Efficiency of a blue organic light-emitting diode enhanced by inserting charge control layers into the emission region*

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We demonstrate high current efficiency of a blue fluorescent organic light-emitting diode (OLED) by using the charge control layers (CCLs) based on Alq_3. The CCLs that are inserted into the emitting layers (EMLs) could impede the hole injection and facilitate the electron transport, which can improve the carrier balance and further expand the exciton generation region. The maximal current efficiency of the optimal device is 5.89 cd/A at 1.81 mA/cm^2, which is about 2.19 times higher than that of the control device (CD) without the CCL, and the maximal luminance is 19.660 cd/m^2 at 12 V. The device shows a good color stability though the green light emitting material Alq_3 is introduced as the CCL in the EML, but it has a poor lifetime due to the formation of cationic Alq_3 species.

Keywords: organic light-emitting devices, charge control layer, current efficiency

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1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention because of their many excellent merits in flat panel display and solid-state lighting since Tang and Vanslyke[1] first reported on an organic electroluminescent device with multilayer structure in 1987.[2–5] No matter whether they are applied to display or illumination, the obtainment of white light is particularly important. As is well known, a blue light-emitting device with excellent electroluminescence (EL) performance is a crucial factor for the development of the white light. It is universally recognized that device efficiency is relevant to the properties of carrier injection and transport as well as the balance between the holes and electrons in the emitting zone.[6,7] In order to enhance the EL performances of a device significantly, various approaches are used to promote device efficiency,[8–10] such as doping the dye in the matrix to form the effect of p/n type doping, inserting buffer layers between ITO anode and hole transport layer (HTL) or LiF/Al cathode and electron transport layer (ETL), fabricating charge control layers (CCLs) as well as multiple quantum wells structure to control the carrier injection and transport in the emitting layer (EML). Among these approaches, inserting the CCL into the EML is the most effective method and easy to operate. For example, Park *et al*.[9] have fabricated a series of red phosphorescent devices each with a multiple quantum well structure, in which the CCL is used as the potential barrier for both electrons and holes. The device with electron transporting material $Bepp_2$ serving as the CCL shows that it has a maximal current efficiency of 12.4 cd/A, and maximal EQE of 14.8%. Given the excellent EL performances of devices with CCLs, the study of blue fluorescent devices with CCLs inserted into the EMLs has not been reported until now.

In this paper, we demonstrate an efficient blue OLED which is realized through adapting Alq_3 as the CCL with the optimal position inserted into the EML to balance the holes and electrons and widen the emitting region where excitons are formed. Also, we illustrate the effect of the CCL structure on device performance and investigate the mechanism for the rapid degradation of current efficiency.

2. Experiment

We conduct an experiment to validate the effect of the CCL structure on the EL performances of a blue device. The control device (CD) has the structure of ITO/NPB (40 nm)/DNCA (40 nm)/Bphen (30 nm)/LiF (0.6 nm)/Al (120 nm), which has no CCL inside the EML deliberately, and Alq_3 used as the CCL is inserted into the emitting layer (DNCA) of the devices A, B, C, and D with a structure of

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ITO/NPB (40 nm)/[DNCA (x nm)/Alq_3 (5 nm)/DNCA (40–x nm)]/Bphen (30 nm)/LiF (0.6 nm)/Al (120 nm), in which the values of x are 10 nm, 20 nm, 30 nm, and 35 nm, respectively. We fix the thickness of Alq_3 layer to be 5 nm initially in order to obtain its optimal position. In general, N,N'-bis (naphthalen-1-yl)-N,N'-bi-s (phenyl)-benzidine (NPB) and 4,7-diphnenyl-1,10-phe-nanthroline (BPhen) are used as HTL and ETL respectively, in view of their similar carrier mobility. A novel blue fluorescent material derivation of N^6,N^6,N^{12},N^{12}-tetrap-tolylchrysene-6,12-diamine (DNCA) is used as EML, in which the electron transporting material tris (8-hydroxyquinoline) aluminum (Alq_3) is used as the CCL. The structures of the devices are shown in Fig. 1. All the organic layers and LiF and Al are deposited on an indium-tin-oxide (ITO) coated glass substrate sequentially without breaking vacuum environment at a base pressure lower than 2×10^{-4} Pa. The evaporation rates are 0.2 nm/s–0.4 nm/s, 0.07 nm/s, and 1 nm/s for the organic layers, the LiF layer, and the Al cathode, respectively. Luminance–current density–voltage and electroluminescent characteristics of the devices are measured by a Keithley model 2400 programmable voltage–current source and a PR650 spectrum scan spectrometer. All the measurements are carried out in ambient atmosphere at room temperature.

