Efficient Organic Light-emitting Diodes by Insertion a Thin Lithium Fluoride Layer with Conventional Structure

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Abstract

Insertion of a thin lithium fluoride (TLF) layer between an emitting layer (EML) and an electron transporting layer has resumed in the developement of a highly efficient and bright organic light-emitting diode (OLED). Comparing with the performance of the device as a function of position with the TLF layer in tris-(8-hydroxyquinoline) aluminum (Alq_3), we propose the optimal position for the TLF layer in the stacked structure. The fabricated OLED shows a luminance efficiency of more than 20 cd/A, a power efficiency of 12 lm/W (at 20 mA/cm^2), and a luminance of more than 22 000 cd/m^2 (at 100 mA/cm^2), respectively. We suggest that the enhanced performance of the OLED is probably attributed to the improvement of carrier balance to achieve a high level of recombination efficiency in an EML.

Keywords : Organic light-emitting diodes (OLEDs), Carrier injection, Thin Lithium Fluoride (TLF) Layer, recombination efficiency

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention due to their potential applications in mobile, large-area full-color flat-panel displays.[1, 2] However, the stability and electric performance of OLEDs remain to be lower than commercial inorganic semiconductor light-emitting devices.[3] A major problem of OLEDs is the thermal degradation caused by excessive current during operation.[3, 4] It therefore, is important, to balance the number of holes and electrons injected into an emitter layer (EML) to archive a high level of recombination efficiency. However, in tris-(8-hydroxyquinoline) aluminum (Alq_3)-based OLEDs that simultaneously use an EML and an electron transporting layer (ETL), the initial electron-hole recombination process is made to occur near between the hole transport layer (HTL) and the EML interface, and then the injected hole from anode diffuse from the EML into the ETL. Finally, light is generated by a direct electron-hole recombination inside the ETL because of different levels of electron-hole mobility and density.[5], [6]

Generally, to prevent the above two mentioned problems, and to improve the carrier injection, and recombination efficiency, OLEDs were fabricated with various methods such as insertion of carrier blocking layers, using triplet emitters, doping processes by p-, n-type dopants, and metal and thin insulator cathodes.[7-11] Here, one of the biggest problems is that layers with a small molecular weight are processed by vacuum evaporation, and it is generally observed that it takes a longer processing time to introduce an additional organic layer. Especially, in the doping process with co-evaporation system, it is hard to maintain the ratio within the range of 0.1 mol % to 1 mol %.[5] A thin insulating layer, especially the lithium fluoride (LiF),[12] is a typical material used to improve the performance of the device as it lowers the lowest unoccupied molecular orbital (LUMO) level in the Alq_3 layer.[13, 14] Other researchers have found that the highest occupied molecular orbital (HOMO) level can be lowered by depositing LiF on an Alq_3 layer before the Al deposition.[15] Kido *et al.*[16] found that devices with an Li-doped Alq_3 anion show lower barrier height for electron injection and enhanced conductivity

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of an Li-doped EML by co-evaporation.

In this work, we present the characteristics of highly efficient and bright OLEDs by inserting of a thin lithium fluoride (TLF) layer between an EML and an ETL with conventional OLED structure furthermore without doping processes. This concept is based on the assumption that the HOMO level can be lowered by band bending, and that the band bending is induced by the different functions of the Alq_3 layer and the LiF layer and consequently, the lowering of the LUMO level. As a result, it enhances the electron injection, carrier balance to achieve a high level of recombination efficiency. As the performance of the device depends on the position of the TLF layer in the Alq_3, we first, investigated the optimal position in which the TLF layer improves the electron injection, carrier balance, and recombination efficiency.

