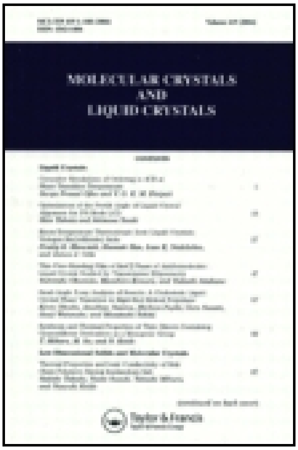

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Energy Transfer and Charge Trapping in Dye-Doped Organic Light-Emitting Diodes

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Energy Transfer and Charge Trapping in Dye-Doped Organic Light-Emitting Diodes

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This paper describes the mechanism of energy transfer and charge trapping in dye-doped organic light-emitting diodes with two dopants, rubrene and coumarin-6. The current efficiency is found to improve significantly compared to undoped cell, which reaches 6.4 cd/A and 9.0 cd/A at 100 mA/cm^2 for the rubrene and coumarin-6 doped cells, respectively. The dopant concentration affects the device performance by changing the location of recombination zone and self-quenching effect. Transient response of pulsed cells shows that carrier trapping changes the detection time of electroluminescence significantly at low voltage. The potential application of doped organic cells in optic-electric conversion is developed.

Keywords: charge trapping; concentration; dopant; energy transfer; organic light-emitting diodes

INTRODUCTION

Since a two-layer organic light emitting diode was first developed in 1987 [1], its promising prospect in flat full-color panel displays [2] and potential application in optical communication [3] have attracted the interest of study in the device performance. Doped organic

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light-emitting diodes (DOLED) have been found to be an effective approach to achieve high efficiency in addition to its color selectivity [4–8], and superior stability [9,10].

In this paper, we study the mechanism of energy transfer in electroluminescence (EL) using two dye species, rubrene and courmarin-6, with varying amounts in light-emitting layer. Another attempt is made to understand the charge trapping by observing the transient response under the electric pulse. Finally, we realize an application of DOLED in the signal transmission as an optical-electric conversion device.

EXPERIMENTAL

We used the vacuum deposition system to fabricate the organic layers and cathode of DOLED upon the indium-tin-oxide coated glass substrate under a base pressure lower than 5.5×10^{-6} Torr. The 4,4′-bis[N-(1-napthyl)-N-phenyl-amino]-biphenyl(α-NPD) and Tris(8-hydroxyquinoline)aluminum (Alq_3) as hole transport layer (HTL) and electron transport layer (ETL), respectively. The light-emitting layer (EML) was co-evaporated using dopants, rubrene and coumarin-6 in the Alq_3 (V/V, %), respectively. In addition, a thin film of hole blocking layer, bathocuproine (BCP) was deposited between ETL and EML for eliminating the potential emission from Alq_3, and improving the device efficiency by enhancing hole/electron ectron ratio in the recombination zone and/or by confining the charge carriers and excitons in the emitting layer. The electron injection layer of 0.5 nm thick LiF and cathode of 300 nm thick Al were evaporated on the top of organic layer. The configuration of devices and molecular structures of dopants are shown in Figure 1.

The current density and luminance for fabricated devices were measured using the HP4140V (Hewlett Packard) and Luminance Colorimeter BM-7 (Topcom), respectively. The transient electroluminescence with the repetition rate of 2.5 MHZ was generated from the pulse generator (Sony Tek AWG410) and recorded by spectroscopy with photomultiplier □Hamamatsu, R7400U-04□ and Oscilloscope (Sony Tek, TDS-680C).

RESULTS AND DISCUSSION

The performances for doped OLEDs and a reference bilayer device are shown in Table 1. The electroluminescence (EL) of doped cells is found to improve significantly comparing to the reference device. The maximum EL of 80000 cd/m^{2}and 52000 cd/m^2, for 1% of coumarin-6 and 3% of rubrene in Alq_3 doped devices were achieved, respectively. The current efficiencies of 9.0 cd/A and 6.4 cd/A for the above two

