Highly Efficient and Stable Narrow-Band MR-TADF Emitter for Top-Emission Red OLED Approaching B.T.2020

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Abstract

We reported two narrowband red MR-TADF emitters KHU-RD-01 and KHU-RD-02 by introducing five-membered heterocyclic scaffolds. These emitters exhibited red emission at 613 nm with narrow band FWHM of 32 nm. The fabricated BE-OLED exhibited high EQE_{max} of 22% with long lifetime of LT_{95} 2039 h @ 1000 cd/m^2 and further to improve the color purity, we optimized TE-OLED with KHU-RD-02 results in high current efficiency of 41.26 cd/A with CIE (x, y) = (0.68, 0.32) approaching near to B.T.2020.

Author Keyword

OLED; Top-emission; red MR-TADF; Narrow FWHM; long-lifetime; B.T.2020

1 Introduction

Organic light emitting diode (OLED)[1] has become the next generation of displays thanks to its flexibility, wide viewing angle, low power consumption and excellent color purity, which makes it perfect for UHD (ultra-high definition) screens. Achieving B.T.2020 color coordinates (CIE) recommended by International Telecommunication Union (ITU) is essential for next-gen UHD display which requires extremely narrow full-width half-maxima (FWHM) for Red (0.70,0.29), Green (0.17,0.79), and Blue (0.13,0.04) (RGB) primary colors. Recently, multi-resonance thermally activated delayed fluorescence (MR-TADF) emitters have gained a significant attention in academia and industry due to ability of efficient triplet-harvesting in achieving 100% internal quantum efficiency (IQE), high photoluminescence quantum yield (PLQY) without need of any heavy metal while maintaining the narrow FWHM[2]. Researchers are focused to develop emitters with narrowband emission, high PLQY, highly efficient and stable materials. Through innovative molecular design many blue and green emitters reaching <20nm with excellent device properties approaching B.T. 2020 have been reported[3,4].

However, despite the promising advancements only a few of red MR emitters have been reported. Introducing acceptor group on the boron para-position or donor group on the peripheral position to the nitrogen atom is one of the well-known molecular designs[5]. Through this approach the enhanced intramolecular charge transfer (ICT) character leads to the red-shifted emission, but the enhanced CT character induces the spectral broadening due to the structural relaxation between the ground and excited state which is unavoidable. The emitter BBCz-R reported by Yasuda et al., is exception, exhibited red emission of 615nm and small fwhm 21 nm, however it exhibited a high intense secondary peak which affected the color purity[6]. Later, Duan et al. demonstrated that double boron-embedded para-B-π-B and N-π-N atomic arrangements cause a substantial ICT effect, resulting in red-shifted emission wavelengths and reported R-BN and R-TBN near infrared (NIR) emitters. Recently Yang et al., introduced oxygen atom into the double boron-based MR framework to reach pure red region BNO1, BNO2 and BNO3 [8,9]. Although, red MR emitters reaching B.T.2020 are in still in search due to the poor color purity in the device. Researchers are focusing on the utilizing of Top-emission OLED (TEOLED) to fabricate narrow band OLED to improve the color purity of the device to achieve B.T.2020 coordinates

Top-emission organic light emitting diodes (TEOLEDs), emitting light from the top electrode in the upward direction, with a strong micro-cavity effect[10]. Normally, TEOLEDs are comprising two highly reflective metal electrodes (thick metal anode and thin metal cathode), wherein semitransparent thin metal electrode generates strong micro-cavity effect. Such micro cavity effect strongly influences the spectral emission by changing internal resonance condition, resulting in small FWHM compared with non-cavity-based device enhance the color purity in the device[11]. The FWHM can be computed as follows and reflects the strength of the micro-cavity effect.

