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We report on the development of highly efficient organic light-emitting diodes (OLEDs) utilized by balancing the energy transfer between multiple dopants, that is, multiple emissions from the multiple dopants were realized by balanced distributed energy transfer. From the cosensitizing fluorescent OLEDs, the peak external quantum efficiency (EQE) of 4.8% at 130 cd/m^2 is demonstrated, which realized theoretical limits of ~5.0% and means that nearly 100% of the singlet excitons are radiative. Also, the optimized device accompanying thickness-modulated electron transport layer for the enhanced light outcoupling demonstrated the highly improved peak EQE and current efficiency of 6.7%, and 23.4 cd/A. ©2009 *American Institute of Physics*

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We report on the development of highly efficient organic light-emitting diodes (OLEDs) utilized by balancing the energy transfer between multiple dopants, that is, multiple emissions from the multiple dopants were realized by balanced distributed energy transfer. From the cosensitizing fluorescent OLEDs, the peak external quantum efficiency (EQE) of 4.8% at 130 cd/m^2 is demonstrated, which realized theoretical limits of ~5.0% and means that nearly 100% of the singlet excitons are radiative. Also, the optimized device accompanying thickness-modulated electron transport layer for the enhanced light outcoupling demonstrated the highly improved peak EQE and current efficiency of 6.7%, and 23.4 cd/A. © *2009 American Institute of Physics*.
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Ever since Tang and VanSlyke[1] from Kodak introduced efficient organic light-emitting diodes (OLEDs), they have been widely investigated because of their attractive possibilities to meet the requirements for the next generation of flexible flat panel displays.[2] Through these research efforts, many achievements have been made.[3–5] And dye doping,[6] which is one of the key methods, has been generally used to enhance the characteristics of the OLEDs. However, by using a single dopant, it is not easy to realize 100% of the exciton radiating systems due to issues that cannot be overcome such as the limited host-guest energy transfer rates, concentration quenching aspects of the dye dopants, etc.[7] To overcome these problems, a codoping technique has been reported, and several attempts have been made in making some headway in achieving enhanced characteristics in the OLEDs.[8–10] But there are no fully singlet radiative methods reported for the fluorescent OLEDs without using the originally synthesized organic materials.

Since it is believed that the balanced energy transfer between the multiple dopants and the possibility of drawing out the full theoretical potential abilities of the dopants, we have demonstrated highly efficient fluorescent OLEDs in this work, realizing almost the full 100% radiative singlet excitons. This work is based on the incomplete cascaded energy transfer (ICET) method which is an incomplete energy transfer between the multiple sensitizing host and the activating dopants used in order to distribute the energies to the multiple dopants rather than transferring all the energy to only one final accepting dopant. The proposed method presented in this paper encapsulates an optimized ICET technique that is capable of reducing the nonradiative quenching and enhancing the efficiency of the OLED device. This optimized ICET is referred to as the "balanced ICET (BICET)" here and it enables a highly efficient electroluminescence (EL).

In this work, seven devices with different doping concentrations have been investigated. The structure and the energy band diagram are shown in Fig. 1. The indium tin oxide is used as an anode; N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)benzidine (α-NPB) as a hole injection layer and a hole transport layer (HTL); tris(8-hydroxyquinoline) aluminum (Alq_3), as the host matrix of the emissive layer (EML) and also as the electron transport layer (ETL); 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7,-tetramethyl-1H,5H,11H - [1]benzopyrano [6,7,8-ij] quinolizin-11-one (C545T) and N,N′-dimethyl-quinacridone (DMQA) as the guest cosensitizing dye dopants; lithium fluoride has been used as an electron injection layer and aluminum as the cathode.

UV-visible absorbance and the PL spectra of the thin films, which are composed of 50-nm-thick 0.5–4.0% single-doped and codoped Alq_3 thermally deposited on the finely

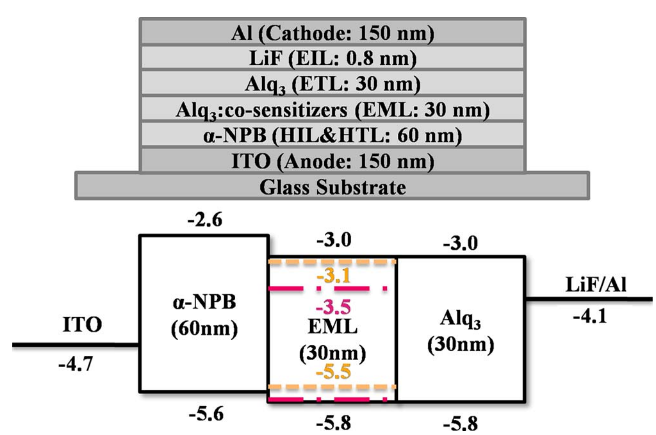

FIG. 1. (Color online) (upper) Device structure and (lower) energy band diagram of the codoped OLED. The energy levels were estimated by cyclic voltammetry and optical energy band gap measurements. The energy levels are illustrated with an arbitrary scale in the vertical axis. The dotted line represents C545T and the dashed-dotted line represents DMQA.

