Photoluminescence quenching of tris-(8-hydroxyquinoline) aluminum thin films at interfaces with metal oxide films of different conductivities

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Photoluminescence quenching of tris-(8-hydroxyquinoline) aluminum thin films at interfaces with metal oxide films of different conductivities

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We report a comprehensive study of photoluminescence (PL) quenching of tris-(8-hydroxyquinoline) aluminum (Alq₃) at interfaces with thin films of tin oxide (SnO₂) using both steady-state and time-resolved measurements. Quenching of excitons generated in the Alq₃ layer increased with increased conductivity of the SnO₂ films, which we relate with the presence of nonradiative energy transfer from excitons in Alq₃ to transitions in SnO₂. In addition, due to the semitransparency of SnO₂, the effects of optical interference on the steady-state PL quenching of Alq₃ are determined. We demonstrate that without accounting for the interference effects in the excitation, the extracted exciton diffusion length (L_d) in Alq₃ is in the range of 10–20 nm. However, when using a numerical model to account for the optical interference effects, we find that L_d is in the range of 5–9 nm, which agrees with L_d extracted from time-resolved measurements (4–6 nm). We conclude that time-resolved measurements are least affected by optical interference, yielding the most accurate measurement of L_d.

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I. INTRODUCTION

Metal oxide thin films have long been used as transparent electrodes in organic optoelectronic devices, but their interaction with excitons in their neighboring organic thin films has seldom been investigated. For example, despite numerous studies of photoluminescence (PL) quenching of organic dyes at interfaces with metallic films, there has not yet been a comprehensive study on PL quenching of excitons in organic films at interfaces with metal oxide layers. Exciton quenching at the interfaces of organic films is manifested in measurements of the exciton diffusion length (L_d), which in this study we measure for evaporated thin films of tris-(8-hydroxyquinoline) aluminum (Alq₃) on top of tin-oxide (SnO₂)-coated glass. The Alq₃ exciton diffusion length reported in literature varies widely, from 5 to 30 nm, at room temperature. In this study, we find that the variation can be attributed to the optical interference in the PL measurements and that the true L_d in Alq₃ thin films is 6 ± 2 nm. To determine L_d, we measured the PL efficiency of Alq₃ films of different thicknesses on the top of the quenching Alq₃/SnO₂ interface. Additionally, variation in conductivity of the quenching layer, and therefore the variation in the quenching layer’s absorption coefficient, allows for the presence of nonradiative energy transfer from Alq₃ to SnO₂ to be probed directly.

II. EXPERIMENT

A. Sample fabrication

Samples were fabricated on clean glass substrates, which were cut from 1-mm-thick electroverre glass sheets manufactured by Erie Scientific Co. SnO₂ films were deposited via radio-frequency sputtering (sputtering target, 99.99% pure, was made by AJA International). The sputtering chamber was evacuated below 5 × 10⁻⁷ Torr prior to SnO₂ deposition. A mixture of argon (Ar) and oxygen (O₂) was used as the plasma-forming gas. Films of different oxygen contents were deposited by varying the oxygen flow rate while fixing the total flow rate at 10 SCCM (SCCM denotes cubic centimeter per minute at STP) and the total pressure at 3 mTorr. Film thickness and deposition rate were monitored using a Sycon STM-100/ME, and the deposition rate was maintained for all samples between 1.3 and 1.5 Å/s. For some samples, as indicated in the text, prior to Alq₃ thin-film deposition a self-assembled monolayer (SAM) was applied to SnO₂ and glass surfaces using 3-aminopropyltriethoxysilane (APTES) as a precursor, manufactured by Pierce Biotechnology, Inc. The following procedure was used: mix 2% APTES with 93% ethanol and 5% de-ionized water by volume; adjust the pH with acetic acid to 4.5–5.5; immerse clean oxide substrates at 100 °C for 10 min. To confirm that a uniform SAM had been coated on the oxide surface, we made contact-angle measurements confirming that the surface is hydrophobic and used atomic force microscopy to characterize the surface morphology. The thickness of the monolayer was measured by a Geartner ellipsometer model L126B. Alq₃ (from TCI) was purified using ultrahigh vacuum thermal-gradient sublimation prior to deposition. Alq₃ films were evaporated onto the substrates via Joule heating in vacuum (<7.0 × 10⁻⁷ Torr). The deposition rate was maintained the same for all samples in a range of 1.2–1.6 Å/s. Completed samples were stored in a nitrogen environment at room temperature with O₂ and moisture levels maintained below 1.0 ppm.

