

# Electron-Induced Quenching of Excitons in Luminescent Materials

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We studied photoluminescence (PL) behavior of tris(8-hydroxyquinoline) aluminum based organic light-emitting devices doped with various fluorescent dyes, under electron currents. The results show that electron currents reduce the PL quantum yield by as much as 50%, depending on the electron density and the doping conditions in the emitter layer. The decrease in luminescence under electron current indicates electron–exciton interaction, which likely plays a role in limiting the efficiency of organic electroluminescent devices.

## Introduction

Hole–exciton interaction effects in luminescent materials have been widely investigated and are known to play an important role in electroluminescence (EL) device performance,<sup>1–5</sup> often leading to a reduction of EL efficiency by over 50% in fluorescent dye doped devices.<sup>1</sup> A parallel process, electron–exciton interaction, however, has received little attention, and the results appear to be inconclusive. For instance, some studies suggested the presence of significant exciton–electron interaction in tris(8-hydroxyquinoline) aluminum (AlQ<sub>3</sub>),<sup>3</sup> while other studies concluded that such interactions were insignificant.<sup>1,6,7</sup> A comprehensive investigation on the behavior of luminescence under electron current is thus warranted to understand the interaction between electrons and excitons. We report here our studies on the photoluminescence (PL) behavior of devices under electron currents. The results show that the PL quantum yield decreases as the electron density increases in the doped emitting layer (EML), pointing to exciton quenching by electrons. The studies also show that electric-field-induced dissociation of excitons<sup>8</sup> does not play a significant role in the quantum yield decrease in the doped EMLs, suggesting that carrier-induced quenching of the excited states is the dominant luminescence loss mechanism.

## Experimental Section

In this study, devices of various structures (structures A–D, as shown in Figure 1a) are used for studying the PL behavior. In these devices, indium–tin–oxide (ITO) and Mg:Ag are used as anode and cathode materials, respectively. *N,N'*-Di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine (NPB) and 4,4'-bis-[2-(4,6-diphenyl-1,3,5-triazinyl)]-1,1,1-biphenyl (BTB)<sup>9</sup> are used to form the hole transport layer (HTL) and electron transport layer (ETL), respectively. Tris-(8-hydroxyquinoline) aluminum (AlQ<sub>3</sub>) is utilized to form the EML, which is optionally doped with various fluorescent dyes. In device structure A, the EML is sandwiched between two HTL layers<sup>10</sup> and includes an electron blocking layer (EBL) composed of tetrafluorotetracyanoquinodimethane (F<sub>4</sub>-TCNQ) doped NPB at the cathode contact. As a p-type dopant, <sup>11</sup> F<sub>4</sub>-TCNQ effectively blocks electron injection, resulting in a hole-only device that allows studying PL of the EML under hole currents (although no EL is detected from device structure A, weak EL is observed from a similar device without the EBL, indicating that limited yet not negligible electron injection can take place at the cathode contact in the absence of the EBL). In device structure B, the EML is sandwiched between two ETL layers and includes a thin Mg anode modification layer (AML)<sup>12</sup> resulting in an electron-only device that allows studying PL of the EML under electron currents (although no EL is detected from device structure B, weak EL is observed from a similar device without the AML, indicating that limited yet not negligible hole injection can take place at the anode contact in the absence of the AML). Device structure C is similar to B (and therefore is also essentially an electron-only device) but further includes a thin layer (5 nm) of NPB between the EML and the lower ETL that partially blocks the transport of electrons, thus leading to a buildup of electron density in the EML layer. Device structure D is a standard three-layer HTL/EML/ETL organic light-emitting device configuration. Energy band diagrams showing the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the EML and the neighboring layers in each of the four device structures are depicted in Figure