$$\mathrm{FWHM} = \frac{\lambda^2}{2L_{cav}} \times \frac{1-\sqrt{R_1R_2}}{\pi\sqrt[4]{R_1R_2}} \quad \text{..... (1)}$$

whereas L_{cav} denotes the cavity length between the two electrodes. λ the wavelength of the emitting light, R is given by the reflectivity of the electrode (R1: anode and R2: cathode). From this equation (1) the TEOLED with a highly reflective electrode and long cavity yields in small FWHM value which improves the color purity in the device. Firstly, we performed the optical simulations to optimize the thickness, enhanced micro-cavity effect and improved device results of TE-OLED. The calculations results demonstrated promising optical properties can be exhibited with the narrower FWHM emitter. In this study we reported a new red MR-TADF emitter with narrow FWHM of 32nm by introducing heteroatom infusion conjugation approach. Furthermore, the fabricated bottom-emission OLED (BE-OLED) employing developed emitters as final dopants results in achieving efficiency EQE of 22% with long lifetime LT_{95} 2039h @ 1000 cd/m^2 with CIE (x, y) (0.67,0.33) on the other hand we fabricated TE-OLED (TOP emission) with KHU-RD-02, demonstrated high current efficiency 41.36 cd/A with narrow FWHM of 21 nm and CIE (x, y) = (0.68,0.32) which approaching B.T.2020.

2 Results and discussion

2.1 Molecular design, Photophysical and electrochemical properties

In this study we designed two red MR-TADF emitters based on the para-B-π-B, N-π-N and O-π-O pairs double boron strategy tuned the emission spectra into pure -red region, while maintaining the narrow FWHM. We successfully synthesized these red emitters namely KHU-RD-01 by linear conjugation, on the other hand KHU-RD-02 by introduced five-membered heterocyclic analogues. The photophysical properties of these emitters KHU-RD-01, and

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KHU-RD-02 were analyzed in dilute toluene solution and the results are shown in fig 1. The Uv-visible and PL of KHU-RD-01 and KHU-RD-02 are 587/611nm and 593/613 nm respectively with gradually bathochromic shift in the emission which is associated with the molecular design strategy. These emitters shown MR-type UV behavior associated with short range charge transfer (SRCT) with a sharp absorption band around ~590 region. KHU-RD-02 shows small stokes shift of 20nm less than KHU-RD-01, due to the effectively suppressed vibronic coupling between $S_1 \rightarrow S_0$ transitions. As a result, a narrow FWHM 32nm of KHU-RD-02 in and 36nm of KHU-RD-01. The S_1 and T_1 energy values were established by assessing the onset point of the RTPL at 300K and the low-temperature photoluminescence (LTPL) spectra at 77K following a 30 ms delay from excitation, respectively. The calculated S_1/T_1 values are 2.16/1.87eV, and 2.12/1.87eV KHU-RD-01, KHU-RD-02 respectively. These emitters show a moderate ΔE_{ST} of 0.25-0.29 eV. The photophysical properties summarized in table 1.

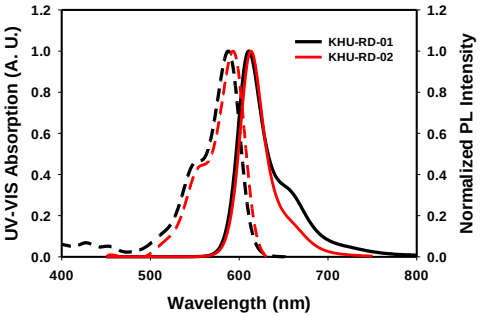

Figure 1. UV-Vis absorption and PL spectra of two emitters in toluene (10^{-5} M)

Table 1. Summary of solution-state photophysical properties

Emitter	λ_{abs} [a] (nm)	λ_{em} [a] (nm)	FWHM (nm)	HOMO/LUMO [b] (eV)	S_1/T_1 [c] (eV)	ΔE_{ST} [c] (eV)	PLQY% [d]
KHU-RD-01	587	611	36	-5.28/-3.29	2.16/1.87	0.29	84
KHU-RD-02	593	613	32	-5.29/-3.29	2.12/1.87	0.25	85

a) Measured in dilute toluene 1× 10^{-5} M solutions at 298 K; b) HOMOs were calculated from CV; LUMO = HOMO + $E_{g,opt}$ c)Estimated from the onset of the spectra in toluene (1 × 10^{-5} M, 77 K) $\Delta E_{ST} = E_{s1} - E_{T1}$ d)Measured in toluene 1× 10^{-5} M