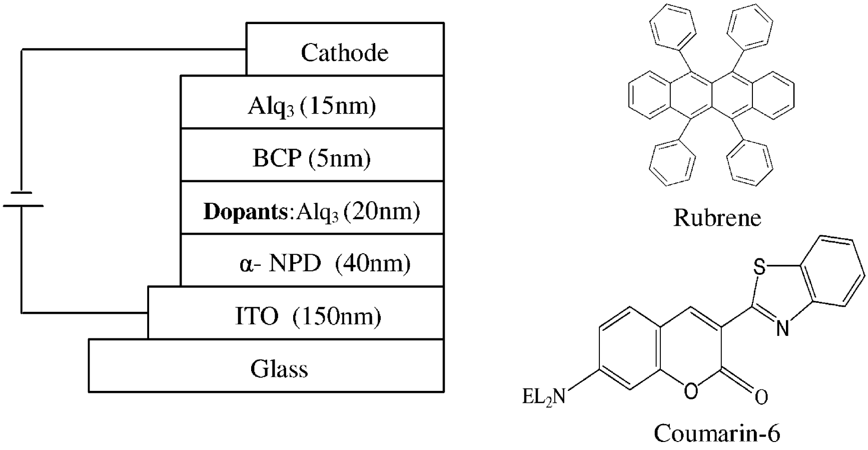

FIGURE 1 Configuration of doped organic light-emitting cells (a) and molecular structure of dopants used in this study (b).

devices were achieved. Improvement of efficiency by doping is assumed to result from two mechanisms, host-guest energy transfer using the Förster formalism [4] or directly electron-hole recombination in dopants as carrier traps [8].

There are two possible energy transfer processes in the guest-host complex, Förster transfer and Dexter transfer [11]. For florescent acceptor (such as rubrene and coumarin 6) in the emitting layer, the transfer mechanism of energy has been demonstrated to be a long range (40–100 □) and fast Förster type [12]. Förster transfer is resonant dipole-dipole coupling of donor and acceptor while Dexter transfer is

TABLE 1 Performance of Cells with Rubrene and Coumarin 6 as Dopants with Different Concentrations

Dopant concentrations in Alq_3 (V/V)	Von^a (V)	EL^b (cd/m^2)	Current efficiency^c (cd/A)
Undoped	2.8	15,000	~ 1.6
Rubrene ~ 1.0%	3.0	42,000	~ 4.8
Rubrene ~ 3.0%	3.0	52,000	~ 6.4
Rubrene ~ 5.0%	3.6	18,000	~ 2.5
Coumarin 6 ~ 1.0%	3.4	80,000	~ 9.0
Coumarin 6 ~ 3.0%	2.8	48,000	~ 4.6
Coumarin 6 ~ 5.0%	2.8	32,000	~ 3.5

^{a}at detectable luminance (~4.0cd/m^2); ^{b}at 1000 mA/cm$^{2;}$ ^{c}at100 mA/cm^2.

the diffusion of excitons from donor to acceptor via the Wigner-Witmer spin conversation rules [11]. The donor and acceptor transitions from the ground to the excited states must be allowed for Förster transfer. For the devices in this work with doping light-emitting layer by fluorescent dyes, rubrene (or coumarin 6): Alq_3, the electron are expected to be trapped in Alq_3 molecules and recombine with the holes injected from the transport layer, to form Alq_3 excitons ($^1D^*$). The singlet excitons transfer energy to the singlet state of the dopant molecule ($^1A^*$) is frequently based on the following Förster process:

$$^1D^* + ^1A \rightarrow ^1D + ^1A^*$$

Here, superscript 1 represents the singlet and triplet states, respectively, and the asterisk the excited state.

An efficient transfer requires that donor emission and acceptor absorption of acceptor be overlapped. Moreover, based on the research of Blasse and Gramaier [13], the energy transfer efficiency of dye-doped OLEDs depends on the overlap integral of the emission spectrum of the host material and the absorption spectrum of the dopant.

Spectral measurement of absorption from dyes and emission from host molecules (Fig. 2) shows that there is a rather good overlap between the absorption of the rubrene or coumarin 6 and emission from the donor molecule, indicating the requirement for Förster energy transfer from the singlet state in the host (Alq_3) to the singlet state in the rubrene or coumarin 6.

