Various Color Long Life EL materials based on a new fused aromatic ring

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Abstract

Excellent organic electroluminescent materials are needed to realize color EL devices with high performance. We have succeeded in realizing bright and efficient devices with long lifetime in red and white color regions, based on a new fused aromatic ring derivative.

1. Introduction

Organic electroluminescence[1] has been studied extensively in order to realize thin, efficient and stable displays with wide viewing angle and fast response[2,3]. The applications such as automotive, mobile and television displays continue to make progress toward a commercial stage of organic EL[2-6]. In response to the progress, the performance of organic EL materials has been improved in lifetime as well as in efficiency.

Material researchers in an organic EL field have concentrated on the development of the emitting materials for full color displays for several years. The practical emitting material in a pure blue region was reported in 2001[7]. A red emitting material has been improved in lifetime and is now recognized to be in a practical use stage [6]. However, the continuing effort is made in order to improve the efficiency and lifetime in red EL. The assist doping method for enhancing the energy transfer [6] and phosphorescent EL for overcoming the theoretical limit of red EL efficiency [8] were reported. Here, we report that we succeeded in realizing a red emitting device with high efficiency and long lifetime by using a new red emitting material. The special features of our system are considerably longer lifetime and lower voltage, compared to the other systems.

On the other hand, white EL materials attract much attention because these applications include displays as well as illuminations. The lifetime over 10000 hr [5] and the luminous efficiency over 10 lm/W [9] were reported. However, there is still demand in improvement of the device stability. For example, the color change of white EL is the problem in the commercialization of white EL devices. Here, we report a new white EL material. By using the material, we succeeded in keeping the color change of white EL less than 0.01 in CIE coordinates. In addition, the lifetime more than 10000 hr was realized not only under DC driving but also under pulse driving.

2. Red EL

The host-dopant system has been used to obtain red EL and the energy transfer from the host to the red dopant plays an important role in the system[6,10]. For many EL devices, Alq [tris (8-hydroxyquinolate) aluminum] as a host and a red dopant have been used as the red emitting layer (EML). However, the following problems prevented us from obtaining practical EL devices with high efficiency.

(1) Energy transfer efficiency is low because of the large energy difference between host emission energy and dopant emission energy.
(2) Red EL is easily quenched in the high dopant concentration region.
(3) Red dopants form carrier traps in the EML because of the small energy gap of the dopant.

So, the following solutions have to be considered for those problems.

(1) Introducing molecules with carrier transporting ability as a dopant emitter.
(2) Introducing sterically bulky substituents inhibiting stack of dopant molecules.
(3) Applying a blended (high concentrated) dopant with a host material.

When the energy transfer is not complete, the host emission is generated in addition to the dopant emission. Then the emission color becomes orange. In order to obtain pure red, it is necessary to increase the dopant concentration. However, the efficiency was found to be low (about 2 cd/A) due to the concentration quenching[10]. Recently, Hamada et al. reported the assist doping method to enhance the efficiency of the red EL[6].

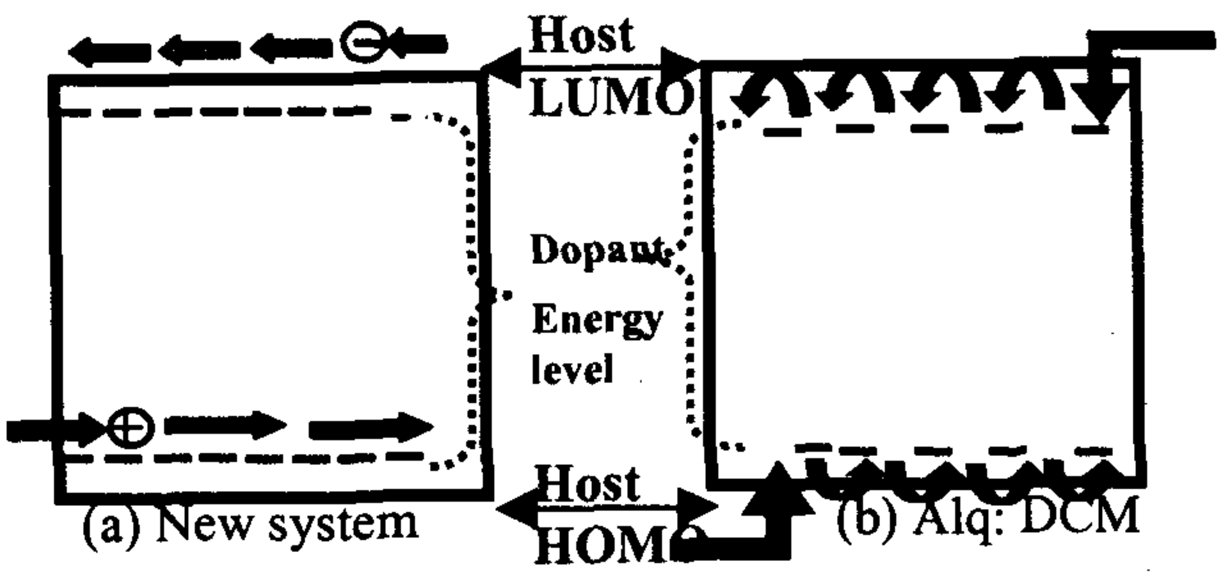

Fig.1: Energy diagram of the red EML

By the use of the assist dopant, cascade energy transfer occurs. The improved efficiency of 2.8 cd/A and the lifetime of 8000 hr were reported for the red EL devices[6].

