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Citation	Applied Physics Letters, 98(18), 181910 https://doi.org/10.1063/1.3582916
Issue Date	2011-05-02
Doc URL	http://hdl.handle.net/2115/45543
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Type	article
File Information	APL98-18_181910.pdf



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Photo- and field-induced charge-separation and phosphorescence quenching in organometallic complex Ir(ppy)₃

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(Received 1 February 2011; accepted 23 March 2011; published online 6 May 2011)

Electric field effects on absorption and photoluminescence (PL) spectra of organometallic phosphorescent emitter Ir(ppy)₃, {tris[2-phenylpyridinato-C²,N] iridium (III)} doped in a film of polymethyl methacrylate (PMMA) have been confirmed at temperatures in the range of 40–295 K. Field-induced quenching of PL observed for Ir(ppy)₃ is attributed to the decrease both of emitting state population and of the lifetime of PL. The quenching is independent of excitation energy as well as temperature. Field-assisted charge separation or dissociation of electron-hole (*e-h*) pair produced by photoexcitation may decrease the population of the emitting state. The Stark shifts on absorption and PL spectra have also been analyzed. © 2011 American Institute of Physics.
[doi:10.1063/1.3582916]

Organometallic phosphor Ir(ppy)₃ complex, which is known for nearly two decades,^{1,2} is now very attractive because of its very high electroluminescence (EL) efficiency in light emitting diodes (LEDs).³ The high quantum efficiency is based on efficient intersystem crossing due to strong spin-orbit coupling of organic complex, which mixes the singlet and triplet states and thus permits to harvest light from the singlet state to the triplet state. During the EL operation, strong electric fields are applied to the sample. As a result, EL quantum yield (QY) may be strongly decreased, which limits the use of organic LEDs (OLEDs) in practical applications. In order to minimize this undesired effect, the knowledge of quenching mechanism is important. Few reports appeared on this issue^{4–6} in which a neat Ir(ppy)₃ film was used as a sample. Here, we have investigated the effects of external electric field on optical absorption, PL and PL-excitation (PL-Ex) spectra as well as PL decay profiles for Ir(ppy)₃ doped in a PMMA film.

Ir(ppy)₃ (Aldrich) was used without further purification. A sample film of Ir(ppy)₃ (~0.5 mol %) doped in PMMA (purchased from Aldrich and purified before use) was deposited on an indium-tin-oxide coated quartz substrate by a spin coating method from dichloromethane solution, and then a semitransparent aluminum film (Al) was deposited on the sample film with vacuum vapor deposition technique. Electroabsorption (E-A), electrophotoluminescence (E-PL), E-PL-excitation (E-PL-Ex) spectra as well as field-induced change in emission decay profile were measured as described elsewhere.^{7–9}

Figure 1 shows absorption, E-A, PL, and E-PL spectra of Ir(ppy)₃. E-A spectra were measured with $\chi=54.7^\circ$. Here χ is the angle between the direction of the applied electric field (*F*) and the electric vector of the polarized excitation light. The E-A signal was proportional to F^2 . The absorption as well as the E-A spectra [Fig. 1(a)] of Ir(ppy)₃ are nearly identical to those reported earlier.^{4,10} PL and E-PL spectra of Ir(ppy)₃ doped in PMMA were measured at ~295 K [Fig.

1(b)] with various field strengths at the excitation wavelength where the E-A signal was negligibly small [Fig. 1(a)]. PL, i.e., phosphorescence, appears with a peak at 511 nm and a shoulder at 540 nm. The E-PL spectra are very different in shape from the PL spectra, while PL as well as E-PL spectra recorded at different excitation wavelengths are essentially the same (see Fig. S1 of Ref. 11). The total integrated intensity of the E-PL spectrum is negative at each of the applied fields (0.2–1.0 MV cm⁻¹), indicating that the emission QY decreases in the presence of *F*. The field-induced change in PL, i.e., ΔI_{PL} , integrated over the entire spectral region of 450–700 nm in the E-PL spectrum, is proportional to F^2 . The fractional field-induced quenching was $1.25 \pm 0.05\%$ at 1.0 MV cm⁻¹. The ratio between E-PL-Ex and PL-Ex is nearly the same at any excitation wavelength, indicating that

