) to confine Flrpic excitons within the EML. On the contrary, the reduced efficiencies in Device B (CzSi) and Device B (CzC) after incorporating the mCP interlayer can be understood as being due to the preferred charge transport ability of the CzSi and CzC host materials. These results

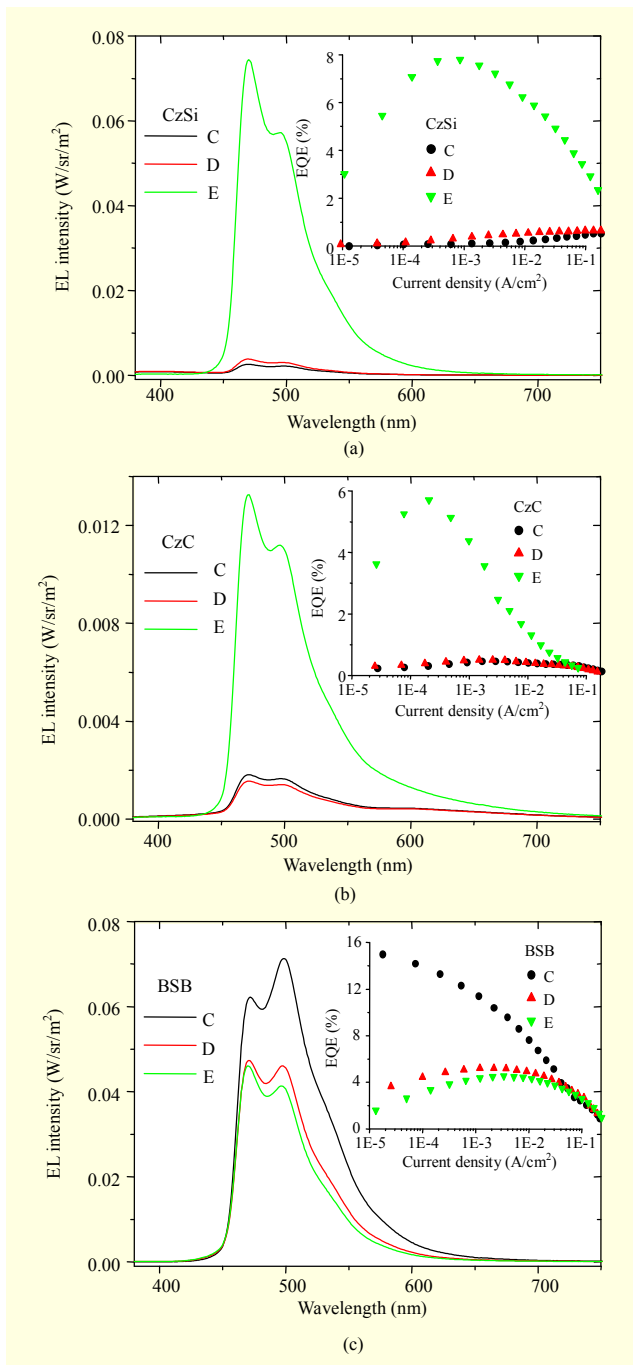


Fig. 6. Electroluminescence spectra of partially doped devices (Device C to E) with (a) CzSi, (b) CzC, and (c) BSB host materials at a driving current of 10 mA/cm² (Inset: EQE vs current density).

indicate that the function of an introduced interlayer is greatly influenced by host properties, such as HOMO/LUMO energy level, triplet energy level, and charge-carrier mobility.

We investigated the location of the recombination zone in blue PHOLEDs with different host materials by using a partially doped EML [15], [25]. Devices C to E were fabricated

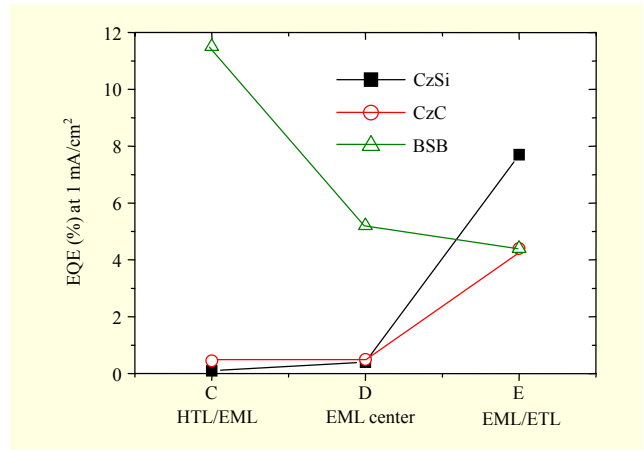


Fig. 7. EQE of partially doped devices (Device C to E) with CzSi, CzC, and BSB host materials at a driving current of 1 mA/cm².

