Highly Efficient and Pure Blue Fluorescent Organic Light-Emitting Diodes with Excellent Device Stability

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ABSTRACT

Blue fluorescent organic light-emitting diodes with a high external quantum efficiency of 9.53% and excellent lifetime ($LT_{95} \sim 1,335$ h) at 1000 cd/m² are demonstrated. The LT_{95} is further enhanced to 3,450 h in the device with a triazine derivative used as an electron transport layer.

1 Introduction

Realizing blue organic light-emitting diodes (OLEDs) with high external quantum efficiency (*EQE*), good color purity, and excellent operational stability is a major challenge in the OLED display application. Despite the success in improving the color purity of high-efficiency blue phosphorescent OLEDs as well as thermal activated delayed fluorescent (TADF) OLEDs [1-3], majority of blue pixels of commercialized OLED displays rely on the blue fluorescent material because of their excellent operation stability. For example, the fluorescent OLED shows excellent LT_{95} exceeding 800 h [4] at a current density of 50 mA/cm², which could correspond to more than 3,000 h if the device was operated at 1,000 cd/m².

EQE of OLEDs can be expressed by EQE =with charge balance factor (γ), the yield of $\gamma \eta_{\rm ex} \phi_{\rm PL} \eta_{\rm out}$, the emissive excited state (η_{ex}), photoluminescent quantum yield (ϕ_{PL}), and out-coupling efficiency (η_{out}). For traditional fluorescent materials, η_{ex} limits at 25%, which is a fraction of singlet exciton ($\eta_{\rm S}$) directly generated by the charge recombination. In fluorescent materials where the energy of the lowest triplet excited states (T_1) is greater than that of half of the lowest singlet excited state (S1), an additional 15% of singlet exciton would be harvested via triplet-triplet annihilation (TTA) [5]. Furthermore, if the twice energy of T_1 is smaller than that of the higher order triplet excited state (T_2), up to 37.5% (η_{TTA}) singlet exciton would be harvested via the TTA process [6]. Consequently, η_{ex} (= η_{S} + η_{TTA}) would reach up to 62.5%. EQE of fluorescent OLEDs is thus achieved up to 12.5% assuming 20% of η_{out} . Indeed, the high EQE (6.91–12.0%) of blue fluorescent OLEDs has been realized by the TTA process [7-10].

In this study, blue fluorescent OLEDs with high *EQE* up to 10.31% were demonstrated by utilizing TTA. The blue device demonstrates outstanding stability such that the LT_{95} measured at 1,000 cd/m² shows 1,335 h while

retaining good device efficiency and color purity. By changing an electron transport material, the LT_{95} can be further enhanced up to 3,450 h.

2 Experiment

We employed a glass substrate coated with indium tin oxide (ITO) as the anode in the devices. We used N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(9-phenyl-9Hcarbazol-3-yl)phenyl)-9H-fluoren-2-amine (HT01) doped with 1% 4,4',4"-((1E,1'E,1"E)-cyclopropane-1,2,3triylidenetris(cyanomethaneylylidene))tris(2,3,5,6tetrafluorobenzonitrile) (PD01) as the hole-injection layer (HIL) and undoped HT01 as the hole-transport layer (HTL). For the electron-blocking layer (EBL), we used N, N-bis(4-(dibenzo[b,d]furan-4-yl)phenyl)-[1,1':4',1"terphenyl]-4-amine (EB01). The emission layer (EML) was composed of 9-(naphthalen-1-yl)-10-(4-(naphthalen-2-yl) phenyl)anthracene (BH01) and N¹,N⁶bis(dibenzo [b,d]furan-4-yl)-3,8-diisopropyl-N¹,N⁶-bis(4isopropylphenyl)-3a¹,5-dihydropyrene-1,6-diamine (BD01) as the blue host and blue dopant, respectively.



Fig.1 Structures of devices and materials used in this study.