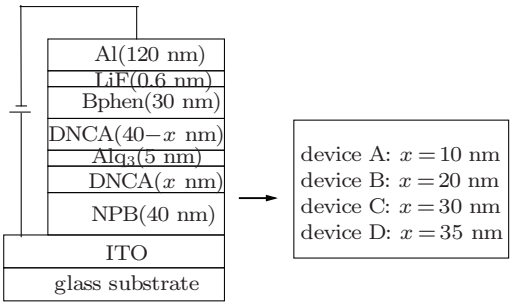


Fig. 1. Structures of the devices.

3. Results and discussion

It is widely accepted that the carrier mobility of hole transport material is much greater than that of electron transport material for general organic materials.[11] This unbalance will depress the recombination rate of hole–electron pairs in EML and lead to the rapid degradation mainly induced from quenching when the recombination zone is close to the metal electrode. Therefore, the carrier balance is a crucial factor for achieving high device efficiency. The energy level diagram of the device is shown in Fig. 2; the highest occupied molecular orbital (HOMO) levels are −5.4 eV, −5.2 eV, −5.7 eV, and −6.4 eV while the lowest unoccupied molecular orbital (LUMO) levels are −2.4 eV, −2.6 eV, −3.0 eV, and −3.0 eV for NPB, DNCA, Alq_3, and BPhen, respectively.

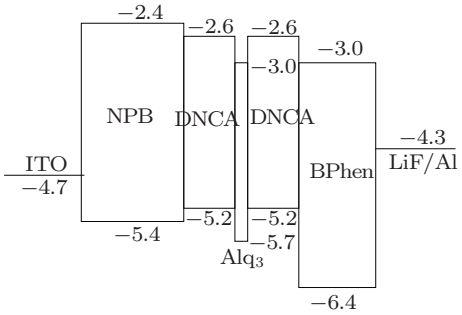


Fig. 2. Energy level diagram of the device, (units in eV).

For the CD, a potential well of 0.2 eV occurs at the NPB/DNCA interface, which indirectly facilitates the injection of holes into the EML. In contrast, there is an energy barrier about 0.4 eV at the DNCA/BPhen interface, which obviously depresses the injection of electrons from BPhen into DNCA. In addition, blue emitting material DNCA is prone to favoring holes transporting relatively. It is expected that this unbalance will largely decrease the recombination rate of holes and electrons and consequently result in the poor performance of device. To achieve the well carrier balance in the recombination zone, we employ Alq_3 used as the CCL which has suitable energy levels in EML.

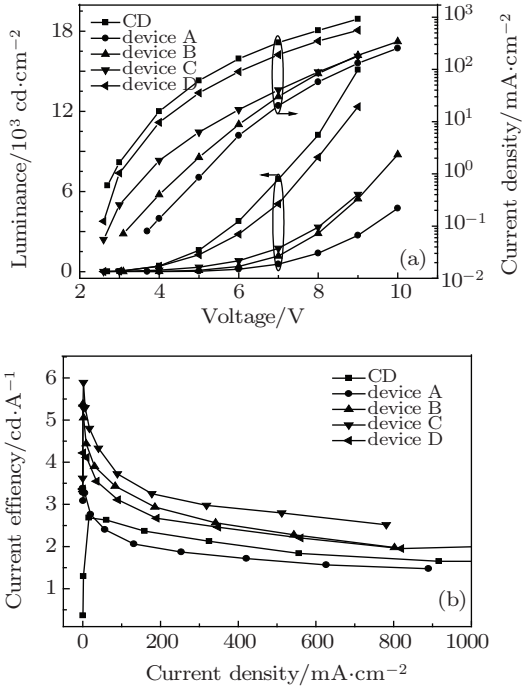


Fig. 3. EL performances for the CD and devices with the different insertion positions of the CCL. Panel (a) shows the dependences of current density and luminance on voltage and panel (b) exhibits the dependences of current efficiency on current density for several devices.

Figures 3 (a) and 3 (b) show the curves of luminance and current density versus voltage and those of the current efficiency versus current density for devices with various insertion positions of CCLs in EMLs, respectively. It is indicated

