Promising operational stability of high-efficiency organic light-emitting diodes based on thermally activated delayed fluorescence

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Organic light-emitting diodes (OLEDs) are attractive for next-generation displays and lighting applications because of their potential for high electroluminescence (EL) efficiency, flexibility and low-cost manufacture. Although phosphorescent emitters containing rare metals such as iridium or platinum produce devices with high EL efficiency, these metals are expensive and their blue emission remains unreliable for practical applications. Recently, a new route to high EL efficiency using materials that emit through thermally activated delayed fluorescence (TADF) was demonstrated. However, it is unclear whether devices that emit through TADF, which originates from the contributions of triplet excitons, are reliable. Here we demonstrate highly efficient, stable OLEDs that emit via TADF by controlling the position of the carrier recombination zone, resulting in projected lifetimes comparable to those of tris(2-phenylpyridinato)iridium(III)-based reference OLEDs. Our results indicate that TADF is intrinsically stable under electrical excitation and optimization of the surrounding materials will enhance device reliability.
In this work, to investigate the possibility of TADF-based OLEDs with high operational stability, we carefully designed a device architecture that included exciton-blocking layers (EBLs) at the interfaces of the emission layer (EML) and optimized the concentration of the emitter. Here we show that expanding the carrier recombination zone to enhance the electron carrier injection efficiency significantly affects the operational stability of the device. We realize lifetimes of more than 2,500 h at an initial luminance of 1,000 cd/m² in TADF-affects the operational stability of the device. We realize lifetimes of zone to enhance the electron carrier injection efficiency significantly.

**Results**

Design of OLED configuration. To maximize the TADF efficiency, we prepared a guest-host system that escapes concentration quenching, similar to conventional fluorescence and phosphorescence based OLEDs. Also, because TADF is based on an up-conversion process of triplet excitons into a singlet state, improper protection of the triplet excitons induces Dexter energy transfer into the surrounding molecules during the lifetime of the guest’s triplet state, which results in exciton quenching. It is therefore necessary to introduce host and carrier transport molecules with higher triplet energies than that of a guest TADF molecule.

The high photoluminescence (PL) quantum efficiency (ΦPL) of an EML is one of the main factors in obtaining a high ηint in OLEDs. The use of 3,3-di(9H-carbazol-9-yl)biphenyl (mCBP) as a host matrix with 6 wt.%-4CzIPN showed a slightly higher ΦPL = 85 ± 2% than the ΦPL = 80 ± 2% of 4,4′-bis(carbazol-9-yl)biphenyl (CBP), as shown in Fig. 1(b), indicating that mCBP with T₁ = 2.90 eV11 traps the triplet excitons of 4CzIPN (T₁ = 2.4 eV) well, and does so better than CBP with T₁ = 2.55 eV. Also, in a dilute concentration of 1 wt.%, the maximum ΦPL = 94 ± 2% was obtained, as shown in Fig. S1(a). We therefore adopted mCBP as the host matrix.

To confirm the confinement behavior of the triplet excitons of 4CzIPN at the interface between a 4CzIPN doped EML and either a hole transport layer (HTL) or an EBL, ΦPL values of co-deposited films of 4CzIPN in various host matrices were evaluated (Fig. 1(b)).

We found that the hole transport materials, such as N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)-benzidine (α-NPD, where T₁ = 2.3 eV, HOMO = 5.5 eV), tris(4-carbazoyl-9-ylphenyl)amine (TCTA, where T₁ = 2.76 eV12, HOMO = −5.9 eV), 1,1-bis(di-4-tolylamino)phenyl)cyclohexane (TAPC, where T₁ = 2.87 eV13, HOMO = −5.5 eV) and 9,9′,9-triphenyl-9H,9′H,9″H-3,3′-3″,3′-tercarbazole (Tris-PCz, where T₁ = 2.7 eV, HOMO = −5.6 eV) completely quench the excitons of 4CzIPN when they are used as hosts, giving very low ΦPL values of 2%, 5%, 7% and 5%, respectively. This is because of the low triplet energy of α-NPD, the strong electron donation ability of the triphenylamine units, and the rather shallow HOMO levels of these materials (Fig. S1(c)). Therefore, a lack of exciton confinement occurs at the interfaces between the HTLs and EMLs. However, we observed no clear reduction in ηEQE in the OLEDs, suggesting that the carrier recombination zone is away from the interface between the HTLs and EMLs.

