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RESEARCH ARTICLE

Efficient Green Phosphorescent Organic Light-Emitting Diodes Depending on Concentration of Lithium Quinolate in Electron Transport Layer

Bo Young Kim[1], Seok Jae Lee[1], Ja Ryong Koo[1], Song Eun Lee[1], Kum Hee Lee[2], Ju An Yoon[3], Woo Young Kim[3], Seung Soo Yoon[2,*], and Young Kwan Kim[1,*]

[1] *Department of Information Display, Hongik University, Seoul 121-791, Korea*
[2] *Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea*
[3] *Department of Green Energy and Semiconductor Engineering, Hoseo University, Asan 336-795, Korea*

Systematic studies on carrier injection and transport are very important for achieving high efficiency in OLEDs. We demonstrate excellent green phosphorescent organic light-emitting diodes (OLED) with lithium quinolate (Liq) doped in 1,3,5-tris(*N*-phenylbenzimidazole-2-yl) benzene (TPBi) as the electron transport layer (ETL). The doping concentration of Liq was varied from 0% to 10%. The optimized green phosphorescent OLED with 5% Liq in the ETL showed the best efficiencies, which were maximum luminous efficiency, power efficiency, and quantum efficiency of 65.76 cd/A, 57.39 lm/W, and 20.03%, respectively. Moreover, high triplet energy states of TCTA and TPBi as a triplet exciton-blocking layer (TEBL) played a role in efficient exciton confinement.

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Keywords: Green Phosphorescent OLEDs, Quantum Efficiency, Triplet Exciton Confinement, Electron Transport Layer.

1. INTRODUCTION

In recent years, research on the efficiency and stability of organic light-emitting diodes (OLEDs) has made significant progress. However, because of their extensive commercial applications, it is clear that supplementary studies of OLEDs are required.[1,2] The most important of several factors is a reduction in operating voltage and improvement in both efficiency and lifetime. It is known that controlling microstructure at an electrode/organic interface can affect the operating voltage and the interface stability. Hence, the use of the electrode/organic interface modification layer in OLEDs has received attention in previous studies.[3,4,7] For example, modifying the electrode/organic interface by introducing a buffer layer, such as LiF, C_{60}, Cs_2O, and Cs_2CO_3,[4–6,13,14] significantly enhances the efficiency and the lifetime of OLEDs.

In addition, the hole and electron blocking layer and the exciton-blocking layer in phosphorescent OLEDs were introduced to block carrier injection from the emitting layer (EML) to the hole and electron transport layer, thus confining both carriers and excitons within the EML. These blocking layers were effective in obtaining high efficiency in phosphorescent OLEDs.[6–10]

In this paper, we verify the significant improvement in device performance to extend the lifetime of excitons and the balance of the charge carrier injection and transport in EML by using mixed ETL with TPBi and Liq. In addition, both 4′,4″-tris(*N*-carbazolyl) triphenylamine (TCTA) and 1,3,5-tris (*N*-phenylbenzimidazole-2-yl) benzene (TPBi) as the triplet exciton-blocking layer (TEBL) were able to confine excitons efficiently. The results of green phosphorescent OLEDs showed low operating voltage and high efficiency as well as reduced efficiency roll-off.

2. EXPERIMENTAL DETAILS

Indium tin oxide (ITO) with a sheet resistance of 10 Ω/sq was used as a transparent anode on glass substrate. The ITO-coated glass was chemically cleaned in an ultrasonic bath using the following sequence: acetone, methanol, de-ionized water, and isopropyl alcohol. Afterwards, pre-cleaned ITO glass was treated by oxygen plasma at the power of 125 W for 2 min at low vacuum of 2×10^{-2} torr. As shown in Figure 1, the device structure was ITO (180 nm)/4,4-bis[*N*-(naphthyl)-*N*-phenyl-amino] biphenyl

*Authors to whom correspondence should be addressed.

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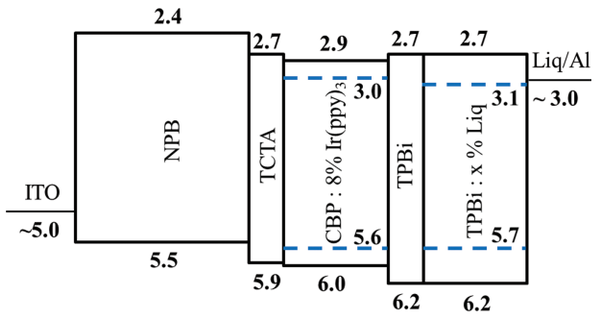

Fig. 1. Energy level diagram of green phosphorescent OLEDs.

