Color tunable organic light-emitting diodes by using europium organometallic complex

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Using the rare-earth special feature of a sharp emission spectrum, voltage-controlled continuous color tuning of organic light-emitting diodes is achieved. Europium(dibenzoylemethanato)$_3$ (bathophenanthroline) is used as the strategic starting point close to the red corner of the Commission International de l’Eclairage chromaticity diagram for a wide color tuning. The end point and path of the color tuning can be engineered by doping the hole-transport emitting layer with dyes. The mechanisms of color tuning have been investigated and explained by the efficiency reduction of the europium complex and the extension of carrier recombination zone with driving voltage. The effect of exciplex on the color tuning is also studied. © 2006 American Institute of Physics. [DOI: 10.1063/1.2405420]

Organic light-emitting diode (OLED) is one of the promising technologies for light display applications. In order to achieve a full-color pixel in display applications, complicated techniques have to be used to accurately fabricate three OLED structures for red, green, and blue emissions in small areas. It will be highly desirable if a single OLED can emit light with a wide range of colors, continuously tunable by changing the voltage for simplifying the fabrication techniques of multi- and full-color devices. Voltage-controlled color tuning has been reported in OLEDs using small molecules and polymers, as well as in light-emitting electrochemical cells. However, more efforts are needed to expand the tuning range and to understand the underlying mechanism.

Rare-earth organometallic complexes have the interesting features of sharp emission spectrum and theoretically high electroluminescent (EL) efficiency. Indeed, high quantum efficiency ($\eta$) of EL of 7.5% was obtained in europium (Eu) complex at low current density. In this letter, a Eu complex is used as the strategic starting point for the color tuning. The sharp red emission close to the corner of the Commission International de l’Eclairage (CIE) chromaticity diagram offers a large space for color tuning. The OLEDs containing Eu(dibenzoylemethanato)$_3$(bathophenanthroline) [Eu(DBM)$_3$]bath acting as the emitting and electron-transport (ET) layers, and $N,N'$-bis(2-naphthalenyl)-N-$N'$-bis(phenylbenzidine) (NPB) as the hole-transport layer are studied. Transient EL, current efficiency, and Eu$^{3+}$ emission $\eta$ are investigated to clarify the mechanism of the color tuning. The effects of exciplex on the color tuning are also addressed. Depending on the emission color of dyes, doping the NPB layer offers various routes of the color tuning on the CIE diagram.

The basic device structure (device A) is indium tin oxide (ITO)/NPB(40 nm)/Eu(DBM)$_3$]bath(40 nm)/Alq$_3$ (20 nm)/LiF/Al. Eu(DBM)$_3$]bath has been shown to have good ET and emitting properties in the earlier studies. The multilayer of Alq$_3$/LiF/Al acts as a composite electron-injection electrode. It should be noted that the ET properties and thus the brightness and $\eta$ of OLEDs can be further enhanced by cohosting the Alq$_3$ based ET layer although the study is out of the scope of this letter. All the organics and the LiF/Al cathode are deposited by thermal vacuum deposition at a pressure of $10^{-6}$ Torr. Transient EL was studied by applying a voltage pulse across the device. By using a monochromator for wavelength selection, the transient spectrum was detected by a photomultiplier and an oscilloscope.

The EL spectra of device A are shown in Fig. 1. At the voltage of 6 V, the EL spectrum shows the solely sharp emission from the Eu complex. At higher voltages a board emission in the shorter-wavelength region appears and its intensity continuously strengthens. Comparing with the photoluminescent (PL) spectrum of NPB, the board emission consists of two parts: one is the emission at $\sim$450 nm from NPB; the other at $\sim$500 nm can be due to either Alq$_3$ or the exciplex forming at the interface between two organic layers. To study the origin of the emission, we replace Alq$_3$ by UV emissive 2,2',2''-(1,3,5-benzinetriyl)-tris (1-phenyl-1H-benzimidazole). The results show that the emission at $\sim$500 nm still exists. This implies that it is the exciplex
emission from the interface of NPB and the Eu complex. The NPB emission becomes dominantly stronger than the exciplex emission as the voltage is further increased. As a result, continuously reversible color tuning from pure red to blue is obtained.

Two reasons may cause the distinct EL spectrum changes. One is the decrease of Eu(DBM)$_3$bath at high voltages; the other is the shift of recombination zone in the device. Transient EL has been used to understand the biexcitonic quenching and decrease of the Eu$^{3+}$ emission in the process of color tuning. Considering that interaction between two excited Eu$^{3+}$ ions causes a quenching channel in the decay process of the excited Eu$^{3+}$ ions, the transient intensity $L(t)$ violates the typical exponential decay rule and follows: $L(t) = L(0) \frac{1}{1 + K_\tau e^{t/\tau}}$.

where $\tau$ is the lifetime of the excited ions due to emissive decay, $L(0)$ is the initial emission intensity, and $K$ is the biexcitonic quench rate. Thus $\eta$ of the Eu$^{3+}$ ions is

$$\eta = \frac{1}{1 + K\tau},$$

where $\tau$ can be obtained from the transient PL and EL under weak excitation intensity. $K$ can be determined by fitting the transient EL decay data with Eq (1).

The decay of Eu$^{3+}$ ions after excitation of pulse voltages are shown in Fig. 2. We set the measured wavelength at 614 nm such that the detected signals only describe the decay of Eu$^{3+}$ ions. The inset of Fig. 2 shows the PL decay of Eu(DBM)$_3$bath characterized by N$_2$ pulse laser excitation.

The inset of Fig. 3 shows the decay of Eu$^{3+}$ ions and the measured current efficiency of device A. The results show that the two trends of reduction with increasing voltage are similar. However, the reduction of the device efficiency is more drastic than that of the Eu$^{3+}$ $\eta$, implying that the recombination zone changes. The inset of Fig. 3 shows the energy diagram of device A. At the interface of NPB and Eu(DBM)$_3$bath the energy barriers for electrons to enter NPB layer and for holes to enter Eu(DBM)$_3$bath are almost the same. Therefore the shift or extension of recomb-
Doping NPB with perylene changes the destination to C2. Consequently, the ending-color adjustable and wide-range color tuning scheme is achieved by doping the NPB layer with dyes. The exciplex emission makes the color tuning path curved instead of a straight line. In our experiments, the \( \eta \) reduction of the Eu complex and extension of carrier recombination zone at higher bias have been shown to be the major reasons for achieving the color tuning. The stability of Eu complex in OLED is still a challenge, further work of new chemically stable Eu complexes are needed in the field.

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In conclusion, making use of Eu\(^{3+}\) featuring a sharp red emission, reversible voltage-controlled continuous color tuning is achieved in the OLEDs by using Eu(DBM)\(_3\) bath as the strategic starting point close to the red corner of the CIE chromaticity diagram. The ending-color adjustable and wide-range color tuning scheme is achieved by doping the NPB layer with dyes. The exciplex emission makes the color tuning path curved instead of a straight line. In our experiments, the \( \eta \) reduction of the Eu complex and extension of carrier recombination zone at higher bias have been shown to be the major reasons for achieving the color tuning. The stability of Eu complex in OLED is still a challenge, further work of new chemically stable Eu complexes are needed in the field.