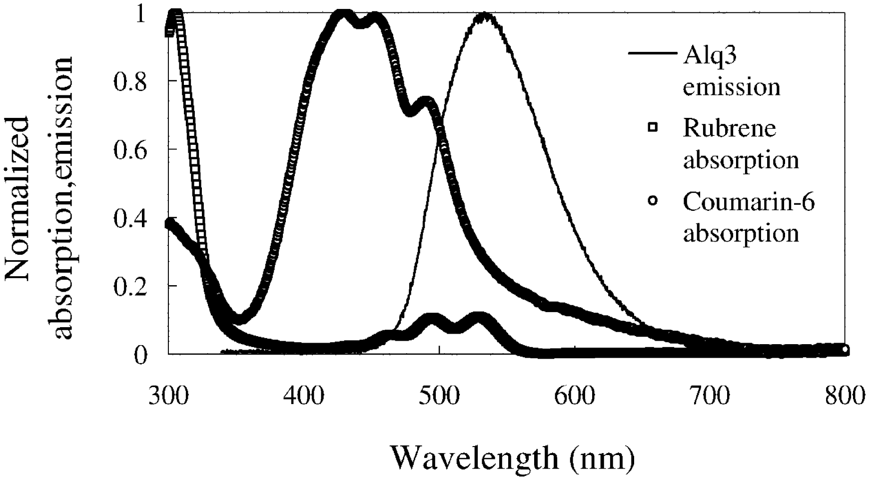

FIGURE 2 Absorption spectra of films of the two fluorescent dyes (rubrene and coumarin 6) and emission spectrum of Alq_3 film.

There is a narrowest full-width at half maximum of emission intensity for coumarin-6 doped device (1%, 67 nm, data not shown here), followed by that of rubrene doped device (1%, 78 nm) and undoped reference cell (97 nm). It is noteworthy that the peak wavelength shifts towards red zone with the increase in the dopant concentrations, as shown in Figure 3, associating with micro-cavity-induced-wave-guiding effect, further supporting the assumption that the dye amount varied recombination zone and exciton diffusion length.

Since Förster transfer dominates singlet-singlet transfer over long distance, only low concentrations of acceptor are needed. Furthermore, it can be found from the Table 1 that the performance of DOLED changes with the concentrations of dopant, because the addition of dopants affects the injection balance of charge and the position of the recombination zone in LEDs [14]. Another reason was assumed that the increased amount of dyes in host would lead to self-quenching of the fluorescence [15], consequently decreased the luminescence and efficiency of cells. Our data show that the optimum dopant concentrations in the host (Alq_3) are 3% (V/V) and 1% (V/V) using rubrene and coumarin-6 as dopant, respectively. The coumarin-6 doped OLED has the higher brightness and efficiency that rubrene-doped cell. It may be contributed from the reasons that there is more overlap of the emission spectrum of Alq_3 and the absorption spectrum for coumarin-6 than that for rubrene, or the hole trapping from the α-NPD to coumarin-6 can slow the mobility of hole, therefore resulting in a more

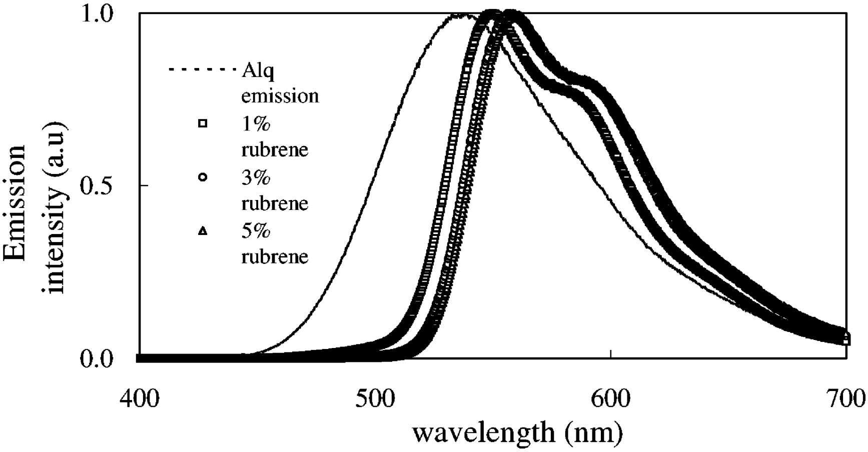

FIGURE 3 Spectral characteristics of rubrene-doped organic light-emitting diodes with varying dye concentrations.

balanced electron/hole recombination than for the device with rubrene as dye species.