2.2 Electroluminescence Properties

To illustrate the abilities of these emitters, the electroluminescence (EL) properties were assessed through the fabrication of the device with the specified configuration. ITO (50nm)/HATCN (10nm)/PCBBiF(80nm)/PCzAC(10nm)/NPB:diDBFTRz (7:3) : 5% KHU-IR : 1% KRD-RD/DDBFT(40nm)/BPPB:Liq (2:1)/Liq/Al. Whereas indium-tin-oxide(ITO) and aluminium (Al) were used as anode and cathode, respectively. Dipyrazino[2,3-f:2′,3′-h]quinoxaline2,3,6,7,10,11-hexacarbonitrile (HATCN), N-(1,1′-biphenyl-4-yl)-N-[4(9-phenyl-9H-carbazol-3-yl)phenyl]-9,9-dimethyl-9H-fluoren-2-amine (PCBBiF) and 9,10-Dihydro-9,9-dimethyl-10- (9-phenyl-9H-carbazol-3yl)-acridine (PCzAC) was utilized as a hole- injection layer, transporting layer and electron blocking layer, respectively. 2,4-Bis(dibenzo[*b,d*]furan-2-yl)-6-phenyl-1,3,5-triazine (DDBFT) and 1,3-bis(9-phenyl-1,10-phenanthrolin-2-yl)benzene (BPPB) were applied for a hole blocking and electron- transporting layers, respectively. The lithium fluoride (LiF) was used as an electron injection layer. In the EML p-type material N,N′-bis(1-naphthalenyl)-N,N′ diphenyl-[1,1′-biphenyl]-4,4′-diamine NPB and n-type material 2-(5 (dibenzo[b,d]furan-4-yl)-[1,1′-biphenyl]-3-yl)-4-phenyl-6-(8-phenyldibenzo[*b,d*]furan-1-yl)1,3,5-triazine (diDBFTrz) which forms a strong exciplex ,reduces the hole trap in the device was chosen as a host matrix and the host ratio was optimized to be NPB:diDBFTRZ(7:3) and sensitizer KHU-Ir:dopant KHU-RD to be 5 wt% and 1 wt% respectively the corresponding energy levels and thickness are shown in fig 2.

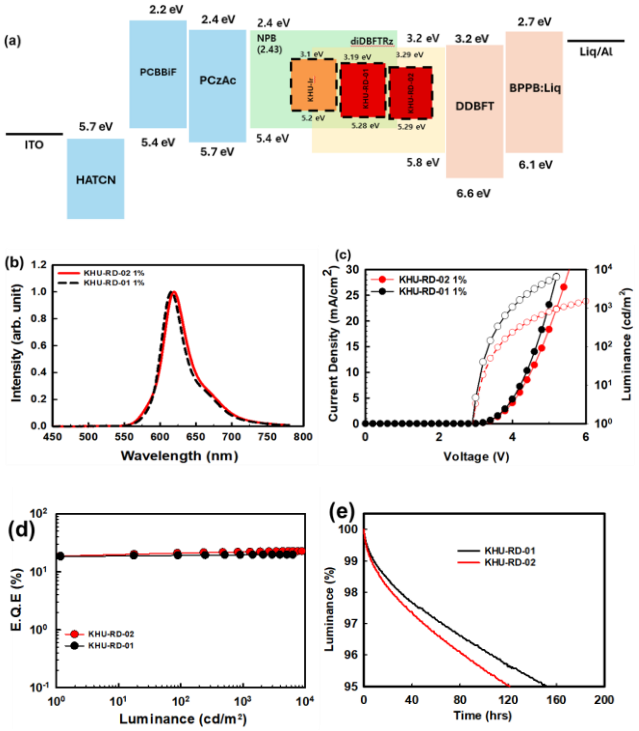

Figure 2. (a)Device architecture and the energy level diagram of BE-OLED, (b) The EL spectra (c) luminescence and current density versus voltage characteristics (d) EQE versus luminance curves (e) Lifetime of the devices measured at 5000 cd m^{-2}

Benefiting from the effective device architecture improved the carrier transportation and suppressed the hole trap in the device leads to the ultralow efficiency roll-off <1% with a high current density of 5000 cd/m^2 in the PSF device. The respected J-V-L shown in fig 2c. The devices employing emitters KHU-RD-01, and KHU-RD-02 exhibits El emission 616nm, and 620nm respectively shows in fig 2d. KHU-RD-02 exhibits pure red emission in device 620nm with narrow FWHM of 40 nm and the corresponding device shows high EQE max of 22.5% with longer lifetime of LT_{95} 2,039 @ 1000 cd/m^2 and CIE coordinates (0.67,0.33) approaching B.T.2020. The bottom emission device (BE-OLED) results are summarized in table 2.