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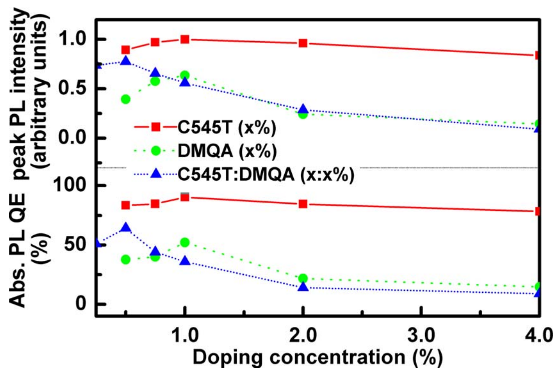

FIG. 2. (Color online) (upper) Peak PL intensity and (lower) Abs. PL QE of doped thin films as a function of doping concentration.

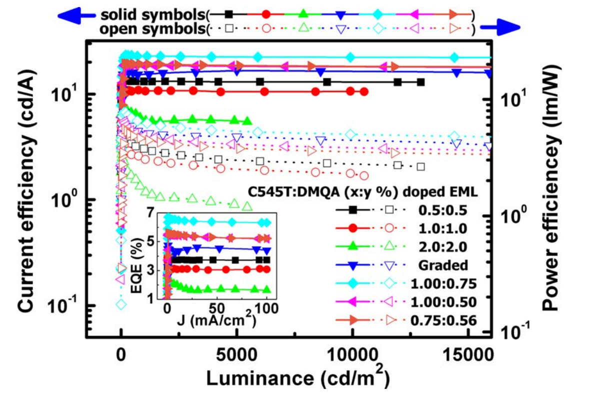

FIG. 3. (Color online) The EL characteristics of codoped OLEDs; current and power efficiency as a function of luminance. The inset shows the EQE as a applied current density.

cleaned quartz substrate, are measured using the 8453 UV-visible spectrophotometer (Agilent Technologies, Inc.) and the F-7000 Fluorescence Spectrophotometer (Hitachi High Technologies America, Inc.), respectively. The absolute photoluminescence quantum efficiency (Abs. PL QE) is measured by a 6 in. integral sphere, 325 nm He:Cd cw laser, and monochromator with photomultiplier tube.[11,12]

The EL characteristics are measured using a PR-670 SpectraScan Spectroradiometer (Photo Research, Inc.) and the Model 237 High-Voltage Source-Measure Unit (Keithley Instruments, Inc.) in a dark box and in air atmosphere.

The PL and EL characteristics of the two dopants with the Alq_3 host matrix has been widely reported as referred to in Refs. 7, 10, and 13–15. The C545T has a smaller overlapping region in the host PL and guest absorption spectra but has a high absorption coefficient and works as a good Förster-type dopant (PL QE ~90%) (Refs. 7 and 10) and also the carrier trapping dopant.[15] Since the DMQA also works as a Förster energy transfer dominant with wider spectra overlapping but has a lower absorption coefficient.[10,13] Comparing both of these dopants, their complementary differences with the spectra overlapping and absorption coefficient and carrier trapping with the Alq_3 host matrix, it is possible to conclude that they are good codoping dopants for distributed energy transfer.

Figure 2 shows the PL characteristics of doped Alq_3 films. The peak PL intensity of C545T and DMQA single-doped Alq_3 shows its maximum at near ~1.0% as in above references. While the codoped Alq_3 shows its maximum at ~0.5:0.5%. This difference in the ideal doping concentration levels between the single-doped and codoped configurations can be explained by the increased energy transfer rate by codoping system. In the Förster energy transfer dominant structure, one of the codopants, having larger singlet energy than the other, works as a secondary host, and also works as the dominant energy transfer medium between the host matrix and the other dopant; the singlet energies of Alq_3, C545T, and DMQA are 2.8, 2.4, and 2.3 eV, respectively. Consequently, the energy transfer rate of the host to the dopant, which has the lowest singlet energy, is relatively higher than the single-doped configuration at the same doping concentration. As a result, the optimized codoping concentration is lower than the optimal single-doping concentration. The Abs. PL QE spectra show the same trends as peak PL intensity, and it strongly supports above explanations.

It is interesting that the overall PL intensity and Abs. PL QE of codoped system are lower than C545T single-doped system, while the codoped OLEDs showed higher EL efficiencies than single-doped OLEDs in previous reports.[10] This kind of difference between the EL and PL are well known to come from the carrier trapping dopant system,[7] and well agree with in this C545T doped system.[15]

Meanwhile, the concentration quenching was strongly observed in the DMQA single-doped and codoped Alq_3. The concentration quenching of the DMQA PL is same with the reported results.[14] It is found that the DMQA-doped Alq_3 thin films shows more dependence on the doping concentration than that of the C545T doped thin films, thus DMQA causes concentration quenching in codoped system. Considering the radiationless concentration quenching of DMQA doped thin films, controlling the DMQA doping concentration is an effective way to improve the overall performance when using the DMQA as an emissive dopant and the activator in OLEDs.

