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Color tunable organic light emitting diodes using Eu complex doping

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Abstract

A voltage-controlled color tunable organic light emitting device has been demonstrated by using a co-evaporated emissive layer of NPB [(*N*,*N*′-bis(naphthalene-1-yl)-*N*,*N*′-bis(phenyl)benzidine)] and an organic Eu complex. As a result of minimized energy transfer from the host (NPB) to the guest emitter (Eu complex), this device can vary the light emission from vivid red to deep blue with increasing bias. Optimal device performance is obtained for a 20 wt.% Eu doping in NPB. This doping concentration is able to yield *x* and *y* chromaticity coordinates in the range of 0.61–0.17 and 0.31–0.12, respectively.
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Keywords: Organic light emitting diodes; Eu complex; NPB; Color tunable device; Energy transfer

1. Introduction

Achieving multiple colors from organic light emitting diodes (OLEDs) has attracted great interest for flat panel display applications [1–5]. In particular, color tunable devices are very attractive because of their potential for producing higher resolution and less complex display units. To date, tuning of the emission color in OLEDs has been achieved by varying either the voltage polarity [6–8] or the current density [9–12]. Two-color emission can be achieved by fabricating a device structure with double emissive layers of either small molecules [6,7] or polymers [8]. By switching the voltage polarity, this device type is able to confine the recombination region in either of these two separate emissive layers. However, efficiency and brightness from these devices are relatively low because of the difficulty in obtaining balanced charge injection for both forward bias and reverse bias operation. Voltage-induced color tunable devices are easier to obtain by simply mixing two polymer or small molecule emissive materials [9–11] to form a single emitter layer. However, devices fabricated with this approach generally do not switch between pure red and blue colors because of the strong energy transfer from the wider-band-gap material (responsible for blue emission) to the narrower-band-gap material (responsible for red emission).

We have previously reported color switchable rare earth doped electroluminescent inorganic (GaN) devices [13], in which the emission color can change from red (due to Eu emission) to green (due to Er emission) with the polarity of applied bias. In this letter, we report a voltage-controlled color tunable organic device which can switch the color from vivid red to deep blue by using a co-evaporated emissive layer of NPB [(*N*,*N*′-bis(naphthalene-1-yl)-*N*,*N*′-bis-(phenyl)benzidine)] and a Eu complex. As shown in Fig. 1a, the device emits red color from 5 V (turn on) to ~10 V and turns into blue emission when the voltage is $\geqslant$16 V. The true blue color of the emission at 18 V is shown in the 4th photograph in Fig. 1a after reducing the emission intensity with a gray neutral filter to prevent saturation of the photographic system.

Eu and other rare earths have characteristic sharp emission bands [14] due to the f^n orbital transitions, while

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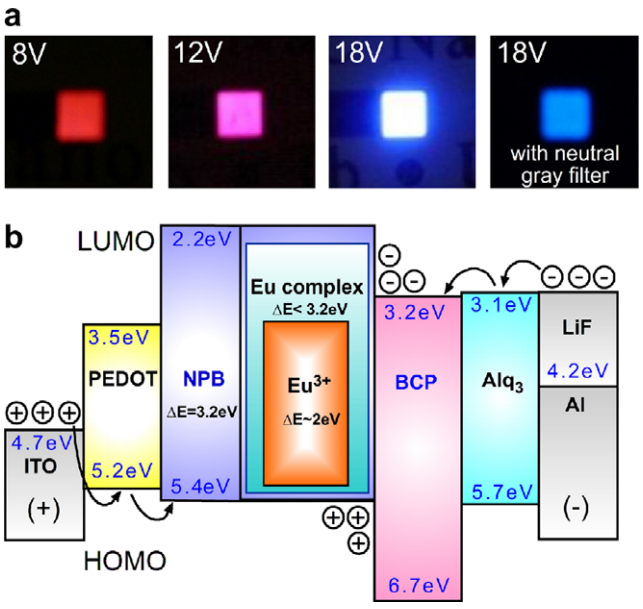


Fig. 1. Color tunable organic light emitting diode operation: (a) photographs showing emission from a 20 wt.% Eu doped device operating at various voltages (note the color change with applied voltage); (b) energy level diagram for the device structure. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

photoemission from polymers/small molecules is quite broad. Eu emits saturated red color. Organic Eu complexes exhibit high internal quantum efficiency [15,16] since the Eu ion is excited by intramolecular through-bond energy transfer from the organic ligand excited state [17,18]. Accordingly, the energy gap for Eu complex is much wider than for the regular organic red emissive materials, thus we can select the Eu complex such that it has a slightly smaller energy gap than the NPB host material. This can result in a minimized energy transfer from the blue emissive material (NPB) to the red emissive material (Eu complex).