2. Experiments

For the structure of the test device, the organic layers composed of copper phthalo-cyanine (CuPc) as a hole injection layer, [N, N`-di(naphthalene-1-yl)-N,N`-diphenyl-benzidine] (α-NPD) as a HTL, and Alq_3 as an ETL. The Alq_3 layer is also the one in which electroluminance process take place. For the anode, we used indium-tin-oxide layer coated onto a glass substrate, and photo-lithographiclly defined an active area of 10 mm × 10 mm. For the cathode, a 1 nm layer of LiF was deposited on top of the ETL. Finally, a 120 nm layer of Al electrode was deposited without breaking vacuum.

Table I shows the structures of each layer and the position of the TLF layer in the Alq_3. The specially designed devices with the light emission peak of 530nm had a total thickness of the Alq_3 of 60 nm and inserted the TLF layer in the Alq_3 to control the thickness of the EML and the ETL with the thickness of the EML, varying from 10nm to 50nm. The thickness of the EML layer was fixed at 1 nm. All layers were deposited by a thermal evaporation method in a ultimate vacuum pressure of around 2.0×10^{-7} torr, and the layers were deposited at rates of 1.0 Å/sec and 10.0 Å/sec, respectively. The electrical properties and operating characteristics were measured using a Keithley 237 SMU unit, hand-held Minolta luminance meter CS-1000, and an Oriel Spectrograph MS125 at room temperature.

Table I. The layer structures of the OLEDs.

Device No.	Layer structures						
	HIL (nm)	HTL (nm)	EML (nm)	TLF (nm)	ETL (nm)	LiF (nm)	Cathode (nm)
A	3	30	0	0	60	1	120
B	3	30	10	1	50	1	120
C	3	30	20	1	40	1	120
D	3	30	30	1	30	1	120
E	3	30	40	1	20	1	120
F	3	30	50	1	10	1	120

3. Results and discussion

Fig. 1 shows the current density-voltage (J-V) characteristics which are extremely sensitive to the position of the TLF layer in the Alq_3. Devices with a TLF layer exhibit two distinct types of behaviours as a function of the layer's position in the Alq_3. For the EML with thinner than 30 nm, the J-V characteristics show much higher currents at lower voltage. However, because the EML is thicker, the voltage is much higher than the voltage of control device A at the same current level. Of all the devices, device C, which has an EML of 20 nm, showed the highest luminance because it has the highest current density of the devices as clearly shown in Fig. 2. Devices B and C show a turn-on voltage for emission (at 1 cd/m^2 of luminance) of approximately 2 V and 3 V, respectively. However, the

