Large electric field effects on photoluminescence of organic Eu^{3+} complex-based electroluminescent emitters ⊘

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Electric field applied to indium-tin oxide (ITO)/organic layer/Au thin-film structure has been shown to strongly (up to 40%) reduce the photoluminescence (PL) of organic films composed of Eu^{3+} complexes-doped diamine derivative (TPD): Polycarbonate thin layers used as red light electroluminescent emitters. Two components of this effect can be extracted from the experiment: (i) electric-field enhanced dissociation of excited states, and (ii) quenching of excited states due to the injected charge. While component (i) reduces PL irrespective of the nature of electrode contacts, the negative values of component (ii) have been observed for some emitters with ITO/organic emitter/ Au structures, tending to an enhancement of the PL. The latter is assigned to the recombination of holes generated by the thermionic emission from ITO (Au) anode and electrons created by exciton reactions at Au (ITO) cathode. The strong PL quenching effects have been attributed to the field increasing occupation of ligands by electrons, competing with excitation energy transfer to them from TPD, the latter being the process responsible for the population of emissive Eu^{3+} ion states. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2168508]

Electric-field-induced photoluminescence (PL) quenching (EPLQ) and the field evolution of electroluminescence (EL) quantum efficiency in organic films become of continuously increasing interest. They are of importance for fundamental knowledge on electronic processes in molecular systems and for practical aims related to optimizing the quantum efficiency of organic light-emitting-diodes (LEDs).[1] In typical organic LEDs, two electrodes injecting electrons (e) and holes (h) in the dark at opposite sides of an organic emitter are used as a rule, the e-h recombination in it leads to the formation of excited emissive states (recombination organic EL). The nonlinear increase of the EL output with the drive current is indicative of the low-field increasing injection efficiency and quenching of excited states including their precursors (mostly coulombically correlated e-h pairs) at high electric fields.[1] The quenching may have at least three reasons: (i) Mutual exciton-exciton annihilation,[2] (ii) field-enhanced dissociation of excited states, and (iii) interaction of excited states with charge carriers distributed in some way in the emitter bulk. To separate these effects weakly injecting Al electrodes have been used and PL quenching observed as a function of exciting light intensity[3] and applied field[4,5] in both fluorescent[3] and phosphorescent[5] organic materials. The mechanisms of emissive state interactions and their field-assisted dissociation could be inferred from those experiments, though the field effect on e-h pairs has not been conveyed by them. Revealing the role of charge carriers in quenching of excited states has remained a challenge in the field of organic EL.

In this study, we used two high work function electrodes, indium-tin oxide (ITO) and Au, to inject holes into the well-defined narrow range emitting Eu^{3+} organic complexes-doped diamine derivative (TPD): Polycarbonate (PC) films, also showing efficient red EL, and examined their PL as a function of applied voltage. The front ITO face observed PL from such a structure has been expected to be free of e-h recombination radiation (EL) because of the high barrier to inject electrons to the TPD conduction level on both ITO and Au contacts ($\Delta E_e \cong 2.5$ eV). Thus, EPLQ at not too high excitation intensities should have been only a combination of mechanism (ii) and (iii), the role of the injected charge to be inferred by comparison with the effect from the same layers provided with Al electrodes, where the EPLQ could be attributed solely to exciton dissociation. It is found that the charge-induced component of the EPLQ can be either positive or negative. We demonstrate that the quenching is principally due to a reduction of the effective concentration of ligands acting as precursor acceptors of energy transferred from excited TPD host molecules to the emissive Eu^{3+} ions. The reduction occurs because the ligands become concurrently occupied with electrons injected by TPD excitons from the negatively biased either ITO or Au electrode. On the other hand, the recombination of TPD transported holes with ligand-trapped electrons can diminish the quenching and even lead to the partial field-increasing PL (negative charge quenching component signal). The difference in the field behavior of EPLQ for Eu complexes with different coligands is discussed in terms of their aggregation ability and disorder effect on the charge carrier mobility in the structures studied.

