

23.2: New Green and Red Phosphorescent Host Materials for Highly-efficient and Long-lifetime OLEDs

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Abstract

We successfully found new phosphorescent host materials. Red host material PRH-01 with a red phosphorescent emitter achieved very high performance of 4.9 V, current efficiency of 20.2 cd/A and half lifetime of 150,000 hrs at an initial luminance of 1,000 cd/m². We designed new molecular structure of green host material focusing on electron transport property and newly developed material PGH-01 achieved very high performance of 5.3 V, 71.9 cd/A and half lifetime of 150,000 hrs at an initial luminance of 1,000 cd/m². It was confirmed by simulation that these host materials have great potential to reduce power consumption of full-color OLED displays. We also studied hybrid white OLEDs with combining the latest blue fluorescent material and the phosphorescent materials. High luminous efficacy of about 30 lm/W and long lifetime over 200,000 hrs at an initial luminance of 1,000 cd/m² without any light outcoupling structure were successfully obtained.

1. Introduction

Full-color Active-Matrix Organic Light Emitting Diode (AMOLED) displays have been rapidly developed and commercialized by some companies in 2007 [1]. In addition, some development projects for highly-efficient OLED lighting are now energetically proceeding in Europe. One of the main issues in order to glow the commercial market of OLEDs is the achievement of comparable power consumption to existing devices such as LCD or LED.

Fluorescent emitting materials are mainly selected in practical OLEDs in the point of lifetime issue. The efficiency of fluorescent OLEDs has been successfully improved in some groups [2], and possibility to the further improvement such as triplet recycling by triplet-triplet annihilation process [3] has been reported. However the limit of the internal quantum efficiency of fluorescent OLED is less than phosphorescent one in principle because of the generation ratio of singlet/triplet exciton. Therefore it is very important for the improvement of power consumption of OLEDs to develop phosphorescent OLEDs with high efficiency and long lifetime.

We have already reported a newly developed phosphorescent host material PRH-01 for red OLEDs [4]. In this report, we mention about the latest performance of phosphorescent red device combining PRH-01 with a red emitter. Very high performance, driving voltage of 4.9 V, current efficiency of 20.2 cd/A and half lifetime of 150,000 hrs at an initial luminance of 1,000 cd/m² were successfully achieved. At the same time, we designed new molecular structure of phosphorescent green host material focusing on the electron transport property of emitting layer. Newly developed material PGH-01 also achieved very high performance of 5.2 V, 71.9 cd/A and 150,000 hrs at an initial luminance of 1,000 cd/m². In order to estimate the contribution of

these host materials to the reduction of power consumption of full-color OLED displays, we estimated power consumption of 2.0" QVGA full-color OLED by utilizing optical simulation. It was confirmed by the simulation that these host materials have a great potential to reduce power consumption.

Furthermore we studied hybrid white OLEDs with stacking the latest deep blue fluorescent material and these phosphorescent materials. High luminous efficacy of about 30 lm/W and long lifetime over 200,000 hrs at an initial luminance of 1,000 cd/m² without any light outcoupling structure were successfully obtained.

2. Results and Discussions

2.1. Phosphorescent red host material

In 2008 we reported a new red phosphorescent host material PRH-01 which shows lower driving voltage and longer lifetime than conventional materials such as Zn-chelate derivatives or 4,4'-N,N-bis(carbazolyl)biphenyl (CBP) [4]. The obtained device performance was driving voltage of 5.2 V, current efficiency of 10.4 cd/A and half lifetime of 72,000 hrs at an initial luminance of 1,000 cd/m² with the device structure as follows.

ITO/HT/HT-1/PRH-01:RD/ET-1/LiF/Al

RD was a conventional red phosphorescent emitter and ET-1 is an electron transport material with high electron mobility developed for fluorescent OLEDs.

However the performance was less than the latest fluorescent OLEDs. Therefore we studied the improvement of performance by combining PRH-01 with new red emitter (RD1). The device structures were as follows;

ITO/HT/HT-1/PRH-01:RD1/HBL/ET/LiF/Al

The initial performance and half lifetime at an initial luminance of 1,000 cd/m² were summarized in Table 1. According to our empirical acceleration factor of 1.85th power, the lifetime values were estimated from the luminance decay curve at an initial luminance of 10,000 cd/m² as shown in Figure 1.

Table 1. Device performance of red OLEDs with PRH-01. Initial performance was at a luminance of 1000 cd/m².