We also determined ΦPL for co-deposited films of 6 wt.%-4CzIPN and various EBLs, including bis(2-methyl-8-quinolinolate)-4-(phenylphenolato)aluminum (BA1q2)14, 9-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-9H-carbazole (CzTRZ) and 2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine (T2T)15 (Fig. 1(b)). A low ΦPL of 22% was obtained in the BA1q2 host, while a high ΦPL of 80% was obtained in the CzTRZ and T2T host matrices. This clearly indicates that the BA1q2 host quenches a triplet exciton of 4CzIPN because of the low triplet energy level of BA1q2.

Based on this preliminary PL experiment, OLEDs were fabricated by the sequential deposition of a 10 nm-thick layer of dipyrazino [2,3-f:2,3-h]quinazoline-2,3,6,7,10,11-hexacarbonitrile (HAT-CN) as a hole injection layer (HIL), a 30 nm-thick layer of Tris-PCz as an HTL, a 30 nm-thick layer of mCBP with various concentrations of 4CzIPN, a 10 nm-thick layer of T2T as an EBL, a 40 nm-thick layer of 2,7-bis(2,20-bipyridine-5-yl)triphenylene (BPy-TP2)16 as an ETL, a 0.8 nm-thick lithium fluoride (LiF) electron injection layer (EIL), and a 100 nm-thick aluminum (Al) cathode. An energy level diagram of the devices used in this study is shown in the inset of Fig. 2(a). We also fabricated a fac-tris (2-phenylpyridinato)iridium(III) (Ir(ppy)3)-based OLED to act as a reference device.

**Electrical characteristics.** The current efficiency (cd/A) vs. current density (J) characteristics of the 3, 6, 10 and 15 wt.% 4CzIPN-doped devices are shown in Fig. 2(a). These devices exhibited high luminance efficiencies of 50 cd/A (ηEQE = 17 ± 0.5%), 49 cd/A (ηEQE = 15.6 ± 0.5%), 48 cd/A (ηEQE = 14.2 ± 0.5%) and 47 cd/A (ηEQE = 14.0 ± 0.5%) at J = 0.01, 0.04, 0.5 and 1.0 mA/cm², respectively. For the 3 and 6 wt.% 4CzIPN-doped devices, the highest ηEQE was observed at low current density (<0.1 mA/cm²). In contrast, the 10 and 15 wt.% 4CzIPN-doped devices showed a gradual increase in ηEQE with increasing J, indicating that the balance of the hole and electron carrier injection changes with the dopant concentration. At rather high current densities, a high ηEQE of 13.8 ± 0.5% (46 cd/A) was obtained at 1,000 cd/m² for the 10 wt.%-doped device, which is higher than those of the 3 and 6 wt.%-doped devices.

We derived the theoretical maximum ηEQE for the 10 wt.%-doped OLED using the following equation:

\[
\eta_{\text{int}} = \eta_{\text{T}} \Phi_F + \left( \eta_{\text{iS}}(1 - \Phi_F) + \eta_T \right) \times \Phi_{\text{RISC}},
\]
efficiency (cd/A) vs. luminance (cd/m²) characteristics for 3, 6, 10 and 15 wt.% 4CzIPN-doped OLEDs. Inset: Energy diagram of the fabricated devices. Figure 2(c) shows the normalized luminance of a 4CzIPN emitter-based OLED as a function of operating time at initial luminance L0 of 1,000 cd/m² and Table 1 summarizes the OLED properties. We observed a significant dependence of the operational lifetime, defined as operation at 90% of the initial luminance (L75), on the 4CzIPN doping concentration. At low doping concentrations, L75 was 200 and 40 h for the 3 and 6 wt.%-doped devices, respectively. In contrast, L75 values of 190 and 253 h were observed for the 10 and 15 wt.%-doped devices, respectively. These results show that the 4CzIPN concentration strongly affects the operational stability of these devices.

To predict L75 for the devices containing 10 and 15 wt.% 4CzIPN at L0 = 1,000 cd/m², we estimated an acceleration factor of 1.92 for each device from the lifetime measurements at L0 = 2,000, 5,000 and 10,000 cd/m² using the following well-known equation:

\[ LT \times L_0^n = \text{constant}, \]

where LT is the operational lifetime and n is an acceleration factor. Based on Eq. (2), L75 is predicted to be 1,900 h for the 10 wt.%-doped device and 2,800 h for the 15 wt.%-doped device, which is comparable to that predicted for a 6 wt.% Ir(ppy)3-doped device (4,500 h), as summarized in Table 1.

