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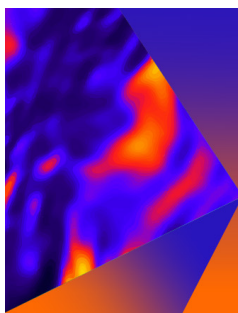


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Red organic light-emitting diodes using an emitting assist dopant

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We propose an emitting assist (EA) dopant system for obtaining organic light-emitting diodes (OLEDs) with pure red emission. The EA dopant (rubrene) did not itself emit but assisted the energy transfer from the host (Alq₃) to the red emitting dopant (DCM2). The cell structure used was {indium tin oxide/hole injection layer [(20 nm), CuPc/hole transport layer (50 nm), NPB/emitting layer (40 nm), Alq₃+DCM2 (2%)+rubrene (5 wt %)]/MgIn}. (CuPc: Copper (II) phthalocyanine, NPB: N, N'-Di(naphthalen-1-yl)-N, N'-diphenyl-benzidine, DCM2: 4-Dicyanomethylene-2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-8-yl)vinyl]-4H-pyran). A stable red emission (chromaticity coordinates: $x=0.64$, $y=0.36$) was obtained in this cell within the luminance range of 100–4000 cd/m². When the cell was not doped with rubrene, the emission color changed from red to orange as the luminance increased. The EA dopant system is a promising method for obtaining red OLEDs. © 1999 American Institute of Physics. [S0003-6951(99)04538-6]

Organic light-emitting diodes (OLEDs) have been expected to find an application as a new type of display since C. W. Tang and S. A. VanSlyke first reported on high-performance OLEDs.¹ The distinctive feature of OLEDs is that they use organic fluorescent dyes as an emitter. Therefore, they are able to produce various emission colors in accordance with a wide selection of organic fluorescent dyes. The green, yellow, and blue OLEDs have high luminance, high efficiency, and long life times.^{2–4} However, red OLEDs with high emitting performance and pure red emission have not been reported.

Conventional red OLEDs have an emitting layer consisting of one material during their early development.⁵ However, these devices are incapable of high luminance because of concentration quenching in the emitting layer. Recently, a doping system is often used in OLEDs in order to prevent this concentration quenching.⁶ The doping system is composed of a host material and a red dopant. When the host layer is doped with a small quantity of the red dopant, which is a fluorescent dye, the red dopant emits with high luminance and without concentration quenching. Tris(8-quinolinolato)aluminum (Alq₃) is widely used as a host material because it features good carrier transporting characteristics, easy film formation, and high stability.

However, the emission obtained from such a doping system is generally not red but orange. There is an emitting peak of Alq₃ in addition to the red peak in this doping system. Alq₃ exhibits strong green fluorescence (peak: 524 nm), and the red dopant shows fluorescence in the range of 600–650 nm. Therefore, the orange emission was the result of a mixture of the two emitting peaks. For this reason the doping system consisting of a host material and a red dopant cannot produce a pure red emission. The energy transfer from Alq₃ to the red dopant could not be made because the excitation

energy of Alq₃ differs greatly from that of the red dopant.

In this letter, we propose a new doping system that can emit pure red with high luminance. An additional dopant, called an emitting assist (EA) dopant, is used with a red dopant in order to prevent the emission from Alq₃. The EA dopant acts as an intermediary since its excitation energy lies between those of Alq₃ and the red dopant. The EA dopant itself does not emit but assists the energy transfer from Alq₃ to the red dopant.

OLED cells were fabricated on indium tin oxide (ITO, anode) substrates which were cleaned by an ultraviolet ozone cleaner immediately before use. Organic layers and a cathode layer (Mg_{0.9}In_{0.1}) were deposited by conventional vacuum vapor deposition in 5×10^{-6} Torr. The emitting area was 2×2 mm. The cell structure used in this experiment was as follows: [ITO/hole injection layer (20 nm, CuPc)/hole transport layer (50 nm, NPB)/emitting layer (40 nm, Alq₃+red dopant+EA dopant)/MgIn].

(CuPc: Copper (II) phthalocyanine, NPB: N, N'-Di(naphthalen-1-yl)-N, N'-diphenyl-benzidine).

4-Dicyanomethylene-2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-8-yl)vinyl]-4H-pyran (DCM2)

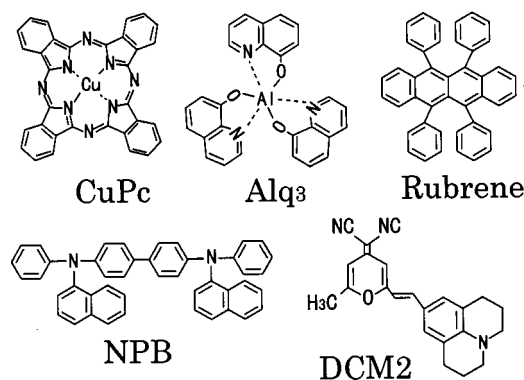


FIG. 1. The molecular structures of the materials.

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TABLE I. The change of chromaticity coordinates in red OLEDs with luminance in the range of 100–4000 cd/m².