However, their used a dicyanmethylenepyran (DCM) derivative as the red dopant forms carrier trap in the red EML and the applied voltage increases due to the trapping effect. Figure 1, (b) shows the energy diagram for the Alq: DCM EML.

The carriers are deeply trapped and the transportation of carriers between traps is inhibited at the low dopant concentration region. Carrier de-trapping is needed for the carrier transport as shown in Figure 1 (b). The large voltage loss exists in the detraping process.

Here, we report a new dopant, which can reduce the operating voltage significantly. The red dopant (P1) with the following properties and performance is a kind of a fused aromatic ring.

<Properties>

a) Reducing the driving voltage below 4 V (@100nit)

b) Performing 3.5cd/A in the high concentration of 20 % to the host material.

c) High-performance red emission in the simple layer (P1:Alq) with no assist dopant.

<Performance>

High Efficiency	3.5 cd/A
(luminous efficiency)	3.0 lm/W
Long Lifetime	> 10,000hr(int.500nit)
CIE coordinates	(0.64, 0.36)

P1 can be doped into red EML at a high concentration. We observed that quenching effect was not remarkable for the red EL device with the P1 dopant. The device structure was reported before [7].

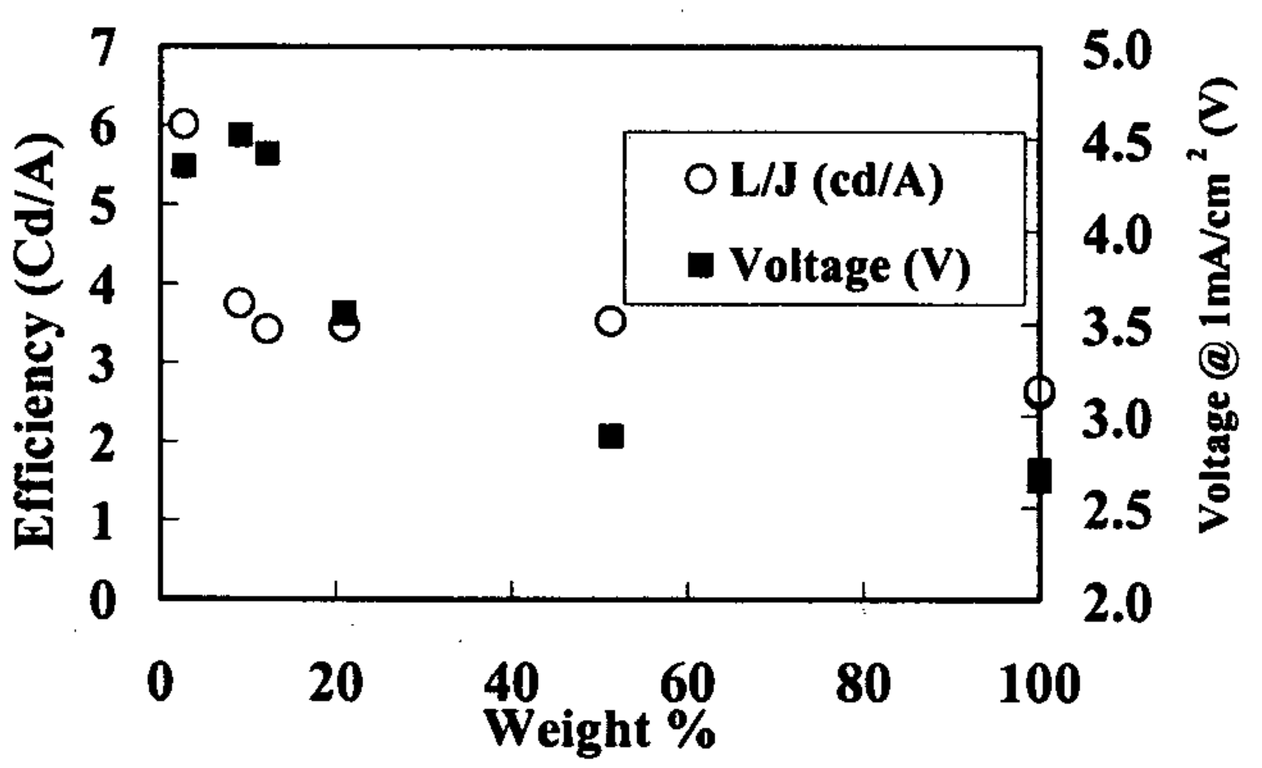

Fig.2: Efficiency and voltage for the doped devices.