2. Device structure and operation

The energy level diagram of the color tunable device structure is shown in Fig. 1b. Values from the literature [19–24] are used for the highest occupied molecular levels (HOMO) and the lowest unoccupied molecular levels (LUMO) of the organic materials and for the work function of the metal electrodes. Indium tin oxide (ITO) serves as the anode, PEDOT [poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate)] functions as a hole injection layer; the first NPB serves as hole transport layer and blue emitter; the second NPB layer is the host for the Eu complex; BCP [2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline] functions as a hole blocking layer; Alq_3 [tris-(8-hydroxyquinoline) aluminum] is used as an electron transport layer and LiF/Al is the low work function cathode.

Under forward bias, holes are injected from the ITO anode into the HOMO states of the organic layers and start to move toward the emitter/BCP interface once they gain sufficient energy to overcome the energy barriers at the ITO/PEDOT (0.5 eV) and PEDOT/NPB (0.2 eV) interfaces. At the same time, electrons are injected from the Al:LiF cathode into the LUMO states of the organic layers and start to move in the opposite direction towards the emitter/BCP interface. Both holes and electrons accumulate at the emitter/BCP interface because of large energy barriers (1.3 eV for holes and 0.9 eV for electrons). Recombination begins to occur in the NPB:Eu layer when electrons gain enough energy to be injected into the emitter layer. NPB has a HOMO/LUMO energy gap of ~3.2 eV, which is slightly larger than that of the Eu complex (~3.1 eV, estimated from the absorption peak wavelength). Recombination and photoemission should first occur in the Eu complex since the lower gap material needs a lower field for electron–hole injection. As the bias increases, recombination and emission from NPB increases as a result of the increased electron–hole injection into NPB molecules.

3. Experimental procedure

The fabrication process for the five-layer device starts with spin-coating of a conductive polymer layer (PEDOT) onto a patterned ITO ($\rho = 60\ \Omega/\square$) glass substrate. Small molecule layers of NPB, Eu complex, BCP and Alq_3 are thermally evaporated at a base pressure of 10^{-8} Torr. The deposition rates of these materials are ~2 Å/s. Different Eu concentrations in the NPB co-evaporated emitter layer are obtained by varying the deposition temperature of both the NPB cell and europium cell while maintaining a total deposition rate at 2–4 Å/s. LiF is evaporated after the organic layers at a rate of 1 Å/s. Then Al is evaporated at 7 Å/s. The final device structure and dimensions are ITO/PEDOT (50 nm)/NPB (30 nm)/NPD:Eu (30 nm)/BCP (20 nm)/Alq_3 (10 nm)/LiF:Al. The active area of the device is $2 \times 2\ mm^2$.

Devices were tested at room temperature without encapsulation. The current density–voltage (J–V) characteristics for the Alq_3 device are obtained with an HP-6634B DC power source controlled by a LabView™ program. The real time luminance is obtained through the transparent glass substrate with a Minolta CS-100 luminance meter. EL spectra are measured with an Ocean Optics SD 2000 fiber optic spectrometer with the optical fiber attached above the OLED normal to the glass substrate.

4. Results and discussion

Eu chelate complex (Keyfluor™ Red from Keystone Aniline) is selected as the dopant because of its excellent PL efficiency when compared to other Eu complexes, such as Eu-DBM and Eu-DBM-DN. Fig. 2 shows the absorption and emission spectra of the Eu complex and NPB. The sharp emission peak at 612 nm is due to Eu red emission, while the broader emission band with a peak at ~440 nm is related to NPB emission. The absorption peak wavelength of NPB at 340 nm is ~10 nm less than that of

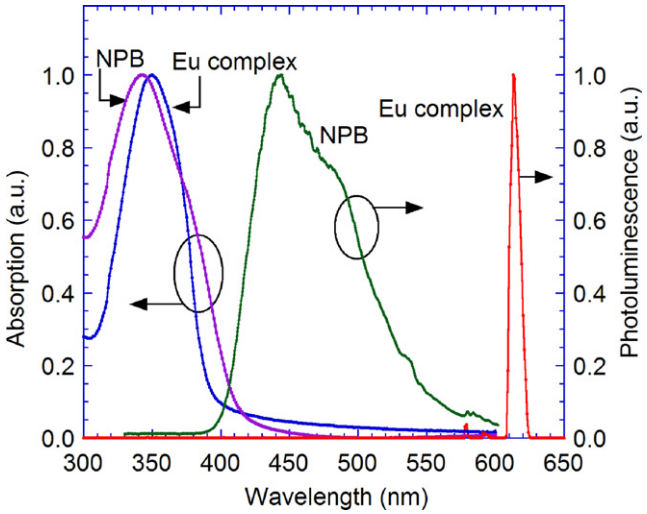


Fig. 2. Absorption and emission spectra of Eu complex and NPB. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

the Eu complex (350 nm), indicating that NPB has a slightly larger HOMO/LUMO gap than that of the Eu complex. Förster energy transfer suggests that exciton interactions of the host/guest molecules are related to the spectrum overlap between the absorption of the host and the emission of the guest. Only a very slight overlap is observed between the absorption spectrum of the Eu complex and the host emission of NPB. These factors indicate that only a very small energy transfer can occur from NPB to the Eu guest.

