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Improved electroluminescent efficiency of organic light emitting devices by co-doping N, N'-Dimethyl-quinacridone and Coumarin6 in tris-(8-hydroxyquinoline) aluminum

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Electroluminescent (EL) efficiency of organic light emitting devices was improved by co-doping N, N'-dimethyl-quinacridone (DMQA) and Coumarin6 (C6) in tris-(8-hydroxyquinoline) aluminum (Alq₃). At 20 mA/cm², superior EL efficiency of 9.33 cd/A was obtained from 1.6% co-doped (0.8% DMQA and 0.8% C6) device, much higher than those of single-doped devices based on 1.6% DMQA (~5.0 cd/A) or 1.6% C6 (~6.0 cd/A). EL efficiency of the single-doped devices with optimal dopant concentration, 0.8% in both cases, are merely 7.13 cd/A for DMQA and 6.43 cd/A for 0.8% C6, respectively. The significant improvement could be attributed to effective utilization of the host energy and depression of concentration quenching. The co-doping technique provides an effective way to overcome the notorious concentration quenching and hence to improve the EL efficiency. © 2005 American Institute of Physics. [DOI: 10.1063/1.2132064]

Organic light emitting diodes (OLEDs) have attracted wide attention in point of view of practical applications for displays and lighting, since the bilayer OLEDs were reported in 1987.¹ Much effort²⁻⁴ has been made to improve electroluminescent (EL) efficiency, which is crucial for display technology. One of the most effective ways to obtain efficient electron-to-photon conversion is to dope fluorescent⁵ or phosphorescent⁶ dyes into host materials in which efficient host-to-guest energy transfer and radiative recombination take place. However, experiments indicated that the optimal concentration of a fluorescent dye in a host is usually ~1%.⁷ High doping concentration, which favors efficient energy transfer, results in aggregation and thus serious self-quenching of dye molecules. On the contrary, low doping concentration limits radiative recombination on dopant sites and the energy of the host cannot be utilized adequately. EL efficiencies in both cases are low. Molecular structure modification has been adopted to minimize the aggregation of dye problem; the constant chromaticity and efficiencies were obtained even at high doping concentration >1%.⁸

Co-doping of two dyes into one host has been proposed to trigger a complete cascade energy transfer process in OLEDs⁹ or to construct white organic light emitting devices,^{10,11} from which combined emissions were observed. In this letter, we adopt a co-doping method to conquer the inter-molecular concentration quenching by two green fluorescent dyes of different molecular structures and excitation mechanisms. Comparing to a typical industrialized application organic green EL device,⁴ N, N'-dimethyl-quinacridone (DMQA) and Coumarin 6 (C6) were chosen as dopants. Im-

proved EL efficiency and pure green light were observed from the co-doped device.

Figure 1 shows the chemical structures of DMQA and C6 and the device configuration. All materials used were commercially purchased. Indium tin oxide coated glass substrates (20 Ω/□) were routinely cleaned¹² then treated in O₂ plasma for 5 min prior to loading into a vacuum chamber; α-naphthylphenylphenylbiphenyl (NPB) and (Alq₃) were used as hole and electron transporting layers, respectively. Organic films, 1 nm LiF layer and Al cathode were deposited by thermal evaporation in high vacuum of 5.0 × 10⁻⁴ Pa during one pump down. Deposition rates and thicknesses of films were monitored by quartz oscillators.

The luminance-voltage (*L-V*) characteristics of the OLEDs are plotted in Fig. 2. It shows that device at the co-dopant concentration of 1.6% by mass has the best *L-V* behavior. The maximum luminance exceeded 50 000 cd/m² at 13 V. The driven voltage for 1.6% co-doped device was only 6 V when the current density reached 10 mA/cm², and the brightness of the device exceeded 900 cd/m², which in-

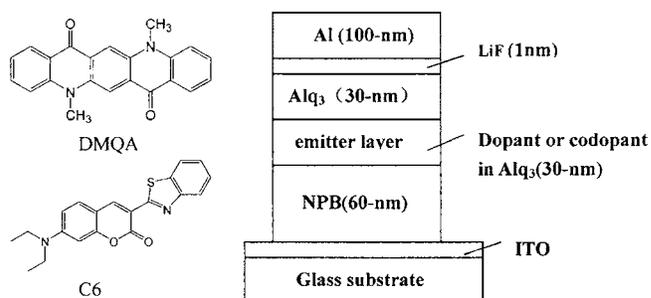


FIG. 1. The chemical structures of DMQA and C6 and the devices' structures.