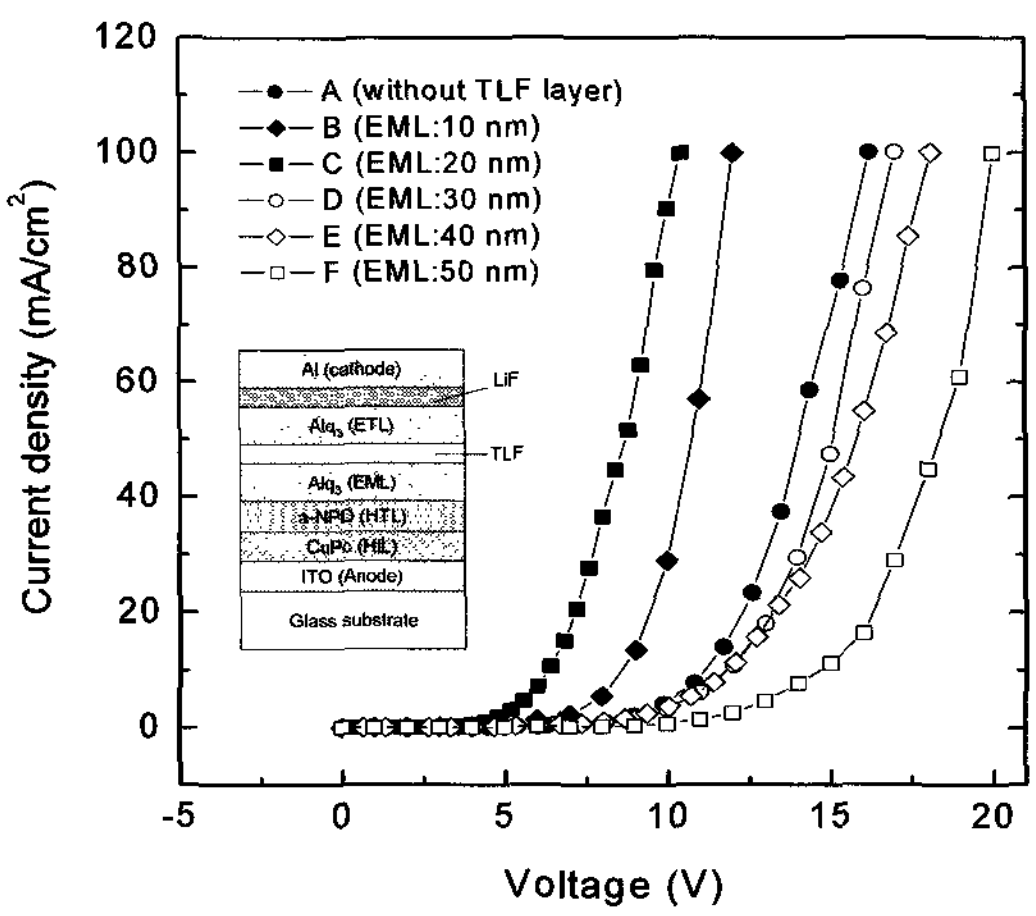

Fig. 1. Current density (J) versus applied voltage (V) for a series of emitting layers with various thicknesses by the insertion of a TLF layer. The symbols of the circle, diamond, square, empty circle, empty diamond, and empty square represent the emitting layer thicknesses of 0 nm, 10 nm, 20 nm, 30 nm, 40 nm, and 50 nm, respectively.

other devices with an EML of up to 30 nm gradually increased over that of device A. The device C, in particular, requires a driving voltage of approximately 10 V to generate a current density of 100 mA/cm^2 and shows a turn-on voltage of around 2 V at 1 cd/m^2. Although the J-V graphs showed a shift to the higher voltage side as the thickness of the EML increased, the devices with the TLF layer showed better lumi-nance characteristics than the device A without the TLF layer.

The current density is mainly determined by the carrier mobility, the conductivity of the organic layer, and the barrier height.[16] For devices with a LiF/Al cathode, we assumed the following: the barrier height for the electron injection from the electrode to the ETL is supposed to be the same as in devices that use the TLF layer. Therefore, the LUMO level is lowered by the TLF layer in the Alq_3. As a result, there is high mobility or conductivity of the electron in the EML and the electron injection, carrier balance, and recombination efficiency of the devices are improved. However, the conductivity of the EML diminishes as the TLF layer is positioned closer to the metal cathode. The J-V graphs show a gradual shift to the right side as the thickness of the EML increases.

Fig. 2 shows that the luminance of all devices increases linearly as the current density increases. When the thickness of an EML increased from 10 nm to 50 nm at the current level of 100 mA/cm^2, the luminance changed to 3 500 cd/m^2 for device A, 12 790 cd/m^2 for device B, 22 350 cd/m^2 for device C, 8 090 cd/m^2 for device D, 6 140 cd/m^2 for device E, and 5 190 cd/m^2 for device F. Device C attained a brightness of 1 000 cd/m^2 but only at 5 mA/cm^2.

Fig. 3(a) shows that the luminance efficiencies for devices A to F at 20 mA/cm^2 are 3.5 cd/A, 12.8 cd/A, 22.4 cd/A, 8.1 cd/A, 6.2 cd/A, and 5.2 cd/A, respectively. The devices with a TLF layer have a higher luminous efficiency than device A. Fig. 3(b) shows the luminance and luminance efficiency as a function of the position of the TLF layer at the same current (100mA/cm^2). The position of the TLF layer in Alq_3 strongly affects the luminance and efficiency properties and also, the device C shows that the electron injection, carrier balance, and re-combination efficiency are enhanced by suitable thickness of the EML. Furthermore, the power efficiency of device C has the highest value of all the devices shown in Fig. 4.

