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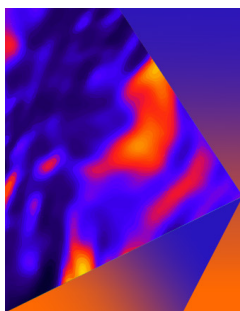
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Electric field-assisted dissociation of singlet excitons in *tris*-(8-hydroxyquinolinato) aluminum (III)

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Results based on the electric-field dependence of electro-modulated fluorescence and steady-state photoconduction in films of *tris*-(8-hydroxyquinolinato) aluminum (III) (Alq_3) are consistent with a model where singlet excitons dissociate into electron-hole pairs through charge transfer state. Dissociation into free carriers or predominantly geminate recombination results from this intermediate state. The quantum efficiency of charge separation is in agreement with predictions based on a model using the three-dimensional Onsager theory of geminate recombination combined with volume (bimolecular) recombination of the photogenerated space charge. This model is used to account for the decrease in the electroluminescence quantum efficiency of Alq_3 -based organic light-emitting diodes at high electric fields. © 2002 American Institute of Physics.
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The metal chelate *tris*-(8-hydroxyquinolinato) aluminum (III) (Alq_3) has been one of the most widely studied luminescent materials since its first use as an emitter and electron transporter in organic light-emitting diodes (LEDs).¹⁻⁴ The electroluminescence (EL) quantum efficiency φ_{EL} of organic LEDs based on a heterojunction involving doped or undoped Alq_3 varies with the applied electric field F , reaching a maximum at a field dependent on the type and concentration of the dopant.⁵

For neat Alq_3 -based LEDs, the $\varphi_{\text{EL}}(F)$ initially increases at low fields (LFs), reaches a maximum value, then decreases at high fields (HFs). In the LF regime, the increase of the $\varphi_{\text{EL}}(F)$ is due to the decrease in the field-dependent recombination-to-transit time ratio.⁶ Various possibilities must be taken into account in order to explain the drop of the $\varphi_{\text{EL}}(F)$ at high electric fields: (i) exciton-exciton annihilation, (ii) exciton quenching by charge carriers, and (iii) field-assisted exciton-dissociation into an electron-hole pair.

In this letter, data obtained from HF photoluminescence (PL) quenching and LF steady-state photoconductivity (PC) measurements in solid films of Alq_3 show evidence for singlet exciton dissociation and explain the observed HF drop in the quantum EL efficiency of Alq_3 -based LEDs.

Films of Alq_3 , typically 0.5–1 μm thick, measured by profilometry, were prepared by thermal vacuum ($\cong 10^{-4}$ Pa) evaporation at a rate 0.3–0.4 nm s^{-1} and deposition onto quartz or glass slides covered by a semitransparent thin layer of Al. A sandwich structure was formed by vacuum deposition of a semitransparent Al top electrode. Alq_3 was purchased from Aldrich and was used as is or purified by sublimation. No systematic difference was observed in the experimental data obtained with such purified material and

that used without further purification. A reduction of trap concentration in the initially purified material, demonstrated recently by the nondispersive photocurrent transients in thick Alq_3 films under vacuum,⁷ was leveled because all measurements were carried out in ambient atmosphere conditions. The electric field modulated fluorescence was studied using a sinusoidal field with a frequency $\omega/2\pi=175$ Hz applied to the sample.⁸ The field amplitude ranged between 10^5 and 2×10^6 V cm^{-1} . The steady-state PC measurements were conducted by irradiating either side of the Alq_3 films sandwiched between two semitransparent Al layers, which could be either a positively or negatively biased electric contact. A Narva 200 W mercury lamp and an Osram 150 W xenon lamp were used as the light sources. The active electrode area of the film was typically 0.1 cm^2 . The photocurrent was measured within the quantal intensity range $10^{11} < I_0 < 10^{15}$ quanta/ $\text{cm}^2 \text{ s}$ and a dc field range between 10^3 and 1.5×10^5 V cm^{-1} . The light intensity dependence of the photocurrent j_{ph} is quasilinear ($j_{\text{ph}} \propto I_0^{0.8}$), suggesting that the discharge of carriers at the electrodes dominates the carrier decay process.⁹ Thus, the carrier decay can be approximated by first order kinetics where the bimolecular recombination contribution is treated as a correction to the effective photodissociation efficiency of the excited states (see discussion below).