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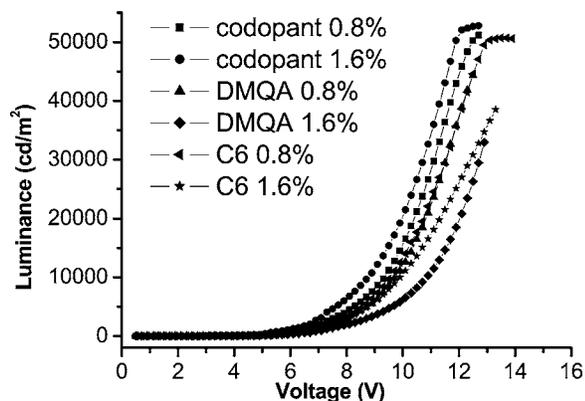


FIG. 2. Luminance-voltage characteristic of the OLEDs.

indicated that the performance of the device for green light EL was excellent.

Figure 3 shows the current efficiency (a) and power efficiency (b) versus current density characteristics based on DMQA, C6 doped and their co-doped devices. The DMQA and C6 single-doped devices were made for reference. For both dyes, optimal doping concentration in EL devices was found to be 0.8%. The detailed EL performances are summarized in Table I. The maximum current efficiency of 1.6% co-doped device reached 9.48 cd/A, in comparison with 7.13 cd/A of 0.8% DMQA-doped device and 6.79 cd/A of 0.8% C6-doped devices. Compared with the single-doped devices based on DMQA and C6 at concentration of 1.6%, the EL efficiency of 1.6% co-doped device was found to be

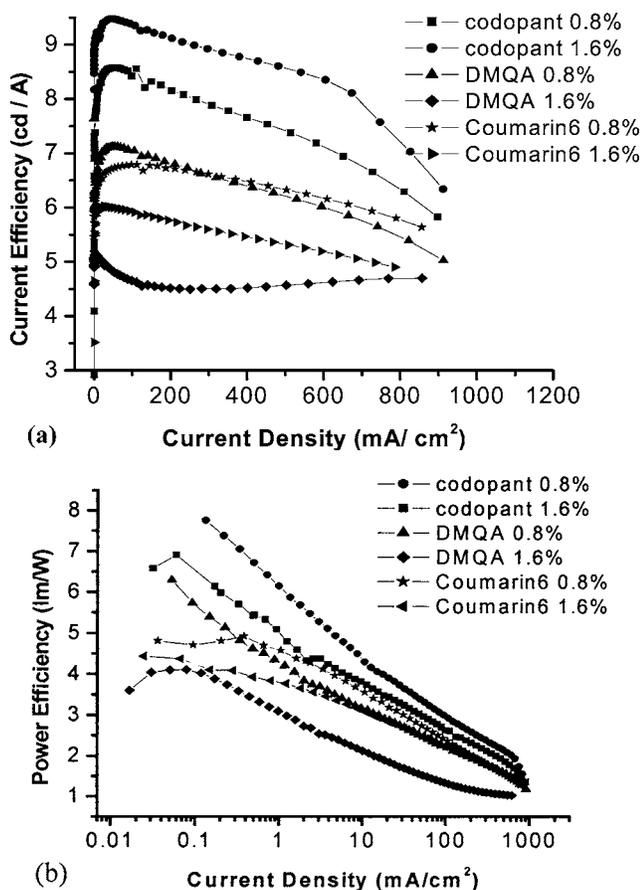
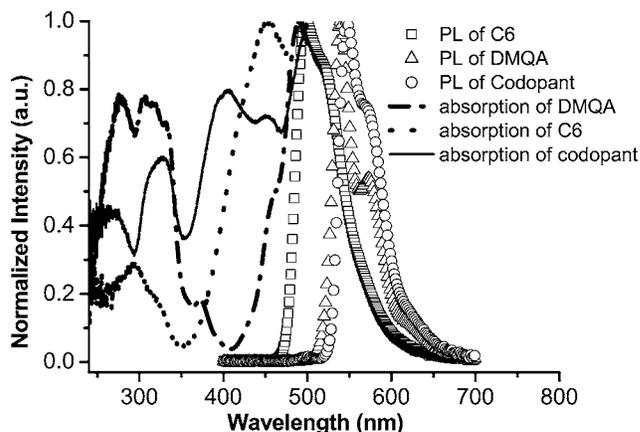


FIG. 3. (a) The current efficiency vs current density, (b) the power efficiency vs current density characteristics.

FIG. 4. (a) The absorption and PL spectra of DMQA, C6 and their 1:1 molar ratio mixture in CHCl_3 , (b) the EL spectra.

improved by 57% and 87%, respectively, strongly indicating that the concentration quenching was effectively depressed in the co-doped device. It was also noticed that, although the maximum current efficiency of C6-doped device was lower than that of DMQA-doped device in our experiments, replaced the half mass of DMQA by C6, the current efficiency of the device (0.4% DMQA and 0.4% C6 co-doped device) reached 8.58 cd/A, 20% higher than that of 0.8% DMQA-doped device. It suggested that concentration quenching was serious even at the so-called optimal concentration. Besides, the phenomenon is the evidence that concentration quenching effect mainly occurs between the same molecules rather than different species. As a result, co-doping of C6 and DMQA increased the total dopant concentration so that the current efficiency was improved, while the respective suitable dopant concentration avoids the further quenching effect. The co-doped device improved current efficiency without increasing drive voltage, so the power efficiency was improved as shown in Fig. 3(b).