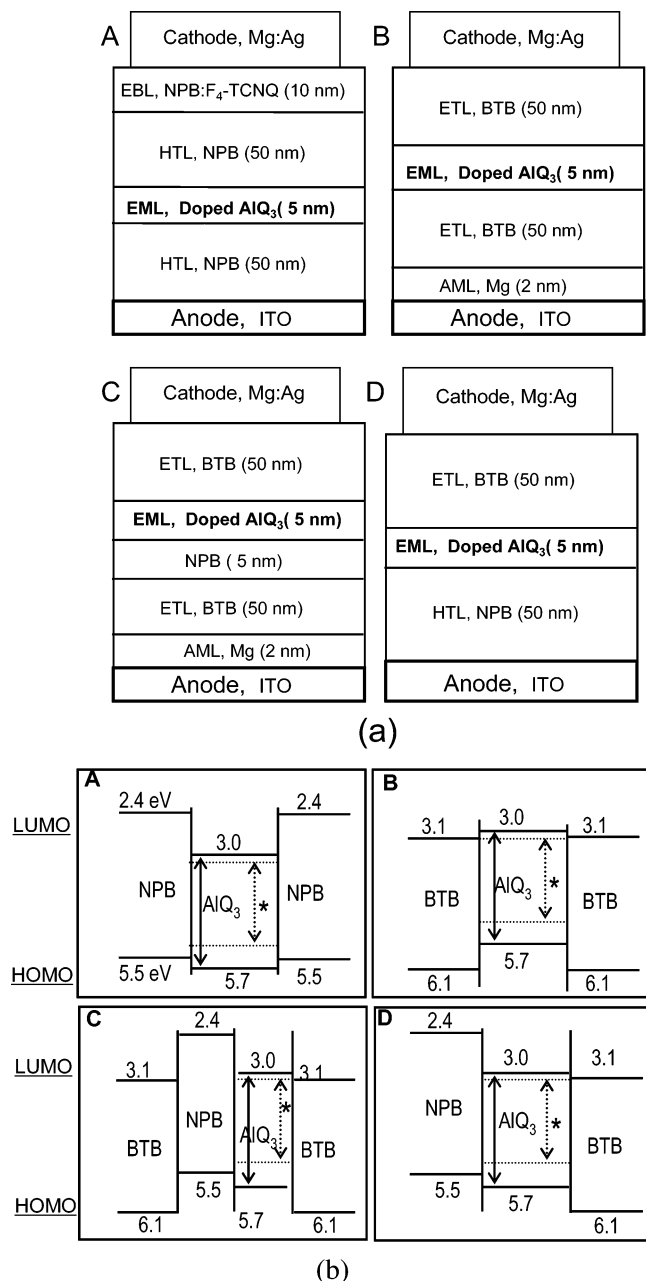
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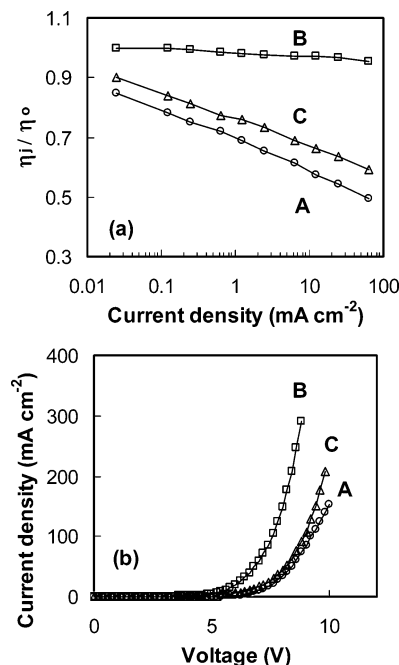


**Figure 1.** (a) Schematic diagrams depicting device structures A–D described in the text. (b) Energy band diagrams showing the HOMO and LUMO levels of the EML and the neighboring layers in each of the four device structures. Note: asterisk (\*) represents the LUMO and HOMO levels of the DCJTJB dopant, which are 3.1 and 5.3 eV, respectively.

1b. Details of device fabrication and PL measurements are as reported elsewhere.<sup>10</sup>

## Results and Discussion

Figure 2a shows normalized PL quantum yield ( $\eta_i/\eta_0$ ), as a function of current density ( $J$ ), for devices of structure A, B, and C, in which the EML is doped with  $\sim 2\%$  (by volume) of 4-[dicyanomethylene]-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTJB) red dye. Results from the device of structure A (hole-only device) show that an increase in  $J$  leads to a rapid decrease in PL. These results are in agreement with those of Young et al. and are attributed to hole-induced quenching of the excited states.<sup>1</sup> Gesquiere et al. showed that the holes can lead to quenching of both singlet and triplet excited states.<sup>2</sup> In the case of device