Figure 2 shows EL efficiency for the doped device with the Alq host material. At a dilute concentration of 2.7 wt%, the efficiency of 6.0 cd/A was obtained. With increasing the concentration, the efficiency decreased to 3.8 cd/A and remained almost constant at 9.1, 21, and 51 wt%. By the use of this nature, the operating voltage can be reduced over 20 wt% as shown in Fig.2. On the other hand, it is usually observed that the red EL from an ordinal red dopant such as DCM is completely quenched in the high concentration region. Therefore, DCM can be used only at a dilute concentration.

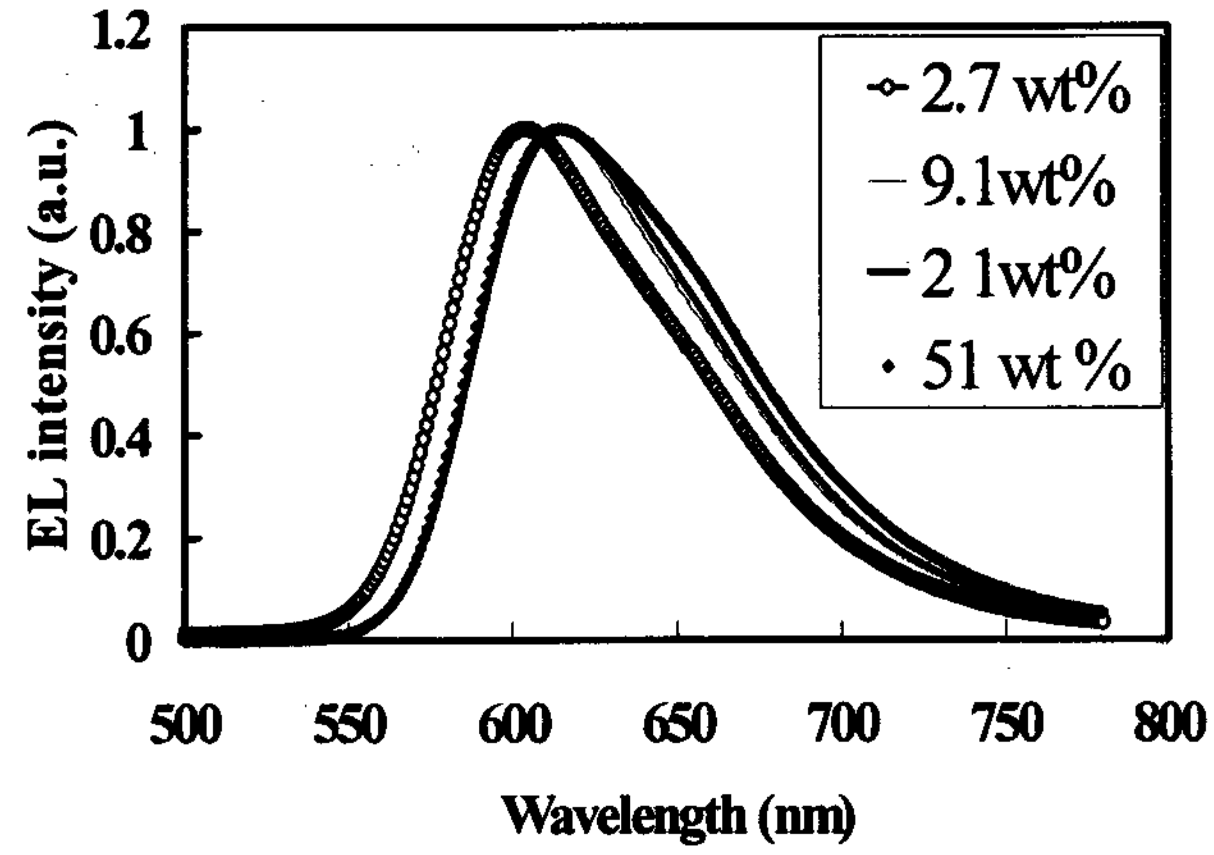

Fig.3: EL spectra for the doped devices.

Figure1 (a) shows the injection and transport mechanism for the P1 doped device. Holes can be transported between dopants in the high concentration region. Furthermore, injection mechanism for the P1 doped device is quite different from that for the other ordinal device. Ionization potential of P1, that of Alq and that of a hole transporting layer is 5.2, 5.7 and 5.4eV, respectively. Considering the energy barrier in hole injection, it is likely that holes can be injected not into the highest molecular orbital (HOMO) of Alq but into HOMO of the P1.

Table1. EL characteristics of the P1 doped devices.

Conc.	Vol.	Luminance	CIE		L/J	Lumi Eff.	EXQ	Peak
wt%	V	nit	X	Y	cd/A	lm/W	%	nm
2.7	4.35	60	0.61	0.39	6.0	4.3	3.5	602
9.1	4.52	38	0.64	0.36	3.8	2.6	2.7	610
21	3.56	35	0.64	0.36	3.5	3.1	2.7	614
51	2.89	35	0.63	0.37	3.5	3.8	2.5	610
100	2.71	26	0.60	0.40	2.6	3.0	1.4	593

The value of current density is constant, $1 mA/cm^2$. Luminous efficiency is denoted as Lumi. Effi. External quantum efficiency is denoted as EXQ.