Figure 1 shows the fluorescence (FL) quenching efficiency [Fig. 1(a)] and dc photocurrent j_{ph} [Fig. 1(b)] as a function of the applied electric field at two different excitation wavelengths. A slightly stronger quenching and higher j_{ph} is apparent for the shorter excitation wavelength, the effect due to the production of higher excited states.⁸ The mechanism by which singlet excitons are quenched by applying an electric field, and charges are photogenerated involves the charge separation process. This is shown in some detail in Fig. 2. The Alq_3 molecules are excited directly by absorption of light $h\nu_{\text{ex}}$ to form the excited singlet states

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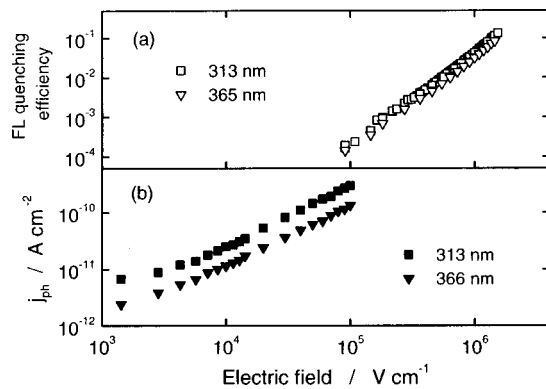


FIG. 1. Fluorescence quenching efficiency (a) and steady-state photocurrent (b) as a function of electric field at two different excitation wavelengths. Three different samples of thickness 0.5 and 0.55 μm (a) and 0.7 μm (b) were used. The photocurrents were measured using a photon flux per unit area $I_0 = 10^{13}$ quanta/cm² s.

Alq_3^* . Alq_3^* may then relax radiatively to the ground state at a rate k_f , or may dissociate into separated electrons e and holes h , i.e., Alq_3^\pm . Other radiationless transitions of Alq_3^* do not alter the electric field effects on fluorescence and production of charge. The initial separation step involves a charge transfer (CT) state formed with a field-independent probability η_0 and a field-dependent CT dissociation process Ω into separated charge carriers.

The overall probability η for excited states to dissociate into separated charge carriers can be expressed as

$$\eta = \eta_0 \Omega (1 - \eta_{\text{VR}}), \quad (1)$$

where $\eta_0 \Omega$ represents the charge separation probability including the geminate recombination step. This process can be reversed to reform the CT state by volume (bimolecular) recombination (VR) and relaxation of the CT state into the original singlet excited state Alq_3^* . The bimolecular recombination efficiency or probability η_{VR} is determined by the recombination time τ_{rec} and transit time τ_t of the carriers to the electrodes $\eta_{\text{VR}} = (1 + \tau_{\text{rec}}/\tau_t)^{-1}$. This recombination probability involves more mobile electrons^{7,10} than holes.¹¹ Assuming the elementary steps in the recombination process are governed by the relative carrier mobility (Langevin's recombination mechanism), the second order recombination coefficient γ can be expressed by the electron mobility μ_e , $\gamma \approx e\mu_e/\epsilon_0\epsilon$, and $\tau_{\text{rec}} = (\gamma n_h)^{-1} \approx \epsilon_0\epsilon/e\mu_e n_h$, where n_h is the concentration of holes. The electron transit time can be approximated by $\tau_t \approx (d/2)/\mu_e F$, where d is the sample thickness. Consequently, Eq. (1) becomes

$$\eta = \eta_0 \Omega (1 + edn_h/2\epsilon_0\epsilon F)^{-1}. \quad (2)$$

According to the scheme of Fig. 2, a field increase of the dissociation efficiency $[\eta(F)]$ should show up as a reduction

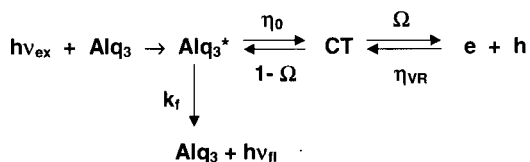


FIG. 2. The photoexcitation and photodissociation of Alq_3^* leading to the charge transfer state and electron (e)-hole (h) pairs, the latter giving rise to the photocurrent flowing in Alq_3 solid films.

