Highly Efficient and Stable Pure Green Phosphor-Sensitized MR-TADF Emitter for B.T.2020 Color Top-Emission OLEDs

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Abstract

In this work, we report a novel green MR-TADF emitter KHU-GD by incorporating naphthalene units to the triazine acceptor, by attaching modified triazine acceptor to the para of MR core. The synthesized material exhibited a narrow FWHM of 22 nm within the pure green region.–The optimized exciplex host assisted phosphor-sensitized system with KHU-GD emitter resulting in high EQE of 29.3% and an extended operating lifetime (LT_{95}) of 6,019 h at an initial luminance of 1,000 cd/m^2. Furthermore, the fabricated top emission OLED with KHU-GD showed pure green emission with narrow FWHM of 20 nm and corresponding CIE coordinates of (0.19, 0.76) approaching BT.2020 requirements.

Author Keywords

Narrowband MR-TADF emitters; Exciplex host; PSF-OLED; TEOLED; Long lifetime

1. Introduction

Thermally activated delayed fluorescence (TADF) emitters in organic light-emitting diodes (OLEDs) have garnered significant interest in display technologies, both in research and commercial levels as a promising alternative to the commercial phosphorescent materials. Since TADF technology can attain 100% of internal quantum efficiencies (IQE) through the reverse intersystem crossing (RISC) mechanism, with a small energy difference between the singlet and triplet (ΔE_{ST}) energy levels. Conventional TADF emitters typically have a donor-acceptor (D-A) configuration, which facilitates a small ΔE_{ST} through the spatial separation between the highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) [1-3]. However, their non-rigid structures often result in broad emission spectra and increased non-radiative decay pathways, which can detract from color purity and luminous efficiency due to significant structural relaxation from the excited to ground states [4-6]. To overcome such issues, corresponds to the color purity, in 2016, Hatakeyama.et al. reported narrow FWHM emitters using multiple resonance (MR) effect by boron and nitrogen atoms [7]. These MR effects enable the alternating distribution of HOMO and LUMO on adjacent atoms, contributing to a rigid structure. Such HOMO-LUMO distribution results in a small ΔE_{ST} and large oscillator strength and the rigidity of MR-type materials resulting in small stokes shift, narrow FWHM, and high photoluminescence quantum yield (PLQY).

Numerous high-performance MR-TADF emitters have been reported since the introduction of DABNA in 2016 [8,9]. Nonetheless, utilizing MR-TADF emitters within a host-dopant emissive layer system, often leads to a severe efficiency roll-off at high current density. The relatively larger ΔE_{ST} in comparison to the conventional D-A TADF materials, resulting in low reverse intersystem crossing (RISC) rate and an increased triplet exciton lifetime subsequently resulting in bimolecular quenching processes such as triplet-triplet annihilation (TTA) in OLEDs, which negatively impacts the device operating lifetime. To address these challenges, researchers utilize a strategy called phosphor-sensitized fluorescence (PSF) technology, wherein phosphorescent materials function as phosphor sensitizers (PS) for narrowband MR-TADF type final emitters. Since PS can utilize both singlet and triplet excitons, and transfers those exciton energies to the final emitter through long-range Förster resonance energy transfer (FRET) process leads to 100% IQE in OLED. A large spectral overlap between the absorption of the final emitter with the emission of the phosphor sensitizer facilitates an efficient FRET process. Furthermore, to mitigate the exciton stress on final MR-TADF emitter for optimal device performance, appropriate energy level alignment of hosts and PS materials are required. Recently, the concept of exciplex hosts were implemented in the EML to reduce the carrier trap in the device and the TADF character of the exciplex host benefits an additional energy transfer process to the both PS and final emitter thereby improving the device efficiency and operational stability.

In this study, we developed a new green MR-TADF emitter by incorporating naphthalene units to the triazine acceptor, by attaching modified triazine acceptor to the para of MR core namely KHU-GD. The synthesize material showed a pure green photo-luminescence (PL) emission of 529 nm with narrow FWHM of 22 nm. The optimized device showed high EQE 29.3% with low efficiency roll-off up to 5000 cd/m^2 and extended device operating lifetime (LT_{95}) of 6,019 h at an initial luminance of 1,000 cd/m^2. In addition, we fabricated top-emission OLED (TEOLED), the corresponding TEOLED showed high current efficiency of 195.3 cd/A and pure green emission at 530 nm with narrow FWHM of 20 nm, corresponding CIE coordinates of (0.19, 0.76) approaching BT.2020 requirements.

