Reduction of Efficiency Roll-Off and Extension of Device Lifetime Through a Double Sensitizer Structure-Controlling Triplet Diffusion

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Abstract

In this study, we propose a novel device architecture for organic light-emitting diodes (OLEDs) by incorporating a double-sensitizer system, which combines a disk-shaped thermally activated delayed fluorescence (TADF) sensitizer and a phosphorescent sensitizer within the emitting layer. A double sensitized (TPDS) device was fabricated by introducing a phosphorescent sensitizer with energy levels strategically positioned between the TADF sensitizer and the terminal dopant. The TPDS device, utilizing the TADF sensitizer and a Pt-based phosphorescent sensitizer, demonstrated enhanced performance by effectively controlling triplet exciton diffusion and reducing triplet exciton density. These improvements suppressed device degradation, leading to significantly lower roll-off at high luminance levels compared to the conventional TADF sensitized fluorescence device, which employs only the TADF sensitizer and terminal dopant. Moreover, the operational lifetime of the TPDS device increased by 53.5%. Through this research, the potential of deep-blue sensitization was explored without the need for a planar n-type host in the TSF system. The double-sensitizing approach provides new possibilities for achieving efficient deep-blue OLEDs.

Keywords

Keywords: Organic light emitting diodes; Thermally Activated Delayed Fluorescence; Phosphorescence; Lifetime; Roll-off;

1. Objective and Background

Exciplex hosts are designed to harvest triplet excitons in organic light-emitting diodes (OLEDs), thereby enhancing device efficiency and performance. In exciplex host systems, the p-type host and n-type host form an exciplex, which facilitates the harvesting of triplet excitons and their transfer to the emitter. While exciplex hosts enable high efficiency and long operational lifetimes, they face limitations in achieving deep-blue emission.(1) The first limitation is that the exciplex formed inherently possesses lower energy, which is insufficient for deep-blue emission. Secondly, the n-type hosts commonly used in exciplex systems often exhibit planar structures to facilitate efficient negative polaron hopping. This planar configuration results in dense packing within the emitting layer (EML) matrix and increases π-π stacking, which subsequently lowers the overall matrix energy. Furthermore, planar n-type hosts tend to form complexes with phosphorescent materials in phosphor-sensitized fluorescent (PSF) systems, negatively impacting both the performance and operational stability of the device. In this study, we explored new possibilities for deep-blue sensitization by simultaneously introducing a disk-shaped thermally activated delayed fluorescence (TADF) sensitizer and a phosphorescent sensitizer into the EML. The disk-shaped TADF sensitizer exhibits a higher photoluminescence quantum yield (PLQY) compared to exciplex hosts and avoids π-π stacking, making it advantageous for deep-blue emission. However, when the disk-shaped TADF sensitizer is used as the sole sensitizer, the density of triplet excitons increases within the TADF layer, leading to higher rates of triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA). These processes negatively impact device lifetime and efficiency roll-off.(2)

To address these issues, we developed a *TADF-phosphorescent double sensitized* (TPDS) device by introducing a phosphorescent sensitizer with a triplet energy (T_1) positioned between the T_1 of the disk-shaped TADF sensitizer and the singlet energy (S_1) of the terminal emitter. The phosphorescent sensitizer, incorporated at a high doping concentration, was designed to suppress the dense accumulation of triplet excitons within the TADF layer, thereby improving device efficiency and operational stability. The TPDS device demonstrated enhanced efficiency and reduced roll-off compared to the TSF device employing only the disk-shaped TADF sensitizer. Moreover, the TPDS device exhibited a significant improvement in operational lifetime, and reduced efficiency roll-off.

2. Results

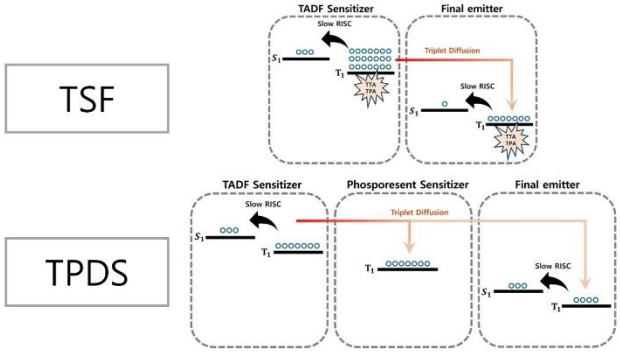

Figure 1. triplet diffusion mechanisms of the TSF and TPDS

The triplet diffusion control mechanisms of the TSF and TPDS devices investigated in this study are illustrated in Figure 1. When using a single p-type host in combination with only a TADF sensitizer, most excitons within the EML are initially formed on the TADF sensitizer (3). Due to its non-planar structure, the disk-shaped TADF sensitizer exhibits reduced overlap of electron and hole distributions between donors and acceptors. Consequently, the disk-shaped p4tCzphbn has a relatively low rate of reverse