The front →ITO and nonsubstrate Al← face excited PL of organic structures: (A) →ITO/6 wt% Eu(1–3):74% TPD:20% PC(150–170 nm)/Au, and (B) quartz/Al/6 wt% Eu(1–3):74% TPD:20% PC (70-100nm)/Al←, respectively, were studied based on Eu^{3+} (L$_1$-L$_3$) phen complexes with the common ligand of phenanthroline (phen) and three different coligands as depicted in Fig. 1. The Eu^{3+} complexes

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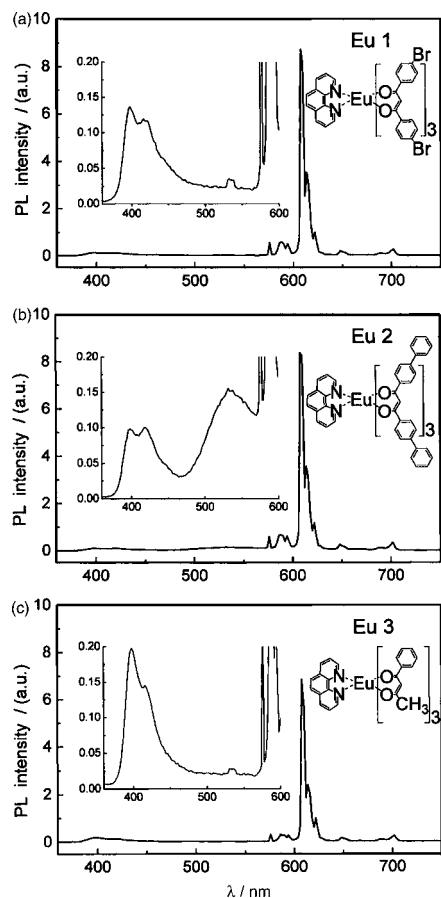
FIG. 1. PL spectra of the Eu complexes studied: (a) (Eu1) Eu(BrBM)$_3$phen-tris(di (bromo) benzoylmethane)mono(phenanthroline) europium(III); (b) (Eu2) Eu(BDBBM)$_3$phen-tris (biphenoylmethane)mono(phenanthroline)europium(III); (c) (Eu3) Eu(BABBM)$_3$phen-tris (benzoyl-lacetonato)mono(phenanthroline)europium(III). The different coligands (L$_1$→BrBM; L$_2$→BDBBM; L$_3$→BABBM)were chosen to examine the coligand role for the EPLQ. The short-wavelength segments of the PL spectra are displayed in the insets. Due to the same ordinate scale in parts (a), (b), and (c), a relative decrease of the emission at the PL maximum may be observed for Eu3-based sample.
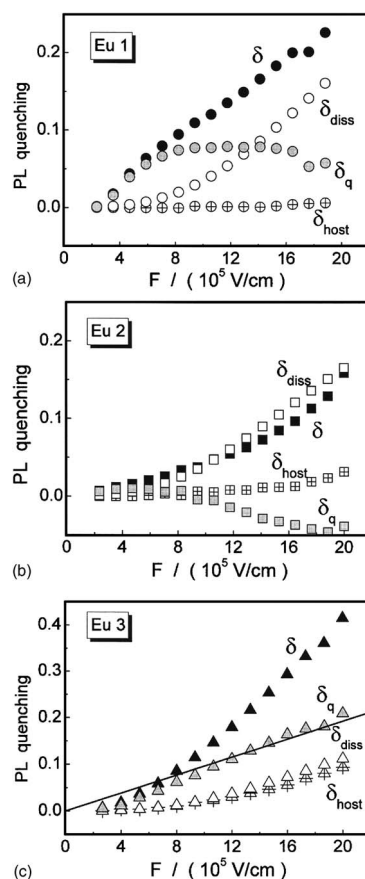

FIG. 2. Comparison of field dependencies of EPLQ for three different Eu^{3+} complex-doped EL emitters as indicated in parts (a), (b), and (c). Filled figures (δ) represent the values measured on Structure (A), open figures (δ_{diss}) are the experimental data for Structure (B), and shadow points (δ_q) are calculated from $\delta_q = \delta - \delta_{host} - \delta_{diss}$. All data obtained with $\lambda_{exc} = 350$ nm, and $I_0 = 7 \times 10^{14}$ quanta/cm^2 s. The data of the EPL for the host fluorescence (TPD), δ_{host}, are displayed by crossed figures for comparison.