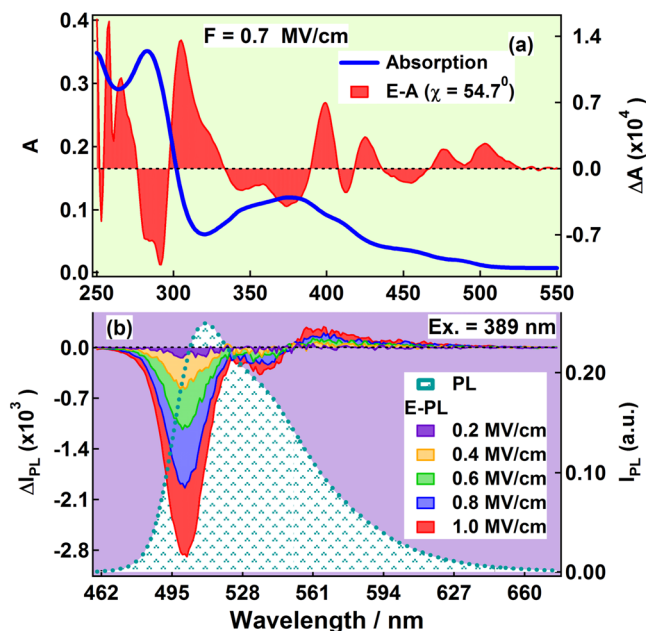


FIG. 1. (Color online) (a) E-A spectrum observed at angle $\chi=54.7^\circ$ with a field strength of 0.7 MV cm⁻¹ and absorption spectrum of a Ir(ppy)₃ doped in a PMMA film, and (b) E-PL and PL spectra observed in vacuum at different field strengths in the range of 0.2–1.0 MV cm⁻¹.

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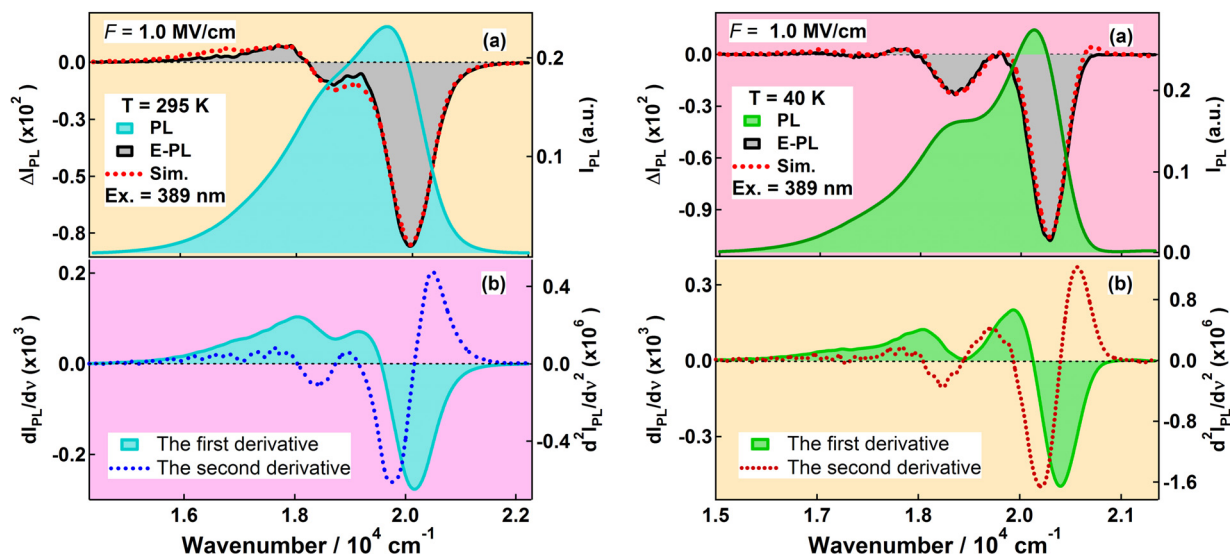