DCM2 (%)	Rubrene (%)	Luminance (100 cd/m ²)	Luminance (1000 cd/m ²)	Luminance (4000 cd/m ²)
1	0	$x=0.57, y=0.42$	$x=0.54, y=0.44$	$x=0.54, y=0.44$
	3	$x=0.62, y=0.38$	$x=0.60, y=0.39$	$x=0.60, y=0.40$
	5	$x=0.59, y=0.41$	$x=0.57, y=0.42$	$x=0.56, y=0.43$
2	0	$x=0.62, y=0.38$	$x=0.62, y=0.38$	$x=0.60, y=0.39$
	3	$x=0.65, y=0.35$	$x=0.64, y=0.36$	$x=0.64, y=0.36$
	5	$x=0.64, y=0.36$	$x=0.64, y=0.36$	$x=0.64, y=0.36$

was used as the red dopant,⁶ and rubrene was used as the EA dopant. Figure 1 shows the molecular structures of these materials. The photoluminescent (PL) peak of DCM2 and rubrene is 650 and 560 nm, respectively. Therefore, rubrene is an intermediary with an excitation energy between those of Alq₃ and DCM2. The doping concentration of DCM2 was 1 and 2 wt % relative to the Alq₃ weight, and that of rubrene was 0, 3, and 5 wt % relative to the Alq₃ weight. The ionization potential of the organic films was measured by atmospheric ultraviolet photoelectron analysis using Riken Keiki AC-1 under ambient atmosphere.

The chromaticity coordinates of these cells at luminance values of 100, 1000, and 4000 cd/m² are shown in Table I. The OLED containing 2 wt % DCM2 was more suitable for obtaining red emission compared to the OLED with only 1 wt %. In particular, the [2,3] cell (DCM2: 2 wt %, rubrene: 3%) and the [2,5] cell exhibited good red color ($x=0.64, y=0.36$). The distinctive feature of cells using an EA dopant is that no change in chromaticity coordinates is observed within the luminance range of 100–4000 cd/m². On the other hand, when the EA dopant is not used, the change in chromaticity coordinates is large. Although the [2,0] cell had reddish emission ($x=0.62, y=0.38$) at a low luminance of 100 cd/m², it had orange emission ($x=0.60, y=0.39$) at a high luminance of 4000 cd/m².

The PL spectra of the [2,5] film (Alq₃+DCM2 2 wt % + rubrene 5 wt %) and the [2,0] film (Alq₃+DCM2 2 wt %) are shown in Fig. 2. The excitation wavelength was 380 nm, which was the same as the absorption peak of Alq₃. In the [2,5] film, only the PL peak of DCM2 (644 nm) was observed. Those of Alq₃ and rubrene were not observed. This indicates that the energy transfer

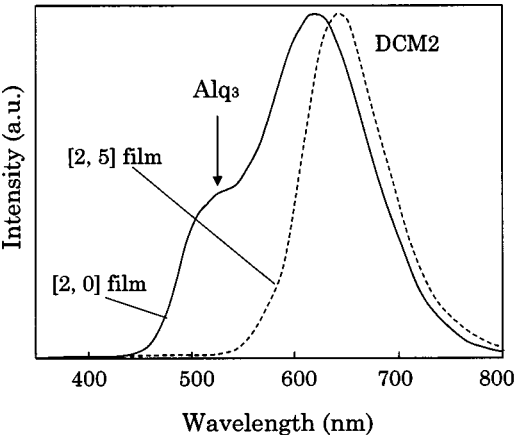


FIG. 2. The PL spectra of [2,5] and [2,0] films.

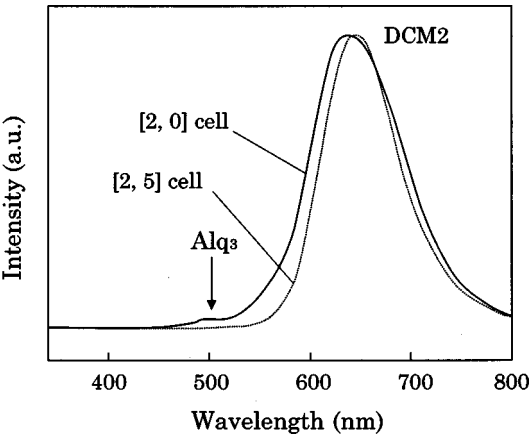


FIG. 3. The EL spectra of [2,5] and [2,0] cells.

from Alq₃ to DCM2 effectively occurred through rubrene in the [2,5] film. However, the large PL peak of Alq₃ near 520 nm was observed with DCM2 in the [2,0] film. This was because the energy transfer did not occur effectively in the rubrene-undoped film.

The electroluminescent (EL) spectra of the [2,5] cell and the [2,0] cell at 100 cd/m² are shown in Fig. 3. The EL peak of the [2,5] cell was 645 nm, which originated from the DCM2. No EL peaks of Alq₃ and rubrene were observed. However, in the [2,0] cell, there was a small peak due to Alq₃ observed along with the DCM2 peak. The emission color changed from red to orange with increasing luminance in the [2,0] cell because the EL intensity of the Alq₃ was relatively enhanced.