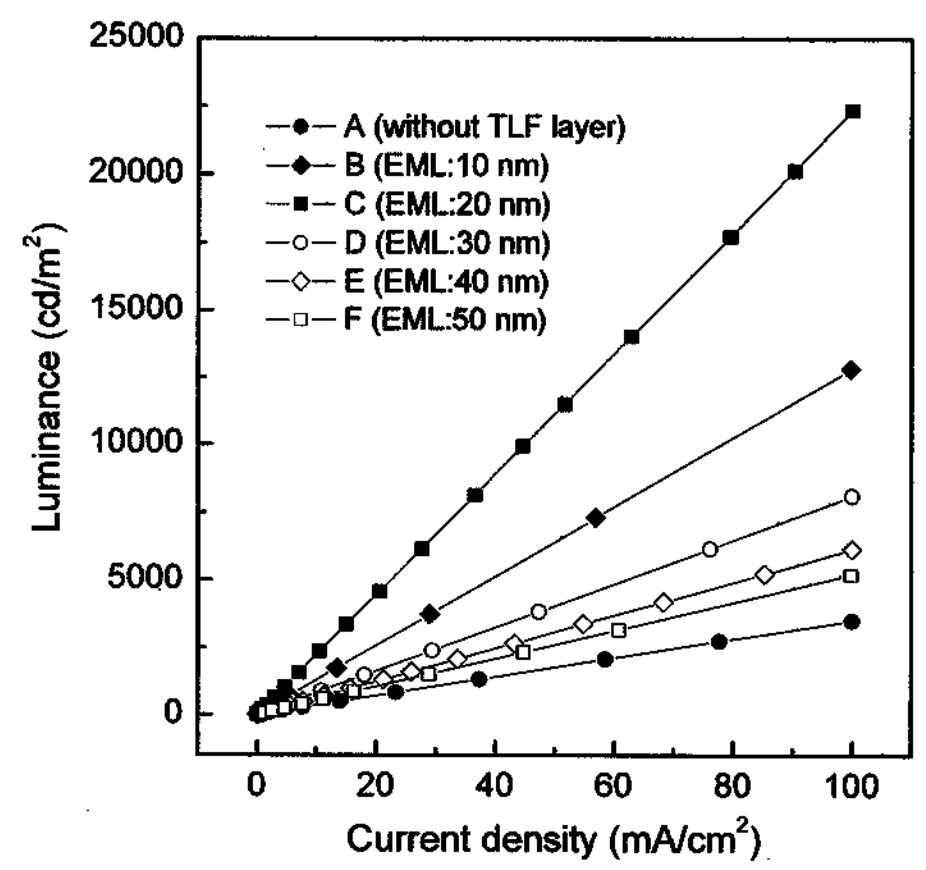

Fig. 2. Luminance (L) - Drive current density (J) with the emitting layer thickness varying from 0 nm to 50 nm. The symbols of the circle, diamond, square, empty circle, empty diamond, and empty square represent the emitting layer thicknesses of 0 nm, 10 nm, 20 nm, 30 nm, 40 nm, and 50nm, respectively.