Table 2. Summary of BE-OLED device performance

	KRD-RD-01 (1%)	KHU-RD-02 (1%)
Turn on voltage (1 cd/m^2)	2.9	2.9
Driving voltage (5,000 cd/m^2)	4.9	5.1
C.E (Max/ 5,000 cd/m^2)	24.30 / 24.25 cd/A	26.83/26.83 cd/A
EQE (Max/ 5,000 cd/m^2)	19.6 / 19.6%	22.5/22.5 %
Max emission peak	616 nm	620 nm
FWHM	39 nm	41 nm
CIE coordinates	(0.66, 0.34)	(0.67, 0.33)
LT95@1000 nits	2,541 h	2,039 h

Further, to improve the color purity in the device we fabricated TE-OLED by incorporating KHU-RD-02 emitters due to its narrow FWHM. We performed Optical simulations using SETFOS commercial tool and the emission according to the hole transporting layer (HTL), electron transporting layer (ETL), and capping layer (CPL) thickness were calculated for better optical properties. Here, the HTL thickness means the distance between anode and EML, and the ETL thickness means the distance between cathode and EML. The TE-OLED was fabricated using the same EML structure of BE-OLED by incorporating exciplex host matrix with optimized thickness the TE-OLED device specified configuration is Ag(150 nm)/ITO (10nm)/N1,N1'-(biphenyl-4,4 '-diyl)bis (N1-phenyl-N4, N4 -di-m-tolylbenzene-1,4-diamine (DNTPD) (75 nm)/HATCN(7 nm)/ PCBBiF (105nm)/PCzAC(15nm)/NPB:diDBFTRz (7:3):5%KHU-IR : 1% KRD-RD/DDBFT(12nm)/BPPB:Liq (2:1)(35 nm)/Liq/Mg : Ag (10:1) (11 nm)/PCBBiF (74 nm)

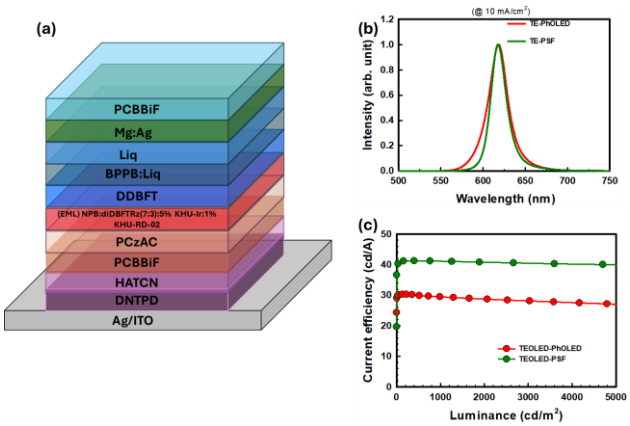

Figure 3. (a)Device architecture and the energy level diagram of TE-OLED, (b) The EL spectra (c) Current efficiency versus luminance curve

The fabricated TE-OLED device exhibited an EL emission of 618 nm with narrow FWHM 21 nm (fig 3b) due to the strong microcavity effect. The current efficiency (C.E) of the TE-PSF was recorded as 41.26 cd/A with a 36% improved in compared to TE-PhOLED and BE-OLED (fig 3c) and the EQE of the TE-OLED is measured as 29.37% (fig 3d) with CIE (x, y) (0.68,0.32) approaching B.T.2020, which is near to B.T.2020 CIE (x, y) (0.70,0.29).The summary of the device results of TE-PhOLED without final emitter KHU-RD-01 and with final emitter are given in table 3.

Table 3. Summary of TE-OLED device performances

TE-OLED	TE-PhOLED	TE-PSF
Turn on voltage (1 cd/m^2)	3.4 V	3.3 V
Driving voltage (5,000 cd/m^2)	7.0 V	5.3 V
C.E. (Max / 5,000 cd/m^2)	30.29 / 27.3 cd/A	41.26 / 40.70 cd/A
Max emission peak	618 nm	618 nm
FWHM	27 nm	21 nm
CIE coordinates	(0.66,0.33)	(0.68 , 0.32)

