Mechanisms of Initial Luminance Loss in Fluorescent Organic Light-Emitting Diodes Unveiled by Time-Resolved Spectroscopies

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ABSTRACT

Time-resolved electroluminescence (EL) of Alq₃-based OLEDs revealed that delayed EL emission via triplet-triplet annihilation (TTA). We found that the initial luminescence loss of the OLED is caused by quenching of not only singlet but also triplet excitons. Triplet quenching by trapped positive charges decrease in singlet excitons created via TTA.

1 INTRODUCTION

The intrinsic degradation mechanisms of organic light emitting diodes (OLEDs) based on tris(8hydroxyquinolinolato) aluminum(III) (Alq₃) has been studied extensively since the electroluminescence (EL) of double-organic layer device was first reported by Tang and VanSlyke.¹ However, the understanding of degradation mechanisms remain limited. For the OLEDs using N, N'di-[(1-naphthaleyI)-N,N'-diphenyI]-1,1' biphenyl-4,4'diamine (α -NPD) layer as a HTL, and Alq₃ as an emitter layer (EML), proposed degradation mechanisms are mainly attributed to quenching or reduced yield of emitter singlet For example, time-resolved excitons. photoluminescence (TRPL) of degraded devices has demonstrated that singlet quenchers formed during device operation could decrease photoluminescence (PL) quantum yield of the Alq₃.² In addition, it has been reported that the decrease in device efficiency could be associated with trapped positive charges at the α -NPD/Alg₃ interface, which could act as non-radiative recombination centers.³ The trapped positive charges could be related to the decomposed α -NPD molecules⁴ or decomposed Alg₃ molecules.⁵ Since the emission of Alg₃-based OLEDs uses both singlet exciton formed by charge recombination and triplet-triplet annihilation (TTA) processes,6,7 the device degradation mechanisms can be ascribed to the decrease in the yield of singlet excitons.

In this study, we have investigated the intrinsic degradation mechanisms of Alq₃-based OLEDs especially at an early stage of device degradation, where less than 10% of the initial luminance is lost. The device degradation related to PL quantum yield of emitter was investigated by the TRPL. The device degradation associated with singlet

exciton formed through the TTA process was investigated by time-resolved electroluminescence (TREL).

2 **EXPERIMENT**

Two OLEDs were fabricated in a vacuum chamber with the base pressure in the order of 10⁻⁹ Torr. Figure 1 shows device structure of OLEDs investigated in this study. Device (A) is composed of multi-layers, such as 150 nm-thick ITO as an anode, a 0.75 nm-thick molybdenum trioxide (MoO₃) layer, a 90 nm-thick α-NPD layer as the HTL, a 70 nm-thick Alq₃ layer as an electron transport layer (ETL) and EML, a 1 nm-thick lithium fluoride (LiF) layer as an electron injection layer (EIL), and a 100 nm-thick aluminum (AI) layer as a cathode. We also fabricated device (B), which was composed of the same HIL, EIL and cathode as in device (A) but different organic layers. In device (B), thin layers of α -NPD (10 nm) and Alq₃ (10 nm) were interposed between two relative thick layers of an 80 nm-thick N,N-bis-(3methylphenyl)-N.N'-bis-(phenyl)-benzidine (TPD) as the HTL and a 60 nm-thick 2,4-di([1,1'-biphenyl]-4-yl)-6-(4pyridin-4-yl)phenyl)-1,3,5-triazine (M4PT) as the ETL.



Fig. 1 Schematic representation of the layers in devices (A) and (B).

To evaluate the operational stability of OLEDs, the EL intensity/initial electroluminescent (EL) intensity-time and the voltage-time characteristics were measured at a constant current density of 50 mA/cm². TRPL was measured with the excitation wavelength of 443 nm to investigate the quenching singlet exciton in the emitter. The capacitance-voltage (C-V) measurement was

carried out with a Precision LCR meter (4284A, Agilent) using the sine wave with an amplitude of 0.05 V and a frequency of 109 Hz. TREL of OLEDs was performed to investigate the dynamics of singlet exciton formed through the TTA process. A rectangular voltage pulse with a width of 120 μ s was applied to the devices. The forward voltage was set to generate 50 mA/cm² and then the voltage was applied to the devices.