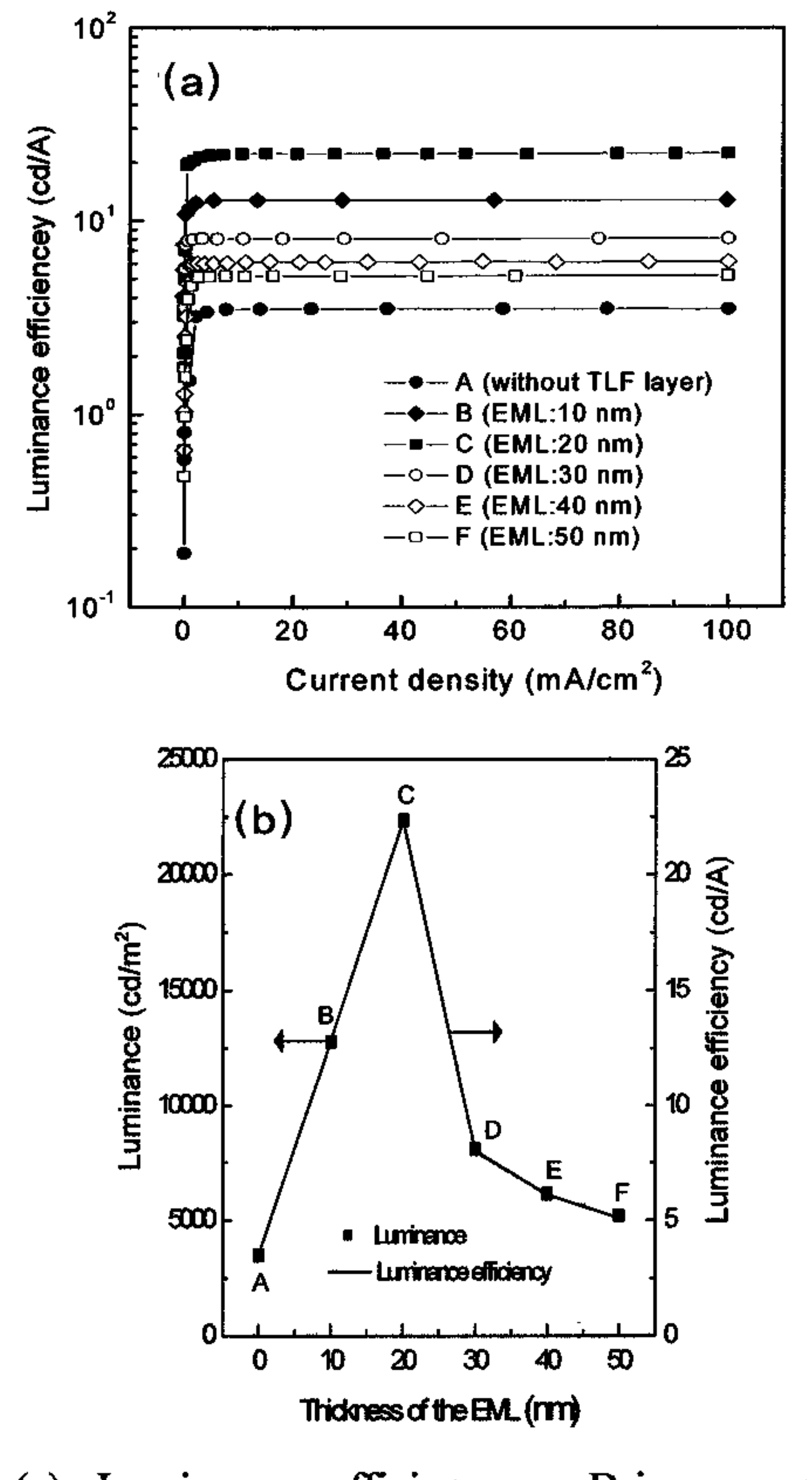

Fig. 3. (a) Luminance efficiency - Drive current density characteristics with the emitting layer thickness varying from 0 nm to 50 nm. The symbols of the circle, diamond, square, empty circle, empty diamond, and empty square represent the emitting layer thicknesses of 0 nm, 10 nm, 20 nm, 30 nm, 40 nm, and 50 nm, respectively. (b) This plot shows luminance and luminance efficiency as a function of the position of the TLF layer in the Alq_3 at 100mA/cm^2

Table II shows the summarized results. The results show that the electron injection, carrier balance, and recombination efficiency decrease when the thickness of the EML increases by more than 30 nm, though devices D, E, and F are more efficient than device A. The lower efficiency is probably due to the quenching of photo-luminescence [17] with the wide thickness of an EML by the TLF layer. The initial carrier recombination occurs within about 5 nm of the interface between of the HTL and EML, and is then diffused from an EML to an ETL.[5] The TLF layer prevents this phenomenon by lowering the barrier height, and by improving the electron injection and recombination efficiency.