**Discussion**

There are several possible reasons for the enhancement of L75 with an increase in the doping concentration. We envisage that the position of the carrier recombination zone strongly affects the operational stability of these devices. In fact, although the EL from only S1 of 4CzIPN was observed at 1,000 cd/m² in all devices, another emission peak around the deep blue region was observed in the 3 and 6 wt.%-doped devices at 20,000 cd/m², suggesting that the carrier recombination zone position changes in these devices, as shown in Fig. 3(a). Also, after the device begins to degrade (L75 = 164 h), an additional emission signal was observed from the 3 wt.%-doped device (Fig. 3(b)). This signal was similar to that observed from the pristine device at 20,000 cd/m², indicating that the carrier recombination zone moves during constant operation. However, no additional emission signal was observed from the 15 wt.%-doped devices (Fig. 3(c)), even after the device began to degrade (L75 = 820 h). These results indicate the absence of the carrier recombination zone at the EML/EBL interface in the 15 wt.%-doped devices.

To determine the effect of the doping concentration on the carrier transport properties, electron-only devices (EODs) and hole-only devices (HODs) were fabricated, as shown in the insets of Fig. 4(a) and (b), respectively. Although the 3 wt.%-doped EOD showed a
very low J of 10^-3 mA/cm² at 10 V, the driving voltage decreased significantly as the 4CzIPN doping concentration was increased, resulting in J values of 0.1 and 0.4 mA/cm² at 10 V for the 10 and 15 wt.%-doped EODs, respectively (Fig. 4(a)). In contrast, the HODs showed almost no dependence on the driving voltage as the 4CzIPN doping concentration increased, as shown in Fig. 4(b). This clearly indicates that only the electron injection/transport efficiency is enhanced by an increase in the doping concentration. Therefore, an increase in the doping concentration enhances the efficiency of electron injection from T2T into the EML and subsequent transport in the EML. These results also suggest that the carrier recombination zone shifts from the EML/ETL interface into the bulk of the EML when the doping concentration is as high as 10 wt.%. The LUMO level of 4CzIPN (−3.4 eV) is located considerably lower than that of mCBP (−2.4 eV), while their HOMO levels are similar (−5.8 and −6.0 eV for 4CzIPN and mCBP, respectively). Therefore, the 4CzIPN molecules in an mCBP host act as strong electron trapping sites, so the recombination process mainly involves direct carrier injection, transport and recombination at the 4CzIPN molecules. A higher dopant concentration expands the exciton formation sites into the bulk of the EML, which produces highly reliable OLEDs18,19. In addition, reduction of the hole accumulation at the interface between the EML and the EBL is another possible reason for the enhancement of the device operational stability20. Also, because the undesired degradation products of carbazole derivatives have been identified after device degradation21, the reduction in the excited state formation on the mCBP host molecules by enhancement of the direct electron injection and transport from a T2T layer to 4CzIPN, e.g., by direct exciton formation at 4CzIPN, is another possible reason for the enhanced device stability.

Table 1 | Comparison of characteristics of OLEDs based on different dopant concentrations. The maximum values were obtained at J = 0.01, 0.04, 0.5, 1.0 and 0.02 mA/cm² in 3, 6, 10 and 15 wt.% 4CzIPN-doped devices and a 6 wt.% Ir(ppy)₃-doped device, respectively

| EML       | Current efficiency [cd/A] (@1,000 cd/m²) | Power efficiency [lm/W] (@1,000 cd/m²) | EQE [%] (@1,000 cd/m²) | LT90 (hour) | LT50 (hour) |
|-----------|-----------------------------------------|----------------------------------------|------------------------|-------------|-------------|
| 3 wt.%-4CzIPN | 50.0 (41.4)                             | 35.7 (20.9)                            | 17.0 (13.4)            | 40          | 506         |
| 6 wt.%-4CzIPN | 49.2 (41.1)                             | 33.5 (19.6)                            | 15.6 (13.1)            | 65          | 685         |
| 10 wt.%-4CzIPN | 47.9 (46.6)                             | 32.7 (28.1)                            | 14.2 (13.8)            | 190         | ca. 1,900   |
| 15 wt.%-4CzIPN | 47.0 (46.5)                             | 30.7 (28.1)                            | 14.0 (13.9)            | 243         | ca. 2,800   |
| 6 wt.%-Ir(ppy)₃ | 42.9 (39.1)                             | 32.1 (19.2)                            | 11.8 (11.1)            | 130         | ca. 4,500   |