as shown in Fig. 2. The blue emitting FIrpic was partially doped with a doping ratio of 5% in EMLs close to an HTL (Device C), close to an ETL (Device E), and at the center of an EML (Device D). The performances of partially doped blue PHOLEDs (Devices C to E) depending on the position of the doped region within the EML are shown in Figs. 6 and 7. In the case of devices with CzSi and CzC host materials, Device C and D exhibited relatively low intensity, whereas Device E showed a strong emission of FIrpic dopant. It can also be seen from Figs. 6 and 7 that EQEs of devices with CzSi and CzC host materials decreased as the FIrpic-doped region moves away from the EML/ETL interface. Both CzSi and CzC are carbazole-based hole-transport-type host materials, and their hole mobility of CzC (5×10^{-4} cm²/V · s) and CzSi (5×10^{-5} cm²/V · s) is higher than their electron mobility [11]. Therefore, most hole/electron recombination probably occurred at an EML close to an ETL in devices with CzSi and CzC host materials. Hence, Devices C and D, which have only host material with no FIrpic dopant at an EML close to an ETL, showed extremely low EQEs. As expected from the above results, Device E, which has FIrpic dopant at an EML close to an ETL, showed a very similar device performance to Device B, which is FIrpic doped in the entire EML. In contrast to CzSi and CzC host materials, the maximum emission and efficiency in cases of BSB host material come from Device C. In accordance with these observations of Devices C to E with BSB host material, we clarified that the location of the hole/electron recombination zone of uniformly doped Device B (BSB) is positioned in an EML close to an HTL. From these results, the introduced mCP interlayer at an HTL/EML interface could be more effective in PHOLEDs whose recombination zone is positioned near the HTL side in an EML, that is, a device with BSB host material. Furthermore, we can

presume that the introduction of an interlayer at an EML/ETL interface will enhance PHOLED performance for devices with CzC and CzSi. Related studies are underway and the results will be reported later.

IV. Conclusion

We have demonstrated that the use of an mCP interlayer as an exciton blocking and hole injection buffer layer in blue PHOLEDs is effective in obtaining high performances. In particular, the EQE of a BSB host-material-based blue PHOLED was enhanced from 0.79% to 17.1% by an mCP interlayer at an HTL/EML interface. Through a recombination zone study, we also found that the effect of the interlayer is quite dependent on the host material properties, such as HOMO/LUMO energy level and charge-carrier mobility.