2. Results and Discussion

2.1 Design Strategy and Photophysical Properties:

Recently, strategies utilizing hydrogen bonds (HBs) have improved TADF emitters by increasing molecular planarity, suppressing non-radiative decay and stabilizing molecular frameworks [10-14]. Hydrogen bonds (HBs), as robust non-covalent interactions, effectively induce rigid molecular conformations and inhibit the complexity of joined rings. Nonetheless, the utilization of HBs in MR-TADF materials is less common than in DA type TADF emitters [15]. In this study, we selected the well-known acceptor unit triazine and integrated two naphthalene units, which facilitates intramolecular N---H hydrogen bonding between the hydrogen in the naphthyl unit and the nitrogen in the triazine scaffold (**Figure 1**). This minimizes the free rotation of naphthyl units relative to phenyl rings in

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excited states, ultimately reducing secondary vibrational peaks and leading to narrowband emission. The synthesis of KHU-GD was carried out by sequential Suzuki coupling reactions from the key intermediate (MR-Core) as shown in **Scheme 1.** The di-naphthyl fused triazine acceptors were synthesized by a controlled Suzuki coupling reaction.

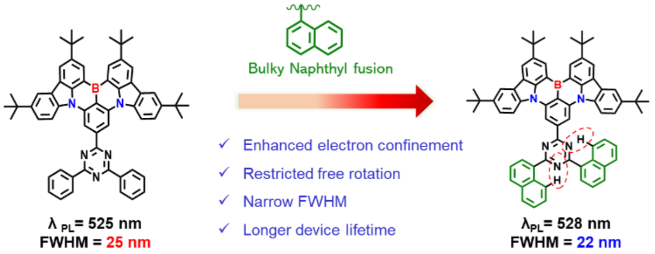
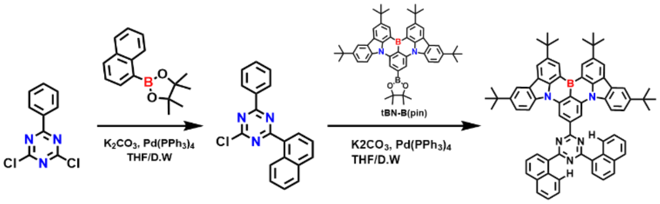


Figure 1. The molecular design strategy for KHU-GD.



Scheme 1. Synthetic route for KHU-GD.

The basic photophysical properties of KHU-GD are measured in toluene at ~ 10^{-5} M conc. and the results are depicted in **Figure 2** and **Table 1.** From figure 2, the PL emission of the emitter is in pure green region at 529 nm with less stokes shift (18 nm) and narrow FWHM of 22 nm. Additionally, the electrochemical properties of KHU-GD wad measured by using cyclic voltammetry (CV) measurements.

Table 1. Photophysical Properties of KHU-GD emitter.

Emitters	λ_{abs} [a] (nm)	λ_{RTPL} [a] / FWHM (nm)	E_{S1} / E_{T1} [b] (eV)	ΔE_{ST} (eV)	HOMO/ LUMO (eV)
KHU-GD	510	529 / 22	2.34 / 2.13	0.21	5.81 / 3.49

[a] UV-vis absorption spectra and Room temperature PL spectra (300 K) measured in toluene solution at 10^{-5} M concentration; [b] Calculated from the onset fluorescence and phosphorescence spectra in toluene solution.

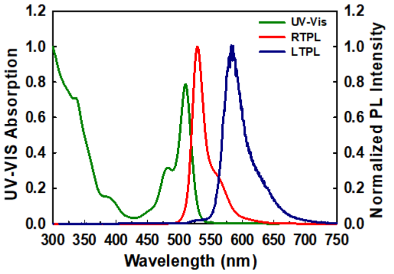


Figure 2. The UV-Vis, room temperature PL and low-temperature PL of KHU-GD.

The formation of exciplex between a P-type host namely, 9 ([1,1′-biphenyl]-4-yl)-9′-phenyl-9H,9′H-3,3′-bicarbazole (BPP-BCz) and two distinct N-type hosts with varying LUMO energy levels namely 2,4-diphenyl-6-bis(12-phenylindolo)[2,3-a]carbazol-11-yl)-1,3,5-triazine (DIC-TRZ) and 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) was investigated by measuring the film PL emission of the individual hosts along with their 1:1 co-deposited film (**Figure 3**). From figure 3, the PL emission of BPP-BCz: diDBFTRz co deposited film showed red-shifted emission in comparison to the individual hosts, confirming the formation of exciplex, whereas the co-deposited film of BPP-BCz: DIC-TRz showed similar PL spectrum with DIC-TRZ, indicating no exciplex formation, acts as mixed host system. The delayed fluorescence lifetime of both the BPP-BCz: diDBFTRz exciplexes is determined by using transient PL (TRPL) analysis. The delayed fluorescence lifetimes are 3.6 µs.