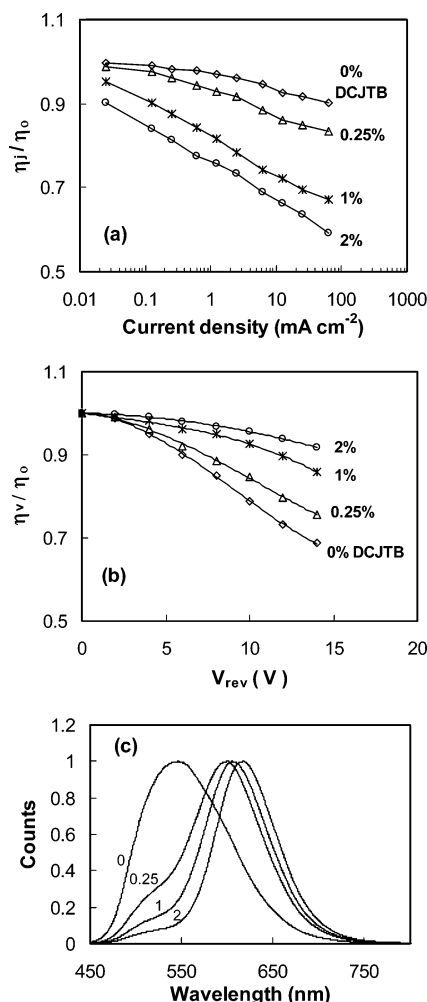


**Figure 2.** (a) Normalized PL quantum yield ( $\eta_i/\eta_0$ ) versus current density ( $\eta_0$  is the PL quantum yield at zero current) for devices of structure A–C, in which the EML is doped with 2% DCJTJB. (b)  $J$ – $V$  characteristics of the same devices.

structure B (electron-only device), on the other hand, an increase in  $J$  leads to a significantly smaller decrease in PL quantum efficiency, also in agreement with previous reports.<sup>1,6,7</sup> Although, on a first look, these results may suggest that electrons are much less efficient in quenching the excited states, inferring that electron–exciton interaction must be insignificant,<sup>1</sup> one must realize that the charge carrier densities in device structures A and B are different, and as such could be a reason behind the difference in PL responses. The difference in carrier density in the two device structures stems from the fact that the EML material used in both devices, AIQ<sub>3</sub>, is essentially an electron transport material with a rather low hole mobility<sup>13</sup> (electron mobility in AIQ<sub>3</sub> is about  $2 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (ref 14) which is 2 orders of magnitude higher than the hole mobility in AIQ<sub>3</sub>)<sup>13</sup> and, therefore, must have a different effect on the transport of charge carriers (holes in device structure A and electrons in device structure B) in each case. In device structure A, the EML acts as a hole blocking layer that partially blocks the transport of holes from the bottom HTL to the top HTL, under the external electric field, resulting in a buildup of positive (i.e., hole) space charges near the bottom HTL/EML interface. In device structure B, on the other hand, the easier transport of charge carriers (in this case electrons) across the EML will not induce a similar buildup of space charges, and hence charge carrier density in the layer remains lower. In fact, a comparison of current density versus voltage ( $J$ – $V$ ) characteristics of devices of structures A and B (Figure 2b) supports this notion, where the lower driving voltage at any given current in the case of device structure B points to the easier (or less “obstructed”) charge carrier transport across

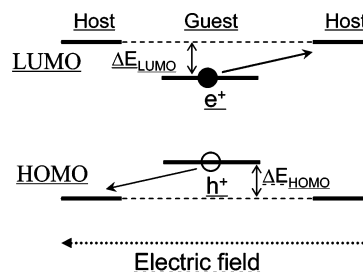
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**Figure 3.** (a) Normalized PL quantum yield ( $\eta_i/\eta_0$ ) versus current density of devices of structure C, in which the EML is doped with 0, 0.25, 1, or 2% DCJTB. (b) Normalized PL quantum yield ( $\eta_v/\eta_0$ ) versus reverse bias ( $V_{rev}$ ) in devices of structure D, in which the EML is doped with 0, 0.25, 1, or 2% DCJTB. (c) Normalized EL from devices with structure D, under forward bias, in which the EML is doped with 0, 0.25, 1, or 2% DCJTB.