3. Conclusion

In conclusion, a series of two red MR-TADF emitters was designed based on the design strategy of double boron-based pairs of para-B-π-B, N-π-N, O-π-O. The reported emitters show excellent solution state photophysical properties with red emission 613nm and narrow FWHM 32 nm. Benefiting from the superior photophysical properties the PSF-OLED was fabricated with the help of exciplex host system and PSF-OLED based on these emitters shows pure red emission of 620nm with narrow fwhm of 41nm, CIE of (0.67,0.33) with a high EQE_{max} of 22.55% and long operational device lifetime of LT_{95} ~2039 h @1000 cd/m^2.Further,we fabricated TE-OLED which demonstrated high current efficiency 41.26 cd/A with color purity of pure red EL emission 618nm with FWHM 21nm due to the strong microcavity effect CIE(x,y) (0.68,0.32) approaching B.T.2020.

4. Impact of Your Research

We report highly efficient and stable narrowband red MR-TADF emitters for top emission OLEDs. Our synthesized KHU-RD-02 emitter exhibited a red emission of 613 nm with narrow band FWHM of 32 nm. The fabricated bottom emission OLED exhibited high EQEmax of 22% with long lifetime of LT_{95} 2039 h @ 1000 cd/m^2. The optimized TE-OLED with KHU-RD-02 results in high current efficiency of 41.26 cd/A with CIE (x, y) = (0.68, 0.32) approaching near to B.T.2020 color. We believe that our approach will provide how we achieve red B.T.2020 color standards with device performances in OLEDs

5. Acknowledgement

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6. References

1. Tang C, VanSlyke S., Organic electroluminescent diodes. *Appl. Phys. Lett.* 21 September 1987; 51 (12): 913–915
2. Hatakeyama, T., Shiren, K., Nakajima, K., Nomura, S., Nakatsuka, S., Kinoshita, K., Ni, J., Ono, Y., and Ikuta, T., Ultrapure Blue Thermally Activated Delayed Fluorescence Molecules: Efficient HOMO–LUMO Separation by the Multiple Resonance Effect. Adv. Mater. 2016, 28, 2777–2781
3. Liu, J., Zhu, Y., Tsuboi, T. *et al.* Toward a BT.2020 green emitter through a combined multiple resonance effect and multi-lock strategy. Nature Communications, 2022, 13:4876.
4. Naveen KR, Lee H, Braveenth R, Yang K, Hwang S, Kwon J, Deep blue diboron embedded multi-resonance thermally

activated delayed fluorescence emitters for narrowband organic light emitting diodes, Chemical Engineering Journal 432 (2022) 134381

5. Y. Qi, W. Ning, Y. Zou, X. Cao, S. Gong, C. Yang, Peripheral Decoration of Multi-Resonance Molecules as a Versatile Approach for Simultaneous Long-Wavelength and Narrowband Emission. *Adv. Funct. Mater.* 2021, 31, 2102017.
6. Yang M, Park, S, Yasuda T Full-Color, Narrowband, and High-Efficiency Electroluminescence from Boron and Carbazole Embedded Polycyclic Heteroaromatics. *Journal of the American Chemical Society* **2020** *142* (46), 19468-19472
7. Zhang Y., Zhang D., Huang T., Gillett A. J., Liu Y., Hu D., Cui L., Bin Z., Li G., Wei J., Duan L., Multi-Resonance Deep-Red Emitters with Shallow Potential-Energy Surfaces to Surpass Energy-Gap Law *Angew. Chem. Int. Ed.* **2021**, *60*, 20498.
8. Zou Y., Hu J., Yu M, Miao J., Xie Z., Qiu Y., Cao X., Yang C., High-Performance Narrowband Pure-Red OLEDs with External Quantum Efficiencies up to 36.1% and Ultralow Efficiency Roll-Off. *Adv. Mater.* 2022, 34, 2201442.
9. Jing Y. Li N., Cao X., Yang C et.al., Precise modulation of multiple resonance emitters toward efficient electroluminescence with pure-red gamut for high-definition displays. *Sci*. *Adv.***9**, eadh8296(2023).
10. Kim S, Lampande R., Kwon J, Technical status of top-emission organic light emitting diodes, J. Infect. Dis. 22 (2021) 115–126
11. Yang H, Cho S, Lee H, Kim S, Pode R, Kwon J, Merits of narrow spectral blue fluorescence emitters in strong micro-cavity top emission OLEDs Organic Electronics 111 (2022) 106658