B. Measurements

For steady-state PL measurements, we used a Coherent Vioflame diode laser (peak wavelength λ=408 nm, 4 mW continuous power) as an excitation source. To avoid photodiodes and organic films, a custom sample chamber had
been constructed such that completed samples could be placed in an airtight nitrogen environment for PL measurements without atmospheric exposure. PL emission was collected via an optical fiber and analyzed with a spectrometer (SpectraPro 300i by Acton Research). The custom sample chamber holds several samples, allowing for multiple PL measurements without changing the alignment of the setup, ensuring consistent input intensity from sample to sample. Time-resolved measurements were carried out using a λ = 395 nm pulse excitation source (pulse width <200 fs) powered by a Coherent Mira 900F mode-locked Ti:sapphire laser. The input intensity was modulated with a Coherent RegA 9000 regenerative amplifier. A repetition rate of 100 kHz was used for all measurements. Emitted photons were collected and analyzed using a Hamamatsu C4780 picosecond fluorescence lifetime system consisting of a Hamamatsu C4334 Streak Camera and a C5094 spectrophotograph. All of the measurements were integrated over 200,000 frames at a frame capture rate of 60 Hz and with a time window of 100 ns. The intensity vs time profile was obtained by integrating the Alq3 emission spectrum from λ = 480 nm to λ = 580 nm.

Optical transmittance and reflectance measurements were performed on an Aquila nkd-8000. For Hall-effect measurements, we used a Keithley 2600 as a current source and an electromagnet to provide a magnetic-field intensity of up to 4.4 ± 0.1 kG.

III. THEORY

Given a number of concurrent and independent processes such as exciton generation, diffusion, and decay, Burin and Ratner\textsuperscript{[15]} proposed that the exciton population density \( N \) at any position \( r \) and time \( t \) in an organic thin film with a quenching interface at \( x = 0 \) can be described by

\[
\frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial x^2} - \frac{N}{\tau_0} \left[ 1 + \left( \frac{x_0}{x} \right)^3 \right] + G
\]

with \( x \) as the distance from the quenching interface into the organic thin film and \( D \), \( \tau_0 \), \( x_0 \), and \( G \) are defined below.

In this model, it is assumed that excitons are generated by photoexcitation only with light incident from \( x = +\infty \). Under steady-state illumination, the generation rate \( G \) is invariant with time; the distance dependence is commonly assumed to follow Beer’s law, viz., \( G(x) = \exp[\alpha(x-d)] \), where \( x = d \) is the illuminated sample surface (thus \( 0 \leq x \leq d \) indicates a position within the organic film) and \( \alpha \) is the absorption coefficient at the excitation wavelength. For films much thinner than \( \alpha^{-1} \), \( G \) can also be assumed to be invariant with distance. The migration of excitons is modeled by a classical non-dispersive diffusion process, with diffusion constant \( D \). It is well known that nonradiative energy transfer can occur near the interface with an absorbing layer (e.g., a metal electrode),\textsuperscript{[1–10]} and the rate of energy transfer has been observed to follow an inverse cubic law with distance.\textsuperscript{[1,2]} Thus, the total exciton decay rate \( \tau^{-1} \) is formulated as

\[
\frac{1}{\tau} = \frac{1}{\tau_0} \left[ 1 + \left( \frac{x_0}{x} \right)^3 \right],
\]

where \( \tau_0^{-1} \) is the total decay rate in the absence of the absorbing layer and \( x_0 \) is the distance at which the probability that an exciton decays by nonradiative energy transfer to the quenching layer is 1/2. A general expression for \( x_0 \) is given by

\[
x_0^3 = \frac{3 \phi \lambda^3 \Theta}{32 \pi^3 n_1} \left( \frac{n_2 \kappa_2}{(n_1^2 + n_2^2 - \kappa_2^2)^2 + 4n_1^2 \kappa_2^2} \right),
\]