EML	HBL	ETL	Voltage (V)	CIE (x, y)	L/J (cd/A)	EQE (%)	Half lifetime @1,000cd/m ² (hr)
PRH-01:RD	none	ET-1	5.2	(0.68, 0.32)	10.4	13.7	72,000
PRH-01:RD1	none	ET-1	4.1	(0.67, 0.33)	19.2	18.6	87,000
PRH-01:RD1	HBL	ET-1	4.6	(0.67, 0.33)	19.7	18.9	110,000
PRH-01:RD1	HBL	ET-2	4.9	(0.67, 0.33)	20.2	19.5	>150,000

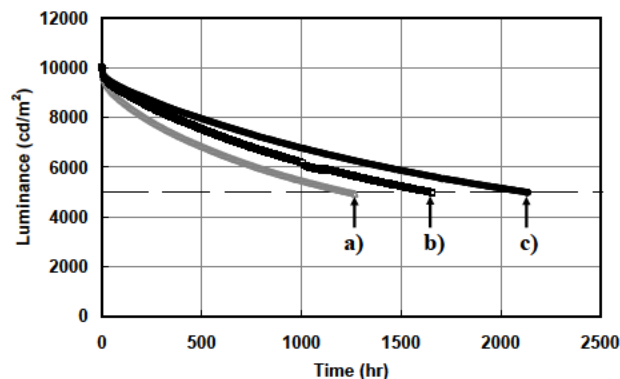


Figure 1. Luminance decay curves of PRH-01 devices with RD1 at an initial luminance of 10,000 cd/m^2 . Device structures are shown as follows, a) PRH-01:RD1/ET-1, b) PRH-01:RD1/HBL/ET-1, c) PRH-01:RD1/HBL/ET-2.

Firstly, the device with RD1 showed 1.8 times higher efficiency of 19.2 cd/A , but the lifetime was almost same as the device with a conventional RD. Here we supposed that the lower lifetime was caused by electron accumulation at the interface between the emission layer (EML) and ET-1 because of the large LUMO-level difference between ET-1 and PRH-01 of about 0.4 eV, followed by the degradation of electron transport layer (ETL) by accumulated electron.

Therefore we studied the effect of hole blocking layer (HBL) and ET materials dependence. The lifetime was highly improved from 87,000 hrs to 110,000 hrs by inserting HBL which has the intermediate LUMO level between PRH-01 and ET-1. Furthermore the device with ET-2 alternative to ET-1 showed the highest efficiency of 20.2 cd/A and the longest lifetime of over 150,000 hrs. We consider that the long lifetime was obtained by the higher electron durability of ET-2 than that of ET-1.

2.2. Phosphorescent green host material

In the latest full-color OLED displays which have high color purity over 100% of NTSC, green pixels need longer lifetime because of higher luminance rather than the device with lower color purity. A phosphorescent green system should be suitable for this requirement due to the higher efficiency than that of a fluorescence. However, the conventional green phosphorescent host material CBP has short lifetime.

Firstly, we fabricated a device with CBP and a phosphorescent green emitter (GD) and estimated its lifetime. The device structure was ITO/HT/HT-1/CBP:GD/HBL/tris(8-quinolynolato) aluminum (Alq_3)/LiF/Al. As shown in Table 2, the lifetime at an initial luminance of 1,000 cd/m^2 was confirmed to be severely shorter lifetime of 8,000 hrs than the latest fluorescent devices of over 100,000 hrs [2].

Table 2. Device performance of green OLEDs. Initial performance was at a luminance of 1000 cd/m^2 .

Host	ETL	Voltage (V)	CIE (x, y)	L/J (cd/A)	EQE (%)	Half lifetime @1,000 cd/m^2 (hr)
CBP	Alq_3	5.6	(0.32, 0.64)	52.6	14.0	8,000
PGH-01	ET-1	5.2	(0.35, 0.62)	71.9	19.2	>150,000

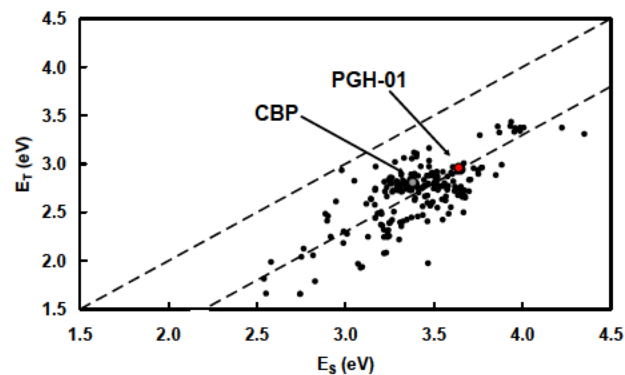


Figure 2. The relationship between singlet (E_S) and triplet energy gap (E_T) of host material: calculated results (black circle), measured results of CBP (gray circle) and PGH-01 (red-circle).