Fig. 2. Device characteristics of OLEDs with EML composed of BH01:BD01 and ETL consisting of ETM01 doped with Liq. (a) current density-voltage characteristics, (b) current efficiency, (c) EL spectra (d) TREL.

Table 1. Initial characteristics at 1,000 cd/m² of OLEDs with ETL composed of ETM01 doped with Liq.

ETL	Voltage (V)	Current density (mA/cm ²)	Current efficiency (cd/A)	Power efficiency (Im/W)	EQE (%)	CIE (x, y)
ETM01:Liq 20%	4.46	10.68	9.34	6.58	7.45	(0.129, 0.167)
ETM01:Liq 50%	3.95	8.65	11.57	9.21	9.53	(0.130, 0.159
ETM01:Liq 70%	4.10	8.14	12.30	9.44	10.31	(0.130, 0.155)

We used two types of the electron-transport layers (ETL), which consisted of 2-(4-(9,10-di(naphthalen-2yl)anthracen-2-ly)phenyl)-1-phenyl-1H-benzo [d]imidazole (ETM01) or 2,4-di([1,1'-biphenyl]-4-yl)-6-(4'-(pyridin-2-yl)-[1,1'-biphenyl]-4-yl)-1,3,5-triazine (ETM02) doped with lithium 8-hydroxyquinolate (Liq). Liq was also used as the electron injection layer (EIL). An aluminum (AI) layer was used as the cathode. All the organic layers and the AI cathode were deposited by vacuum deposition. After the deposition of all layers, the devices were transferred to a glove box filled with nitrogen and encapsulated with a UVcurable epoxy resin with a desiccant.

The devices characteristics including current densityvoltage characteristics, current efficiency and EQE of OLEDs were measured with a source meter (2400, Keithley), a luminance meter (BM-9, TOPCON), and an integrating sphere equipped with a calibrated Si photodiode. For stability test, the devices were operated at a constant current density to obtain initial luminance of 1,000 cd/m². Time-resolved photoluminescence (TRPL) was measured at room temperature. An optical pulse at a wavelength of 443 nm was used for the excitation of BD01. Time-resolved electroluminescence (TREL) was measured by applying an electrical pulse (120 µs of pulse width) at a current density of 15 mA/cm². TRPL and TREL were measured with a streak camera in a single photon counting mode.

3 Results

Figure 2 shows device characteristics of OLEDs with the ETL composed of ETM01 doped with Liq at a concentration of 20, 50, and 70%. The initial device characteristics of the devices at 1,000 cd/m² were summarized in Table 1. Current efficiency (CE), EQE and Power efficiency (PE) of OLEDs increase with increasing Lig concentration due to the enhanced electron current by the Liq doping. The CE of 12.30 cd/A and EQE of 10.31% were observed in the device with the Liq doping concentration of 70%. EL spectra were independent of the Lig concentration and show a peak at 464 nm with narrow emission (full-width half maxima of 43 nm). The fact that all devices exceed EQE larger than 5.0% suggests that the TTA is taking place in these devices. Indeed, as shown in Fig. 2d, delayed EL was observed in all devices with the time scale of a few tens of µs, which is three orders of magnitude longer than the fluorescent lifetime of BD01 (~2.05 ns). The contribution of delayed emission clearly increases with increasing Liq concentration. Thus, the high efficiency observed in the blue devices should be originated from the TTA process.

To get more insight about TTA, we have measured TREL of OLEDs with EML without the blue dopant BD01. A similar decay time of delayed EL was observed in the OLEDs without the blue dopant BD01 in EML. (Fig.3b) This result indicates that the TTA occurs by triplet excitons of host (BH01) and generate singlet exciton of BH01 followed by the energy transfer to BD01.