Figure 4(a) shows the absorption spectra of DMQA, C6 and their 1:1 molar ratio mixture (0.1 M in CHCl_3) as well as corresponding photoluminescence (PL) spectra under excitation of 315 nm. It can be seen that the absorption of the mixture solution originated apparently from the simple addition of respective absorptions of C6 and DMQA. However, the PL spectrum of the mixture was mainly attributed to DMQA emission, which could be due to efficient Förster energy transfer from C6 to DMQA according to the well overlapping between absorption spectrum of DMQA and PL spectrum of C6. But the EL spectra in Fig. 4(b) clearly showed that in the co-doped device both emissions of C6 and DMQA contributed to EL output. It is interestingly observed that the shoulder at the long-wavelength edge of the emission spectra, which should attribute to the emission of DMQA aggregations, disappears in EL spectrum of co-doped device. The CIE coordinates of the co-doped device were (0.313, 0.630), better for green color display than DMQA (0.338, 0.663) single-doped device.

From above results we can conclude that improved EL efficiency based on co-doping method was mainly owed to the successful suppression of the concentration quenching. To single dye doped devices, concentration quenching was caused by the molecular aggregation and formation of excimer state at high concentration,^{13,14} which resulted in broadened emission band and low efficiency. When concentrations

TABLE I. Performances of different dopant (co-dopant) or dopant (co-dopant) concentrations of doped devices.

| Dopant concentration | Turn on voltage (V) | Current efficiency (cd/A) | | | Power efficiency (lm/W) | |
|----------------------|---------------------|---------------------------|------|------|-------------------------|------|
| | | a | b | c | b | c |
| 0.8% co-dopant (1:1) | 2.7 | 8.58 | 8.16 | 8.41 | 3.78 | 3.40 |
| 1.6% co-dopant (1:1) | 2.7 | 9.48 | 9.20 | 9.33 | 4.30 | 3.91 |
| 0.8% DMQA | 2.7 | 7.13 | 6.72 | 6.95 | 3.14 | 2.88 |
| 1.6% DMQA | 2.9 | 6.02 | 5.10 | 5.02 | 2.12 | 1.87 |
| 0.8% Coumarin6 | 2.9 | 6.79 | 6.44 | 6.43 | 3.54 | 3.20 |
| 1.6% Coumarin6 | 2.9 | 5.06 | 5.94 | 5.90 | 3.10 | 2.82 |

^aMaximum current efficiency.^bAt 10 mA/cm².^cAt 20 mA/cm².

of both co-dopants were kept at their respective optimized values, the negative factors could not prevail in EL processes. The dispersal of the dye in the host had no change when the other dye was introduced. The increased probabilities of dye aggregation, in fact, are not between themselves but between one another. In DMQA- and C6-doped EL devices the excitation mechanisms of the two dopants have been proved to be Förster energy transfer¹⁵ for the former and charge trapping or Dexter electron exchange¹⁶ for the latter, respectively. When the two dyes were co-doped in Alq₃, the energies transferred from Alq₃ and adjacent C6 to DMQA by Förster energy transfer mechanism were consistent with the dominant emission of DMQA in the PL spectra of the mixture. Differing from photoexcitation mechanism of the thin film which does not generally lead to free carriers,¹⁷ the emissions of C6 contributed to the EL spectra of co-doped device, indicating that C6 trapped the charge carrier from Alq₃ and adjacent DMQA excitons. Thus we can conclude that C6 gave an efficient EL emission although part of its energies was transferred to DMQA molecules. The competition process of energy transfer might be utilized the energy of host more adequately, therefore the efficiency was improved greatly. It was found that charge trapping process was much faster than Förster energy transfer process,¹⁷ which might weaken the interaction between the excitons of DMQA and C6, so that excimer formation could be fully avoided and efficiency improved. The absence of spectrum broadening of EL emission and high EL efficiencies confirmed that no excimer was formed.

In summary, we report an effective co-doping way to improve the EL efficiencies of green OLEDs. Co-doping two fluorescent dyes into the same host, an efficient device without undesirable excimer was obtained at high dye concentrations because the excitons' interaction between two kinds of emitter centers were distinguished from the exciton interaction between the same dye that would lead to self-quenching. The co-doping technique can be further used to improve EL efficiency in other material systems, especially for the im-

provements of EL performances under the background of the industrial applications. The efficiencies were improved but no change was found in the electrical field distribution and driving voltage of the co-doped device compared with the single-doped ones. From that point we can predict that its lifetime will be improved too, in which we will be further actively interested.

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