Fig. 3 shows the combined (host + guest) luminous efficiency as a function of total luminance for various Eu concentrations from 10 to 40 wt.% and for a device with Eu-only emitter layer (i.e. no NPB in the emitter layer). These devices show the same trend: a fairly rapid initial increase of efficiency with increasing brightness, reaching a maximum value and then followed by a decreasing trend. Interestingly, the maximum luminous efficiency occurs at $\sim$10 cd/m^2 for all NPB:Eu co-emitter devices. The highest efficiency value of 0.7 cd/A is achieved for the 20 wt.% europium doping concentration.

Fig. 4a shows the *L–J–V* characteristics for the 15 wt.% Eu device, with NPB emission and Eu emission separated by using a color filter. Red emission from Eu^{3+} is observed to start 1 V less than the blue emission. This is because the HOMO/LUMO gap of the Eu complex is slightly narrower than that of NPB, resulting in a lower field requirement for electron–hole injection. When the applied voltage is greater than 10 V, emission from NPB begins to exceed that from Eu complex. Fig. 4b shows the efficiency trend for the same device. The luminous efficiency for the Eu^{3+} emission starts

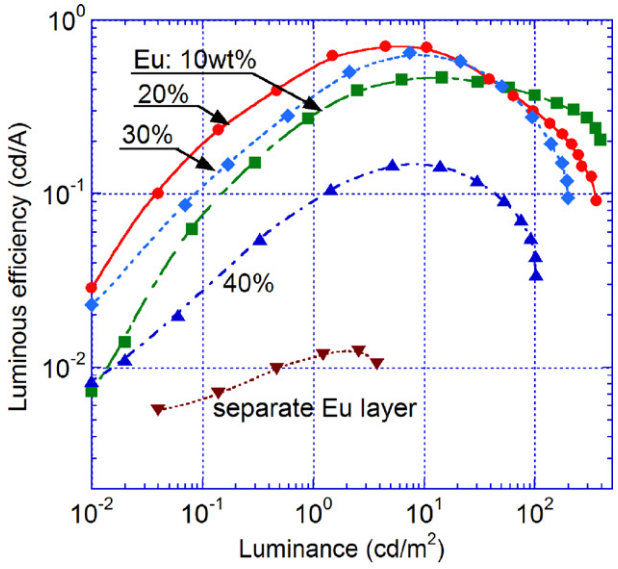


Fig. 3. Luminous efficiency as a function of luminance for color tunable devices with different Eu doping concentrations. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

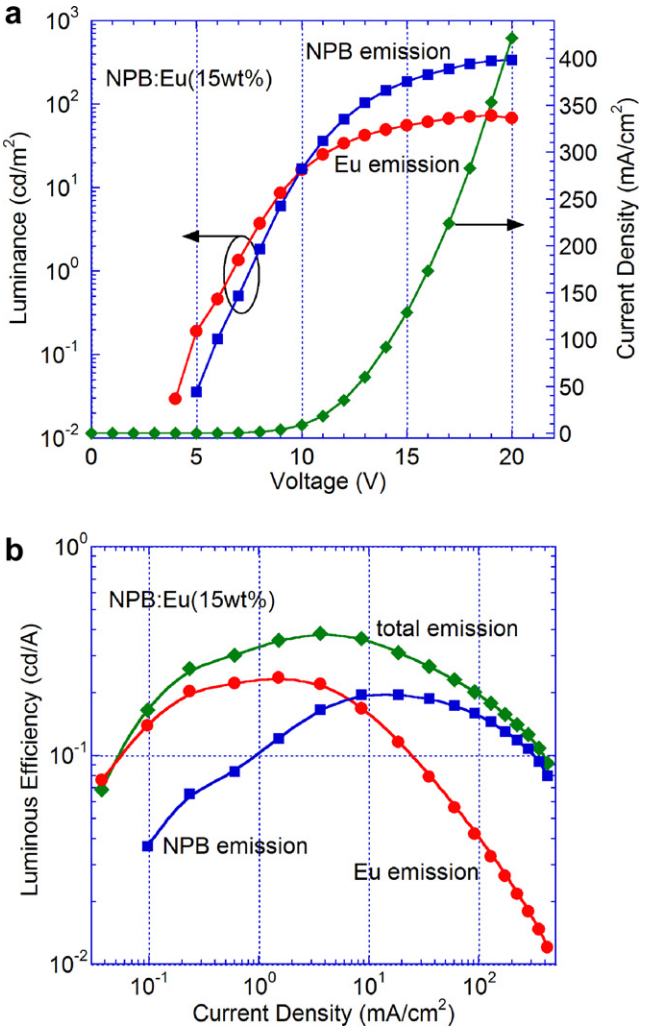


Fig. 4. Characteristics of 15 wt.% Eu device with the emission from NPB and Eu complex separated by using color filter: (a) luminance–current density–voltage characteristics; (b) luminous efficiency as a function of driving current density. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