(NPB, 50 nm)/TCTA (10 nm)/8% fac-tris(2-phenypyridine) iridium(III) [Ir(ppy)$_3$] doped in 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP, 30 nm)/TPBi (10 nm)/TPBi mixed with *X*% lithium quinolate (Liq) ($X = 0$, 3, 5, and 10%, 30 nm)/Liq (2 nm)/aluminium (Al, 100 nm). OLEDs were fabricated by thermal evaporation in a high vacuum under 5×10^{-7} torr.[11] The deposition rate was 0.3–0.5 Å/s for organic materials and 0.1 Å/s for Liq, respectively. After the deposition of the organic layers without a vacuum break, the Al as cathode was deposited at curves. The current density values of devices C and D with 5% and 10% Liq, respectively, doped in the ETL were at the rate of 10 Å/s. The deposition rate was controlled using a quartz crystal monitor. The emitting area in the pixel of devices was 3 mm × 3 mm. The current density–voltage (*J*–*V*) characteristics of the OLEDs were measured by using a source-measure unit (Keithley, model-236) with DC voltage. The optical and electrical properties of the OLEDs, such as the luminance (*L*), electro-luminescence (EL) efficiencies, Commission Internationale de L'Eclairage (CIE) coordinates, and EL spectra characteristics, were analyzed using a chromameter (Konica Minolta, CS-1000). The lifetime property was measured using the OLED lifetime test system (McScience, M6000) under a constant electric current. All measurements were carried out under ambient conditions at room temperature.

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3. RESULTS AND DISCUSSION

The device structure and energy diagram are shown in Figure 1. TCTA and TPBi function as both the charge-transporting layer (HTL and ETL, respectively) and triplet exciton-blocking layer (TEBL). Four types of OLEDs (Devices A∼D) with different Liq doping concentration were fabricated to investigate their charge transport ability on doping concentrations of Liq in ETL. The standard device structure was device A without Liq in ETL (30 nm).

Devices B, C, and D were fabricated with Liq as the key material were 3, 5, and 10% doped in ETL (30 nm), respectively. Generally, Liq is one of the organometallic complexes that have been demonstrated to adjust electron injection, which is because of the low binding energy

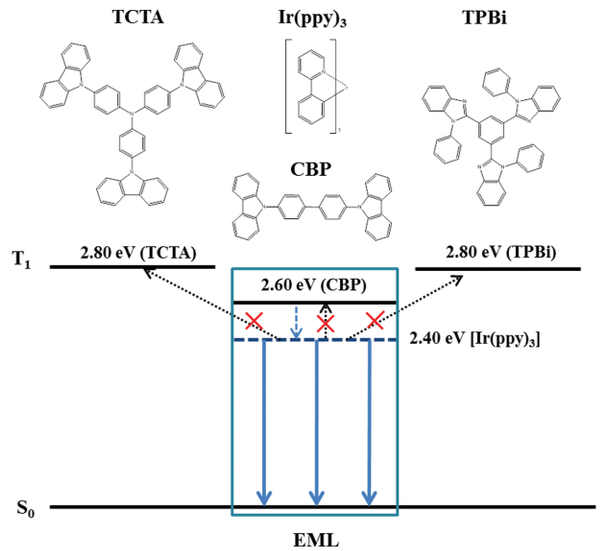

Fig. 2. Chemical structures and triplet energy level diagram of TCTA, CBP, TPBi, and Ir(ppy)$_3$. Path of exothermic energy transfer in EML and exciton confinement between TCTA and TPBi is showed.

between Li and quinolate ligand. When the Liq is doped in ETL, electrons can be easily injected from the cathode into the lowest unoccupied molecular orbital (LUMO) of mixed ETL instead of the TPBi alone. In addition, when Liq exists as a thin layer between the ETL and the cathode, it is possible to inject the carriers. On the other hand, a thick Liq layer reduces carrier transport because it has an insulating property with a high dielectric constant.[12–14] Thus, we expected that a suitable Liq doped in the ETL would easily lead to the effective injection of electrons from the cathode to the ETL.