3 RESULTS AND DISCUSSION

The relative EL intensity and operation voltage as a function of the operation time of device (A) is shown in Fig. 2a. After the device operation at a constant current density of 50 mA/cm² for 56 h, the EL intensity reaches 90% of the initial luminance of 1,616 cd/m², and the operation voltage increases to approximately 0.7 V. The current density–voltage characteristics of the degraded device showed an increase in the operation voltage (Fig. 2b). The pristine and degraded OLEDs demonstrate identical EL spectra with the emission peak at 523 nm (Fig. 2c). The external quantum efficiency (η_{ext}) of the degraded device at 50 mA/cm² decreases to 1.04%, which is 90% of the pristine ones (1.15%), thus suggesting the observed small (10%) degradation is irreversible.



Fig. 2 (a) lifetime, (b) *J–V*, (c) EL spectra, and (d) η_{ext} of pristine and degraded OLEDs

The decrease in EL intensity was investigated in terms of the parameters of the η_{ext} . The η_{ext} of OLEDs can be expressed by the following equation

$$\eta_{ext} = \gamma \,\eta \,\phi_{PL} \,\eta_{out} \,\,, \tag{1}$$

where γ is the charge balance factor, η is the yield of the emissive excited states, ϕ_{PL} is the PL quantum yield, and η_{out} is the optical out-coupling efficiency. Considering the fraction of singlet formed by the charge recombination (η_S) and the TTA process (η_{TTA}) of triplets, the eq. (1) can be rewritten as the following⁸

$$\eta_{ext} = \gamma(\eta_S + \eta_{TTA})\phi_{PL}\eta_{out}.$$
 (2)

Assuming γ and η_{out} are constant as devices age, the decrease in the η_{ext} can be attributed to from the decrease in ϕ_{PL} and/or ($\eta_{S} + \eta_{TTA}$).

The decrease in the ϕ_{PL} was investigated with TRPL measurements. PL lifetime (τ) of emitter singlet exciton of degraded device (A) demonstrated negligible change compared to that of the pristine one. Since the degradation takes place in a narrow region in the EML adjacent to the HTL, it is necessary to employ a device that contains thin Alq₃ layer (~10 nm thick) to properly examine the decrease in the ϕ_{PL} of the degraded devices. Figure 3 shows the TRPL of pristine and degraded device (B). The τ of the singlet exciton of Alq₃ was 14.3 ns, which is similar to the reported values.9,10 After the degradation, the τ decreases to 13.5 ns, which suggests that the ϕ_{PL} decreases by guenching the singlet exciton. This result indicates that singlet quenchers form during device operation, which may be attributed to decomposed α -NPD⁴ and/or decomposed Alq₃ molecules.5 These decomposed compounds might generate at the α -NPD/Alg₃ interface and could act as trapping sites for positive charges.3



Fig. 3 TRPL of pristine and degraded device (B). The TRPL was measured with an excitation wavelength of 443 nm at 25 °C.

The formation of a trapped positive charge was investigated by C-V measurements. It has been reported that the Alq3-based OLEDs demonstrates the presence of a negative interfacial charge at the α -NPD/Alq₃ interface.¹¹⁻¹³ To measure the negative interfacial charge in our devices, we performed the C-Vmeasurements for pristine and degraded device (A) (Fig. 4). At a reverse bias below -2 V, an observed constant capacitance corresponds to the series capacitance of a-NPD and Alq₃ layers. When the bias becomes larger than the transition voltage (V_t), holes are injected to the device, and capacitance is raised. After the device degradation, the Vt shifts from -1.65 V (pristine) to -1.05 V (degraded). The change of the Vt indicates the formation of the trapped positive charges, which would compensate the net negative interfacial charge.

The negative interfacial charge density (σ_0) can be calculated from the following equation

$$\sigma_0 = \frac{Q_0}{A} = \frac{\varepsilon_0 \varepsilon_r}{d_{Alq_3}} (V_t - V_{bi}), \tag{3}$$

where Q_0 is the negative interfacial charge, A (4 mm²) is the device area, ε_0 is the permittivity of free space, ε_r (3.5) is the relative dielectric constant of Alq₃,¹⁴ d_{Alq3} (70 nm) is the thickness of the Alq₃ layer, and V_{bi} (2.27 V) is the builtin potential. Accordingly, the negative interfacial charge density of the pristine device is -1.72±0.01 mC/m², which is consistent with the reported value.¹⁴ In the degraded device, the negative interfacial charge density decreases to -1.46±0.01 mC/m². The formation of trapped positive charge at the α -NPD/Alq₃ interface is responsible for the decrease in the net negative interfacial charge density. As we discussed previously, the decomposed molecules would act as the quencher of singlet exciton and lead to a decrease in the PL lifetime of the degraded device.