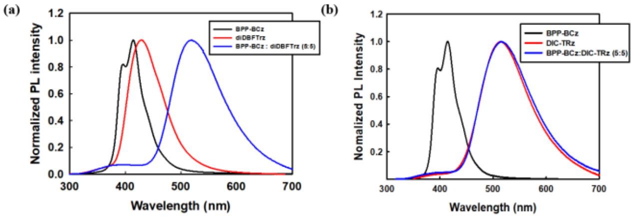


Figure 3. Room temperature PL of (a) BPP-BCz: diDBFTRz, (b) BPP-BCz: DIC-TRz

2.2 Electroluminescence Properties:

The electroluminescence performance of KHU-GD was investigated by using a phosphor sensitized fluorescence system within both exciplex host and mixed host systems, where Ir(mppy)3 is utilized as a phosphor sensitizer. The optimized PSF device structure to investigate KHU-GD as final emitter are as follows: ITO / HATCN (90 Å) / PCBBiF (720 Å) / PCzAC (120 Å) / BPP-BCz: DIC-TRz/diDBFTRz (7:3): 5% Ir(mppy)3: 1% KHU-GD (300 Å) / DDBFT (100 Å) / BPPB: Liq (470 Å) / Liq (15 Å) / Al (1,000 Å). The device architecture and electroluminescent performance are illustrated in **Figure 4** and detailed in **Table 2**.

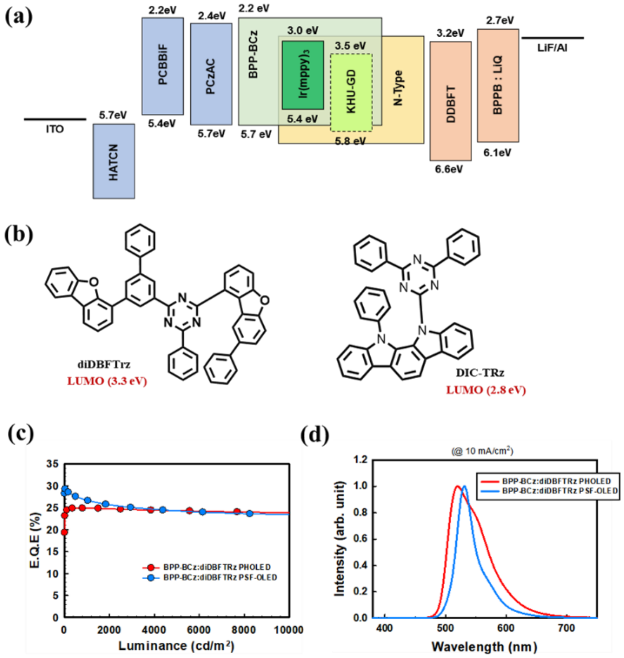


Figure 4. (a) The exciplex host assisted PSF-OLED device structure (b) Chemical structures of N-type materials (c) EQE vs Luminescence and (d) EL spectra of BPP-BCz: diDBFTRz exciplex device.

Both devices exhibited a low turn-on voltage of 2.7 V and a driving voltage of 4.3 V at 5,000 cd/m². The PSF device utilizing a mixed host system exhibited a pure green emission at 531 nm with a narrow FWHM of 36 nm and a high EQE of 29.3%. Despite attaining a high EQE_{max}, a significant efficiency roll-off was observed at high current density due to the unexpected direct exciton recombination in the final emitter. Furthermore, the PSF device utilizing an exciplex host exhibited a high EQE of 29.3% with EL emission at 531 nm with narrow FWHM of 35 nm. Unlike the mixed host system, the exciplex host-based system showed reduced-efficiency roll-off at high current density, attributed to the reduction of electron trapping and exciton stress on KHU-GD within the device. Benefiting from these, the exciplex host-based device showed extended lifetime (LT95) of 360 h at an initial luminance of 5,000 cd/m2. Additionally, the lifetime (LT95) at the commercial luminance of 1,000 cd/m2 was calculated by assuming the acceleration factor (n) as 1.75, be 6,019 h. The improved device lifetime of KHU-GD is attributed to the structural rigidity resulting from hydrogen bonding and high bond dissociation energy (BDE).

Table 2. Summary of Electroluminescence Properties using tCzphB-Fl.