to be abbreviated as Eu1 (with coligand L$_1$), Eu2 (L$_2$) and E3(L$_3$), were purchased from SANDS Corp., TPD from Aldrich, and PC of mw 32000–36000 from Polysiences Inc., all used as supplied. Electromodulation of the PL in Structure (A) was performed by applying a progressively increasing dc voltage and taking an average PL intensity over a time of 10 s before (Φ_0) and after (Φ) the voltage rise step for each value of the voltage. The PL intensity was sampled every 0.3 s with a Spex Fluorolog 2 spectrofluorimeter, the results displayed by the ratio $\delta = |\Phi_0 - \Phi(F)|\Phi_0$ as function of electric field (F) within the emission ranges corresponding to the weak host fluorescence of TPD ($\lambda_{max} \cong 420$ nm) and strong guest emission of Eu^{3+} ion ($\lambda_{max} \cong 610$ nm) (see emission spectra in Fig. 1). The PL from Structure (B) was modulated by a sinusoidal field as described elsewhere.[4] The second Fourier harmonic of the modulated PL signal was transformed into the steady-state quenching ratio δ to be compared with that for Structure (A).

The δ for TPD fluorescence does not exceed 10% and can be attributed to mechanisms (ii) and (iii) operating on TPD singlet excitons,[6] the PL quenching for Eu^{3+} emission exceeds largely 10% (up to 40% for Eu3) and cannot be rationalized on the basis of these mechanisms only. The mea-

sured total PL quenching effect (δ) of the latter as a function of the applied electric field for Structure (A) along with that (δ_{diss}) for Structure (B) is displayed in Fig. 2. The charge quenching component (δ_q) of Structure (A) is extracted from the approximate equation $\delta \cong \delta_{host} + \delta_{diss} + \delta_q$, using the δ_{host} measured on Structure (A). As may be seen, the dissociation component, δ_{diss}, observed with Structure (B), is roughly the same (≤ 0.15) for all three Eu complexes studied. On the contrary, the field evolution of component δ_q takes on completely different shapes, changing from monotonous increase for Eu3, through a broad maximum with a tendency to drop at the highest fields for Eu1, and reversing the sign at the inset of the high field region (~ 0.8 MV/cm) and reaching a minimum of about -3% at 1.8 MV/cm for Eu2.

In order to understand these results, the field dependence of the charge concentration in the samples must be addressed. It can be inferred from the current (j)-field (F) characteristics presented in Fig. 3. The important message that follows from them is high photoconductivity of all of the samples, the photocurrent (j_{ph}) exceeds at least two orders of magnitude the dark current (j_{dark}) [Fig. 3(a)] and within the statistical error does not depend on the bias of the illuminated electrode. However, both at high electric fields (>0.8 MV/cm) follow a space-charge-limited-current (SCLC) pattern of the j-F characteristic, $j \cong \epsilon_0 \epsilon \theta \mu F^2 / d$, either in the mobility $\mu(F) =$ const and the free-to-total carrier
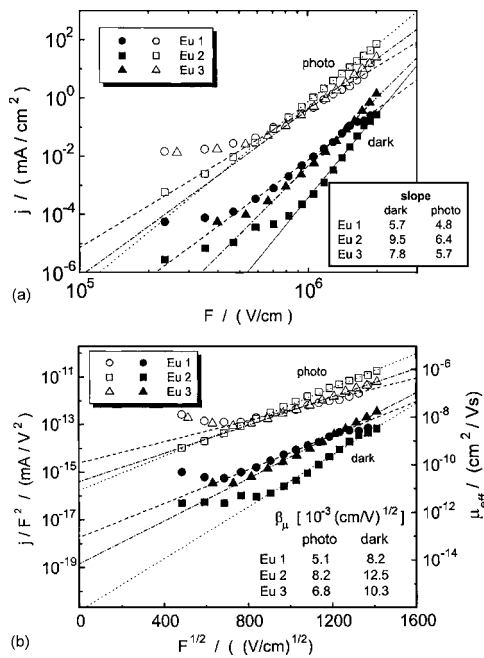
FIG. 3. Current-electric field characteristics of Structure (A) taken in the dark (filled points) and under illumination (photo) through the ITO anode (open points) in the log$j$-log F (a) and log(j/F^2)-$F^{1/2}$ (b) representations. Photocurrents were generated with light of $\lambda_{exc} = 350$ nm and intensity $I_0 = 7 \times 10^{14}$ quanta/cm^2 s. The straight lines are high-field fits to the data assuming SCLC conditions in $\mu(F) = $ const (a) and $\theta(F) = $ const (b) approximations. Their slopes give characteristic parameters for the approximations used. μ_{eff} on the right-hand ordinate stands for the effective mobility calculated as $\mu_{eff} \cong \theta\mu = jd/\epsilon_0\epsilon F^2$.