Figure 3 shows EL spectra for the P1 doped devices. Table 1 shows EL characteristics for the devices. With increasing the concentration, red shift of the peak occurs. At a concentration of 21 wt%, the luminous efficiency of 3.1 lm/W was obtained in red color region. This considerably high value is partially due to the low operating voltage. The voltage was only about 4 V at a luminance of 100 nit. It is noted that voltage of 7 or 8 V was needed to obtain the luminance of 100 nit for an Alq: DCM device. In addition, P1 doped devices possess a simple structure without any assist dopant and the EML can be easily formed by evaporation because the color coordinates do not change in the wide concentration range.

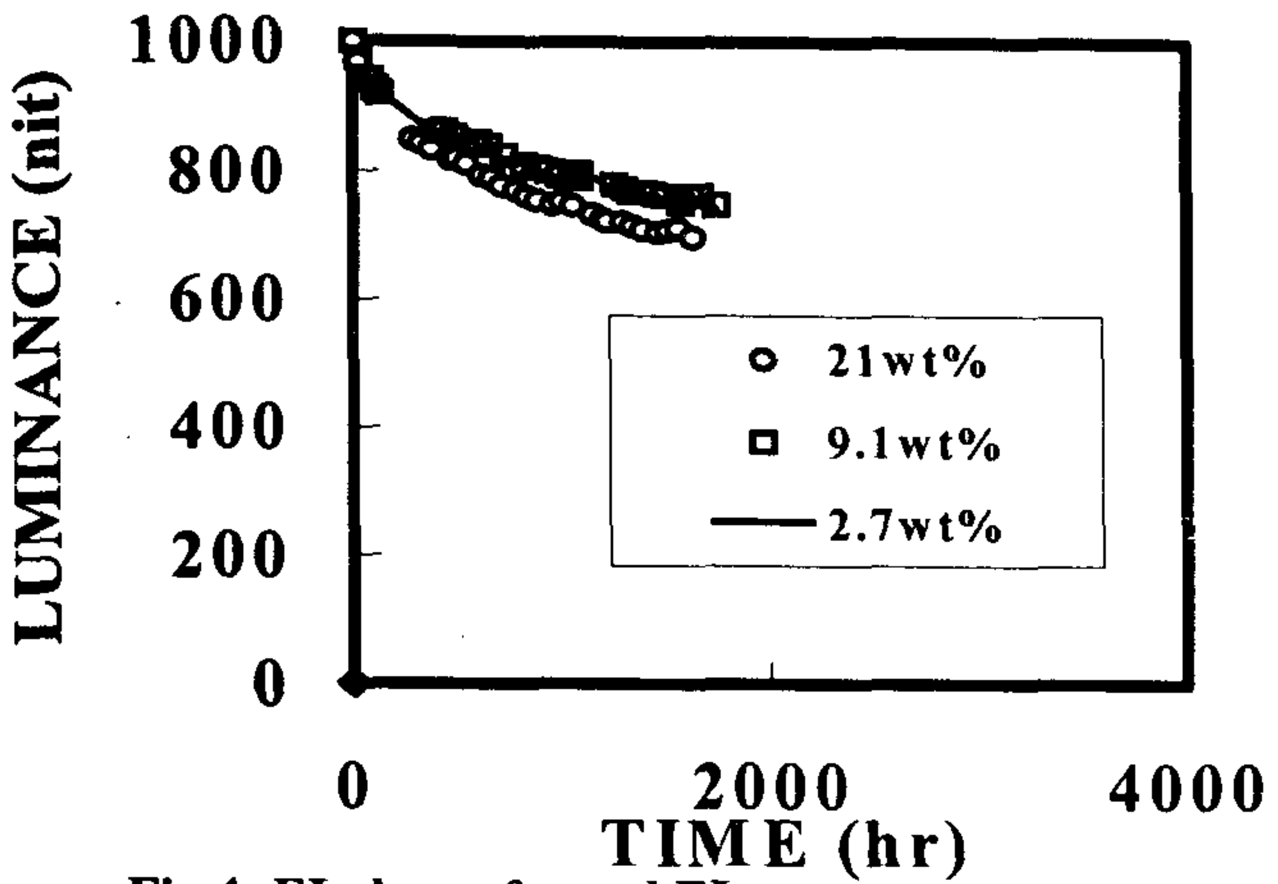

Fig 4: EL decay for red EL.

Figure 4 shows the luminance decay curve in the acceleration test under the constant DC current. The half lifetime over 5000 hr was estimated at an initial luminance of 1000 nit. This indicates that the half lifetime over 10000 hr can be realized at an initial luminance of 500nit. This value is one of the longest ever reported for organic red EL.

As described above, we succeeded in realizing highly efficient red EL devices with long lifetime by blending a new dopant P1 with the Alq host. Operating voltage was found to be reduced, due to the new hole injection and transportation effect.