Fig. 4 C–V of pristine and degraded device (A) measured at 109 Hz.

We measured the TREL of device (A) to examine the effect of the trapped positive charge on the device degradation in terms of the η_{TTA} . As shown in Fig. 5, the EL signal decays within 16 µs, which is shorter than the lifetime of Alq₃ triplet excitons (25-170 µs).7,15-17 The EL spectra measured under the current pulse and that of the delayed EL were identical. These results suggest that the delayed EL is generated via the TTA process of triplets Since a reduction of the delayed EL intensity was observed in the degraded device, the degradation is likely caused by the decrease in the η_{TTA} . For example, the degraded device demonstrates a 28% reduction of the integrated delayed EL intensity in the time range of 1-16 μs compared to that of the pristine device. The decrease in the delayed EL intensity could be due to the nonradiative recombination of the trapped positive charge³ and/or quenching of the triplet by trapped positive charges.



Fig. 5 TREL of pristine and degraded device (A). After a forward bias was switched off, 0 V reverse bias was applied.

First, we investigated the possibility of nonradiative recombination on the trapped positive charge being the reason for the decrease in the delayed EL intensity. Suppose that the nonradiative recombination on the trapped positive charge accounts for the additional 4% decrease in the η_{ext} operated at 50 mA/cm², the number of excitons generated at this current density would decrease by 4%. In other words, the effective current density to generate the singlet and triplet excitons should be smaller than 50 mA/cm². We measured the current density dependence on the delayed EL intensity to see the effect of the reduction of current density on the delayed EL intensity, as shown in Fig. 6. Even though the current density was reduced from 50 to 20 mA/cm², the TREL of pristine device (A) shows no change in the delayed EL intensity. By further reducing the current density to 1 mA/cm², the delayed EL intensity decreases by the reduction of the triplet exciton density. Hence, we exclude the nonradiative recombination on the trapped positive charge as the reason for the decrease in the delayed EL intensity. This implies that the decrease in the delayed EL intensity may be caused by the quenching of the triplet exciton by the trapped positive charge.



Fig. 6 TREL of pristine device (A). The device was operated at current density of 1, 20, 50 mA/cm².

To examine the triplet quenching by positive charges, we measured the TREL of the pristine devices by applying different reverse voltages after the forward bias voltage. Figure 7a shows the TREL of pristine device (A) measured at the different reverse bias voltages of either 0 or -8 V. The decrease in the delayed EL intensity in the time range of 1–5 μ s would be due to the removal of residual charges, which may recombine after turning off the forward voltage. The delayed EL intensity after 6 µs slightly increases by applying a reverse voltage of -8 V. This result suggests that triplet quenching may be suppressed by sweeping out the charges under the reverse bias. Time of flight (TOF) measurements demonstrated that the hole mobility of α -NPD was 10⁻⁴ cm²/Vs, which is approximately two orders of magnitude higher than the electron mobility of Alq₃.¹⁸ This indicates that excessive positive charge exists at the α -NPD/Alq₃ interface during EL operation, which may lead to interaction with triplet excitons. To further confirm the triplet quenching by positive charge, we measured the TREL of device (B), which contains a 10 nm-thick Alg₃ layer. Since MPT has a wider optical band gap than Alq₃, the excitons generated by charge recombination would be confined within the Alq₃ layer in device (B). This situation may cause enhanced interaction between the excitons and the positive charge accumulated at the α -NPD/Alq₃ interface. The TREL of device (B) demonstrates that the delayed EL intensity is drastically reduced when no reverse bias was applied (Fig. 7b). Thus, the triplet quenching by the positive charge is enhanced in device (B). The delayed EL intensity was completely recovered by applying the reverse bias. This result clearly shows that the quenching of triplet exciton by positive charge takes place.



Fig. 7 (a) TREL of pristine device (A), and (b) pristine device (B). After a forward bias was switched off, different reverse bias voltage (either 0 or -8 V) was applied to the devices.

4 CONCLUSIONS

We have investigated the degradation mechanisms of fluorescent OLEDs at an early stage of device degradation via TRPL and TREL. The TRPL demonstrated decrease in PL lifetime of singlet exciton of the emitter, suggesting that device degradation is associated with the decrease in PL quantum yield. The TREL of devices shows delayed EL in the microsecond time range originated from TTA. The TREL of the degraded device demonstrates decrease in the delayed EL intensity, suggesting that the device degradation is also related to the reduced yield of singlet exciton formed through the TTA process. The decrease in yield of singlet exciton is attributed to the quenching of triplet excitons by trapped positive charges.

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