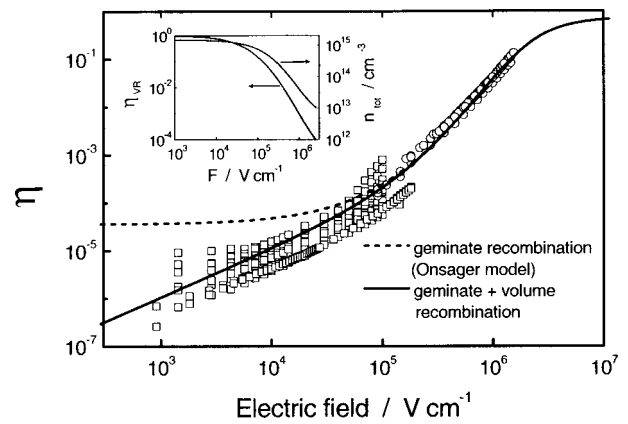


FIG. 3. The electric field dependence of photogeneration efficiency shown for eight different samples of Alq_3 . The squares represent the steady-state photoconduction measurements for six samples, and the circles represent FL quenching measurements for two samples. The dashed line was calculated using the 3D Onsager theory. The solid line is the prediction using the scheme in Fig. 2, plotted according to Eq. (2). The field evolution of the bimolecular recombination efficiency η_{VR} and the total concentration of holes n_h used in the fitting procedure are given in the inset.

in the population of the emitting excited states (Alq_3^*). Thus, the fluorescence intensity at $F=0$, $\text{FL}(0)$, would decrease under an electric field F applied to the Alq_3 film $\text{FL}(F) \approx \text{FL}(0)[1 - \eta(F)]$. The experimental ratio $[\text{FL}(0) - \text{FL}(F)]/\text{FL}(0) \approx \eta(F)$ is a measure of the field-induced fluorescence quenching. The fractional fluorescence change due to an applied electric field directly provides the value of the dissociation probability of the emitting excited states (Alq_3^*). These changes have been measured by applying a sinusoidal electric field to the sample, which monitor the time-dependent fluorescence signal at the second harmonic and thus reflects fluorescence quenching only. A detailed description of the experimental technique has been published elsewhere.^{12,13}

Data for eight Alq_3 films with varying thickness, taken at different excitation wavelengths and light intensities, are shown in Fig. 3. The dissociation efficiency η plotted as a function of electric field is obtained from Fig. 1. The experimental data for the LF portion ($F < 10^5$ V/cm) and the HF portion ($F > 10^5$ V/cm) were obtained from the PC measurements and the FL quenching, respectively. The overlapping values of η in the intermediate range (around 10^5 V/cm) suggest that there is a common origin between the FL quenching and the photogeneration process. Since the LF photogeneration quantum yield is very low, the three-dimensional (3D) Onsager model of geminate recombination¹⁴ can be used to describe the charge separation process in solid Alq_3 .

The application of the Onsager theory to the photoionization in solids has been described in detail in many studies.¹⁵ It predicts that the overall photogeneration efficiency is the product of the initial field-independent charge separation step probability η_0 and the efficiency Ω_{Ons} of the diffusion governed further separation under the combined effects of the Coulomb attraction and the applied field $\eta_{\text{Ons}} = \eta_0 \Omega_{\text{Ons}}$. The essential parameters in the Onsager formalism are η_0 and r_0 , the latter being the initial separation distance of the geminate $e-h$ pair. The dashed line in Fig. 3 was calculated according to the 3D Onsager model assuming