3. Orange EL

The orange EL with long lifetime can be obtained by doping P1 into a distyrylarylene host material (IDE120) [7]. The luminance and the efficiency of the doped device were 231 nit and 11 cd/A at a voltage of 5.0 V (current density=2.1 mA/cm^2), respectively. The CIE coordinates were (0.56,0.43), The half lifetime was estimated to be 16000 hr (initial luminance is 1000 nit) as a result of the acceleration lifetime test as shown in Fig.5.

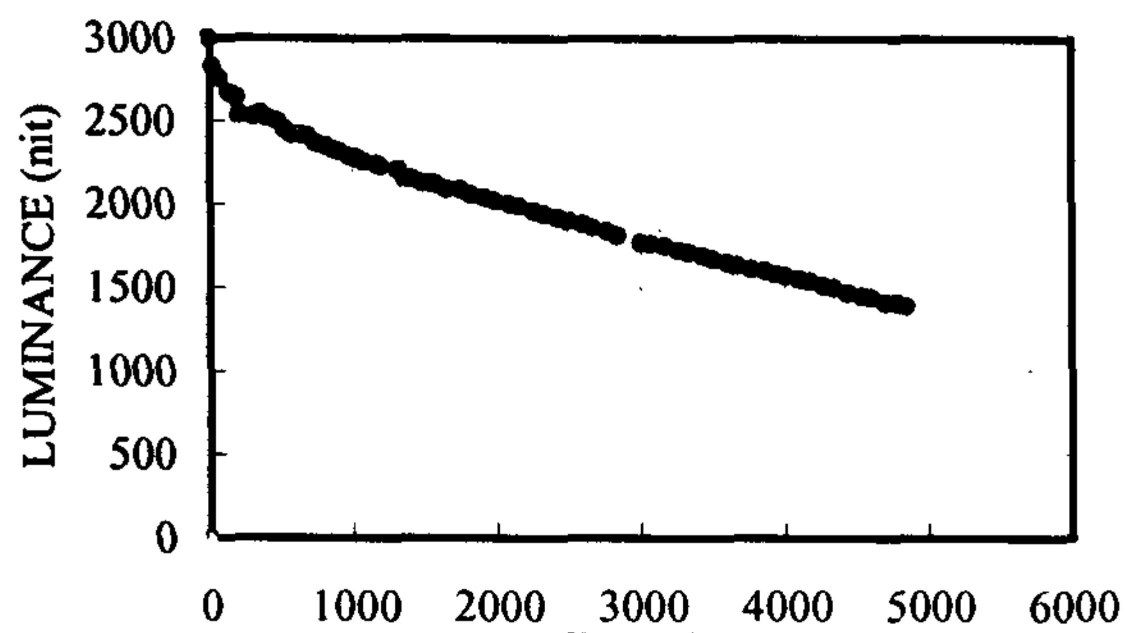

Fig.5: EL decay curve of orange EL.

4. White EL

Various white EL devices have been developed and reported [5,7,9]. The lifetime over 10000 hr [5,7] under the constant DC current and the efficiency over 10lm/W [9] have been reported. However, there are still problems as mentioned in the following.

(1) White color coordinates change with operating white EL devices.

(2) Lifetime is not long enough for practical use under the pulse driving.

We succeed in overcoming the problems by using the dopant P1 with a new host material (NB). Here, we report the detailed characteristics for the white EL device. The glass transition temperature of NB is over 120 degree centigrade. The light blue dopant, IDE102 is also used for the EL device. The EML structure was a two-layered type as reported before [7]. The first EML was an orange EML with the P1 doping into the NB host. The second EML was a blue EML with IDE102 doping into the NB host. This two-layered EML enabled us to obtain highly efficient devices with longer lifetime, compared to that reported before.

As the typical characteristics, the luminance, the CIE coordinates, and the efficiency were 114 nit, (0.31,0.34), and 11.4 cd/A at a voltage of 5.5 V (current density=1.0 mA/cm^2), respectively.

