

Electroluminescence Properties of Organic Light-Emitting Diodes with a Red Dye Doped into Alq₃ : Rubrene Mixed Host

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We have studied the electroluminescence (EL) properties of devices with a red fluorescent dye, 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTb), doped into a mixed matrix of tris-(8-hydroxyquinoline)aluminum (Alq₃) and rubrene. The devices doped with DCJTb in the Alq₃:rubrene mixed host show an efficient red emission from DCJTb with negligible EL emission from both Alq₃ and rubrene. The QE increases with increasing rubrene concentration and reaches a maximum of about 3.6 % for a DCJTb doping concentration of about 5 % in the Alq₃:rubrene mixed (50:50 % ratio by weight) host, and then decreases at higher rubrene concentration, due to the concentration quenching effect. At a given bias voltage, the current density increases with increasing rubrene doping concentration, but it decreases with increasing DCJTb doping concentration. The results imply that the injected electrons and holes can transport via hopping through the energy levels of rubrene molecules while DCJTb acts as traps.

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I. INTRODUCTION

Organic light-emitting diodes (OLEDs) emerge as a new flat-panel display technology having excellent display characteristics such as high luminous efficiency, low driving voltage, low power consumption, fast response time, and wide viewing angle [1–3]. The performance of OLEDs has been enhanced very rapidly to a level adequate for commercial display applications [1].

The doping technique has been widely used for fabricating OLEDs in order to improve device characteristics or change the emission color. Doping the light-emitting layer with appropriate fluorescent or phosphorescent dopants can tune the emission color or enhance the electroluminescence (EL) efficiency and the stability, compared with the undoped devices [4–6]. The EL emission from the dopant is attributed to the exciton energy transfer from the host to the dopant molecules or to the direct recombination of electrons and holes trapped at the dopant molecules [9,10].

Recently, Hamada *et al.* reported that the EL efficiency of red fluorescent dyes doped into the tris(8-hydroxyquinoline)aluminum (Alq₃) host can be further improved by using an emission-assisting dopant of

rubrene [9]. Furthermore, Liu *et al.* reported that luminous efficiency of a red fluorescent dye, 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTb), could be improved by doping it into the mixed (1:1 by weight) layer of Alq₃ and rubrene [10]. The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of rubrene are positioned in between those of the host molecule of Alq₃ and the red

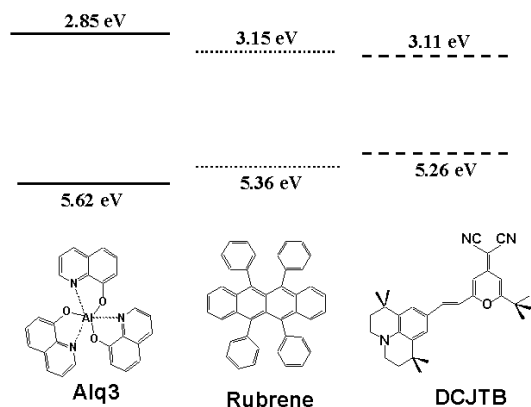


Fig. 1. HOMO and LUMO levels of Alq₃, rubrene, and DCJTb, and their molecular structures.

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dopants [9,11]. Figure 1 shows the HOMO and LUMO levels of Alq₃, rubrene, and DCJT_B and their molecular structures. The enhanced red emission from the dopant molecules is explained by an efficient energy transfer of the exciton formed in the Alq₃ host through the intermediary of rubrene to the dopant molecules [9,12]. Recently, we reported that the direct formation of excitons occurs on rubrene and the subsequent energy transfer to DCJT_B dominates in a device with a host of 1:1 mixture of Alq₃ and rubrene, compared with the host of Alq₃ only [13].

In this paper, we have extended our study in order to fully understand the effect of rubrene molecules on the exciton energy transfer and the charge-trapping processes for the devices with the emitting layer of DCJT_B doped into the Alq₃:rubrene mixture of various concentration ratios. The undoped Alq₃ is used as an electron-transporting layer, and 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]-biphenyl (α -NPD) is used as a hole-transporting layer.

II. EXPERIMENTS

The devices were fabricated on precleaned ITO glass substrates (sheet resistance of about 10 Ω/\square). To enhance the device performance, 3,4-polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS, Baytron P4083) was deposited by spin coating from solution at 4000 rpm for 30 s, followed by drying at 100 °C for 1 hour in vacuum. Organic layers were deposited on top of the PEDOT:PSS layer by successive vacuum deposition of α -NPD (500 Å), the emitting layer (300 Å), Alq₃ (400 Å), LiF (5 Å), and Al electrode, without breaking vacuum. The emitting layer was deposited by simultaneously evaporating DCJT_B, Alq₃, and rubrene with appropriate evaporation rates for controlling the doping concentrations of DCJT_B and rubrene. The overlap area of the Al and ITO electrodes is about 2.5 mm².