Figure 3 shows the EL characteristics of the fabricated codoped OLEDs where, out of the 0.5:0.5–2.0:2.0% codoped OLEDs, the 0.5:0.5% codoped OLED show the highest EL efficiencies, as well as the peak current efficiency (CE) and external quantum efficiency (EQE) of 13.9 cd/A and 4.0%, respectively. This is an identical trend as that of the PL intensity of the codoped thin films, as shown in Fig. 2.

To develop the optimal doping concentration, the concentration quenching of the DMQA is reduced. The C545T-fixed and DMQA-graded OLED was fabricated, and the doping concentration of the DMQA is graded from 0.5% at the HTL interface, to 0.8% at the ETL interface, with an average of 0.65%, thereby, being lower than 1.0%. The EL characteristics of the graded codoped OLEDs are also shown in Fig. 3 where it can be seen that the EL efficiencies are much higher than that of the 0.5:0.5% codoped OLEDs, as expected. While the 1.0:1.0% codoped OLED shows a lower performance than the 0.5:0.5% codoped OLED, the reduced doping concentration of DMQA, from 1.0% to an average of 0.65%, gives a significant improvement in the EL efficiency.

The summarized performances of fabricated OLEDs are shown in Table I. The peak CE and EQE of graded doped OLED were 17.3 cd/A and 4.8%, respectively. These are 24% and 20% higher than the 0.5:0.5% codoped OLED case. Also, the observed peak luminance of 15 900 cd/m^2 at 100 mA/cm^2 was 23% higher than the 12 950 cd/m^2 of the 0.5:0.5% codoped OLED. The reduced energy transfer into the DMQA obtained by lowering the DMQA doping concen-

TABLE I. Summarized performances of OLEDs.

Doping profile (%)	Luminance (cd/m^2)		CE, EQE (cd/A, %)		PE (lm/W)	
	a	b	a	b	a	b
0.5:0.5	12,950	110	13.0,3.7	13.9,4.0	2.6	4.2
1.0:1.0	10,500	42	10.5,3.1	12.4,3.8	2.2	3.3
graded	15,900	130	15.9,4.4	17.3,4.8	4.0	6.3
1.00:0.75	22,010	195	22.0,6.3	23.4,6.7	4.6	7.7
1.00:0.50	17,820	158	17.8,5.2	18.9,5.5	3.6	6.3

[a]At 100 mA/cm^2.
[b]At peak current efficiency.

tration, prevents concentration quenching and improves the EL efficiency of the codoped OLED. The peak EQE of 4.8% for the graded doped OLED means that balanced and ICETs (BICET), between the host matrix and cosensitizing fluorescent dyes, realized the quenchingless emissions in the fluorescent OLEDs.[16]

Finally, to derive the optimized devices, OLEDs, having C545T:DMQA $(x:y\%)$ doped EML, have been fabricated. Also, the thickness of the ETL has been increased from 30 to 50 nm for enhanced light-out coupling. The EL characteristics of the optimized devices are also shown in Fig. 3, where it can be seen that the OLED doped with 1.00:0.75% show the highest EL efficiencies; the peak CE, EQE, and a power efficiency of 23.4 cd/A, 6.7%, and 7.7 lm/W are obtained at the luminance of 195 cd/m^2.

In conclusion, under the Förster energy transfer dominant system, the best codoping concentration has been limited by the dopant having the smallest singlet energy. Due to the increased energy transfer from the host matrix and the other dopant, the dopant with the smaller singlet energy works as a final accepter of the energy transfer. This dopant becomes a concentration quenching site, even at the ideal single-doping concentration level. The codoped OLED, with an optimized codoping concentration, whose dopant with a smaller singlet energy having a lower doping concentration than the optimal single doping concentration, shows a balanced energy transfer between multiple dopants followed by balanced multiple emissions of the multiple dopants. The optimized device shows the highest EL efficiencies at 195 cd/m^2; current, EQE, and a power efficiency of 6.7%, 23.4 cd/A, and 7.7 lm/W, respectively. Also, the optimized OLED shows the low roll-off efficiency of −8.6% from 0.9 to 400 mA/cm^2; CE of 21.2 cd/A, at 400 mA/cm^2 with peak luminance of 84,900 cd/m^2. This optimized device demonstrates that reducing concentration quenching and balancing the distributed emission from the host matrix and the guest dye sensitizers by BICET, highly improves the EL efficiencies. Efficiency values of more than sixfold higher than those from conventional undoped Alq_3 devices have been realized. The demonstrated peak CE and EQE of 23.4 cd/A and 6.7% is the highest result of all previously reported Alq_3-based devices with conventional structures.

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[16]See EPAPS supplementary material at http://dx.doi.org/10.1063/1.3243689 for clarity of multiple emission of multiple dopants in graded configuration, the photoluminescence time resolved emission spectroscopy (TRES) of codoped thin films is performed. The Fig. s-1 in supplemental shows the TRES spectra which is the direct evidence of energy transfer, and it supports the explanations.