To investigate the location of the charge recombination zone in the device, we have deconvoluted the EL spectra of the OLEDs by PL spectra of BH01 and ETM01.(Fig. 4) At the low Liq concentration, the EL spectra of the device are dominated by the emission of



Fig. 3. (a) EL spectra of OLED with BH01 as the EML (b) TREL of OLEDs with and without blue dopant BD01 in EML, (c) emission mechanism of OLED with EML consisting of BH01:BD01



Fig. 4. Deconvolution of EL spectra of OLED using BH01 as the EML by PL spectra of BH01 and ETM01.

ETM01 with a smaller contribution of BH01. This result indicates that the charge recombination zone locates near the EML/ETL interface. Since the contribution of the emission of BH01 increase with increasing Liq concentration, the recombination zone moves toward the inside of the EML.

Although the high doping concentration of Liq improves the initial device characteristics, increasing Liq concentration brings about a negative impact on the device stability. Figure 5 shows the changes of operation voltage and normalized EL intensity of blue devices measured at the initial luminance of 1,000 cd/m². Although the OLED with ETM01 doped with 70% of Liq showed the best power efficiency, LT_{95} of this device was limited to 400 h. On contrary, LT_{95} of over 1,000 h was observed in the devices with lower Liq concentrations.

The degradation mechanism of the OLEDs was investigated by examining the possible loss of η_{ex} using TREL. Figures 6a and 6b demonstrate the EL spectra and TREL of pristine and degraded OLEDs with the EML composed of BH01:BD01. Whereas the EL spectra did not change after the degradation, the delayed EL intensity gradually decrease with the progress of the degradation. As discussed before, the delayed EL was originated from the TTA on the host molecule, the decrease in the delayed EL intensity can be ascribed to the decrease in η_{TTA} on the host molecule. This assumption was confirmed by the TREL of the degraded OLED with the EML composed of BH01 (Fig.6d). EL spectra of the degraded devices exhibited the increase in the contribution of the emission of ETM1. This spectral change seems to be the same with that of the OLED with ETL doped with varying the Liq concentration. That is, by lowering the Liq concentration,



Fig. 5. Stability test of OLED with EML composed of BH01:BD01 as EML and ETM01 doped with difference concentration of Liq as ETL. (a) operation voltage vs time characteristics and (b) normalized luminance vs time characteristics measured at 1,000 cd/m².

the recombination zone in the EML moves towards the inside of the EML. By considering this result, we could assume that the EL degradation took place due to the shift of the recombination zone during the device operation.



Fig. 6. EL spectra and TREL of pristine and degraded OLED. (a, b) OLED with EML composed of BH01:BD1, (c, d) OLED with EML composed of BH01.

We have fabricated an OLED with the ETL composed of ETM02 doped with 50% of Liq. The OLED demonstrates excellent device characteristics comparable to those of the OLED using ETM01, such as high *EQE* (8.54%) and pure blue with the CIE(x, y) of (0.129, 0.159). We have found that the device demonstrates superior LT_{95} of 2,900 h at 1,000 cd/m². The LT_{95} was further increased up to 3,450 h in the



Fig. 7. Stability test of OLEDs with ETL composed of ETM01 (or ETM02) doped with 50% of Liq measured at 1,000 cd/m². (a) operation voltage vs time characteristics, (b) normalized luminance vs time characteristics. Fitting of the data has been done by a double exponential decay function.

Table 2. Initial characteristics at 1,000 cd/m^2 of OLEDs with ETL composed of ETM01 or ETM02 doped with 50% of Liq.

ETL	Voltage (V)	Current density (mA/cm ²)	Current efficiency(cd/A)	Power efficiency (Im/W)	EQE (%)	CIE (x, y)	LT ₉₅ (h)
ETM01:Liq 50%	3.94	8.65	11.58	9.23	9.55	(0.130, 0.159)	1335
ETM01	5.07	11.68	8.55	5.30	6.83	(0.128, 0.167)	2026
ETM02:Liq 50%	4.07	9.65	10.38	8.01	8.54	(0.129, 0.159)	2900*
ETM02	4.67	11.40	8.78	5.90	6.79	(0.128, 0.174)	3450*

* Fitting of the data has been done by a double exponential decay function.