Table 2. The performance comparison of the devices with various thickness of emission layer.

Device No.	Turn-no Voltage (V) at 1 cd/m^2	Luminance (cd/m^2) at 100 mA/cm^2	Luminance Efficiency (cd/A) at 20 mA/cm^2	Power Efficiency (lm/W) at 1 000 cd/m^2
A	5	3 500	3.5	0.8
B	3.2	12 790	12.8	4.7
C	2.5	22 350	22.4	12.2
D	5.2	8 090	8.1	2.0
E	7.0	6 140	6.2	1.4
F	7.2	5 190	5.2	0.9

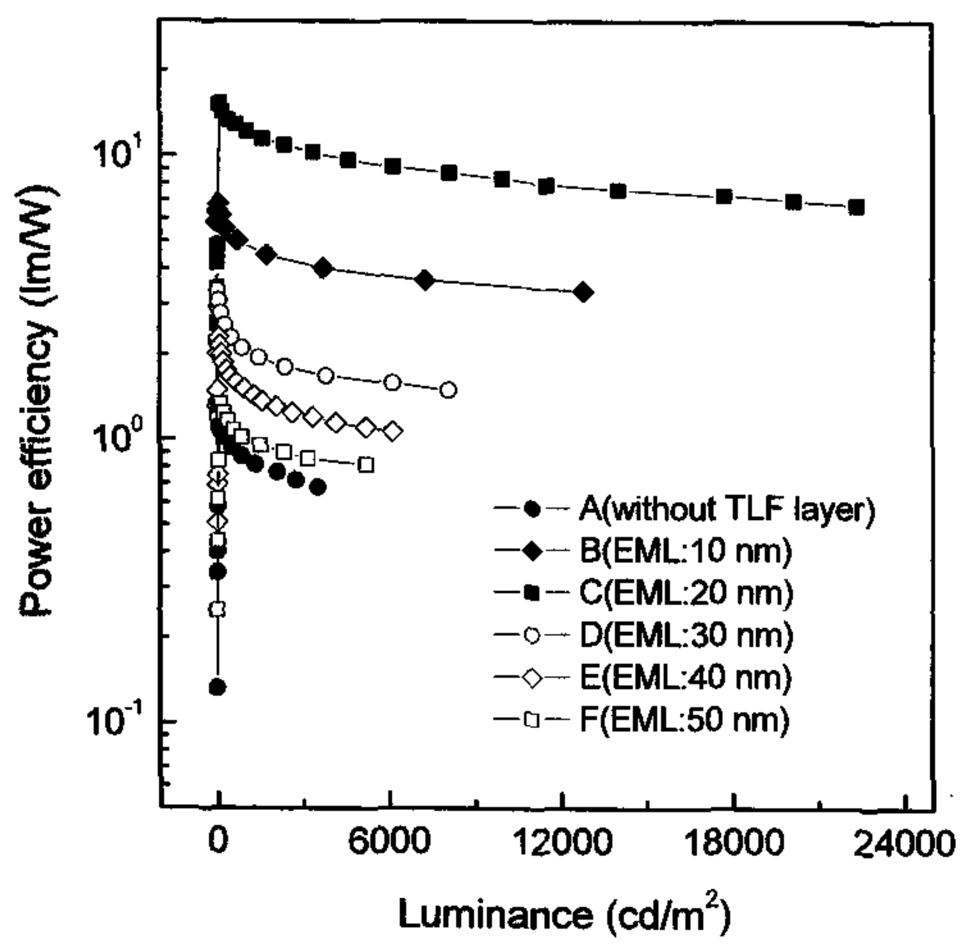

Fig. 4. Power efficiency characteristics as a function of luminance with the emitting layer thickness varying from 0 nm to 50 nm. The symbols of the circle, diamond, square, empty circle, empty diamond, and empty square represent the emitting layer thicknesses of 0 nm, 10 nm, 20 nm, 30 nm, 40 nm, and 50 nm, respectively.