In addition to EML-doping, the previous studies revealed that doping the HTL with rubrene could slower the transport of hole [16] and consequently reduced the lifetime of the unstable Alq_3 cationic species [17]. However, our experiment of doping HTL (Rubrene:α-NPD (1%)/BCP/Alq_3) or doping ETL(α –NPD/Alq_3/BCP/Rubrene:Alq(1%)) %)) can't achieve as obviously high brightness and efficiency as doping EML (data not shown here). This suggests that the energy transfer from the Alq_3 excitation to dye excitation play a more important role in the enhancement of EL efficiency.

The sequential capture of carriers into dye serving as recombination center was also found to be the prevalent EL excitation mechanism according to on the Pschenitzka's research [18]. The evidence about carrier trap by dopant molecular can be further tested from the measurement of transient response. Our previous study showed that delay time of transient EL (time for EL to be detected after the pulse voltage switched on) was mainly determined by the transport process of charge carriers [19]; therefore, delay time can be an important index to investigate the carrier traps in OLED. By observing the transient EL of undoped and dye-doped devices, we found that that the delay and rise time of transient EL for rubrene-doped cell decreased significantly at low applied voltage, comparing to undoped one. This is mainly attributed by that the holes and electrons are favorably expected to be trapped by rubrene molecules [5], particularly the increase of electron mobility by rubrene doping, which create new electron hopping site on rubrene (Fig. 4a). For rubrene, the optical energy gap (E_g) and ionization energy (I_p) are 2.21 and 5.36 eV, respectively, less than those of the host molecule ($E_g = 2.77\,\text{eV}$, $I_p = 5.62\,\text{eV}$), indicating the most possible role of dopant working as carrier traps. In the other hand, for the DOLED with courmarin-6 as dopant, its E_g (2.47 eV) is less while I_p (5.65 eV) is a little higher than those of host molecule. Accordingly, the energy transfer from Alq_3 exciton to the singlet state of coumarin-6 molecule, rather than hole trap and then recombination with electron on coumarin-6 molecule, was expected. Furthermore, the delay time that the EL for coumarin 6-doped cell was detected is found to be a little slower than that for undoped cell. We attribute the difference in response time for DOLED with two species of dyes, to their different diffusion length and lifetime of exciton [20], or to one assumption we proposed here: the mobility of carriers couldn't increase as there is energy barrier for the hole trapping from α-NPD to coumarin-6 molecule, which is contrary to the case of rubrene, as shown in Figures 4-a and 4-b. Therefore, dopants are

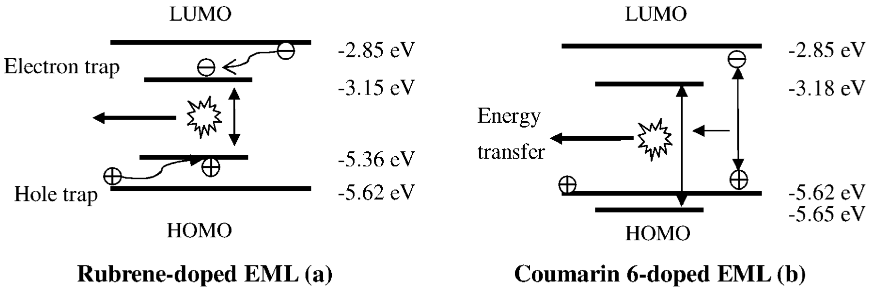

FIGURE 4 Energy transfer and charge trap for the doped light-emitting layer with two species of dopants, rubrene (a) and coumarin 6 (b).

expected to work favorably as carrier traps for rubrene and Förster energy transfer for coumarin 6.

Using the developed doped devices, we have successfully realized the transmission of pulse signal with 100 Mbps on the rubrene-doped devices with an active area of 0.02 mm^2 and real-time video signal using DOLED as an Electric/Optical conversion device in transmission system. The output response from the small-size dye-doped cells was then converted from optical to electric signal through pin-photodiode (Hamamatsu S6468–05) and recorded by oscilloscope. It was observed that the transmitted signal was completely consistent with input one, demonstrating that a novel role of doped organic light-emitting diodes can now added in its application list.

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