

# High Performance Green Hyperfluorescence Devices with New BODIPY Materials

Hyun Seung Lee, Chae Yeon Jeon, Hyuna Lee, Jang Hyuk kwon

jhkwon@khu.ac.kr

Department of Information Display, Kyung Hee University, 26, kyunghedae-ro, Dongdaemun-gu, Seoul, Korea

Keywords: OLED, hyperfluorescence, BODIPY, TADF

## ABSTRACT

Here, we report the new deep green BODIPY fluorescence emitters and efficient deep green hyperfluorescence (HF) devices. The KHU-FD1 exhibits the pure and bright deep green emission peak at 531 nm with 22 nm of narrow spectral width. With 30 wt% of 4CzIPN and 0.5 wt% of KHU-FD1, HF device exhibited the 20.5% of the maximum efficiency, and 531 nm of emission peak with 29 nm of narrow full-width at half maximum.

## 1 Introduction

The thermally activated delayed fluorescence (TADF) can obtain high internal quantum efficiency through reverse intersystem crossing (RISC) process from dark triplet exciton harvesting. However, it showed low color purity due to intramolecular charge transfer (ICT) characteristics. In order to solve this problem, hyperfluorescence (HF) device is highly desired and regarded as the most suitable for the next generation in OLED display. In HF system, the TADF acts as assistant host and transfers the singlet exciton to narrow full-width at half maximum (FWHM) of fluorescence emitter [1-2]. However, it is still challenging to develop good fluorescent emitters with proper color and FWHM characteristics.

As the final emitter, well-known 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) core can be an appropriate candidate due to its high photoluminescence quantum yield (PLQY) and narrow FWHM characteristics. The BODIPY utilization in the HF system can overcome the challenge of color purity with the help of TADF assistant host. In 2020, Duan *et al.* reported tPhBODIPY as a promising green final emitter [3]. Reported HF device with tPhBODIPY exhibits 19.0% of maximum external quantum efficiency ( $EQE_{max}$ ) and 520 nm of emission peak with 32 nm of FWHM. However, its emission wavelength was not satisfactory for deep green color.

In this study, we report new green BODIPY core fluorescence emitter, KHU-FD1 and KHU-FD2, and fabricate the highly efficient green HF devices with deep green emissions with our KHU-FD as final emitters. With 25wt% of 4CzIPN and 0.5 wt% of KHU-FD1, HF device exhibited the 20.5% of  $EQE_{max}$ , and 531 nm of maximum emission peak with 29 of FWHM.

## 2 Result and discussion

The tPhBODIPY exhibited the high PLQY, but the emission color is 520 nm. Thus, target of molecular design is to achieve a 530 nm of green emission without influencing on high PLQY and narrow FWHM characteristics. In general, it was reported that the *meso* position of BODIPY core can change PLQY and reactivity of the material, and the addition of a substituent to the *alpha* or *beta* position increases the conjugation. [4] Thus, we modified the tPhBODIPY by attaching a substituent on the *alpha* or *beta* position. Finally, we designed and synthesized two new materials KHU-FD1, KHU-FD2.

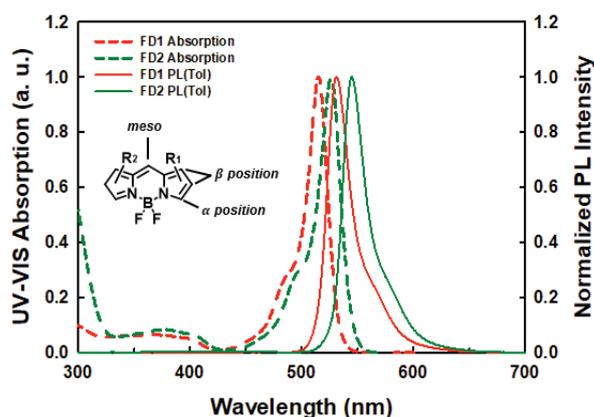


Figure 1. The absorption and emission spectra of KHU-FD1, KHU-FD2, respectively.