FIG. 2. (Color online) (a) E-PL and PL spectra and (b) derivatives of the PL spectra of a $\text{Ir}(\text{ppy})_3$ doped in PMMA film observed at a temperature of 295 K (left panel) and 40 K (right panel). Simulated spectrum is shown in (a) of both panels by a dotted red line. Excitation wavelength was 389 nm, and the field strength was 1.0 MV cm^{-1} .

the field-induced quenching is independent of the excitation energy (see Fig. S2 of Ref. 11), in contrast with this, the field induced quenching depends critically on excitation energy in OLEDs materials of the π -conjugated polymers.⁸

The E-PL can be reproduced with a linear combination of the zeroth-, first- and second-derivatives of the PL spectrum [left panel of Fig. 2(a)].^{7,8,12,13} QY does not depend on excitation energy irrespective of F . The change in polarizability and electric dipole moment, i.e., $\Delta\bar{\alpha}$ and $|\Delta\mu|$ between the emitting state and the ground state was evaluated to be $680 \pm 15 \text{ \AA}^3/f^2$ and $8.0 \pm 0.5 \text{ D}/f$, respectively. Here, f is the internal field factor. These values are different from the ones evaluated from the E-A spectra; E-A spectra showed that the maximum value of $|\Delta\mu|$ for the first excited singlet state was $5.0 \pm 0.5 \text{ D}/f$ and the average molecular polarizability change was $20 \pm 5 \text{ \AA}^3/f^2$ for the first five bands,⁴ indicating that the emitting state is different from the optically excited state. The value of $\Delta\bar{\alpha}$ determined from the E-PL spectra is much larger than that of the metal complex tris(8-hydroxyquinoline)aluminum (Alq_3), $\Delta\bar{\alpha}^- (=200 \text{ \AA}^3/f^2)$,¹⁴ but similar to the one of the OLED polymers,⁸ while the change in $|\Delta\mu|$ determined in the present study is similar to the ones of the metal complexes Alq_3 or $\text{Ru}(\text{ppy})_3$.^{14,15}

E-PL and PL spectra were also measured as a function of temperature from 40–295 K with a field of 1.0 MV cm^{-1} . On decreasing temperature, the PL spectrum becomes narrower, but the peak position remains unchanged (see Fig. S3 of Ref. 11). The vibronic bands observed at $\sim 540 \text{ nm}$ are well resolved at a low temperature of 40 K.^{16,17} E-PL spectra at 40 K show a similar trend as the one at 295 K for the field-induced quenching [Fig. 2(a)]. The magnitude of the quenching at 40 K, i.e., $1.26 \pm 0.05\%$, is nearly the same as that at 295 K, i.e., the field-induced quenching is essentially independent of the temperature. The molecular parameters $\Delta\bar{\alpha}$ and $|\Delta\mu|$ determined from E-PL/PL at a temperature of 40 K are $430 \pm 10 \text{ \AA}^3/f^2$ and $7.0 \pm 0.5 \text{ D}/f$, respectively. The difference in polarizability change $\Delta\bar{\alpha}_{295 \text{ K}} - \Delta\bar{\alpha}_{40 \text{ K}} = 250 \text{ \AA}^3/f^2$ may be due to the orientational polarizability

and $\Delta\bar{\alpha}_{40 \text{ K}} (=430 \text{ \AA}^3/f^2)$ may be purely molecular polarizability (rotational motion is restricted).⁷

The field-induced quenching of PL, i.e., Ph, of $\text{Ir}(\text{ppy})_3$ was further examined with the time resolved experiments.