Emitting Layer	V_{on} (V)[a]	EQE_{max} [b] / 5,000 cd/m² (%)	$C.E._{max}$ [c] / 5,000 cd/m² (cd/A)	$λ_{EL}$ [d] (nm)	FWHM[e] (nm)
BPP-BCZ: DIC-TRz PHOLED	2.7	25.8 / 24.0	80.6 / 75.5	518	65
BPP-BCZ: DIC-TRz PSF	2.7	29.3 / 18.0	103.8 / 61.9	531	36
BPP-BCZ: diDBFTRZ PHOLED	2.7	24.9 / 24.3	78.2 / 76.0	520	69
BPP-BCZ: diDBFTRZ PSF	2.7	29.3 / 24.5	102.3 / 84.2	531	35

[a] Turn on voltage at 1 cd/m^2; [b] Maximum external quantum efficiency; [c] Maximum current efficiency; [d] Electroluminescence peak wavelength; [e] Full-width half maximum.

To further improve the color purity to reach BT.2020 standards, we fabricated top-emission organic light emitting diode (TEOLED). TEOLEDs consist of two highly reflecting metal electrodes: a thick metal anode and a thin metal cathode, with the semitransparent thin metal electrode producing a pronounced micro-cavity effect. The micro cavity effect significantly affects spectrum emission by altering internal resonance conditions, leading to a narrower full width at half maximum (FWHM) compared to non-cavity-based devices. The optimized PSF-TEOLED structure is as follows: Ag (1500 Å) / ITO (100 Å) / DNTPD (750 Å) /HATCN (70 Å) / PCBBiF (650 Å) / PCzAc (100 Å) / BPP-BCz: DIC-TRz (7:3): 5% of Ir(mppy)3: with 1% KHU-GD (250 Å) / DDBFT (100 Å) / BPPB: Liq (400 Å) / Liq (15 Å) / Ag (250 Å) / DNTPD (700 Å). The device results are shown in **Figure 5** and summarized in **Table 3**.

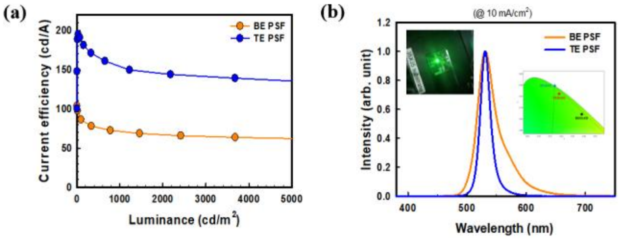


Figure 5. (a) Current efficiency vs Luminance, (b) EL spectra of KHU-GD based TEOLED.

The fabricated TEOLED exhibited an improved current efficiency of 195.3 cd/A showing EL emission at 530 nm with a narrow FWHM of 20 nm. The corresponding CIE coordinates are (0.19, 0.76) which closely align with the BT.2020 standards for green emission, i.e. (0.17, 0.79).

Table 3. Summary of Electroluminescence Properties using KHU-GD.

Emitting Layer	V_{on} (V)[a]	EQE_{max} [b] / 5,000 cd/m² (%)	$C.E._{max}$ [c] / 5,000 cd/m² (cd/A)	$λ_{EL}$ [d] (nm)	FWHM[e] (nm)
KHU-GD (Bottom Emission)	2.7	29.3 / 24.5	102.3 / 84.2	531	35
KHU-GD (Top Emission)	2.7	-	195.3 / -	530	20

[a] Turn on voltage at 1 cd/m^2; [b] Maximum external quantum efficiency; [c] Maximum current efficiency; [d] Electroluminescence peak wavelength; [e] Full-width half maximum.

3. Conclusions

In summary, we synthesized a novel green MR-TADF emitter, KHU-GD, by integrating naphthalene units into the triazine acceptor and attaching a modified triazine acceptor to the para position of the MR core. The synthesized material had a narrow full width at half maximum (FWHM) of 22 nm in the pure green spectrum. The optimized exciplex host-assisted phosphor sensitized system was then utilized with the KHU-GD emitter, achieving a high external quantum efficiency (EQE) of 29.3%. Furthermore, the fabricated top-emitting OLED demonstrated enhanced color purity with a pure green emission at 530 nm, characterized by an exceptionally narrow FWHM of 20 nm and associated CIE coordinates of (0.19, 0.76), nearing BT.2020 standards. The PSF-OLED showed an extended device lifetime (LT_{95}) of 6,019 hours at an initial brightness of 1,000 cd/m².

4. Impact of Your Research

We presented how we have to designed green MR-emitters for TEOLEDs. Our synthesized material exhibited a narrow FWHM of 22 nm with a pure green emission. Fabricated phosphor-sensitized green OLED with our MR-emitter results in high EQE of 29.3% and an extended operating lifetime (LT95) of 6,019 h at an initial luminance of 1,000 cd/m2. Furthermore, TEOLED was optimized for reaching BT.2020 coordinates. The obtained lifetime and color coordinates are one of the best among reported green MR TADF materials.

5. Acknowledgements

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