The mechanism to improve the device performance is based on the following theory; The highest occupied molecular orbital (HOMO) level can be lowered by band bending, and that the band bending is induced by the different functions of the Alq_3 layer and the TLF layer, which leads to the lowering of the lowest unoccupied molecular orbital (LUMO) level. The lowering LUMO level infers a shift of the Fermi level towards the Alq_3 LUMO that is indicative of an increase in the carrier density in the bulk [18]. It has been understood that the LUMO level lowering induces the lowering of the electron-injection barrier and the enhan-cement of OLED performance. Also, a hole accumulated in the interface of Alq_3 and LiF. Therefore, a thin LiF layer plays a role of improving the carrier balance property. For a α-NPD/Alq_3 bilayer device, it is well known that α-NPD/Alq_3 interface possesses an electron injection barrier of about 0.6 eV from Alq_3 to α-NPD, and a hole injection barrier of about 0.3 eV from α-NPD to Alq_3. Lowering the LUMO and HOMO level improves the electron injection into EML and accumulates a hole at the interface between α-NPD and Alq_3. Thus, the high local charge density at the interface between α-NPD and Alq_3 increases the recombination probability of the electrons and holes.

From this study, device C exhibits the highest luminance efficiency of all the devices. Thus, we can conclude that the optimum thickness for an EML is 20 nm and for an ETL 40 nm.

4. Conclusions

In this paper, we have demonstrated the high efficiency and brightness characteristics of OLEDs by inserting the TLF layer in different positions in Alq_3 with conventional structure.

In an ideal condition, the current density, luminance, and efficiency are determined by the recombination rate. Electron-hole recombination in organic materials is thought to follow the Langevin bimolecular recombination model [19], [20]. In the Langevin model, the recombination current from bipolar equilibrium carrier densities N_e and N_p with carrier mobilities μ_e and μ_p is given by

$$R = \gamma N_e N_p = e(\mu_e + \mu_p) / \varepsilon N_e N_p$$

where γ is called the Langevin recombination coefficient. As the recombination coefficient gradually increases, the current density decreases owing to a decrease in the neutralization of the space charge. The recombination current decreases as well because of the lower current density, but the efficiency increases owing to fewer carriers being collected without their undergoing recombination. Therefore, efficiency is strongly dependent on the recombination rate.

In most realistic cases, when the mobilities of two carriers are different, recombination takes place closer to the electrode injecting the carrier with the lowest mobility. The TLF layer prevents this phenomenon by lowering the barrier height and by improving electron injection and recombination efficiency.

Another reason is that the effective conductivity and density of LiF may vary according to the position of LiF in the Alq_3. The diffusion length of LiF and conductivity in the organic bulk layer is varied by the thickness of organic layer. As the thickness of organic layer becomes thicker than diffusion length of LiF, the high local field generated by accumulated space charges exists around cathode side. Therefore, recombination zone shift to metallic electrodes and the position of LiF in the Alq_3 may affect the device performance and quench the excitons. However, as the most investigated buffer in OLEDs, LiF shows quite different optimal thickness at different interfaces, the range of which varies from several angstroms to several nanometers.

It is suggested that the enhanced performance of the OLED with the optimal thickness of an EML and ETL by TLF layer is attributed to the improvement of the electron injection, carrier balance, and recombination efficiency in an EML. Finally, with simple fabrication, the device structure by the excellent TLF layer enables highly efficient and bright OLEDs to be realized.

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