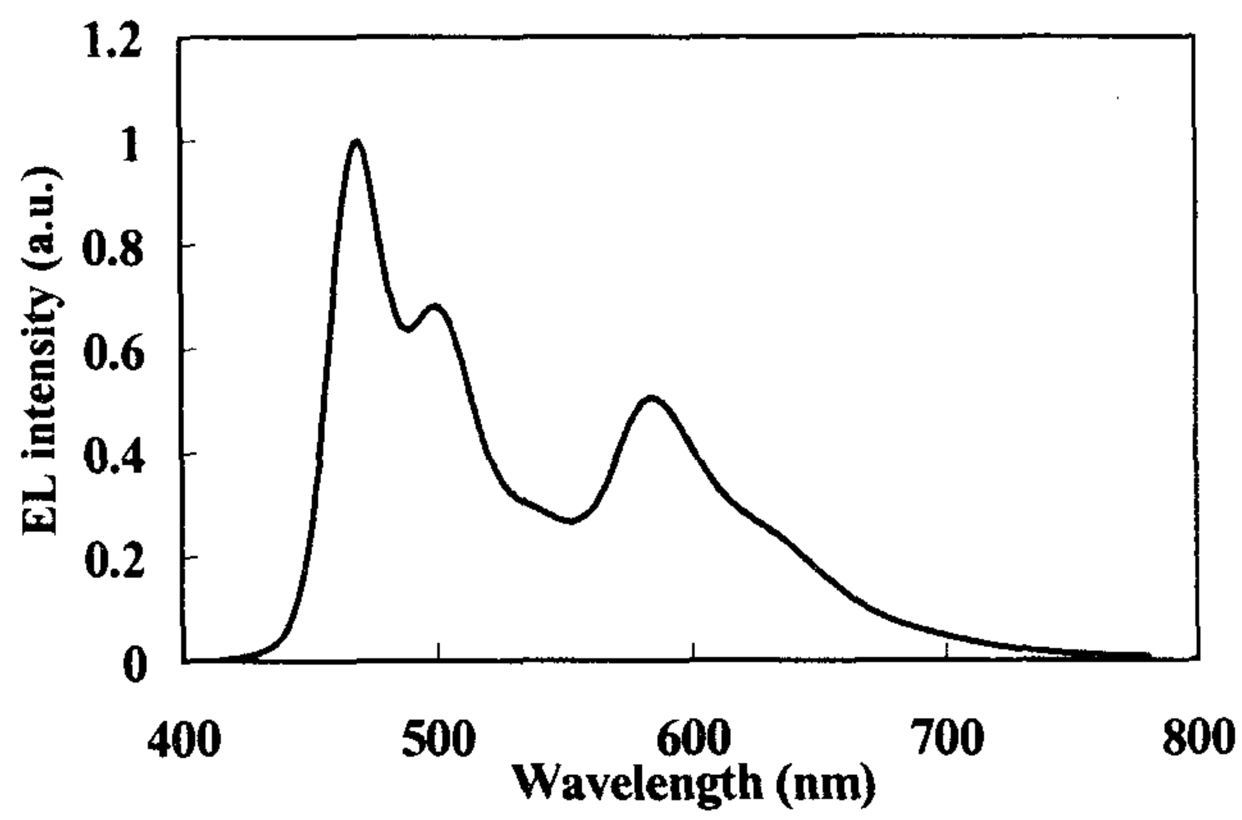

Fig.6: EL spectrum of white EL.

Figure 6 shows EL spectrum for the device with two-layered EML. The EL spectrum consists of a 472 nm band and a 586 nm band. If the degradation speeds of two bands are different, the color coordinates of the white EL may change with operating the device. The color coordinates could easily change if degradation of dopants and the occurrence of carrier imbalance occurred. In order to observe the color shift of white EL, we performed an acceleration test under the pulse driving at a duty ratio of 1/100 (the initial luminance was 500 nit). We found that the color coordinates of the white EL remained constant over the 1500 hr, as shown in Fig.7.

