Stable Pure-Blue Hyperfluorescence OLEDs

<u>Chin-Yiu Chan</u>¹, Yi-Ting Lee¹, Masaki Tanaka¹, Yiu-Wing Wong¹, Hajime Nakanotani¹, and Chihaya Adachi¹

chinyiu.chan@opera.kyushu-u.ac.jp, adachi@cstf.kyushu-u.ac.jp ¹Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan Keywords: OLED, Pure-Blue, TADF, Hyperfluorescence, Device stability

Abstract

Pure-blue hyperfluorescence (HF) OLEDs with high-efficiency, narrow-emission and good stability have been demonstrated. The design is based on a two-unit stacked tandem HF-OLED with an improved singlet-excited energy transfer process from a sky-blue TADF assistant dopant to a pure-blue terminal emitter.

1. Introduction

The search for a narrow emissive, a highly stable, a highly efficiency pure-blue OLED has been challenged for more than 20 years in OLEDs. Thus, conventional pure-blue fluorescence materials have been still used as a blue emitter in commercial products. One of the critical reasons for the very short operational lifetime of pure-blue OLEDs exhibiting 100% of internal quantum efficiency (IQE) is due to the presence of the highly unstable triplet excitons that are generated through exciton annihilation events of long-lived triplets such as triplet-triplet and triple-polaron interaction,¹³⁻¹⁶ leading to a device degradation. Additionally, in order to confine high-energy excitons of a pure-blue emitter that utilizes triplet excitons, the surrounding peripheral materials have to possess a higher triplet energy than that of the emitter. Meanwhile, the singlet excited state energies of those molecules are always higher than that of the triplet, in which a high-triplet-energy material possesses a much higher singlet energy. Both high singlet and triplet energies are the critical issue in molecular design. To enhance an operational lifetime of pure-blue OLEDs, an unwarranted chemical reaction through triplet-excited state of both pure-blue emitter and surrounding materials must be removed. Therefore, for achieving stable pure blue OLEDs, we must design a new emitting layer (EML) that an emitter possesses short triplet lifetime for maintaining its high electro-chemical stability, and an OLED architecture that enables a quick consumption of triplet excitons to reduce triplet-exciton density inside the devices.

In this study, we show a proof-of-concept of using not only a blue/deep-blue but also a sky-blue energy donor exhibiting thermally-activated delayed fluorescence (TADF) as an assistant dopant (AD) to sensitize a 'pure-blue' terminal emitter (TE), i.e., hyperfluorescence (HF). According to a broad distribution of energy state of the charge-transfer excited states in TADF emitters, the electrically generated energy of the sky-blue assistant dopant can be exothermically transferred to the excited state of the pure-blue emitter with energy confinement even if the assistant dopant emits sky-blue emission. In addition, an unwarranted chemical reaction through the triplet excited state can be suppressed by an acceleration of a spin-flip rate from the triplet to singlet excited states of the TADF-type assistant dopant and FRET efficiency. Also, we mention the importance of eliminating carrier trapping by TE by proper energy alignment in OLEDs.

2. Method

We newly designed a hetero-donor-type TADF (HDT) emitter, that is TPh2Cz2DPhCzBN (HDT-1) (**Fig. 1A**). Compared to the

previously reported bluish-green HDT emitter of 3Cz2DPhCzBN ($\lambda_{em} = 495 \text{ nm}$)¹⁷, a bulky *m*-terphenyl unit was introduced to blueshift the photoluminescence (PL) in HDT-1. Meanwhile, the bulky *m*-terphenyl not only prevents molecular aggregation in the film state that eventually maintains the color purity in the device, but it should also enhance device stability by inhibiting bimolecular interactions with the rigid molecular structure.