When the concentration of DCM2 was 1 wt %, the emission color changed with increasing luminance, even in rubrene-doped cells, such as the [1,3] and [1,5] cells. This was because the concentration ratio of DCM2 and rubrene was not suitable for preventing this shift in emission color.

Figure 4 shows the luminance–voltage curves of the [2,0], [2,3], and [2,5] cells. The maximum luminance of all three cells was almost the same ([2,0] cell: 7130 cd/m², [2,3] cell: 7840 cd/m², and [2,5] cell: 7780 cd/m²). However, only

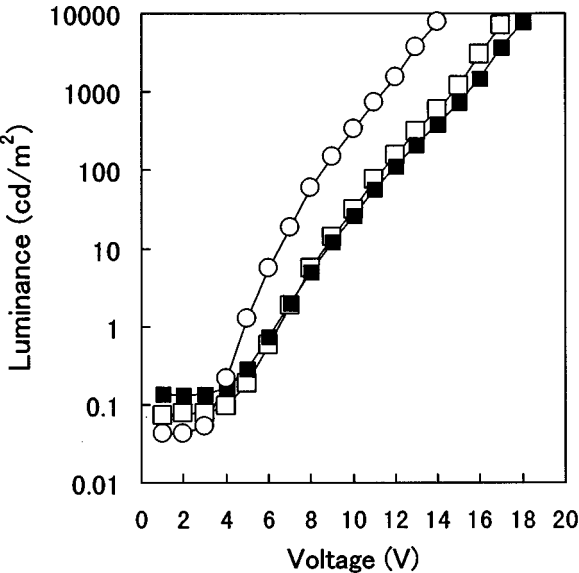


FIG. 4. The luminance–voltage characteristics of [2,0], [2,3], and [2,5] cells: □ [2,0] cell, ■ [2,3] cell, and ○ [2,5] cell.

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the luminance–voltage curve of the [2,5] cell shifted toward the low-voltage region in comparison with those of the [2,0] and [2,3] cells. The turn-on voltage (at 1 cd/m²) of the [2,5] cell was also the lowest of all cells ([2,0] cell: 6.5 V, [2,3] cell: 6.3 V, and [2,5] cell: 4.8 V). This decrease in voltage was due to the increase in the concentration of rubrene.

There are three possible emission processes in the rubrene-doped cells:

- (1) Injected electrons and holes recombine on the host molecules (Alq₃). The Alq₃ molecules enter an excited state, and the excitation energy of the host molecules is directly transferred to DCM2 molecules; or it is transferred to DCM2 molecules by the intermediation of rubrene. The DCM2 molecules then produce the light.
- (2) Injected electrons and holes recombine on the rubrene molecules, and the rubrene molecules enter an excited state. The excitation energy of rubrene is transferred to DCM2, and the DCM2 molecules produce the light.
- (3) Injected electrons and holes directly recombine on the DCM2 molecules, and the DCM2 molecules produce the light.

Processes (1) and (3) may exist in the [2,0] cell. Process (1), however, would dominate. The process in which Alq₃ itself emits is limited to process (1) because the energy transfer from Alq₃ to DCM2 is slightly difficult.

All three processes may be active in [2,3] and [2,5] cells. However, it is thought that process (1) dominates in the [2,3] cell and process (2) dominates in the [2,5] cell due to its having a higher rubrene concentration. We have reported previously that rubrene was the dopant responsible for carrier trapping.⁷ The recombination of holes and electrons readily occurred on the rubrene molecules when rubrene was used as a dopant.

Figure 5 shows the energy diagram of the [2,5] cell. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of rubrene exist between the HOMO and LUMO of Alq₃. Therefore, injected holes and electrons in the Alq₃ layer transfer into the HOMO and LUMO of rubrene, which have lower barriers compared to those of Alq₃. The recombination of carriers then occurs

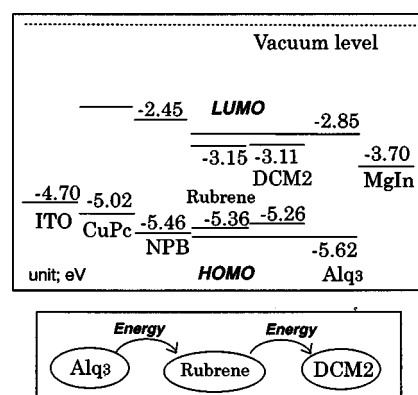


FIG. 5. The energy diagram of [2,5] cell.

on the rubrene molecules. As the concentration of rubrene increases, the recombination on rubrene molecules occurs more readily. Therefore, when process (2) dominates, the drive voltage of the [2,5] cell is lowered. Also, the excitation energy of the rubrene molecules is transferred efficiently to the DCM2 molecules because the HOMO and LUMO of DCM2 are nearly equal to those of rubrene.

An EA dopant, such as rubrene, is very useful in obtaining pure red emission. When an EA dopant is used, the change of the emission color from red to orange is prevented and the drive voltage is lowered. The EA dopant system would improve the performance of other OLEDs.

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