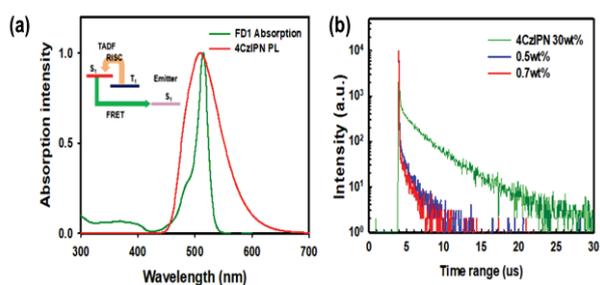
	PL peak (nm)	FWHM(nm)	Stoke shift(nm)	HOMO/LUMO(eV)	PLQY
tPhBODIPY	520 nm	23 nm	14 nm	5.8 / 3.5	0.97
KHU-FD1	531 nm	22 nm	16 nm	5.8 / 3.5	0.97
KHU-FD2	545 nm	22 nm	19 nm	5.9 / 3.6	0.97

Table 1. Photophysical properties of tPhBODIPY, KHU-FD1, KHU-FD2.

The photophysical properties of KHU-FD1, KHU-FD2 were measured in toluene at a concentration of  $10^{-5}$  M as shown in Figure 1. A narrow absorption spectrum peak at 515, 526 nm was observed with high extinction coefficient ( $\epsilon$ ) at around 74,000. High extinction coefficient value can be the great advantage in HF

system, since the FD can absorb the larger amount of energy from the TADF material emission. The sharp and narrow emission peak was appeared at 531, 546 nm, respectively with FWHM of 22 nm. Narrow emission can be attributed to improvements in locally excited (LE) properties in rigid and symmetric molecular structures, so the emission wavelengths of CT interactions are rarely seen and only sharp emission wavelengths are observed. In addition, both emitters have high PLQY at 0.97. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were measured using cyclic voltammetry. The HOMO energy levels of KHU-FD1 and KHU-FD2 were measured to 5.8, and 5.9 eV, and the LUMO was measured to 3.5, and 3.6 eV, respectively. Since the -BF<sub>2</sub> group in BODIPY core has a strong electron withdrawing strength, our BODIPY emitters also have deep LUMO energy level. Additional photophysical properties of KHU-FD1 and KHU-FD2 is summarized in Table1.

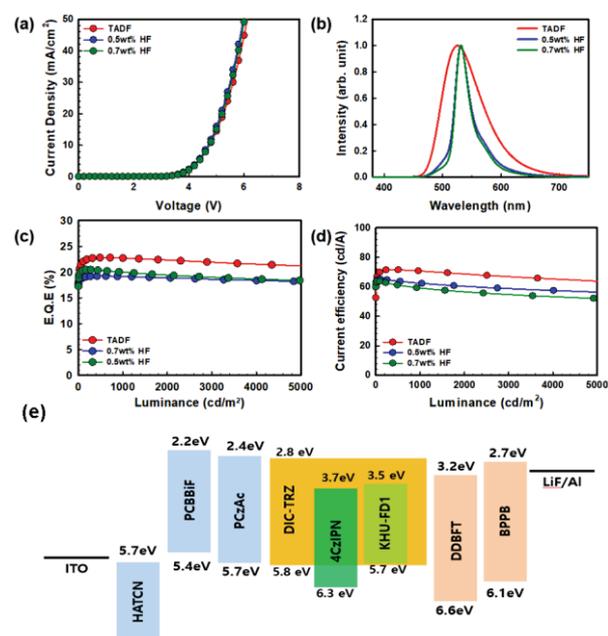
Since the emission wavelength of KHU-FD1 is much suitable as deep green color, we utilized the KHU-FD1 as a final emitter in the HF device. For successful HF system, efficient Förster resonance energy transfer (FRET) from TADF to final emitter is important. For efficient FRET, large spectrum overlap between TADF assistant material and final emitter is crucial. The 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene, 2,4,5,6-tetrakis(9H-carbazol-9-yl)isophthalonitrile (4CzIPN), well known as green TADF can be a good candidate for our green TADF sensitizer. 4CzIPN has 510 nm emission peak and KHU-FD1 also has high extinction coefficient ( $\epsilon$ ) value at 515 nm, the good FRET efficiency can be expected. In addition, as aforementioned, BODIPY-core material has significantly deep LUMO level of 3.5 eV, which can easily occur the electron trap. In that point of view, 4CzIPN has deep LUMO of 3.7 eV, trapping emission issue can be solved. In order to confirm the efficient energy transfer, time resolved photoluminescence (TRPL) was measured as Figure 2 (c). With 0.5 and 0.7 wt% of KHU-FD1 in 30 wt% of 4CzIPN, it can be observed that delayed fluorescence ratio and the lifetime was decreased, indicating the efficient singlet exciton transfer.