3. Result and Discussion

3.1 Photophysical process in hyperfluorescence emitter In the oxygen-free toluene solution, the lowest singlet excited state (S₁) and lowest triplet excited state (T₁) energy of HDT-1 were estimated to be 2.90 eV and 2.88 eV from the onset of the fluorescence and phosphorescence spectrum, respectively. The PL quantum yield (PLQY) of the solution was 99±1%. Furthermore, even in the solid-state thin film, that is 20 wt% of doped in 3,3'-di(9H-carbazol-9-yl)-1,1'-biphenyl HDT-1 (mCBP) host matrix, a high PLQY of 86% was obtained. The film exhibited a clear temperature-dependent delayed emission component with a remarkably short delayed emission lifetime (τ_d) of 2.9 µs at 300 K. The faster τ_d of 2.9 µs in HDT-1 comparing to that of 3Cz2DPhCzBN (5.7 µs) was due to a reduction of the energy gap between the high-lying localized triplet excited state (3LE) and the lowest charge transfer triplet excited state $({}^{3}CT_{1})$ because we can expect more strong mixing of the states between ³LE and ³CT₁ in HDT-1 (Fig. 1B).¹⁷ The rate constant for reverse intersystem crossing (kRISC) of HDT-1 in the film was calculated to be 9.2×10^5 s⁻¹, indicating the high TADF activity of HDT-1 by the contribution of short triplet lifetime with high delayed fluorescence efficiency.

Generally, TADF-OLEDs are always accompanied by very broad electroluminescence (EL) spectra due to CT nature, which are undesirable for display applications. In fact, although the emission peak wavelength of HDT-1 is 476 nm, the emission color of HDT-1 is positioning at sky-blue region. Regarding the EL color purity issue, hyperfluorescence technology that a narrow-emission TE is co-deposited with an AD in the host matrix can be applied to solve this issue.¹⁸ In this study, a narrowenergy-distributed blue emitter exhibiting TADF, that is v-DABNA, is chosen as a TE for the pure-blue OLED, even though the reported operational lifetime of the OLED is quite short.¹⁹ Moreover, although v-DABNA exhibited bluer emission than that of HDT-1, the Förster resonance energy transfer (FRET) from S1 of HDT-1 to S1 of v-DABNA should occur because the absorption spectrum of v-DABNA is considerably overlapped with the emission spectrum edge of HDT-1 (Fig. 1A). To evaluate the FRET process in the hyperfluorescence system, the PL characteristics of the 0.5 wt%-v-DABNA:20 wt%-HDT-1 in a mCBP host film was studied. The narrowed blue emission mainly originated from v-DABNA with a high PLQY of 97% was confirmed (Fig. 1A), meaning the occurrence of the FRET process between them. The FRET efficiency can be estimated by the ratio of the emission intensities of the binary and ternary films at 575 nm. Thus, the FRET efficiency from HDT-1 to v-DABNA was calculated to be 64%.



Figure 1: (A) Energy transfer mechanism of hyperfluorescence system; (B) Transient decay profiles.

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Table 1.	. Device	charact	eristics	of	tested	devices

Device	λ_{EL}	Voltage	EQE	PE	CE	CIE	LT ₉₅	FWHM				
	(nm)*	(V) ⁶	(%)°	(lm/W) ^d	(cd/A) ^e	(x,y)*	(h) ^f	(nm)*				
Control I	471	5.5/8.5/11.5	3.7/3.7/3.5	1.0/1.0/0.8	2.9/2.9/2.7	(0.12,0,11)	4	17				
Control II	486	3.2/4.6/7.0	22/21/19	53/35/20	54/51/44	(0.19,0.40)	29	80				
Device A	470	3.0/4.2/5.6	27/24/20	41/26/16	39/36/31	(0.15,0.20)	11	18				
Device B	470	6.5/9.0/11.5	41/39/32	23/16/10	72/70/59	(0.13,0.16)	18	19				
Ref 17	469	3.4/-/-	-/33/26	-/21/12	-/30/23	(0.12,0.11)	<1 ⁸	18				

⁴⁰ At 1,000 cd m⁻². ¹⁰ Voltage at 1 cd m⁻², 100 cd m⁻² and 1,000 cd m⁻². ⁰¹ External Quantum Efficiency maximum, value at 100 cd m⁻², value at 1,000 cd m⁻², ⁴⁰ Power Efficiency: maximum, value at 100 cd m⁻², value at 1,000 cd m⁻². ¹⁰ Current Efficiency: maximum, value at 100 cd m⁻², ¹⁰ P5% of an initia huminance of Dinot din m⁻². ¹⁰ Dinital huminance = 100 cd m⁻².