Figure 3 | EL spectra of OLEDs containing TADF emitters. (a) EL spectra of 3, 6, and 10 wt.% 4CzIPN-doped OLEDs at luminance of 20,000 cd/m². (b) EL spectra of 3 wt.% 4CzIPN-doped OLEDs before and after device degradation. (c) EL spectra of 15 wt.% 4CzIPN-doped OLEDs before and after device degradation.

Figure 4 | J-V characteristics of single carrier transport devices. (a) J vs. V characteristics for 3, 6, 10 and 15 wt.% 4CzIPN-doped EODs. Inset: Energy diagram of the EODs. (b) J vs. V characteristics for 3, 6, 10 and 15 wt.% 4CzIPN-doped HODs. Inset: Energy diagram of the HODs.
Finally, we consider the possibility of further enhancement of the device reliability. In this study, we adopted conventional host and carrier transport materials and obtained comparable degradation lifetimes for 4CzIPN and Ir(ppy)$_3$. This is an encouraging sign that the emitter itself is quite stable for redox and oxidation processes under electrical excitation. Thus, because Ir(ppy)$_3$ derivative-based OLEDs with optimum materials and device architectures have realized very long lifetimes of over 100,000 hrs.$^{22,23}$, we can expect further improvements in the device reliability when TADF is combined with the best possible combination of surrounding materials and device architectures.

In summary, we clarified that the operational lifetime of 4CzIPN-based OLEDs depends strongly on the emitter concentration in the EML and demonstrated highly efficient TADF-based OLEDs ($\eta_{\text{EQE}}$ of 13.9 \% at 1,000 cd/m$^2$) with excellent operational stability, showing L75 of 2,800 h at 1,000 cd/m$^2$ and of over 10,000 h at 500 cd/m$^2$. We also found that the 4CzIPN molecules act as strong electron trapping sites in the mCBP EML, and that the position of the recombination zone strongly affects the operational lifetime of these devices. Our results confirm that TADF-based OLEDs show great potential for realization of both high efficiency and operational stability.

**Methods**

Sample preparation and characterization for photoluminescence. Samples for the optical measurements were fabricated by co-depositing host materials and 6 wt.$\%$ carrier transport materials and obtained comparable degradation device reliability. In this study, we adopted conventional host and showing LT50 of 2,800 h at 1,000 cd/m$^2$ and of over 10,000 h at 500 cd/m$^2$. We also found that the 4CzIPN molecules act as strong electron trapping sites in the mCBP EML, and that the position of the recombination zone strongly affects the operational lifetime of these devices. Our results confirm that TADF-based OLEDs show great potential for realization of both high efficiency and operational stability.

Sample preparation and characterization for electroluminescence. Green TADF-based OLEDs with an effective area of 1 mm$^2$ were fabricated on 110 nm-thick indium tin oxide (ITO)-coated glass substrates with a 2 mm stripe pattern. Deposition was performed under vacuum at pressures from 5 \times 10^{-5} to 5 \times 10^{-6}$ Pa. After deposition, the devices were immediately encapsulated with glass lids using epoxy glue in nitrogen-filled glove boxes (O$_2$ \% at 1,000 cd/m$^2$) with excellent operational stability, showing L75 of 2,800 h at 1,000 cd/m$^2$ and of over 10,000 h at 500 cd/m$^2$. We also found that the 4CzIPN molecules act as strong electron trapping sites in the mCBP EML, and that the position of the recombination zone strongly affects the operational lifetime of these devices. Our results confirm that TADF-based OLEDs show great potential for realization of both high efficiency and operational stability.

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**Author contributions**

The experiments were conceived and designed by H.N. and K.M., and were carried out by H.N., K.M. and J.N. H.N. and C.A. wrote the manuscript. The project was supervised by T.S.

**Additional information**

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CORRIGENDUM: Promising operational stability of high-efficiency organic light-emitting diodes based on thermally activated delayed fluorescence

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This Article contains an error the chemical structure shown for 4CzIPN in Figure 1a. The correct Figure 1a appears below as Figure 1.

![Chemical structures](image-url)