**Figure 2.** (a) Spectrum overlap with 4CzIPN PL and KHU-FD1 absorption. (b) The PL decay curves of films of 30 wt% 4CzIPN with x wt% KHU-FD1. (x = 0.0, 0.5, 0.7)

Next, the device was fabricated in the following order of ITO / 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HATCN) (7 nm)/ N-(1,1'-biphenyl-4-yl)-N-[4-(9-phenyl-9H-carbazol-3-yl)phenyl]-9,9-dimethyl-9H-fluoren-2-amine (PCBBiF) (55nm) /9,9-dimethyl-10-(9-phenyl-9H-carbazol-3-yl)-9,10-dihydro acridine (PCZAC) (10 nm) / (2,4-diphenyl-6-bis(12-phenylindolo)[2,3-a]carbazole-11-yl)-1,3,5-triazine (DIC-TRZ): x wt% 4CzIPN: x wt% KHU-FD1 (30 nm) / 2,4-bis(dibenzo[b,d]furan-2-yl)-6-phenyl-1,3,5-triazine (DDBFT) (10 nm) / 1,4-bis(4-(phenylethynyl)phenylethynyl)benzene (BPPB)(40 nm) / LiF (1.5 nm) / Al (100 nm). Besides, PCZAC and DDBFT was used as triplet exciton confinement layer and DIC-TRZ was used as high triplet energy host.

When fabricating the HF device, we first optimized TADF concentration to get high efficiency. With 30 wt% of doping concentration, 4CzIPN TADF device showed the 22.7% EQE<sub>max</sub> with 526 nm of emission peak. After optimizing the TADF doping concentration, HF devices were fabricated by manipulating the doping concentration of final emitter. Increasing the emitter doping rate improves the efficiency of FRET. However, as the distance between TADF and emitter gets closer, non-radiative process of the Dexter energy transfer (DET) occur more dominantly. Therefore, we need optimized the doping concentration of the final emitter, KHU-FD1 to 0.5 and 0.7wt% in 4CzIPN TADF system.



**Figure 3.** (a) Current density-voltage curves. (b) The electroluminescence spectra. (c) The EQE – luminescence curve, (d) current efficiency – luminescence curve, and (e) the energy levels of HF device.

Consequently, HF devices with 30 wt% of 4CzIPN and 0.5 and 0.7wt% of KHU-FD exhibited the 20.5 and 19.2% of EQE<sub>max</sub>, respectively, with 531 nm of maximum emission peak with 31 and 29 nm of FWHM. The following Commission Internationale de Photométrie (CIE) coordinates were (0.28, 0.69) and (0.29, 0.69), respectively. Detailed device performances and analysis will be discussed on the presentation.

### 3 Conclusions

We designed new BODIPY based core structure as a fluorescence emitter and fabricated HF device with 30 wt% of 4CzIPN and 0.5% of KHU-FD1 exhibited the maximum external quantum efficiency of 20.5%, and 531 nm of emission peak with 31 nm of FWHM. Such device performance is the best among reported green BODIPY based HF devices.

### 4 Acknowledgement

This work was supported by the Technology Innovation Program (20006464) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea)

### References

- [1] Chan, Chin-Yiu, et al. "Stable pure-blue hyperfluorescence organic light-emitting diodes with high-efficiency and narrow emission." *Nature Photonics* 15.3 pp.203-207. (2021):
- [2] Baldo, M. A. et al. Highly efficient phosphorescent emission from organic electroluminescent devices. *Nature* 395, pp.151–154 (1998)
- [3] Song, Xiaozeng, et al. "Strategically modulating carriers and excitons for efficient and stable ultrapure - green fluorescent OLEDs with a sterically hindered BODIPY dopant." *Advanced Optical Materials* 8.15: 2000483 (2020)
- [4] Squeo, Benedetta Maria, and Mariacecilia Pasini. "BODIPY platform: A tunable tool for green to NIR OLEDs." *Supramolecular Chemistry* 32.1: 56-70. (2020)