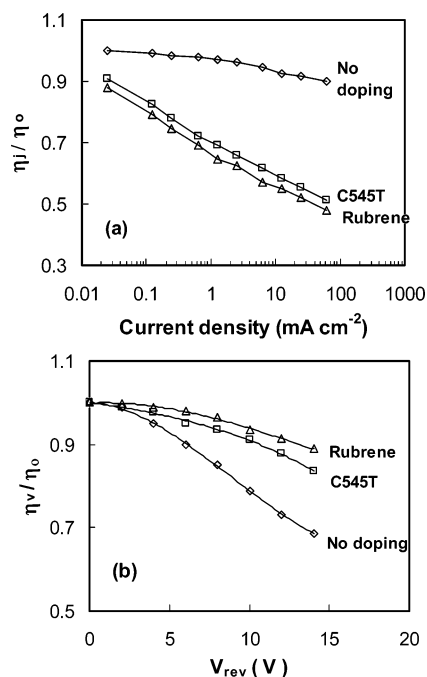
the device. Therefore, the smaller decrease in PL quantum efficiency upon increasing  $J$  in device structure B could simply be due to the significantly lower charge-carrier density in the EML and not necessarily an indication that electrons are not effective in quenching excitons. In order to study the effect of electron currents on PL in more comparable space charge environments to those existing in device structure A, we investigated a device of structure C which includes a thin NPB EBL. The presence of the thin EBL partially blocks electron transport from the top ETL to the bottom ETL, under the external electric field, and therefore leads to the buildup of a space charge (in this case negative) in the EML. As expected, the introduction of the NPB layer in a device of structure C shifts the  $J$ - $V$  characteristics to higher voltages with respect to device of structure B (Figure 2b), pointing to the effect of the thin NPB layer in partially blocking the electron transport and the subsequent buildup of electron space charge in the EML. PL measurements on device C show that an increase in  $J$  leads to a rapid decrease in PL quantum efficiency, not unlike in the case of device A, as shown in Figure 2a. The results, therefore, suggest that electrons may also be effective in quenching excited states, contrary to previous reports.<sup>1,6,7</sup>



**Figure 4.** Schematic diagram illustrating the dissociation process of excitons in the doped system. An exciton on a guest molecule is less susceptible to dissociation by an electric field because of the energy barriers  $\Delta E_{LUMO}$  and  $\Delta E_{HOMO}$  that the electron and hole will have to overcome in the dissociation process.

However, it is not possible to conclude, based on the above results alone, that electron-induced PL quenching is indeed happening in device C. The reason is that there are two other possible mechanisms that, in principle, can also lead to exciton quenching, namely: (i) exciton-exciton annihilation<sup>15,16</sup> and (ii) electric-field-induced dissociation of excitons into electron-hole pairs.<sup>17,18</sup> Exciton-exciton annihilation strongly correlates with exciton density and, in general, becomes more significant only at high exciton densities.<sup>15</sup> Given the typically low exciton density produced during our PL measurements and the fact that it cannot increase with current density (because of negligible hole injection from the anode, as evident from the absence of any detectable EL), exciton-exciton annihilation cannot be significant in device C and can therefore be ruled out. Electric-field-induced exciton dissociation, on the other hand, cannot be ruled out, especially because the local electric field in the EML of device structure C must be higher than in device structure B. To investigate whether electric-field-induced dissociation of excited states is playing a role in the decrease in PL upon increasing current in electron-only devices, we tested a series of devices of structure C and D, in which the EML was doped with various concentrations of DCJTB (red dye). Figure 3a shows normalized PL versus  $J$  from a series of devices of structure C with 0%, 0.25%, 1%, and 2% of DCJTB in the EML, whereas Figure 3b shows PL versus reverse voltage ( $V_{rev}$ ) from a series of devices of structure D with the same DCJTB concentrations in the EML. The reason for carrying out the measurements under reverse bias in the latter case was twofold: (i) to avoid the generation of EL during the PL measurements and (ii) to prevent the injection of charge carriers into EML from electrodes and, thus, preclude carrier-induced PL quenching effects. The results show that although doping with DCJTB leads to less PL quenching upon increasing the reverse voltage (Figure 3b), in agreement with our recent findings,<sup>8</sup> it, conversely, leads to more PL quenching upon increasing the current (Figure 3a). Since PL quenching at higher reverse voltages is exclusively due to the electric-field-induced dissociation of

