Spectral Narrowing and Efficiency Enhancing in Deep-Red Organic Light Emitting Diode

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ABSTRACT

We developed both thermally activated delayed fluorescence materials with high performances and spectral-narrow fluorescent dopants for deep-red organic light-emitting diodes. We achieved the efficiency of 46 cd/A at 10 mA/cm^2 and the LT95 of around 90 hours at 50 mA/cm^2 in the top emission device at CIEx = 0.679.

1 INTRODUCTION

Even after realizing the organic light-emitting diodes (OLEDs) for practical mobile and large-sized screens, the evolution of OLEDs are keeping on going the field of size enlargement and high definition, or improving shape flexibility. The development of OLEDs that can express brighter and more vivid colors will be required for the various expanded applications to be realized in near future.

From the viewpoint of material developments, two subjects are presently discussing, a) the realization of luminescent materials with higher color purity, and b) the electro-excited system for high internal quantum efficiency (IQE) with practical durability.

The strict control of emission spectrum is very important for further enhancing both efficiency and color purity. By improving the color purity of emission from an OLED material itself, it can lead to reduction of color filter loss and, as a result, it can also enhance the efficiency in Bottom-emission (BE) devices. Particularly in the Top-emission (TE) devices, although it is necessary to consider the viewing angle dependency for each color pixel, reducing the full width at half maximum (FWHM) of emission is directly reflected in the enhancement of front efficiency by applying the cavity effect.

On the other hand, as the methods for improving IQE of OLED, we proposed the blue fluorescent device using Triplet-Triplet Fusion process with high color purity in TE devices[1]. Efficient green and red devices using room-temperature phosphorescence by heavy metal complexes have been realized[2]. Furthermore thermally activated delayed fluorescence (TADF) has been reported in recent years[3]. Both phosphorescence and TADF can achieve the theoretical limit IQE of 100%, but the two mechanisms suffer from relatively large FWHMs due to the properties of the luminescent material itself such as utilizing the charge transfer state, and the color purity in the device is insufficient.

To overcome the issues, the system that combines the advantages of high IQE by TADF and small FWHM of fluorescent material has been proposed[4].

We constructed the device called TADF-Matrixed Electrofluorescence (TMEF) by combining a TADF material, a matrix which disperses TADF, and an appropriate fluorescent red dopant (FRD) with narrow FWHM and controlled emission peak.

In this paper, we report both BE and TE OLEDs exhibit deep-red emission with high efficiency and improved lifetime based on TMEF mechanism.

2 RESULTS AND DISCUSSIONS

2.1 BE Devices with Deep-Red Fluorescent Dopant

In order to improve the efficiency of TMEF devices, it is necessary to consider from the points of view electrically and photophysically.

On the electrical side, it is necessary to design the device that charge recombination occurs on the TADF, not on the FRD to achieve high IQE through the triplet-singlet up-conversion process on the TADF molecule.

Regarding on the photophysical side, it is important to increase the efficiency of Förster energy transfer from the singlet exciton generated on TADF molecules to FRD, and to suppress quenching of the triplet exciton on TADF molecule by Dexter-interaction with FRD at the same time. Moreover the suppression of concentration quenching between FRDs is also important.

Firstly, the performance of the TMEF device was confirmed using the BE configuration. For the emitting layer, TRM-1 was used as matrix, in addition TRH-1 was used as the TADF. FRD-1 was utilized as the fluorescent dopant which showed strong fluorescence on deep-red region with high color purity. The concentration of FRD for each device in this report was fixed to be 1wt%.

The device configuration was as follows,

BE device A:
ITO/HI/HT/EB/TRM:TRH:FRD-1(25, 25wt%, 1wt%) /HB/ET/LiF/Al (unit: nm)

Here, numbers in parentheses indicate thickness of each layers (unit: nm).

Device A-1 showed pure-red electroluminescence (EL) derived from FRD-1. It peaked at 630 nm and kept the FWHM of 43 nm as same as the PL result shown in Table 3. The external quantum efficiency (EQE) of 12.6% at 10 mA/cm^2 and LT95 of 80 hours at 50 mA/cm^2 was observed.

In case of Device A-2, changing the matrix from TRM-1 to TRM-2 reduced the voltage to 4.1 V and increased the EQE to 13.7%, while the LT95 was reduced to 61 hours.

In order to recover the lifetime and improve the EQE, we tested the combination of TRM-2 and TRH-2 in Device A-3. As a result, A-3 showed the voltage of 4.4 V, the EQE of 14.3 % at 10 mA/cm^2, and the LT95 of 96 hours at 50 mA/cm^2.

Table. 1 EL performances with combinations of TRM and TRH in Device A at a current density of 10 mA/cm^2.