The device performance was studied by measuring the current-voltage-luminance (I-V-L) characteristics and the EL spectra at room temperature. The I-V-L characteristics were measured with a Keithley 236 source-measure unit and a Keithley 2000 multimeter equipped with a PMT through an ARC 275 monochromator. The external quantum efficiency (QE) of the EL, defined as the ratio of the emitted photons to the injected electric charges, was calculated from the EL intensity measured by the calibrated Si photodiode placed at the normal angle to the device surface, while assuming that the device is a Lambertian source.

III. RESULTS AND DISCUSSION

Figure 2 shows the EL spectra for the devices with various concentrations of DCJT_B doped into the

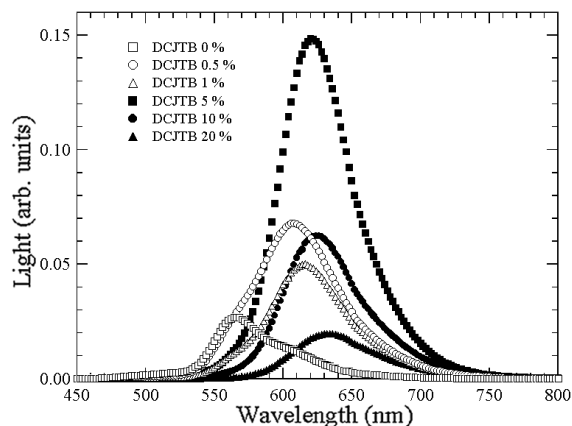


Fig. 2. EL spectra for devices with various concentrations of DCJT_B doped into the Alq₃:rubrene mixed (50:50 % ratio by weight) host at room temperature, under a current density of 20 mA/cm².

Alq₃:rubrene mixed (50:50 % ratio by weight) host at room temperature under a current density of 20 mA/cm². The device structure is ITO/ α -NPD/DCJT_B (x %):(Alq₃:rubrene)/Alq₃/LiF/Al. The device with a DCJT_B doping concentration of 0 % corresponds to the emitting layer with the 50:50 % mixture of Alq₃ and rubrene. It emits a yellow color with the peak at 564 nm, corresponding to the photoluminescence (PL) peak of rubrene. The EL emission from Alq₃ is negligible. Since the HOMO and LUMO levels of rubrene lie inside the energy gap of Alq₃, as shown in Figure 1, and the concentration of rubrene is similar to that of Alq₃, the majority of the injected electrons and holes recombine at rubrene molecules, although there is some contribution from the energy transfer from Alq₃ to rubrene. As the DCJT_B concentration increases, the yellow EL emission from rubrene diminishes and the red emission from DCJT_B increases. The devices with the DCJT_B concentration higher than 0.5 % show a very strong red emission and a negligible EL emission from rubrene. Thus, the exciton energy transfer from rubrene to DCJT_B appears to be very efficient. The energy transfer between the host and fluorescent dopant is usually explained by the Förster energy-transfer process in which the nonradiative energy transfer from an excited (donor) to an unexcited (acceptor) molecule results from the dipole-dipole interaction between donor and acceptor molecules [14]. The Förster mechanism of energy transfer depends on the spectral overlap between donor fluorescence and acceptor absorption [14]. Therefore, the energy transfer from rubrene and DCJT_B is very efficient, since there is a large spectral overlap between the PL of rubrene and the absorption of DCJT_B [11,12].

The EL spectra in Figure 2 also show that the red EL emission peak shifts toward longer wavelength as the DCJT_B concentration increases. The EL peak is at about 616 nm for 1-% DCJT_B doping, and it reaches 634 nm for 20-% DCJT_B doping. It is considered that

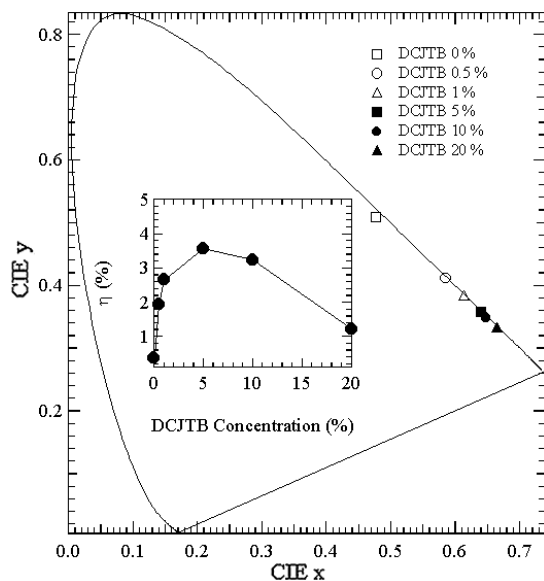


Fig. 3. Commission Internationale d'Eclairage (CIE) chromaticity coordinates for the EL spectra shown in Fig. 2. The inset shows the quantum efficiency (η) as a function of the DCJTB concentration in the Alq₃:rubrene mixed (50:50 % ratio by weight) host.