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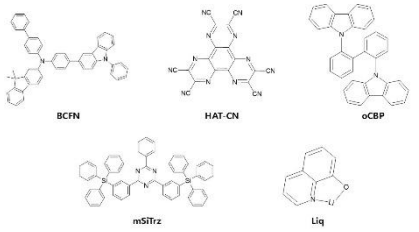
intersystem crossing (RISC). As a result, in TSF devices, efficiency roll-off becomes more pronounced under high current densities, leading to reduced operational lifetimes.(4)

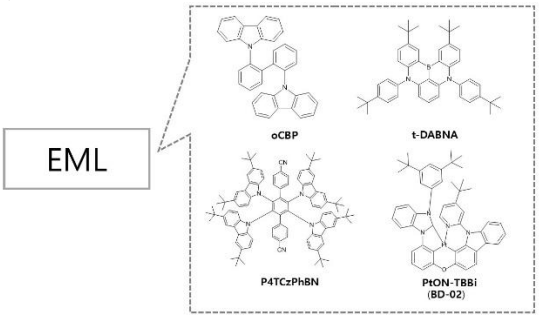
In contrast, in the TPDS device incorporating a phosphorescent sensitizer with a T_1 energy positioned between the T_1 of the TADF sensitizer and the S_1 of the terminal emitter, the triplet diffusion from the TADF sensitizer predominantly occurs toward the phosphorescent sensitizer if its doping concentration is sufficiently higher than that of the terminal emitter. This reduces the overpopulation of triplets on the TADF sensitizer, thereby mitigating non-radiative processes such as TTA and TPA.

Furthermore, the phosphorescent sensitizer can effectively transfer excitons directly from its T_1 state to the S_1 of the terminal dopant via Förster resonance energy transfer (FRET), which helps to disperse triplet exciton density and prevents bimolecular quenching processes. As a result, the TPDS device exhibits reduced efficiency roll-off at high current densities and mitigates device degradation, leading to a significantly longer operational lifetime compared to the TSF device.

LiF(1.5 nm)/Al(200 nm)
mSi-Trz:Liq(20nm :50 wt%)
mSi-Trz (5 nm)
EML(30 nm)
oCBP(10 nm)
BCFN(45 nm)
HATCN(10nm)
ITO(50 nm)



(a)



(b)

Figure 2. (a) Device structure and chemical structure of common layers and (b) chemical structure of EML materials.

In this study, four OLED devices with varying EML structures were fabricated while maintaining identical common layers for performance comparison (Figure 2). The device structure employed dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN) as the hole injection layer, N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-N-(4-(9-phenyl-9H-carbazol-3-yl)phenyl)-9H-fluoren-2-amine (BCFN) as the hole transport layer. 2,2'-di(9H-carbazol-9-yl)-1,1'-biphenyl (oCBP) as the electron blocking layer, 2-phenyl-4,6-bis(3-(triphenylsilyl)phenyl)-1,3,5-triazine (mSiTrz) was used as the hole blocking layer, and mSiTrz doped with 50% 8-hydroxyquinolinolato-lithium (Liq) using as the electron transport layer, with LiF as the electron injection layer.

The EML compositions were as follows:

- **Device 1**: oCBP doped with 1% 2,12-di-tert-butyl-5,9-bis(4-(tert-butyl)phenyl)-5,9-dihydro-5,9-diaza-13b-boranaphtho[3,2,1-de]anthracene (t-DABNA.)
- **Device 2**: oCBP doped with 5% PtON-TBBi(BD-02) and 1% t-DABNA.
- **Device 3**: oCBP doped with 30% 2',3',5',6'-tetrakis(3,6-di-tert-butyl-9H-carbazol-9-yl)-[1,1':4',1"-terphenyl]-4,4"-dicarbonitrile(p4tCzphbn) and 1% t-DABNA.
- **Device 4**: oCBP doped with 30% p4tCzphbn, 5% BD-02, and 1% t-DABNA.

In the EML materials, oCBP functioned as the host facilitating hole transport, p4tCzphbn acted as the disk-shaped TADF sensitizer, BD-02 served as the phosphorescent sensitizer, and t-DABNA was the final emitter.

Table 1. Summarized performance of device 1, 2, 3, 4

		Device 1	**Device 2**	**Device 3**	**Device 4**
Driving Voltage[(a)] (V)		6.6	5.3	4.9	4.2
EQE (%)	Maximum	11.3	12.1	20.6	21.3
	300cd/m^2	3.2	7.5	13.5	15.2
EQE roll-off (%)		71.6	36.8	34.5	28.6
Power Efficiency (lm/W)		6.2	10.7	18.1	21.1
Color coordinate		(0.134, 0.077)	(0.131, 0.086)	(0.135, 0.092)	(0.135, 0.092)