Device	Matrix:TADF	V [V]	EQE [%]	EL Peak [nm]	FWHM [nm]	CIE	LT95@ 50mA/cm^2 [hrs]
A-1	TRM-1:TRH-1	4.4	12.6	630	43	(0.66, 0.34)	80
A-2	TRM-2:TRH-1	4.1	13.7	632	43	(0.67, 0.33)	62
A-3	TRM-2:TRH-2	4.4	14.3	632	42	(0.68, 0.32)	96

2.2 Optimization of Material Combinations

As the next step, Device B was fabricated by optimizing the transport materials for further improvement of EQE. TRM-2 was used as the matrix. The device configuration was as follows,

BE device B:
ITO/HI/HT/EB/TRM-2:TRH:FRD(25, 25wt%, 1wt%) /HB/ET/LiF/Al (unit: nm)

EL performances of Device B were summarized in Table 2. When TRH-1 and TRH-2 were utilized as TADF in Device B, B-1 and B-2 showed the EQE of 15.0% and 15.5%, respectively. While further improvement of EQE was observed, the LT95s were almost halved compared to the corresponding Device A (A-2 and A-3 in Table 1).

On the other hand, it was found that TRH-3 could enhanced both EQE and lifetime in the configuration of Device B. Much improved EQE of 16.5% and enhanced LT95 of 101 hours were achieved in B-3.

Table. 2 EL performances of Device B with FRD-1 and FRD-2 at a current density of 10 mA/cm^2.

Device	TADF:FRD	V [V]	EQE [%]	EL Peak [nm]	FWHM [nm]	CIE	LT95@ 50mA/cm^2 [hrs]
B-1	TRH-1:FRD-1	4.2	15.0	631	44	(0.66, 0.34)	29
B-2	TRH-2:FRD-1	4.3	15.5	630	43	(0.67, 0.33)	51
B-3	TRH-3:FRD-1	4.4	16.5	632	42	(0.68, 0.32)	101
B-4	TRH-3:FRD-2	4.3	16.7	616	37	(0.66, 0.34)	88

The PL properties of FRD-2 are shown in Table 3. FRD-2 shows FWHM of 38 nm and keeps relative PLQY of 0.92 vs. FRD-1. It is expected to show higher color purity and enhancement of efficiency, especially when it is applied into TE device.

As a result of applying FRD-2 instead of FRD-1 in B-3, B-4 showed EL peaked at 616 nm and reduced FWHM of 37 nm as expected, and achieved EQE of 16.7% at 10 mA/cm^2, LT95 of 88 hours at 50 mA/cm^2

Table. 3 Photoluminescent properties of FRDs in doped film at concentration of 1wt%.

Dopant	PL peak [nm]	FWHM [nm]	PLQY*
FRD-1	630	44	1
FRD-2	615	38	0.92

*Relative value vs. FRD-1 as Ref.

2.3 TE Device Performances

Finally, we confirmed the performance of TE devices by adopting the best combination based on B-4. The optical cavity length was adjusted by the thickness of HT. Ag-alloy/IZO was used as reflective substrate. The device configuration was as follows.

TE device C:
Ag-alloy/IZO/HI/HT(x)/EB/TRM-2:TRH-3:FRD-2 (25, 25wt%,1wt%)/HB/ET/LiF/Mg:Ag/CAP (unit: nm)

Table. 4 TE device performances and variation of cavity length by changing HT thickness at a current density of 10 mA/cm^2.

Device	Total HT thickness [nm]	V [V]	L/J [cd/A]	EL Peak [nm]	FWHM [nm]	CIE	LT95@ 50mA/cm^2 [hrs]
C-1	ref	4.3	57	614	32	(0.664, 0.335)	88
C-2	+5	4.4	58	616	32	(0.670, 0.330)	91
C-3	+10	4.4	53	619	33	(0.675, 0.325)	88
C-4	+15	4.4	46	621	35	(0.679, 0.320)	92

The four devices in Table 4 showed various EL colors and efficiencies when the total HT thickness was changed in increments of 5 nm. Regarding the LT95 at 50 mA/cm^2, it was found that they reproduced the LT95 of around 90 hours as almost same level as BE device.

Especially in case of C-2 and C-4, they exhibited L/J of 58 cd/A at CIEx = 0.670, and L/J of 46 cd/A at CIEx = 0.679, respectively. Normalized TE spectra of each device were shown in Figure 1. All devices exhibited very narrow FWHMs that reflected the FWHM in PL, and it was confirmed that they contributed to the high luminous efficiency in TE devices.