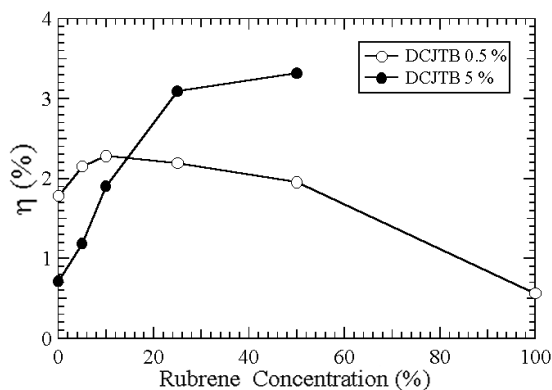


Fig. 4. Quantum efficiency measured at a current density of 20 mA/cm² for devices with DCJTB doping concentrations of 0.5 and 5 % as a function of rubrene concentration in Alq₃ host.

the red shift of the EL peak arises due to the polarization effects of dopant molecules with a dipole moment in the Alq₃ host [15]. As the EL peak shifts toward longer wavelength with increasing DCJTB concentration, the Commission Internationale d'Eclairage (CIE) chromaticity coordinates approach toward the pure red point, as shown in Figure 3. These CIE chromaticity coordinates correspond to the EL spectra shown in Figure 2. The CIE chromaticity coordinates are (0.665, 0.334) for the device with 20 % DCJTB. The inset of Figure 3 shows the quantum efficiency (QE) of the devices with various DCJTB concentrations. The QE (η) increases with the DCJTB doping concentration and reaches a maximum of about 3.6 % for a DCJTB doping concentration

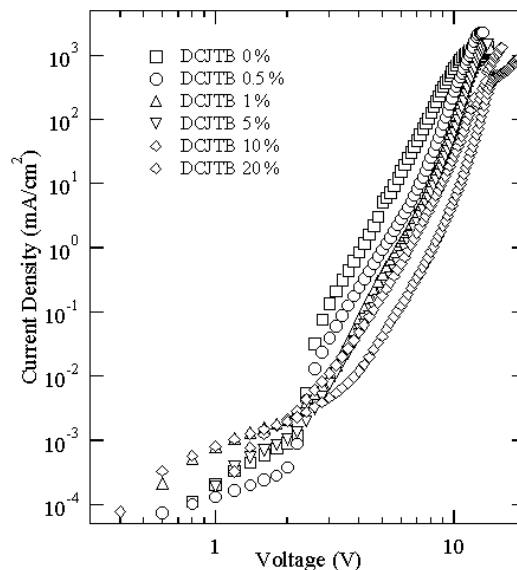


Fig. 5. I-V-L characteristics for the device of ITO/ α -NPD/DCJTB (x %):(50:50 % mixture of Alq₃:rubrene)/Alq₃/LiF/Al with various doping concentrations of DCJTB at room temperature.

of about 5 % in the Alq₃:rubrene mixed (50:50 % ratio by weight) host. It decreases at higher doping concentrations of DCJTB, due to the concentration-quenching effect, which is common for many organic dyes [16].

Figure 4 shows the QE for the devices with DCJTB doping concentrations of 0.5 and 5 % as a function of rubrene concentration in Alq₃ host. The QE is measured for the devices under a current density of 20 mA/cm². For the device with the DCJTB doping concentration of 0.5 %, the QE increases with the rubrene concentration and reaches a maximum at around 10 % of rubrene, and then it decreases at higher doping concentrations of rubrene, due to the concentration-quenching effect. Compared with the device with 0.5 % DCJTB, the device with 5 % DCJTB shows lower QE at low concentration of rubrene, again due to the concentration-quenching effect, but its QE increases continuously with the rubrene concentration up to 50 %. Therefore, the QE of the device with 5-% DCJTB is higher than the device with 0.5-% DCJTB for rubrene concentration higher than about 20 %. These results are consistent with the efficient energy transfer from rubrene to DCJTB. Since the energy levels of the HOMO and the LUMO of rubrene are in between those of Alq₃ and DCJTB, rubrene acts as an intermediary for the energy transfer from Alq₃ to DCJTB, as previously reported by Hamada *et al.* [9]. Therefore, more excitons are formed in rubrene and then transferred to DCJTB as the rubrene concentration increases.