concentration ratio $\theta(F) = $ const approximations. A plausible explanation for j_{ph} is efficient injection of electrons by TPD excitons from the negatively biased electrode (either ITO or Au). The current becomes the double-injection current exceeding largely the unipolar hole-injection current in the dark. The difference between β_μ is to be expected as it concerns holes only for the dark- and holes+electrons for the photocurrent. Once accepting the high-field j_{ph} to be SCLC, the average concentration (n) of the charge in the sample bulk is simply proportional to the applied field,[1] $n = (3/2)\epsilon_0\epsilon F/ed$. The nonlinear dependence of δ_q on F for Eu1 and Eu2 rules out the quenching based on the exciton-charge carrier collision, $\delta_q = \gamma_q n \tau$, where τ is the intrinsic lifetime of the exciton, and γ_q is the second-order interaction rate constant.

We propose that the PL output is limited by the TPD exciton transfer to the effectively available ligands. Their number decreases with applied voltage due to increasing concentration of electrons trapped on the ligands up to fully saturate these energy acceptor sites. Only molecularly dispersed Eu complexes act as emitters, their aggregates assumed to form nonemissive energy acceptors. The aggregation factor, "f", standing for a fraction of aggregated N_0 complex molecules, largely affects the energy transfer rate to ligands of guest molecules, $\gamma(1-f)N_0$, where γ is the second-order energy transfer rate constant, and N_0 is the nominal concentration of guest molecules. The charge-

induced effect on the guest emission, δ_q^{guest}, follows from the kinetics of excited states,[6]

$$\delta_q^{guest} \cong \frac{n(F)}{(1-f)N_0}. \tag{1}$$

Equation (1) implies δ_q^{guest} to be positive (PL quenching) and varying between 0 (no quenching) up to 1 (total quenching). Moreover, it predicts $\delta_q^{guest}(n)$ to be a linear function of n (thus F). This would explain the results with Eu3 [Fig. 2(c)], yielding the aggregation factor $f = 0.98$ with $N_0 = 5.3 \times 10^{19}$ cm^{-3}. A slight deviation of the low-field points from the straight line is due to the non-Ohmic injection, the SCLC sets in at about 0.8 MV/cm (see Fig. 3). We ascribe the nonmonotonic field evolution of δ_q for Eu1 and Eu2 to the bimolecular e-h recombination that contributes to the guest emission, the process weakening of the overall δ_q^{guest} effect. In a limiting case when the increment of the recombination radiation exceeds the PL quenching, we would expect $\delta_q^{guest} < 0$, i.e., $\delta < \delta_{diss}$ as is the case with Eu2 [Fig. 2(b)]. Such a situation can be linked to the carrier mobility. Its relatively high value for the Eu2-doped structure [cf. Fig. 3(b)] presumably increases the e-h recombination coefficient. Otherwise, a decreased aggregation ability could reduce the contribution of the quenching ratio (1) as compared with that for Eu1- and Eu3-doped emitters. The latter is supported by increased emission intensity observed for Eu1 and Eu2 (see Fig. 1).

In summary, we demonstrated how to distinguish between EPLQ due to the exciton dissociation and action of the injected charge by comparing the EPLQs from Eu^{3+} complex-doped EL emitters provided with a pair of high- and low-work function electrodes. We have elucidated the EPLQ mechanisms, showing the crucial role of the exciton-induced injection of electrons from negatively biased high-work function ITO and Au electrodes. The emitter layers containing three Eu^{3+} (L_1-L_3) phen complexes with different coligands (L_1-L_3) have been shown to reveal similar exciton dissociation component of the EPLQ, but completely different EPLQs imposed by injected charge. This suggests that the coligands differentiate between the high degree ($\cong 98\%$ for Eu3) of guest molecules aggregation and disorder in the emitters.

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