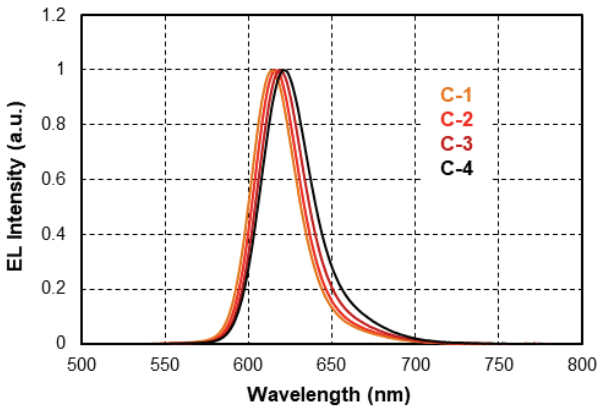

Fig. 1 Normalized TE spectra of Device C at a current density of 10 mA/cm^2.

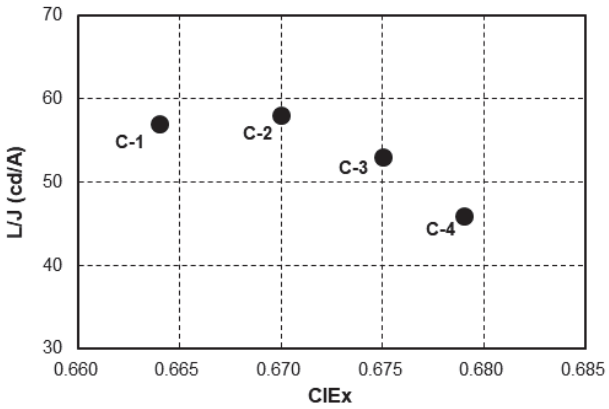

Fig. 2 CIEx coordinate vs. L/J in Device C at a current density of 10 mA/cm^2.

Figure 2 summarizes the CIEx coordinate vs. L/J in Device C at a current density of 10 mA/cm^2. Although it strongly depends on the internal emission spectral shape, the L/J showed the maximum value around CIEx = 0.670 at the optimal cavity length when FRD-2 was used, but it tended to decrease in the larger CIEx region.

Figure 3 shows the L/J dependency as a function of current density in Device C. The all four devices showed same tendency and it was found that they could provide the L/J curves with a flat dependency at less than 1 mA/cm^2. Maximum value of L/J reached at 65 cd/A in C-2 which showed CIEx = 0.670.

From the result of C-4 shown as black line in Figure 3, it suggests that more than 50 cd/A at CIEx = 0.68 is potentially realized by suppressing the roll-off of efficiency at high current density.

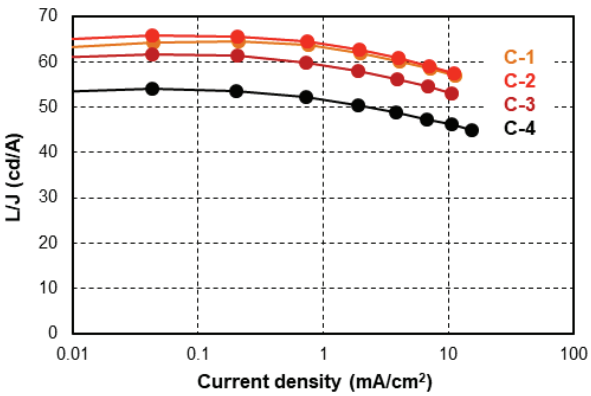

Fig. 3 Current density vs. L/J curves in Device C.

3 CONCLUSIONS

We developed both TADF materials with high performances and spectral-narrow fluorescent dopants for deep-red OLEDs. We tested the several devices based on TMEF mechanism and achieved the L/J of 46 cd/A at 10 mA/cm^2 and the LT95 of around 90 hours at 50 mA/cm^2 in the TE device which showed CIEx = 0.679.

It suggested that the TMEF mechanism could be a promising way to realize the pure color and high efficient OLED in deep-red region.

REFERENCES

[1] T. Masuda, Y. Nakano, Y. Takahashi, H. Ito, K. Okinaka, E. Kambe, Y. Kawamura, and H. Kuma, “Highly efficient fluorescent blue materials and their applications for top-emission”, J. Soc. Information Display 26, pp146-152 (2018).

[2] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, M. E. Thompson, “Highly phosphorescent bis-cyclometalated iridium complexes: synthesis, photophysical characterization, and use in organic light emitting diodes”, J. Am. Chem. Soc., 123, pp4304-4312 (2001).

[3] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, and C Adachi, “Highly efficient organic light-emitting diodes from delayed fluorescence”, Nature 492, pp234-238 (2012).

[4] H. Nakanotani, T. Higuchi, T. Furukawa, K. Masui, K. Morimoto, M. Numata, H. Tanaka, Y. Sagara, T. Yasuda, and C. Adachi, “High-efficiency organic light-emitting diodes with fluorescent emitters“, Nat. Commun., 5, pp4016-4022 (2014).