In order to analyze the degradation mechanisms of the CBP device, we measured the carrier mobility of CBP by time of flight method. The results were that the hole mobility of $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$ was larger than the electron mobility of $4 \times 10^{-4} \text{ cm}^2/\text{Vs}$ at an electric field of 0.25 MV/cm .

From the results we supposed the degradation mechanism as follows. Excess hole was injected into ETL because of the hole transport property of CBP which has carbazole units, and it was likely to occur the degradation of ETL by the injected hole.

Therefore we designed electron transport host structures without carbazole structure in order to improve the hole durability of device structure. From many types of candidate structures except chelate derivatives, we selected some structures with suitable singlet and triplet energy level E_S and E_T by utilizing quantum chemical simulation technique. As reported in the past, chelate derivatives are likely to degrade under the existence of hole. As the result, we obtained electron-transport-type host material PGH-01 which is non-chelate and has no carbazole unit. Figure 2 shows the relationship between singlet and triplet energy gap of host material. The E_T of PGH-01 is about 3.0 eV which is enough to confine the triplet exciton on green phosphorescent emitters that have the E_T of around 2.4 eV. The carrier mobility values of PGH-

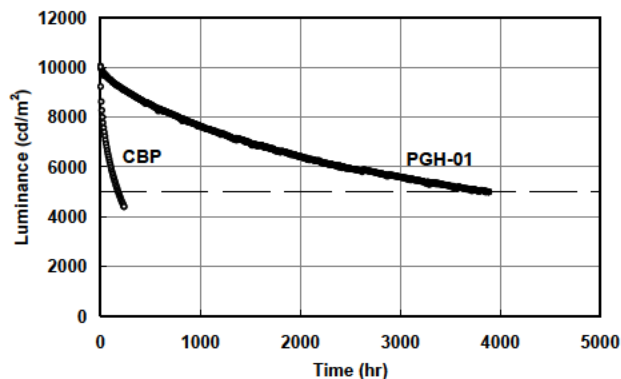


Figure 3. Luminance decay curves of green devices at an initial luminance of 10,000 cd/m^2 .

01 at an electric field of 0.25 MV/cm were 10^{-6} cm²/Vs (hole) and 6×10^{-4} cm²/Vs (electron).

We evaluated the device performance with PGH-01. The device structure was;

ITO/HT/HT-1/Host:GD/HBL/ET/LiF/Al.

The performance of PGH-01 was also shown in Table 2. PGH-01 achieved high current efficiency of 71.9 cd/A at 1,000 cd/m² (67.4 cd/A at 10 mA/cm²) and long lifetime of over 150,000 hrs by combining with ET-1. The acceleration factor of 1.7th power was used. High efficiency and long lifetime indicate that the triplet exciton and carrier were successfully confined in the EML by applying PGH-01 as the host. Figure 3 shows the lifetime test results of green devices at an initial luminance of 10,000 cd/m². We consider that degradation of ETL by hole was drastically decreased by using electron transport host material.

2.3. Performance simulation of full-color display

We estimated power consumption of full-color OLED displays with the newly developed host materials in order to confirm the effect on reduction of power consumption. Specifications of estimated display panel are as follows; Panel structure:2.0" QVGA and top emission type with polarizer (T = 45%), brightness:300 cd/m² (100% ON, Aperture ratio 40%), color coordinate of white: (0.31,0.32), NTSC ratio:100% and operating voltage 5 V (R, G, B). Each pixel luminance is 565 cd/m² (blue), 3006 cd/m² (green) and 1429 cd/m² (red). The CIE coordinate and current efficiency of each pixel was estimated by optical simulation method by using experimental results of bottom emission devices [5].

Estimated results were summarized in Table 3. It was confirmed that both PGH-01 and PRH-01 can contribute the reduction of power consumption by 50 mW compared to the case of all fluorescent type display. However, the half lifetime of phosphorescent green pixels was estimated to be about 25,000 hrs which was much shorter than fluorescent green pixels of 126,000 hrs. Furthermore, the lifetime of fluorescent blue pixel was the shortest and power consumption of that was the largest. In future we must try to improve materials for both phosphorescent green and fluorescent blue and contribute to the improvement of OLED display performance.

Table 3. Estimated results of 2.0" QVGA display performance. The power by TFT is not included.

	CIE _x	CIE _y	L/J (cd/A)	Voltage (V)	Power (mW)	Half lifetime (hr)
All fluorescence						
Blue	0.13	0.08	5.1	5	91	19,000
Green	0.21	0.69	37.1	5	67	126,000
Red	0.67	0.33	20.8	5	57	230,000
				total	215	
Blue:Fluorescence, G,R:Phosphorescence						
Blue	0.13	0.08	5.1	5	91	19,000
Green	0.24	0.71	77.5	5	32	25,000
Red	0.67	0.33	26.9	5	44	>600,000
				total	167	

Table 4. Device performance of fluorescent blue device and phosphorescent red/green stacked devices (type A, B) at 10 mA/cm².