relatively high and increases quickly with the driving current. It reaches its maximum at ~2 mA/cm^2 and starts to fall rapidly when the driving current increases further. A somewhat different trend is observed for the case of NPB emission. The luminous efficiency starts lower than that of Eu^{3+}, and it increases slowly with the driving current. It reaches its maximum at ~20 mA/cm^2 and begins to fall slowly as the driving current increases further. The strong contrast between the red/blue emissions is the result of the different efficiency trends for Eu^{3+}/NPB emission.

Fig. 5 shows the color coordinates of the 20 wt.% Eu device operated at different bias voltages in the 1931 Commission Internationale de l'Eclairage (CIE) diagram. From 6 V to 10 V, the emission color is mainly red (corresponding to Eu emission). The emission color ranges from red to pink, purple and finally to blue once the voltage exceeds 16 V. The x and y coordinates decrease with voltage, indicating the increased blue emission from the NPB material. The ranges for the x and y values are from 0.61 to 0.17 and from 0.31 to 0.12, respectively.

There are two possible mechanisms involved in the red emission: (1) energy transfer from the NPB host to the Eu complex; (2) excitons directly formed on the Eu complex. Since the energy gap difference between NPB and Eu complex is very small, the host/guest energy transfer will be quite limited. The insert of Fig. 5 shows emission spectra at voltages of 8 V, 12 V and 18 V. As a result of the weak energy transfer from the blue emitter to the red emitter, a strong contrast between the absolute intensity of blue and red emission is achieved at high bias voltage as shown in the spectrum taken at 18 V. The emission intensity from both the Eu complex and NPB increases with voltage as a result of increasing total number of injected electrons and holes. Therefore, when the device operates in the blue region, the device luminance is much higher than when it is operated at the red region (also shown in Fig. 1a). The color tuning is the result of the much faster rate of increase of emission from NPB.

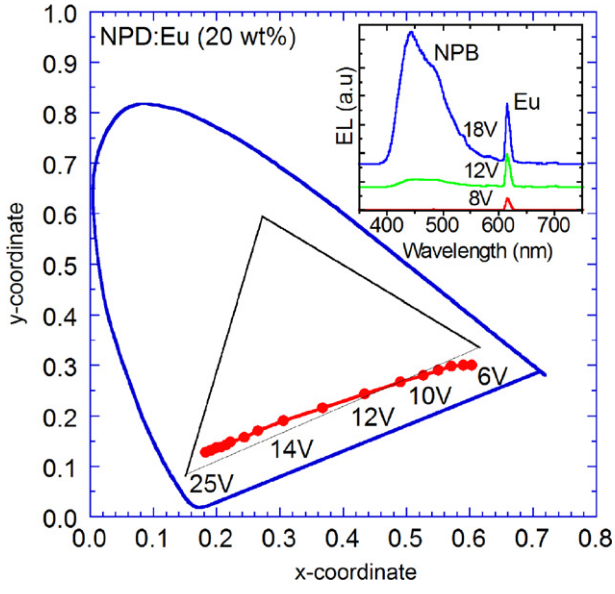


Fig. 5. Color coordinates in the CIE diagram, showing color changes with operating voltage for the 20 wt.% Eu doped device. Insert: output spectra at selected voltages. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

Ideally, we would like to be able to control the brightness and emission color of the OLED independently of each other. Under conventional DC or fixed frequency AC operations that is not feasible. However, one can accomplish this goal by operating the device under AC bias and adjusting the duty ratio. By changing both the voltage and the duty ratio one can obtain the same color with different levels of brightness and different colors with the same brightness.

5. Summary

In summary, we have reported a device structure that contains a co-evaporated emissive layer of NPB and Eu complex responsible for blue and red emission, respectively. Voltage-induced color tuning capability from saturated red to deep blue was demonstrated with this simple method. The Eu complex has an energy gap approximately equal to that of NPB. This results in minimized energy transfer from NPB to Eu complex. Accordingly, a strong contrast between the absolute intensity of blue and red emission is achieved. The maximum luminous efficiency of 0.7 cd/A is obtained for a Eu doping concentration of 20 wt.% in NPB. This doping concentration resulted in CIE coordinates which can be tuned over $\Delta x = 0.44$ and $\Delta y = 0.19$.

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