$r_0=1.5$ nm and $\eta_0=0.8$. Above 9×10^4 V cm⁻¹, the results are in good agreement with those predicted from the Onsager theory. At low electric fields, however, the efficiency is much lower and its field increase much stronger than that predicted by the Onsager theory. This discrepancy was also observed in earlier studies (see e.g., Ref. 16), and cannot be resolved by adjusting the different parameters (r_0 and η_0), and/or by the introduction of an exponential or Gaussian distribution of the initial separation parameter. Instead, the experimental data are well fitted (the solid line in Fig. 3) based on the predictions derived from Eq. (2) and assuming that $\eta_0\Omega_{\text{Ons}}$ is diminished by the VR of the separated carriers. The fitting procedure requires the concentration of holes and, consequently, the VR efficiency, being high at low electric fields, to decrease by orders of magnitude above 10^5 V cm⁻¹ (see the inset in Fig. 3). For $n_h \leq 10^{15}$ cm⁻³, the second term in the denominator of Eq. (2) is much smaller than unity and $\eta \approx \eta_0\Omega$. This means that in the LF region the discharge of the separated carriers at their exit contacts is not efficient enough to suppress volume recombination (the recombination-to-transit time ratio is <1). We note that the field dependence of n_h is a result of the field-dependent carrier generation and carrier decay processes. The latter involves the field-dependent carrier mobilities. For Alq₃ with $\mu_e \gg \mu_h$,⁷ the electron decay is largely dominated by discharge processes. A simple expression for the hole concentration $n_h = [(ed/2\epsilon_0\epsilon F) + (2\mu_h F/\eta I_0)]^{-1}$ can be derived from the kinetics of holes decaying in both VR and electrode discharge processes. Note that $n_h < 2\epsilon_0\epsilon F/ed$ which is roughly the capacitor charge. The n_h decreases at high fields as the field-dependent product $\mu_h(F)F$ increases more rapidly than $\eta(F)$. At higher fields the space charge is reduced due to the more efficient hole discharge at the cathode, caused by increasing carrier mobilities^{10,11} and the applied field. As a result, the concentration of charge becomes predominantly controlled by the charge separation efficiency in accordance with the Onsager formalism as shown in Fig. 3. A previous analysis of the field-induced FL quenching data in solid films of Alq₃ showed their good fit with a model, that assumes a high zero-field carrier separation efficiency, and the field effect belonging solely to further separation in the course of classical carrier hopping.⁸ Such an approach is justified under the premise that the emission is a result of radiative decay of a trapped (charge-transfer) state.¹² The similarity between the PL spectra of dilute solution of Alq₃ and those from thin evaporated films³ suggests that the emission originates from well-localized molecular singlet states. Hence, the good fit of the experiment with the hopping separation model in this case must be considered as fortuitous and reinforces the present interpretation based on the 3D Onsager theory.

The field-assisted dissociation of singlet excitons reduces the emission efficiency by a factor $(1 - \eta)$. Hence, the

probability that an excited state Alq₃^{*} relaxes radiatively is $P_f = [k_f/(k_f + k_n)](1 - \eta)$, k_n being the rate constant for nonradiative decay pathways other than exciton dissociation. Using the experimental value of the absolute PL efficiency $\varphi_{\text{PL}} = k_f/(k_f + k_n) = 25\%$,⁵ $P_f = 0.23$ is obtained with $\eta = 0.07$ at a field $\approx 10^6$ V cm⁻¹ (see Fig. 3). This would lead to about a 10% drop in EL quantum efficiency φ_{EL} of Alq₃. The φ_{EL} decrease defined as $[\varphi_{\text{EL}}^{(\text{max})} - \varphi_{\text{EL}}(F)]/\varphi_{\text{EL}}^{(\text{max})}$ has been found to be on the order of $\approx 20\%$ at F of about 10^6 V cm⁻¹, which agrees within a factor of two with the above prediction.

In summary, we have shown that the dissociation of singlet excitons can be considered as a common basis for the electric field-induced fluorescence quenching and steady-state photoconduction experiments performed on solid films of Alq₃. A simple kinetic model is presented to describe the experimental results. The model includes the charge separation and volume (bimolecular) recombination of the separated charges. Charge separation appears to follow the 3D Onsager model, and controls the relationship between the concentration of excitons and charge carriers at high electric fields. At low fields volume (bimolecular) recombination must be invoked, whereas, the 3D Onsager mechanism applies to the singlet exciton dissociation of Alq₃ at high electric fields. Whenever the recombination-to-transit time ratio is negligible with respect to unity, the singlet exciton dissociation process becomes a process limiting the electroluminescence quantum efficiency.

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