Device	Voltage (V)	CIE (x,y)	L/J (cd/A)	EQE (%)
Blue	4.9	(0.14, 0.11)	6.6	6.8
R/G type A	3.9	(0.45, 0.53)	43.9	15.7
R/G type B	3.9	(0.41, 0.57)	66.5	20.1

Here it should be noted that the estimated structure in this paper was no optimized one and the joint development between Sony and Idemitsu has already contributed to highly efficient and long lifetime fluorescent deep blue device with optimized structure [6].

2.4. Fluorescent/phosphorescent-stacked hybrid white OLEDs

In recent years we have developed all fluorescent type white OLEDs and achieved very high efficiency of over 16 lm/W and long lifetime of 88,000 hrs at 1,000 cd/m². However the external quantum efficiency of the device has reached to 8.4%, which is close to the limit of all fluorescent system in principle, and further improvement of efficiency has been desired in order to improve performance of white with CF full-color display or OLED lighting system.

Therefore, we studied both fluorescent and phosphorescent stacked hybrid white OLEDs with PGH-01, PRH-01 and the latest fluorescent blue materials. The performance of fluorescent blue material used for the white OLEDs is CIE coordinate of (0.14, 0.11), voltage of 4.9 V, current efficiency of 6.6 cd/A and EQE of 6.8% at 10 mA/cm². Desirable color coordinate of red/green phosphorescent device was estimated to be (0.44, 0.53) in order to achieve good white color by combining with (0.14, 0.11) of blue. We developed two types of phosphorescent red/green stacked devices type A and B as shown in Table 4. We note that both green and red phosphorescent emitters in white OLEDs are conventional materials. Type A device achieved the CIE coordinate of (0.45, 0.53) which is very close to the ideal value for white. The color of type B turned slightly greenish but the EQE of over 20% was observed.

Finally we made some trial fabrications of hybrid white OLEDs. We developed two types of hybrid white OLEDs type I and II that are based on Type B structure for the red/green component due to its high EQE. The estimated device performances at a luminance of 1,000 cd/m² without any light outcoupling structure were summarized in Table 5. Lifetime was estimated from the results at an initial luminance of 10,000 cd/m² by using the acceleration factor of 1.7th power (Figure 6).

Table 5. Device performance of hybrid white OLEDs (type I, II) at 1,000 cd/m².

Structure	CIE (x, y)	fficacy lm/W)	Lifetime (hr)
Type I	(0.37, 0.40)	27.4	>200,000
Type II	(0.32, 0.42)	35.8	94,000

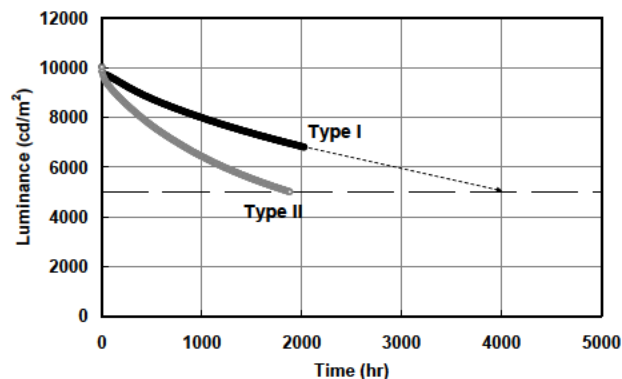


Figure 5. Luminance decay curves of hybrid white OLEDs at an initial luminance of 10,000 cd/m².

High luminous efficacy of 30 lm/W and long lifetime of about 200,000 hrs were successfully achieved. CIE y value of over 0.40 may not be suitable for display application, and we will improve color and efficiency in future by optimizing the device structure.

3. Summary

We successfully found new phosphorescent host materials. Red host material PRH-01 with a red phosphorescent emitter achieved very high performance, driving voltage of 4.9 V, current efficiency of 20.2 cd/A and half lifetime of 150,000 hrs at an initial luminance of 1,000 cd/m². At the same time, we designed new molecular structure of green host material focusing on electron transport property of emitting layer. Newly developed material PGH-01 also achieved very high performance of 5.3 V, 71.9 cd/A and half lifetime of over 150,000 hrs at an initial

luminance of 1,000 cd/m². These host materials will make great contributions to the reduction of power consumption of full-color OLED displays. Furthermore we studied hybrid white OLEDs with combining the latest blue fluorescent material and these phosphorescent materials. High luminous efficacy of about 30 lm/W and long lifetime over 200,000 hrs at an initial luminance of 1,000 cd/m² without any light outcoupling structure were successfully obtained.

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