a) Data were measured at 300 cd/m^2

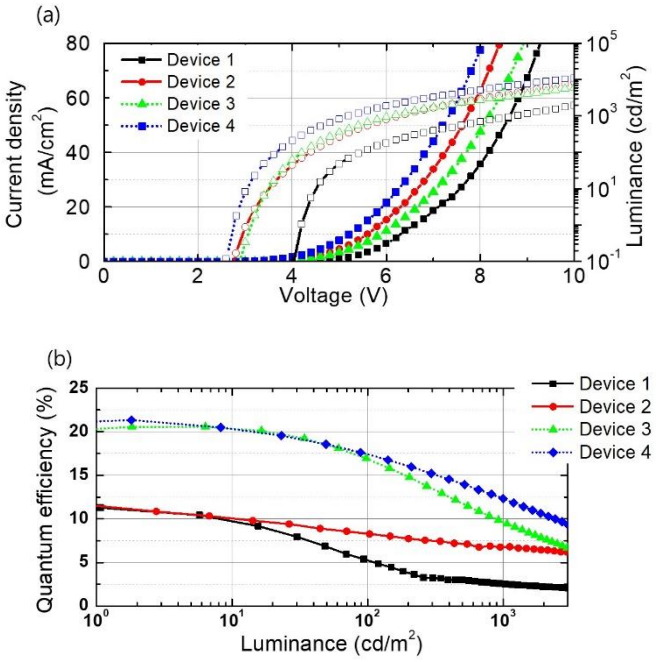


Figure 2. (a) J-V-L, (b) EQE-L of Device 1, 2, 3, 4.

Figure 3 presents the current density-voltage characteristics and external quantum efficiency-luminance curves of the four devices. For Device 1, which consists solely of the host (oCBP) and the final dopant (t-DABNA), the electron injection barrier is significantly high. As a result, the device exhibits a high turn-on voltage of 4.2 V and a driving voltage of 6.6 V at 300 cd/m².In contrast, Devices 2–4 demonstrate reduced turn-on and driving voltages compared to Device 1, with steeper slopes in the current density versus voltage curve. The steepest slope is observed in the TPDS Device 4, indicating that the addition of the TADF and phosphorescent sensitizers in the EML creates new channels for both negative and positive polarons.

At a luminance of 300 cd/m², the current densities are 5.2 mA/cm² for the phosphor sensitized fluorescence (PSF) Device 2, 2.7 mA/cm² for the TSF Device 3, and 2.4 mA/cm² for the TPDS Device 4. The higher current densities in the PSF and TSF devices compared to the TPDS device suggest a greater presence of non-radiative components, requiring a larger number of excitons to achieve the same luminance.

Regarding maximum EQE, Devices 1 and 2 achieve relatively low values of 11.3% and 12.1%, respectively. Devices 3 and 4 show higher maximum EQEs of 20.6% and 21.3%, respectively, with comparable peak efficiencies. However, Device 4 exhibits the smallest efficiency roll-off at high luminance levels (Table 2). This improvement in Device 4 is attributed to the addition of the phosphorescent sensitizer BD-02, which effectively regulates triplet diffusion, reducing the density of triplet excitons within the EML. This reduction mitigates intermolecular interactions such as TTA and TPA, which are known to decrease device efficiency.

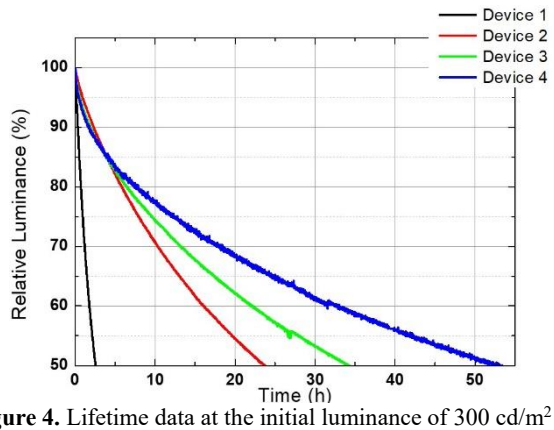


Figure 4. Lifetime data at the initial luminance of 300 cd/m^2

Figure 4 illustrates the operational lifetimes of the devices, measured as the luminance decreases from an initial brightness of 300 cd/m². Based on LT50 values, the lifetimes of Devices 1–4 are recorded as 2.6, 24.7, 34.2, and 52.5 hours, respectively.

Devices 3 and 4 display a trend where the luminance decay is steep initially but becomes more gradual over time. This behavior is attributed to the initial luminance drop. Following this initial decrease, the more gradual luminance decay observed in Devices 4 indicates effective suppression of degradation processes driven by intermolecular interactions.(5) Ultimately, through the regulation of triplet diffusion, the TPDS device (Device 4) demonstrates an extended operational lifetime, surpassing the PSF device (Device 2) and the TSF device (Device 3) by 112.6% and 53.5%, respectively.

3. Impact of Research

In this study, we explored the potential for deep-blue sensitization by developing various devices employing a novel structure that replaces conventional n-type hosts with disk-shaped TADF materials. Specifically, the combination of disk-shaped TADF and Pt-based phosphorescent sensitizers was introduced to regulate triplet diffusion and reduce triplet exciton density. This approach effectively suppressed exciton quenching, resulting in enhanced device lifetime and reduced efficiency roll-off. The findings from this research provide new guidelines for designing devices to sensitize high-energy regions.

4. References

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