that the devices with CCLs exhibit lower current densities and lower luminances but higher current efficiencies than those with the CD; the maximal current efficiencies are 3.37 cd/A, 5.38 cd/A, 5.89 cd/A, and 4.22 cd/A for the devices with the corresponding locations of CCLs at 10 nm, 20 nm, 30 nm, and 35 nm far from the anode, respectively. By employing the CCL in the EML, a hole barrier of about 0.5 eV will significantly resist the injection of holes from DNCA into Alq_3. Therefore, the accumulation of holes at the DNCA/Alq_3 interface would occur as a result of the higher hole barrier and the weak hole-transporting property of Alq_3. While the number of electrons injected from the cathode is almost the same as that of the CD, the transporting ability is increased, owing to the existence of the CCL. Additionally, the accumulation of holes may create an internal electric field, whose direction is contrary to that of the driving electric field, which will further restrain the injection and transport of holes as well as recombination rate in two emitting regions.[12] The farther away from the anode the insertion position, the weaker the internal electrical field becomes. We can find that the values of current density (J) and luminance (L) of the devices first decrease with the CCL increasing compared with those with the CD under a certain driving voltage, then increase gradually with the value of x increasing from 10 nm to 35 nm. As shown in Fig. 3(b), the maximal current efficiency and luminance of device are 5.89 cd/A and 19660 cd/m^2, respectively, when the CCL is located at 30 nm far from the anode. Apparently, the current efficiency of the optimal device above is 2.19 times higher than that of the CD (2.68 cd/A), which elucidates that the optimal position is obtained where the carrier balance and a high recombination rate are assured. With the continuous moving of the CCL away from the anode, the significant decline of current efficiency is ascribed to the destruction of charge balance. Additionally, the current efficiency of the device not only depends on the recombination rate of the charge carriers, but also relates to extension of the emitting region where excitons are formed. By utilizing the structure of the CCL, the original emitting zone is broadened and separated by inserting Alq_3 into the EML, consequently the concentration quenching is avoided. Moreover, it should be noted that the device efficiency sharply decreases with current density increasing compared with that of the CD. For example, the peak efficiencies of the optimal device C and the CD decrease rapidly from 5.89 cd/A (at 1.81 mA/cm^2), 2.68 cd/A (at 15.69 mA/cm^2) to 3.25 cd/A (at 177.68 mA/cm^2), 2.36 cd/A (at 159.34 mA/cm^2), respectively. Obviously, employing the CCL structure in the device increases the efficiency roll-off more than three times, which can be illustrated by the degradation mechanism of Alq_3, as Hany *et al*.[13] have confirmed that the unstable cationic Alq_3 species formed by capturing the holes is a primary factor for the current efficiency degradation. In fact, the introduction of the CCL has dual functions: one is that it blocks the hole injection and promotes the electron migration, further equalizing the charge mobility to realize an excellent charge balance, and the other is that it expands the distribution zone of excitons to avoid the concentration quenching.[14]

Figure 4 shows the normalized EL spectra of the devices with CCLs at various positions at a fixed bias of 8 V. It can be clearly seen that the emitting peak of the optimal device is located at 484 nm, but the peaks of other devices are all located at 480 nm. Compared with the dominant emitting peak of the CD (480 nm), a negligible red-shift, which may come from the exciplex emission, occurs for the optimal device.[15–17] At the same time, it is noted that there is no obvious emitting peak of Alq_3 for the device with CCL inserted into the EML, so it seems that the main emission comes from the blue emitting layer rather than the thin CCL.[18] The inset of Fig. 4 reveals the CIE chromaticities of the devices fabricated in this experiment at the driving voltages ranging from 3 V to 8 V, which implies that the high color stability is successfully achieved for the device with the CCL. The red-shift of the emitting peak will appear if the CCL becomes very thick, which will provide a clue for our next research.

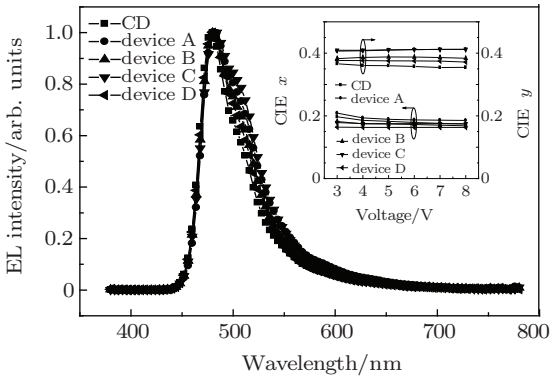


Fig. 4. Normalized EL spectra of devices with CCLs at a driving voltage of 8 V. The inset shows the CIE chromaticities of devices in a voltage range of 3 V–8 V.

4. Conclusion

In the present paper, an easy approach to the improvement of the EL performance of blue fluorescent OLED is actualized by using the CCL with optimal position in the EML. These devices with CCLs exhibit the enhanced current efficiencies and the good color stabilities contributed to the excellent carrier balance in active layers and the broadening of the emission region. The optimal device exhibits a maximal current efficiency of 5.89 cd/A, which is 2.19 times higher than that of the CD (2.68 cd/A). Our experiment may provide some valuable hints on how to achieve an excellent carrier balance in the EML, broaden the exciton distribution region and finally improve the EL performances of devices.

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