Figure 2 shows the chemical structures and the triplet energy level diagram of TCTA, CBP, TPBi, and Ir(ppy)$_3$. As can be seen in Figure 2, it was supposed that the possible triplet energy (T_1) transfer path for emitters in

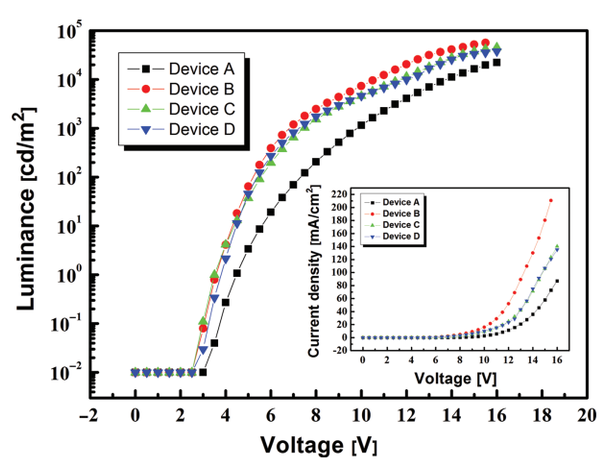

Fig. 3. Luminance–voltage (Inset: current density–voltage curves) of green phosphorescent OLEDs.

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the EML, TCTA and TPBi were inserted between HTL and EML, and between EML and ETL for efficient triplet exciton confinement, respectively, because the T_1 of both TCTA (2.80 eV) and TPBi (2.80 eV) were higher than that of $Ir(ppy)_3$ (2.40 eV), which means that efficient exothermic energy transfer was maintained in the EML.[15]

Figure 3 shows the luminance (L)–voltage (V) characteristics of green phosphorescent OLEDs with diverse ETL structure. The turn-on voltages of devices B, C, and D were lower than that of the device A. Hence, the turn-on voltage was reduced by doping a small amount of Liq in ETL. It was also assumed to have good interfacial contact by Liq molecules between the cathode and the ETL. The luminance values of devices B, C, and D were higher than that of device A within all voltage ranges. As shown in the energy band diagram (Fig. 2), easier electron injection from the cathode was expected for the Liq-doped ETL than for the non-doped ETL because of the low LUMO level of Liq. These results showed that a charge balance between holes and electrons was enhanced by doping a suitable Liq in EML. Furthermore, the effects of exciton confinement were increased because of TCTA and TPBi as TEBL.

The inset of Figure 3 shows current density–voltage curves. The current density values of devices C and D with 5% and 10% Liq doped in the ETL were decreased because of the low electron transporting properties of Liq and the obstruction of electrons movement by the existence of many shallow traps in the Liq molecules. These results suggested that an optimal Liq doping ratio would enable the production of OLEDs with excellent performance. These results affected power efficiency (PE) as shown in Figure 4(a).[17] The maximum power efficiencies of devices A, B, C, and D were 34.64, 34.82, 57.39, and 31.93 lm/W, respectively. Device C with 5% Liq doped in ETL, showed the best power efficiency.

Figure 4 shows power efficiency (PE), luminous efficiency (LE), and quantum efficiency (QE)-luminance curves. Device C shows the best luminous efficiency and quantum efficiency value at 65.76 cd/A and 20.03%, respectively. As expected, TCTA and TPBi as TEBL contributed to increasing the efficiency, as shown in the energy level diagrams in Figures 1 and 2. More importantly, the mixed ETL structure by suitable Liq molecules significantly reduced the efficiency roll-off of the fabricated devices at high luminance value.[16]

Figure 5 shows the lifetime curves of the four-OLEDs with diverse ETL under constant current density. Device A shows the shortest lifetime, but the other devices show gradually increased lifetimes. The results showed that the use of a proper Liq doped ETL as an interface modification