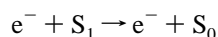
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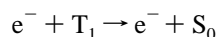
**Figure 5.** (a) Normalized PL quantum yield ( $\eta_i/\eta_0$ ) versus current density of devices of structure C, in which the EML is undoped, doped with 2% of C545T, or doped with 2% of rubrene. (b) Normalized PL quantum efficiency ( $\eta_v/\eta_0$ ) versus  $V_{\text{rev}}$  of device D, in which the EML is undoped, doped with 2% of C545T, or doped with 2% of rubrene.

excitons, it follows, from the opposite trends, that PL quenching in device structure C cannot be due to the same mechanism. Therefore, electric-field-induced dissociation of excitons cannot be a dominant factor behind the decrease in PL yield upon increasing the current in structure C devices. It follows, therefore, that electron-induced quenching of excited states is indeed the main factor behind the decrease in PL at high currents in electron-only devices.

In fact, the PL quenching by high electron currents (Figure 3a) can be well explained in terms of electron–exciton interaction phenomena, analogous to what was initially proposed for hole–exciton interaction in hole-only devices before:<sup>2</sup>



and



where  $e^-$ ,  $S_1$ ,  $S_0$ , and  $T_1$  represent an electron, a singlet exciton, the ground state, and a triplet exciton, respectively. The increased PL quenching (Figure 3a) in the doped devices versus in the undoped device upon increasing the current can be attributed to the higher density of trapped electrons on guest molecules and hence a higher electron–exciton interaction probability.<sup>19,20</sup> The inclusion of the NPB EBL and the subsequent increase in electron density in the EML increases the density of these populated guest trap sites, leading to the stronger PL quenching observed in device C compared to in B. On the other hand, the less pronounced PL quenching in the doped devices versus in the undoped

device upon increasing the reverse voltage (Figure 3b) can be attributed to the existence of the DCJTB guest molecules in a wider energy band gap host material,<sup>21</sup> which makes electric-field dissociation of excitons on the guest molecules more difficult. As depicted in Figure 4 and explained in our earlier work in more detail,<sup>8</sup> an exciton on a guest site with an energy gap smaller than that of the host is less susceptible to dissociation by an electric field because of the energy barriers  $\Delta E_{\text{LUMO}}$  and  $\Delta E_{\text{HOMO}}$  that the electron and hole, respectively, will have to overcome in the dissociation process. The fact that the electric-field-induced PL quenching decreases upon increasing the DCJTB concentration (Figure 3b) gives further support to this argument, since increasing dopant concentration results in an increase in the fraction of excitons residing on the guest molecules (as evident from the EL spectral shifts shown in Figure 3c) and hence the decrease in electric-field-induced dissociation of excitons.

It is worthwhile mentioning that the use of other dopant materials has been found to give the same effect. Figure 5 shows results from devices of structures C and D as described above in which the EML layer is doped with 10-(2-benzothiazolyl)-2,3,4,6,7-tetrahydro-1,1,7,7-tetramethyl-1*H*,5*H*,11*H*-[1]-benzopyrano[6,7,8-*ij*]quinolizin-11-one (C545T) green dye or 5,6,11,12-tetraphenylnaphthacene (rubrene) yellow dye. Again, introducing the C545T or the rubrene leads to increased PL quenching when the current is increased (Figure 5a), whereas it leads to the expected decrease in PL quenching when the reverse voltage (and therefore the electric field) is increased (Figure 5b). The results further show that the increased luminescence quenching observed at high electron currents is predominantly attributed to electron-induced quenching of excited states rather than to electric-field dissociation effects.

### Summary

We studied PL behavior of tris(8-hydroxyquinoline) aluminum based organic light-emitting devices, doped with various fluorescent dyes, under electron currents. The results show that electron currents reduce the PL quantum yield by as much as 50%, depending on the electron density and the doping conditions in the emitter layer. The decrease in luminescence under electron current is attributed to electron–exciton interaction phenomena and shows that the presence of electrons in a luminescent material can lead to significant exciton quenching, similar to what has been observed from holes before. Such electron–exciton interaction phenomena likely play a role in limiting the efficiency of organic electroluminescent devices.

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