where \( \lambda \) is the emission wavelength, \( \phi \) is the luminous yield, \( n_1 \) is the real part of the refractive index of the host medium, \( n_2 \) and \( \kappa_2 \) are the real and imaginary parts of the complex refractive index of the quenching medium, and \( \Theta \) is a geometry factor for different dipole orientations with respect to the quenching layer, viz., \( \Theta = 2 \) for a vertical dipole and 1 for a horizontal dipole. But for broad emission materials such as Alq3, Eq. (3) should be recast in a fashion that integrates over the entire spectrum,

\[
x_0^3 = \frac{3 \phi \Theta}{32 \pi^3} \int_0^\infty \frac{n_2 \kappa_2 f(\lambda)}{(n_1^2 + n_2^2 - \kappa_2^2)^2 + 4n_1^2 \kappa_2^2} \lambda^3 d\lambda,
\]

where \( f(\lambda) \) is the area-normalized emission spectrum of the host.

To estimate the extent of energy transfer from Alq3 to SnO2 with Eq. (4), we assume that the real refractive index of Alq3 is \( n = 1.70 \) and constant over its emission spectrum.\textsuperscript{[19]} We use the area-normalized emission spectrum \( f(\lambda) \) as determined by our measurements. The complex refractive index of pure SnO2 used is that reported by Martín-Palma and Martínez-Duart.\textsuperscript{[20]} The PL yield used is \( \phi = 0.32 \),\textsuperscript{[12]} and we set \( \Theta = 4/3 \) as for a randomly oriented dipole.\textsuperscript{[9]} The overlap between the Alq3 emission and the SnO2 extinction coefficient is plotted in Fig. 1. Integrating Eq. (4) for \( \lambda \) from 400 to 800 nm, we find that \( x_0 = 32 \) Å.

In the steady state, Eq. (1) is set to 0 and can be rewritten as

\[
\frac{\partial N}{\partial t} = \frac{\partial^2 N}{\partial x^2} - \frac{N}{\tau_0} \left[ 1 + \left( \frac{x_0}{x} \right)^3 \right] + G.
\]
time-resolved measurements. We also observe similar quenching effects from in the case with a metallic electrode.1–10 Below, we demonstrate of the quencher and the emission spectrum of Alq3, as ciently large spectral overlap between the absorption spec-
energy transfer can become significant if there is a suffi-
icient, the average exciton decay rate increases with decreasing Alq3

$$\frac{d^2 N}{dx^2} - \frac{N}{L_d} \left( 1 + \frac{x^3}{x^2} \right) + G' = 0,$$  \hspace{1cm} (5)

where \(L_d = \sqrt{D\tau_0}\) is the exciton diffusion length. We note that a more precise definition has that \(L_d = \sqrt{2D\tau_0}\) where \(Z=2\) for strictly one-dimensional diffusion, \(4\) for two-dimensional diffusion, and \(6\) for three-dimensional diffusion.13 But in literature, \(Z\) is usually taken as unity.8,15–17,21,22 Therefore, we follow the same convention for direct comparison.

We evaluate the numerical solution by considering three boundary conditions: (1) no surface quenching, (2) partial quenching, and (3) complete quenching. If surface quenching does not occur, then the net flow of excitons to the interface is zero, viz., \(\frac{dN}{dx}=0\). This condition also applies to the inert air/organic interface. For a partial quenching condition, the net flow of excitons to the quenching interface is balanced by the rate at which excitons are quenched, viz., \(D\frac{dN}{dx}=\nu N\), where \(\nu\) is the quenching velocity. If \(\nu\) is large, then the interface becomes a perfect quencher, and the exciton population density at the quenching surface is always zero. From the solution to Eq. (1), the PL quantum efficiency can be obtained by finding the rates of absorption (\(A\)) and emission (\(F\))

$$A(w) = \int_0^w G dx, \quad \frac{F(w)}{w} = \int_0^w \frac{N}{\tau_r} dx, \hspace{1cm} (6)$$

where \(\tau_r^{-1} = \phi \tau_0^{-1}\) is the radiative decay rate. Thus, the PL efficiency for a film of thickness \(w\) is \(\frac{F(w)}{w}/A(w)\).