3.2 OLED performance of hyperfluorescence based emitter

The energy transfer from the S1 of 'sky-blue' TADF dopant to the S₁ of 'pure-blue' dopant enabled the progressive improvement of EL color purity. Table 1 and Figure 2 summarized the OLED performances. To obtain elevated pureblue OLED performance, the hyperfluorescence system was optimized in device A (EML: 0.5 wt%-v-DABNA:20 wt%-HDT-1:mCBP). Device A resulted in a maximum EQE of 27% with a remaining high EQE of 20% even at 1,000 cd m^{-2} . The EQE value is higher than that of the control device I (EML: 1 wt%-v-DABNA:mCBP). It can be ascribed to the help of horizontal orientation of the transition dipole moment (TDM) of v-DABNA in the doped film (TDM vector (S) = -0.42). The EL peak maximum at 1,000 cd m⁻² was found to be blue-shifted emission (471 nm) with a narrower FWHM of 18 nm (Fig. 2B), when comparing to the control device II (EML: 20 wt%-HDT-1:mCBP) (486 nm), resulted in the pure-blue EL of the CIE coordinates of (0.15, 0.20). By fitting the EL spectrum of device A to the EL spectra of control devices I and II with an equation $y = a(EL_I)+b(EL_{II})$ from 450 to 750 nm, where EL_I and EL_{II} are the individual EL spectrum of control device I and II, and, a and b are the corresponding constants. The constants were found to be 0.88 and 0.12. Additionally, the area ratio of 0.88(ELI)/0.12(ELII) was found to be 2:1. Thus, 67 % of the EL emission of device A was come from v-DABNA, which is also matched with the FRET efficiency estimated from the PL



Figure 2: HF-OLED characteristics.

spectra. Furthermore, the LT95 of over ten-hour was confirmed. Note that the major reason for the shortened device lifetime comparing to that of control device II is due to the injection of a high current density (3.2 mA cm^{-2} in device A vs. 1.7 mA cm⁻² in control device II) into the device to obtain same level of luminance ($1,000 \text{ cd m}^{-2}$). This is due to the significant blue-shift of the EL spectrum in the device A.

To further boost the pure-blue OLED performances, we designed the two-unit-stacked tandem OLED (Device B). Device B shows the smallest y-value of CIE coordinates, that is (0.13, 0.16). Furthermore, device B exhibited an extraordinary maximum EQE of 41% (corresponding to the current efficiency of 72 cd A-¹ and the power efficiency of 23 lm W⁻¹) with well-suppressed efficiency roll-off characteristics, that is a high EQE of 32% was still maintained even at 1,000 cd m^{-2} (Fig. 2C). Note that the power efficiency of device B is slightly lower than that of device A. This might be attributed to the intrinsic charge loss from the inefficient charge generation at the charge generation layer interfaces. Therefore, it is possible to further boost the OLED performance with equal power efficiency by employing optimized CGL. Nonetheless, at a luminance of 1,000 cd m⁻², device B not only resulted in a high EQE and a narrow blue emission, but also an outstanding LT95 of 18 h (Fig. 3). Based on the acceleration aging test of the OLED (Fig. 3 inset), the LT95 and LT50 can be predicted to be over 300 and 10,000 hours at the initial luminance of 100 cd m⁻², respectively.²¹ Device B thus definitely represents the best pure-blue OLED with the narrow emission, a high efficiency and a long operational stability among the literatures reported.9,10

In hyperfluorescence OLEDs (device A and B), *v*-DABNA mainly functionalizes as a terminal fluorescence emitter only, rather than as a TADF emitter, in which an improved emission color was realized by the FRET process from HDT-1 to *v*-DABNA. The dramatic enhancement of operational lifetime of the pure-blue OLED compared to that of the previously reported *v*-DABNA-OLED (LT50 = 31 hour at initial luminance of "100" cd m⁻² in *Ref. 19*) can also be ascribed to the much larger k_{RISC} of HDT-1 (8.6 × 10⁵ s⁻¹) that can contribute to a rapid

consumption of triplet excitons than that of ν -DABNA (2.0×10^5 s⁻¹). Thus, HF-OLEDs that produce only ν -DABNA' singlet excitons displayed promising prolonged stabilities with pure blue emissions. Due to the instabilities of their triplet states, when ν -DABNA were used solely as a TADF emitter (control I), relatively short device lifetimes were observed.