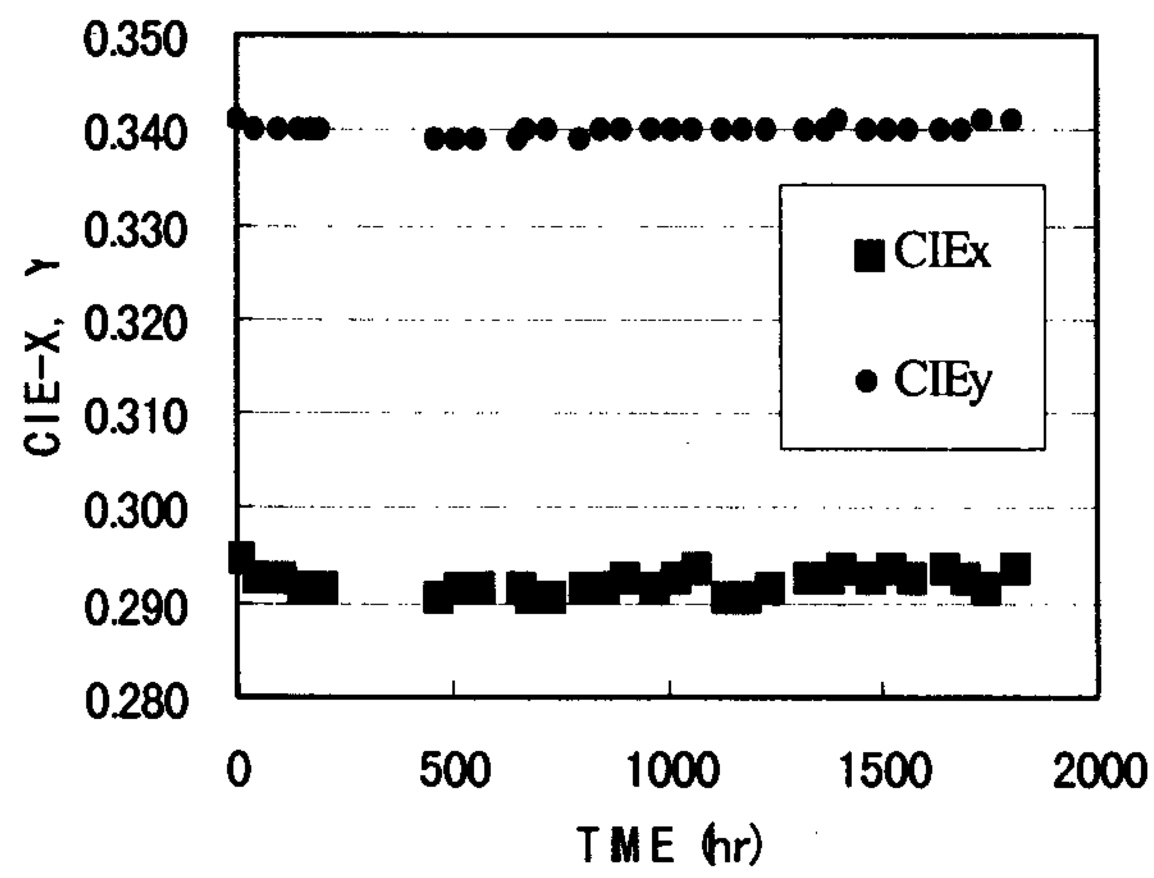

Fig.7: Color coordinates under pulse driving.

Furthermore, the lifetime of 5000 hr was estimated under the high duty pulse driving, as shown in Fig.8. Therefore, the lifetime at an initial luminance of 300 nit can be estimated to be 12000 hr on our experimental results that the lifetime is inversely proportional to 1.8 th power of luminance under the 1/100 duty pulse driving.