IV. RESULTS AND DISCUSSION

A. Photoluminescence quenching by SnO2

In Fig. 2, we show PL quenching of a series of thin films of Alq3 by SnO2 through steady-state PL measurements with varying Alq3 thickness. Figure 2(a) shows that the normalized emission spectra peak at \(\lambda = 523 \pm 3\) nm. Relative peak intensity of each sample is plotted in Fig. 2(c), which shows a significant decrease in the photoluminescence of Alq3 with thickness. We also observe similar quenching effects from time-resolved measurements (Fig. 3), which show that the average exciton decay rate decreases with decreasing Alq3 thickness.

In subsequent analysis, we consider two most likely external quenching mechanisms: (1) surface quenching at the Alq3/SnO2 interface and (2) nonradiative energy transfer to SnO2 transitions. The former can occur at type II heterointerfaces for which the band offset is greater than the exciton binding energy. In this case, excitons in Alq3 can dissociate into separate charge carriers upon arrival at the Alq3/SnO2 interface, as illustrated in Fig. 4(a). Alternatively, dangling bonds at the SnO2 surface could result in formation of mid-gap states that could act as recombination sites for Alq3 excitons. The efficiency of this process depends on the energy levels and the contact between the two layers. Nonradiative energy transfer can become significant if there is a sufficiently large spectral overlap between the absorption spectrum of the quencher and the emission spectrum of Alq3, as in the case with a metallic electrode.1–10 Below, we demonstrate that Alq3 can energy transfer to SnO2, as illustrated in Fig. 4(b), via two experiments: (1) modifying the optical properties of sputtered SnO2 and (2) applying a SAM to the oxide surface.

Optical and electrical properties of SnO2 can be modified by tuning the film deposition conditions. In Fig. 5, we show...
that as-deposited SnO$_2$ films become less absorptive with excess oxygen introduced into the sputtering ambient. Through ellipsometry measurements at a select wavelength, we find that there is no significant variation in the real index of refraction of SnO$_2$ with varying oxygen content. Consequently, only the extinction coefficient is strongly affected by the introduction of oxygen. Furthermore, the decrease in absorption with increasing oxygen content is accompanied by a decrease in the carrier density, as determined by Hall-effect measurements (Fig. 6). Thus, it is likely that excess oxygen reduces the oxygen vacancies, which are intrinsic donors,$^{25}$ in the sputtered SnO$_2$ films, thereby removing those energy states that are responsible for the absorption in the visible spectrum.

By measuring the steady-state PL spectra of Alq$_3$ on these SnO$_2$ films, we find that the emission intensity rises steadily with the SnO$_2$ oxygen content, as shown in Fig. 7(a), which indicates a reduction in PL quenching. To estimate the absorption of the Alq$_3$ layer, we implement a thin-film dielec-

FIG. 4. Two examples by which excitons can be quenched: (a) exciton dissociation at the Alq$_3$/SnO$_2$ interface and (b) nonradiative energy transfer from Alq$_3$ to SnO$_2$. Energy levels are denoted by conduction band (CB), valence band (VB), lowest unoccupied molecular orbital (LUMO), and highest occupied molecular orbital (HOMO). Their values are obtained from literature (Refs. 23 and 24).

FIG. 5. Optical properties of 700 Å SnO$_2$ samples sputtered in different oxygen content (measured by ratio of the oxygen flow rate to the total gas flow rate): (a) transmittance, (b) reflectance, and (c) absorption.

FIG. 6. Change in the carrier density and Hall mobility as a function of the oxygen content.

FIG. 7. Photoluminescence of 100-Å-thick Alq$_3$ thin film on SnO$_2$ substrates sputtered with different oxygen content: (a) 700-Å-thick SnO$_2$ films and (b) 300-Å-thick SnO$_2$ films with and without application of a SAM.
PHOTOLUMINESCENCE QUENCHING OF TRIS-(8-...
this microcavity effect is too weak to induce a large variation in the luminescence extraction efficiency.

C. Extraction of the exciton diffusion length

We extract the exciton diffusion length from steady-state and time-resolved measurements using the models described in Sec. III. In Figs. 9 and 10, we compare the relative PL efficiency from Fig. 2 calculated with and without any interference correction. Supposing that these samples do not exhibit strong interference effects, the generation term can be approximated by either a uniform absorption rate or by Beer’s law. Conversely, for the case in which optical interference is assumed to play a significant role, a correction factor is estimated for the absorption using the $T$-matrix simulations, and excitons are assumed to be generated uniformly throughout the organic film. Key parameters for each theoretical fit are tabulated in Table I. Overall, we find that with all input parameters optimized, each model provides a good fit to the experimental results. In particular, without any optical correction, the exciton diffusion length ($L_d$) in Alq3 varies from 10 to 20 nm, a range that is commonly reported in literature. With the $T$-matrix absorption correction, however, $L_d$ is shortened to a range of 5–9 nm.