Figure 3: OLED device lifetime.

3.3 Advanced HF system with faster FRET with less carrier trapping

The pure-blue OLED performance, especially operational lifetime, could be further boosted up with the development of more stable "sky-blue" TADF assistant dopant, which should possess a faster kRISC. In fact, sky-blue (or green) TADF emitters exhibiting larger kRISCS with one order of magnitude higher than that of HDT-1 have been realized through a strict control of the excited state alignment between a CT state and a LE state.²² The concept presented here can be applied to other advanced TADF materials to realize more stable pure-blue OLEDs. In addition, we should note that a suppression of direct carrier trapping on a terminal dopant can also improve the operational lifetime. In the transient EL spectrum of our fabricated devices, a spike EL was found in device A with an enhanced emission intensity at 0 µs, which was not observed in control device II, indicating the existence of trapped charge carriers in device A.23 The origin of the carrier traps formation is due to the shallower HOMO level of v-DABNA (-5.4 eV) than that of HDT-1 (-5.7 eV), leading to an unwarranted triplet exciton formation in the terminal dopant. Thus, the OLED performances presented here are still nonoptimized. A commercialized device structure (not top emission but bottom emission type device architecture) with a fluorescent blue emitter was fabricated in the same chamber as a comparison. At 1,000 cd m⁻², the corresponding device demonstrated an EQE of 7% with CIE coordinates of (0.13,0.16). The emission maximum of the EL was found to be 465 nm with a FWHM of 40 nm. The LT95 was found to be 84 h at an initial luminance of 1,000 cd m⁻². It is expected that with a strict controlling of device fabrication environments and procedures ²⁴⁻²⁶, it has a high possibility to catch up on the same level of LT95 of the commercialized fluorescence-based blue OLEDs.

Further, very recently, a new series of blue-emission emitters are developed, which are capable of showing narrow FWHMs and high PLQYs.²⁷ Blue HF-OLEDs resulted in high EQE of 21.9%, high color purity, and high brightness ($L_{max} = 63,777$ cd m⁻²). From the transient PL analysis, we confirmed the presence of very efficient FRET between AD and TE. Further, by analyzing the transient EL spectra of the HF-OLEDs, it is found that a smaller E_{HOMO} difference between AD and TE efficiently helps to decrease hole trapping inside the emitting layer, hence resulting in a lower efficiency rolloff and a longer operational

device lifetime. HF-OLEDs based on CzBNCz as a TE having the closest E_{HOMO} to that of AD showed a maximum EQE of 21.9% together with a reduced efficiency rolloff (EQEs of 21.2% and 19.8% at 100 and 1000 cd m⁻², respectively). This provides a designing principle for a TE in HF-OLEDs with well-matched energy levels towards reaching the requirements of commercial displays.

4. Conclusions

Pure-blue (CIEx, y color coordinates of [0.13, 0.16]) OLEDs with high-efficiency (external quantum efficiency of 32 % at 1000 cd m⁻²), narrow-emission (full-width half maximum of 19 nm), and good stability (LT95 of 18 hours at an initial luminance of 1000 cd m⁻²) have been reported. The design is based on a two-unit stacked tandem hyperfluorescence (HF)-OLED with an improved singlet-excited energy transfer process from a sky-blue TADF-AD (HDT-1) to a pure-blue TE (v-DABNA). Moreover, with a careful energy alignment of the HOMO energy levels of TADF-AD and TE, device lifetimes have been enhanced.

Acknowledgement: We sincerely acknowledge Prof. Takuji Hatakeyama for providing v-DABNA and fruitful discussions. This work is financially supported by the JSPS Core-to-Core Program and Kyulux Inc..

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