Figure 5 shows the effect of DCJTB doping concentration on the I-V-L characteristics at room temperature. The device structure is ITO/ α -NPD/DCJTB (x %):(50:50 % mixture of Alq₃:rubrene)/Alq₃/LiF/Al. As the concentration of DCJTB increases, the current den-

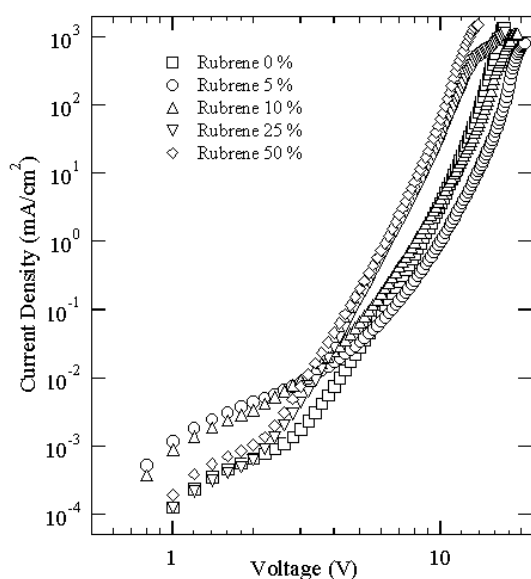


Fig. 6. I-V-L characteristics for the device of ITO/ α -NPD/DCJTB (5 %):(Alq₃:rubrene y %)/Alq₃/LiF/Al with various mixing concentrations of rubrene in the Alq₃ host at room temperature.

sity decreases at a given bias voltage. This result indicates that DCJTB acts as traps for electrons and holes, since the HOMO and LUMO levels of DCJTB lie deeply inside the energy gap of rubrene and Alq₃, as shown in Figure 1. Therefore, the EL onset voltage and the operating voltages at the same luminance level increase with increasing DCJTB doping concentration.

Figure 6 shows the effect of rubrene:Alq₃ mixing ratio on the I-V-L characteristics for the device doped with 5 % DCJTB, ITO/ α -NPD/DCJTB (5 %):(Alq₃:rubrene y %)/Alq₃/LiF/Al. At low concentration of rubrene doping, the current density decreases at a given bias voltage, similar to the DCJTB doping. For rubrene concentration higher than about 10 %, however, the current density increases at a given bias voltage, in contrast to the effect of DCJTB doping (see Figure 5). These results can also be understood based on the energy level diagram shown in Figure 1. The HOMO and LUMO levels of rubrene are positioned in between those of Alq₃ and DCJTB. Therefore, at low concentration of rubrene, the injected electrons and holes transport through the energy levels of Alq₃ molecules and rubrene molecules act as traps, like DCJTB. However, the injected electrons and holes can transport via hopping through the energy levels of rubrene molecules, rather than the energy levels of Alq₃, for high concentration of rubrene. Therefore, the operating voltage at the same luminance level decreases with increasing rubrene concentration in the Alq₃:rubrene mixed host. The lower operating voltage for these devices using Alq₃:rubrene mixed host results in not only higher luminous efficiency but also the ability to use lower supply voltage to the thin film transistors that drive the EL pixels for an active-matrix display [8].

IV. CONCLUSIONS

We have studied the EL properties of devices with DCJTB doped into the Alq₃: rubrene mixed host. The current-voltage-luminescence characteristics, the quantum efficiency, and the EL spectra were measured for devices with varying concentrations of DCJTB and rubrene in Alq₃. The devices doped with DCJTB, in the Alq₃:rubrene mixed host show an efficient red emission from DCJTB with negligible EL emission from both Alq₃ and rubrene. The QE increases with increasing rubrene concentration and then reaches a maximum, whose value also depends on the doping concentration of DCJTB, and then decreases at higher rubrene concentration, due to the concentration-quenching effect. At a given bias voltage, the current density increases with increasing rubrene doping, since the injected electrons and holes can transport via hopping through the energy levels of rubrene. However, it decreases with increasing DCJTB doping concentration, since the energy levels of DCJTB lie inside the energy gap of Alq₃ and rubrene and thereby DCJTB acts as traps for electrons and holes. We find that the best device performance can be obtained by adjusting the doping levels of DCJTB (about 5 %) and rubrene (about 50 %) in the Alq₃. In such devices, recombination of injected electrons and holes occurs on rubrene and the subsequent energy transfer to DCJTB is very efficient, resulting in higher luminous efficiency and lower operating voltage at a given luminance.

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