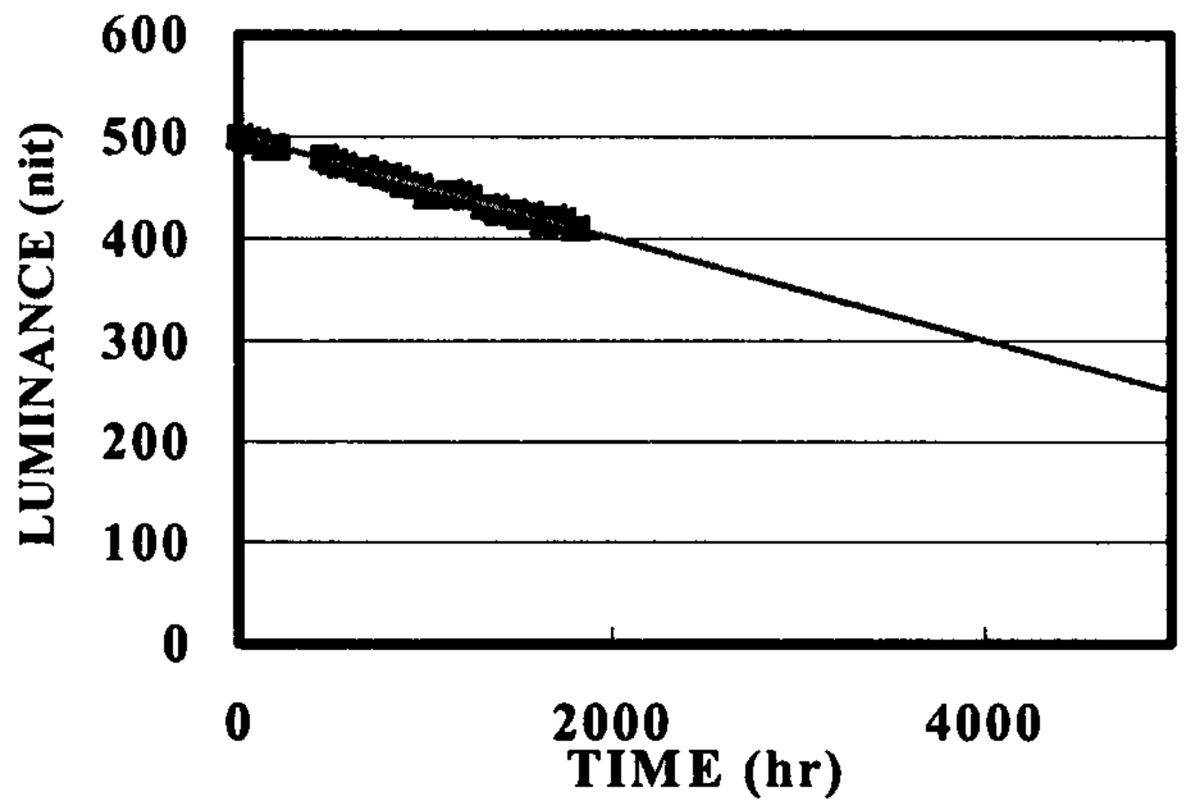

Fig.8: Decay curve of white EL under pulse driving

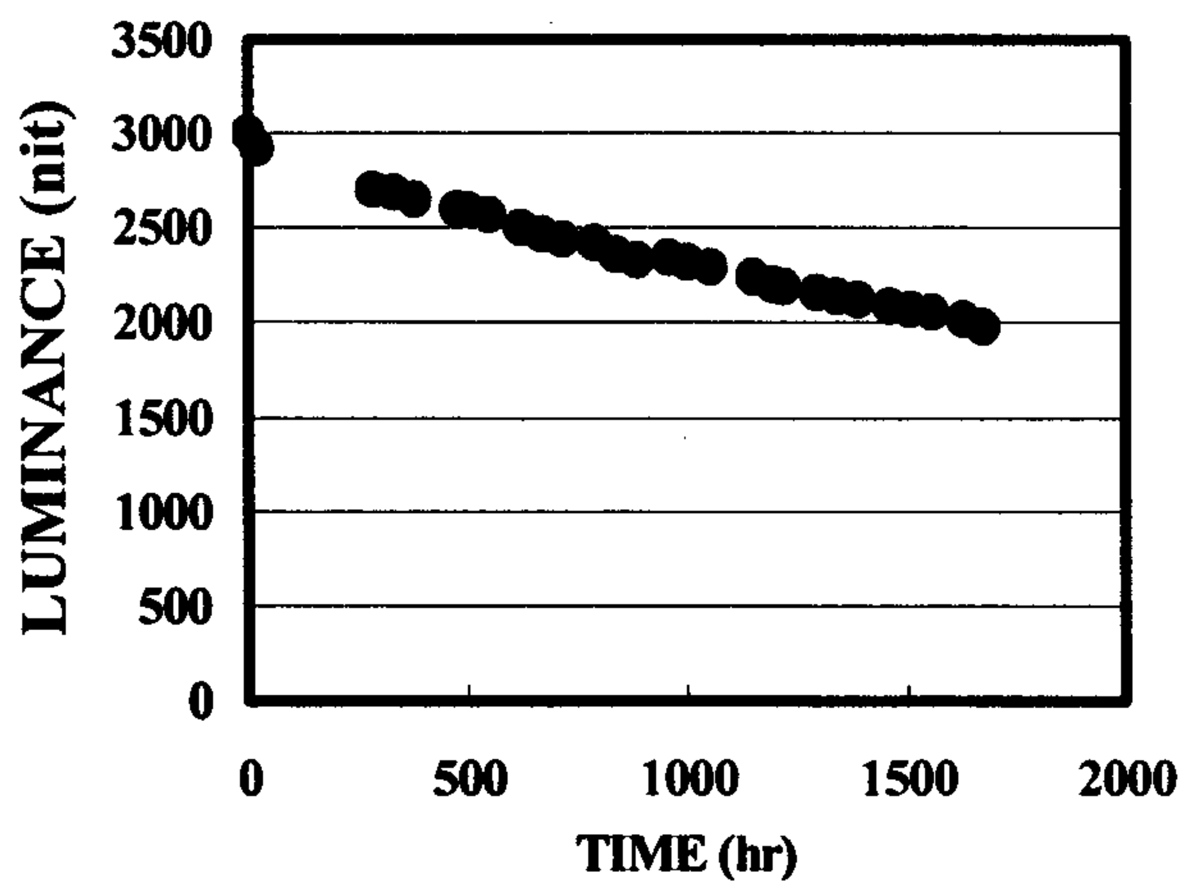

Fig 9: Decay curve of white EL under DC driving .

Under DC constant current, the lifetime was measured to be about 2800 hr at an initial luminance of 3000 nit, as shown in Fig.9. Therefore, the lifetime at an initial luminance of 1000 nit can be estimated to be 10000 hr on our experimental results that the lifetime is inversely proportional to 1.2 th power of the luminance. To our knowledge, this value is one of the longest ever reported for organic white EL.

<Performance>

a) White color coordinates are extremely stable with operating its device

b) Operating lifetime reaches 10,000hr (int.1,000nit) under DC.

As described above, the white EL material reported here shows high performance. The lifetime is long enough to apply the material to passive matrix displays driven by high duty pulses. The additional feature that color change is negligibly small also indicates the material is promising for the EL display. It should be emphasized that high luminance of 50000 nit (500nit under 1/100 duty driving) can be achieved at a considerably low voltage of 13 V

The operating voltage can be reduced when using alkali metal doping technology in our devices [9,11]. The luminance of 100 nit at a low voltage of 3V was reported. The luminous efficiency over 12 lm/W can be expected for the white EL material reported here as a result of improvement by the alkali metal doping. Therefore, the white EL material is suitable not only for passive matrix displays but also for illuminations. The color display based on filtered white EL is also promising.

5.Summary

《We get the excellent red devices!》

We have reported the detailed characteristics for the excellent devices with a new dopant P1. The red devices with the dopant P1 show the low operating voltage and the high luminous efficiency. In addition, the lifetime over 10000 hr was obtained. The red EL material is suitable for full color displays.

《We get the excellent white devices!》

We succeeded in obtaining an excellent white EL material. Extremely long lifetime and highly efficient device was obtained in white color region. In addition, almost no change of color was realized by the use of white EL material.

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