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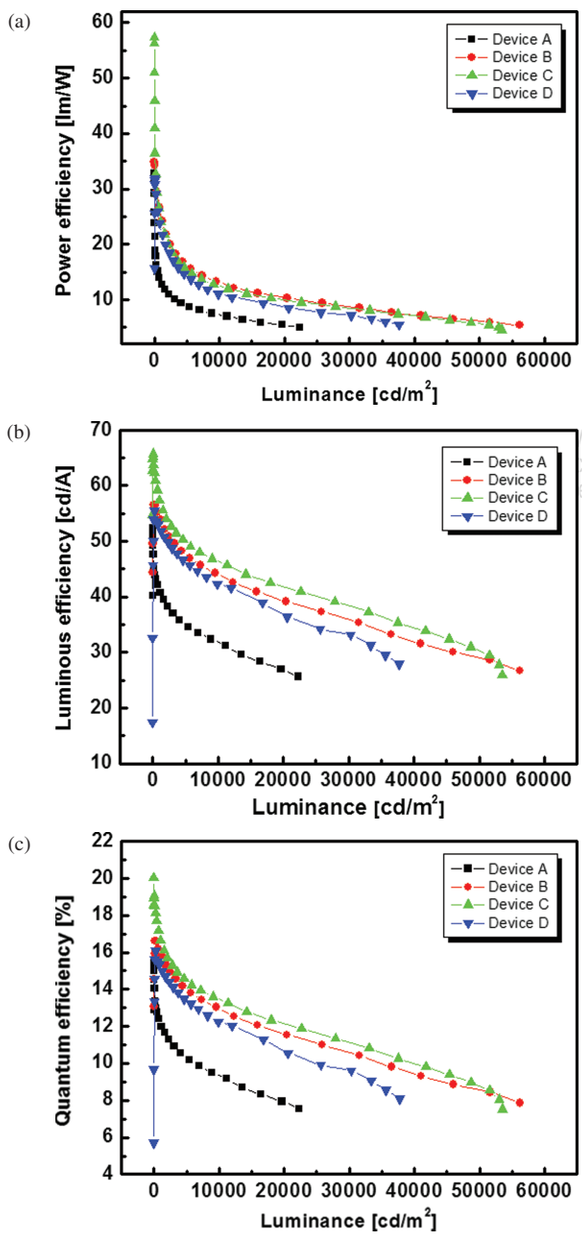

Fig. 4. (a) Power efficiency (b) luminous efficiency, and (c) quantum efficiency-luminance curves of green phosphorescent OLEDs.

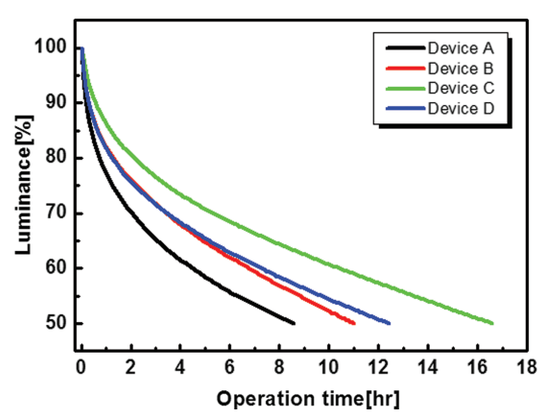

Fig. 5. Luminance change on operation time under constant current density for green emission.

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Table I. Various EL performances of all OLEDs including maximum luminance, luminous efficiency, power efficiency, quantum efficiency, CIE_{XY} coordinates, and lifetime.

Device	V_{on}^{a} [V]	L^{b} [cd/m^2]	LE^{c} [cd/A]	PE^{c} [lm/W]	QE^{c} [%]	τ^{d} [hr]
Device A	4.0	22330	52.34	34.65	15.44	8.57
Device B	4.0	56180	56.58	34.82	16.62	11.00
Device C	3.0	53480	65.76	57.39	20.03	16.58
Device D	3.5	37680	55.47	31.93	16.07	12.41

Notes: [a]Turn-on voltage; [b]Maximum luminance; [c]Maximum values; [d]Lifetime at 50% of initial luminance.

layer significantly reduced operating voltage and improved both efficiencies and lifetime. The EL performances of fabricated green phosphoresent OLEDs are summarized in Table I.

4. CONCLUSION

We clearly demonstrated electrical properties, such as driving voltage, efficiencies, and lifetime of green phosphorescent OLEDs, which were improved by the modification of the electron transport layer and the efficient exciton confinement system within the emitting layer. In particular, electrons can be easily injected by improved interfacial contact from cathode into LUMO of mixed ETL when a suitable Liq adjusts an electron injection barrier at ETL. The higher triplet energy states of TCTA and TPBi as TEBL also showed efficient exciton confinement, which directly affected the devices' stability in green phosphorescent OLEDs with suitable Liq doping. Consequently, device C with 5% Liq doped in ETL showed the most improved EL performance among the other devices.

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