For the energy transfer only cases, since the energy-transfer distance ($x_0$) and $L_d$ cannot both be determined independently, we extract $L_d$ by fixing $x_0$ at a particular value in a range between 1 and 60 Å. We find that for small $x_0 (<5$ Å), the extracted $L_d$ approaches that from the partial quencher case. When $x_0$ is in the range of 5–20 Å, the energy-transfer rate near the interface becomes sufficiently fast that the exciton population at the interface is virtually zero regardless of the surface quenching velocity. Thus, the extracted $L_d$ approaches that from the perfect quencher case. This analysis shows that for the purpose of extracting $L_d$ alone, it is reasonable to use the energy transfer model only to obtain the upper and lower bounds.

We apply similar analysis to the time-resolved measurements. Fitting each decay profile with a single exponential function, we obtain the average exciton decay time for each sample (Fig. 11). We solve Eq. (1) by making the following assumptions: (1) the initial exciton population is uniform at $t=0$, (2) exciton generation is zero for $t>0$, and (3) excitons are quenched by energy transfer only. The extracted $L_d$ is found to be in the range of 40–60 Å for $x_0$ between 40 and 5 Å. Since only the change in the emission intensity with time is relevant in time-resolved measurements, results from this analysis are less likely to be affected by optical interference in the same samples. Thus, the exciton diffusion length extracted from time-resolved measurements is more precise than that extracted from steady-state measurements. Conversely, our analysis also shows that $T$ matrices correctly
TABLE I. Comparison of different models: without any optical correction, the exciton diffusion length ($L_d$) is found to be in the range of 10–20 nm; with the $T$ matrices, $L_d$ is found to be in the range of 5–9 nm. Other parameters are denoted by $v$ (surface-quenching velocity) and $x_0$ (energy-transfer distance).

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<th>Model</th>
<th>Absorption</th>
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<td><strong>Perfect quencher</strong></td>
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<tr>
<td>Uniform</td>
<td>122.5 ± 12.3</td>
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<tr>
<td>Beer’s law$^a$</td>
<td>139.6 ± 16.1</td>
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<tr>
<td>$T$ matrices</td>
<td>88.9 ± 13.2</td>
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<tr>
<td><strong>Partial quencher$^b$</strong></td>
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<td></td>
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<tr>
<td>Uniform</td>
<td>641</td>
<td>160.3 ± 59.3</td>
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<tr>
<td>Beer’s law$^a$</td>
<td>535</td>
<td>218.2 ± 88.4</td>
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<td>$T$ matrices</td>
<td>4.3 × 10$^5$</td>
<td>88.8 ± 44.8</td>
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<td><strong>Energy transfer only</strong></td>
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$^a$The absorption coefficient is fixed at $\alpha=5.6 \times 10^4$ cm$^{-1}$.

$^b$The bulk exciton decay time is fixed at $\tau_0=17.4$ ns (Ref. 19).

capture the interference effects by helping to establish an agreement between the steady-state and the time-resolved measurements.

V. CONCLUSIONS

In this paper, we demonstrate that surfaces of thin films of SnO$_2$ quench the luminescence of Alq$_3$ and that nonradiative energy transfer plays a major role in this process due to the dependence of quenching magnitude on the carrier concentration in SnO$_2$. We characterize optical interference in the excitation using the emission spectra of Alq$_3$ deposited on varying thicknesses of SnO$_2$. Finally, we compare the exciton diffusion length extracted from theoretical fittings with and without any interference correction. We show that for steady-state measurements without any interference correction, the exciton diffusion length in Alq$_3$ is in the range of 10–20 nm, but with the interference correction, the exciton diffusion length is shortened to a range of 5–9 nm. The latter agrees with the range derived from time-resolved measurements, which is in the range of 4–6 nm. Our study suggests that a wide range of exciton diffusion length reported in literature may have resulted from not accounting for optical interference in measured samples.

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