OLED using undoped ETM02 as ETL. Interestingly, operation voltage of this highly stable device gradually decreases after reaching the maximum value at around 250 h. The reason for the observed excellent device stability has not been clarified yet. It could be due to the fixing the recombination zone in the EML and/or photochemical stability of the triazine core of ETM02 compared to the benzoimidazole core of ETM01.

4 Conclusions

Highly efficient pure blue OLEDs with the *EQE* of 9.55%, CIE(x,y) of (0.130,0.159) have been demonstrated by enhancing the delayed EL via the TTA process. The blue device demonstrates excellent LT_{95} of 1,335h at the initial luminance of 1,000 cd/m². Longer LT_{95} of 3,450 h was realized in the OLED with ETL composed of the triazine derivative ETM02.

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References

- [1] K. Klimes, Z. Q. Zhu and J. Li, "Efficient Blue Phosphorescent OLEDs with Improved Stability and Color Purity through Judicious Triplet Exciton Management", Advance Functional Materials 29, 1903068 (2019).
- [2] J. Y. Kim, T. R. Hong, I. R. Choe, J. A. Lee, H. G. Ryu, B. M. Seo, J. H. Yang, C. W. Han, J. H. Baek, H. C. Choi and I. B. Kang, "Lifetime Improvement of TADF-OLEDs", SID Symposium Digest of Technical Papers, 51, 53-56 (2020).
- [3] C. Y. Chan, M. Tanaka, Y. T. Lee, Y. W. Wong, H. Nakanotani, T. Hatakeyama and C. Adachi, "Stable pure-blue hyperfluorescence organic light emitting diodes with high efficiency and narrow emission" Nature Photonics, 15, 203-207 (2021).
- [4] T. Ishimoto, N. Hashimoto, S. Nomura, T. Okuyama, H. Nowatari, T. Suzuki, S. Seo, S. Yamazaki, "Ultralong-life Deep Blue OLED device achieved by controlling the carrier recombination site" SID Symposium Digest of Technical Papers, 52, 236-239 (2021).
- [5] B. H. Wallikewitz, D. Kabra, S. Gelinas, and R. H. Friend, "Triplet dynamics in fluorescent polymer light emitting diodes" Physical Review B, 85, 045209 (2012).
- [6] C. J. Chiang, A. Kimyonok, M. K. Etherington, G. C. Griffiths, V. Jankus, F. Turksoy and A. P. Monkman, "Ultrahigh efficiency fluorescent single and bi-layer organic light emitting diodes: The key role of triplet fusion" Advanced Functional Materials, 23, 739-746 (2013).
- [7] B. Kim, Y. Park, J. Lee, D. Yokoyama, J. H. Lee, J. Kido, and J. Park, "Synthesis and electroluminescence properties of highly efficient blue fluorescence emitters using dual core chromophores" Journal of Materials Chemistry C, 1, 432-440 (2013).
- [8] T. Suzuki, Y. Nonaka, T. Watabe, H. Nakashima, S. Seo, S. Shitagaki and S. Yamazaki, "Highly efficient long life blue fluorescent organic light emitting diode exhibiting triplet-triplet annihilation effect of enhanced by novel hole transporting material" Japanese Journal of Applied Physics, 53, 052102 (2014).
- [9] Y. H. Chen, C. C. Lin, M. J. K. Hung, Y. C. Wu, W. C. Lin, R. W. Chen-Cheng, H. W. Lin and C. H. Cheng, "Superior upconversion fluorescence dopants for highly efficient deep blue electroluminescent devices" Chemical Science 7, 4044-4051 (2016).
- [10] A. Salehi, C. Dong, D. H. Shin, L. P. Zhu, C. Papa, A. T. Bui, F. N. Castellano and F. So, "Realization of high-efficiency fluorescent organic light-emitting diodes with low driving voltage" Nature Communications, 10, 2305 (2019).