References

- [1] B.W. D'Andrade and S.R. Forrest, "White Organic Light-Emitting Devices for Solid-State Lighting," *Adv. Mater.*, vol. 16, no. 18, 2004, pp. 1585-1595.
- [2] K.T. Kamtekar, A.P. Monkman, and M.R. Bryce, "Recent Advances in White Organic Light-Emitting Materials and Devices (WOLEDs)," *Adv. Mater.*, vol. 22, no. 5, 2010, pp. 572-582.
- [3] S. Reineke et al., "White Organic Light-Emitting Diodes with Fluorescent Tube Efficiency," *Nature*, vol. 459, 2009, pp. 234-239.
- [4] J. Lee, J.I. Lee, and H.Y. Chu, "Improved Performance of White Phosphorescent Organic Light-Emitting Diodes through a Mixed-Host Structure," *ETRI J.*, vol. 31, no. 6, 2009, pp. 642-646.
- [5] J. Lee, J.I. Lee, and H.Y. Chu, "Efficient and Color Stable Phosphorescent White Organic Light-Emitting Devices based on an Ultra Wide Band-Gap Host," *Synth. Met.*, vol. 159, no. 11, 2009, pp. 991-994.
- [6] C. Adachi et al., "Nearly 100% Internal Phosphorescence Efficiency in an Organic Light Emitting Device," *J. Appl. Phys.*, vol. 90, 2001, pp. 5048-5051.
- [7] C. Adachi et al., "Endothermic Energy Transfer: A Mechanism for Generating Very Efficient High-Energy Phosphorescent Emission in Organic Materials," *Appl. Phys. Lett.*, vol. 79, 2001, pp. 2082-2084.
- [8] H. Inomata et al., "High-Efficiency Organic Electrophosphorescent Diodes Using 1, 3, 5-Triazine Electron Transport Materials," *Chem. Mater.*, vol. 16, 2004, pp. 1285-1291.
- [9] S.J. Su et al., "Pyridine-Containing Bipolar Host Materials for Highly Efficient Blue Phosphorescent OLEDs," *Chem. Mater.*, vol. 20, 2008, pp. 1691-1693.
- [10] R.J. Holmes et al., "Efficient, Deep-Blue Organic Electrophosphorescence by Guest Charge Trapping," *Appl. Phys. Lett.*, vol. 83, 2003, pp. 3818-3820.
- [11] M.H. Tsai et al., "Triphenylsilyl- and Trityl-Substituted Carbazole-Based Host Materials for Blue Electrophosphorescence," *ACS Appl. Mater. Interfaces*, vol. 1, 2009, pp. 567-574.
- [12] J.J. Lin et al., "A Highly Efficient Host/Dopant Combination for Blue Organic Electrophosphorescence Devices," *Adv. Funct. Mater.*, vol. 18, 2008, pp. 485-491.
- [13] S.J. Su et al., "Highly Efficient Organic Blue- and White-Light-Emitting Devices Having a Carrier- and Exciton-Confining Structure for Reduced Efficiency Roll-Off," *Adv. Mater.*, vol. 20, 2008, pp. 4189-4194.
- [14] J. Lee, J.I. Lee, and H.Y. Chu, "Investigation of Double Emissive Layer Structures on Phosphorescent Blue Organic Light-Emitting Diodes," *Synth. Met.*, vol. 159, 2009, pp. 1460-1463.
- [15] J. Lee et al., "Influence of Doping Profile on the Efficiency of Blue Phosphorescent Organic Light-Emitting Diodes," *Appl. Phys. Lett.*, vol. 92, 2008, pp. 133304-1-3.
- [16] S.H. Eom et al., "Low Voltage and Very High Efficiency Deep-Blue Phosphorescent Organic Light-Emitting Devices," *Appl. Phys. Lett.*, vol. 93, 2008, pp. 133309-1-3.
- [17] J. Lee et al., "Enhanced Efficiency and Reduced Roll-Off in Blue and White Phosphorescent Organic Light-Emitting Diodes with a Mixed Host Structure," *Appl. Phys. Lett.*, vol. 94, 2009, pp. 193305-1-3.
- [18] J. Lee et al., "Improved Performance of Blue Phosphorescent Organic Light-Emitting Diodes with a Mixed Host System," *Appl. Phys. Lett.*, vol. 95, 2009, pp. 253304-1-3.
- [19] J. Lee et al., "Effects of Interlayers on Phosphorescent Blue Organic Light-Emitting Diodes," *Appl. Phys. Lett.*, vol. 92, 2008, pp. 203305-1-3.
- [20] S.O. Jeon et al., "High Efficiency Blue Phosphorescent Organic Light Emitting Diodes Using a Simple Device Structure," *Appl. Phys. Lett.*, vol. 94, 2009, pp. 013301-1-3.
- [21] J. Lee et al., "Stable Efficiency Roll-Off in Blue Phosphorescent Organic Light-Emitting Diodes by Host Layer Engineering," *Org. Electron.*, vol. 10, 2009, pp. 1529-1533.
- [22] S.H. Kim, J. Jang, and J.Y. Lee, "High Efficiency Phosphorescent Organic Light-Emitting Diodes using Carbazole-type Triplet Exciton Blocking Layer," *Appl. Phys. Lett.*, vol. 90, 2007, pp. 223505-1-3.
- [23] V.I. Adamovich et al., "New Charge-Carrier Blocking Materials for High Efficiency OLEDs," *Org. Electron.*, vol. 4, 2003, pp. 77-87.
- [24] H. Aziz, Z.D. Popovic, and N.X. Hu, "Organic Light Emitting Devices with Enhanced Operational Stability at Elevated Temperatures," *Appl. Phys. Lett.*, vol. 81, 2002, pp. 370-372.
- [25] E. Polikarpov et al., "Emission Zone Control in Blue Organic Electrophosphorescent Devices through Chemical Modification of Host Materials," *Appl. Phys. Lett.*, vol. 96, 2010, pp. 053306-1-3.



Jonghee Lee received the BS, MS, and PhD in chemistry from Korea Advanced Institute of Science and Technology (KAIST) in 2002, 2004, and 2007, respectively. During his graduate period, he conducted research on conjugated polymers and related organic semiconductor devices. He joined ETRI in 2007 and has worked on white organic light emitting diodes (WOLEDs) for display and lighting applications.



Jeong-Ik Lee received the BS, MS, and PhD in chemistry from Korea Advanced Institute of Science and Technology (KAIST) in 1992, 1994, and 1997, respectively. After graduation, he joined IBM Almaden Research Center, San Jose, CA, USA, as a post-doctoral researcher, where he worked on organic light emitting materials. He moved to ETRI, Korea, in 1999, and has been continuing his research on organic light emitting materials and devices.



Joo-Won Lee received the MS and PhD in physics from Kyung Hee University in 2003 and 2006, respectively. After graduation, he joined the Department of Materials Engineering, Auburn University, Alabama, USA, as a post-doctoral researcher. He moved to ETRI, Korea, in 2008, and has been continuing his research on transparent organic light emitting devices and light extraction techniques.



Hye Yong Chu received the BS and MS in physics from Kyung Hee University in 1987 and 1989, respectively. She joined ETRI, Korea in 1989. She earned the PhD degree in information display from Kyung Hee University in 2008. Her current research interests include novel device architectures in organic light emitting devices.