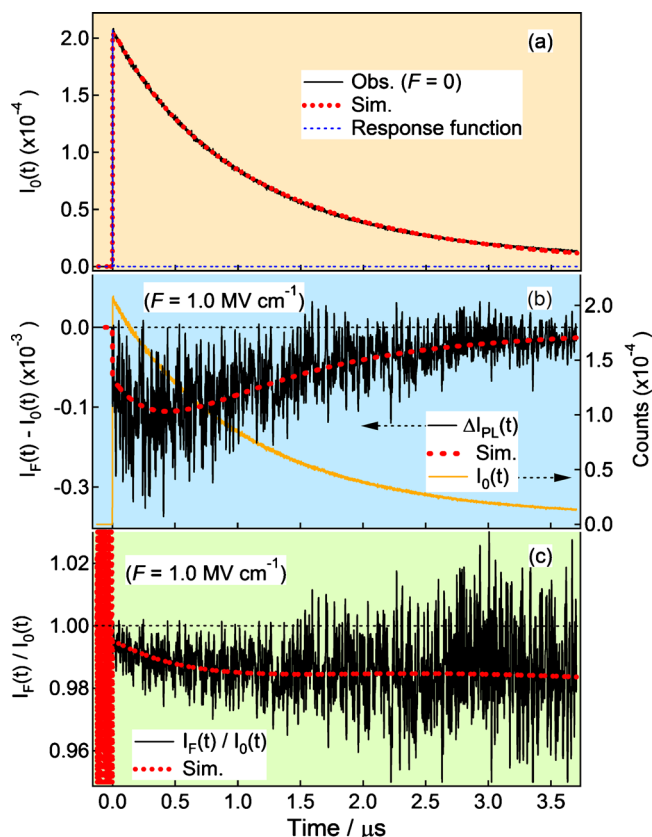


FIG. 3. (Color online) (a) PL decay of $\text{Ir}(\text{ppy})_3$ doped in a PMMA film (solid black line) observed at zero field at 295 K, simulated curve (dotted red line) and instrumental response function (dotted blue line). (b) The difference (solid black line) between the PL decays observed at 1.0 MV cm^{-1} and at zero field, the simulated difference (dotted red line) and the decay profile at zero field (solid yellow line). (c) The ratio of the decay observed at 1.0 MV cm^{-1} relative to that at zero field (solid line), and the simulated one (dotted red line). Excitation and emission wavelengths were 389 and 511 nm, respectively.

TABLE I. Lifetimes and pre-exponential factors of each component of the PL decay of Ir(ppy)₃ complex doped in a PMMA film at zero field and at 1.0 MV cm⁻¹; λ_{ex}=389 nm and λ_{em}=511 nm.

F (MV cm ⁻¹)	τ_1 (μ s)	τ_2 (μ s)	τ_{av} (μ s)
0	0.563 ± 0.003(0.283 ± 0.001)	1.460 ± 0.002(0.717 ± 0.002)	1.212 ± 0.005
1.0	0.541 ± 0.003(0.281 ± 0.001)	1.454 ± 0.002(0.714 ± 0.002)	1.196 ± 0.005

This was done by the measurement of four decay profiles, corresponding to positive, zero, negative and zero sample bias (Fig. 3).⁹ All the decay profiles were simulated by assuming a bi-exponential decay, i.e., $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, and lifetimes and pre-exponential factors were determined, as given in Table I (τ_1 and τ_2 are the lifetimes and A_1 and A_2 are the pre-exponential factors).

A single exponential decay with a lifetime of 1–2 μ s was observed in dilute solution.^{2,18,19} However, a faster non-exponential decay whose average lifetime (τ_{av}) is shorter by one order of magnitude than that in solution were observed in neat films.^{19–22} A single exponential decay with a lifetime between 48–56 ns was observed for neat Ir(ppy)₃ film in the presence of the electric field.⁶ The observed lifetimes agree with the ones in dilute solution (Table I).

The difference between two decay profiles, i.e., $I_F(t) - I_0(t) \cong \Delta I_{PL}(t)$ [Fig. 3(b)] as well as the integral of $\Delta I_{PL}(t)$ over the observation period are both negative, indicating that the field-induced quenching of PL occurs, which agrees with the E-PL spectra. The time profile of $\Delta I_{PL}(t)$ is different in shape from the decay profile of $I_F(t)$, indicating that the lifetime is influenced by the electric field. In fact, the lifetime becomes shorter in the presence of F .

If the initial population of the emitting state of PL is not affected by application of electric fields, the ratio $I_F(t)/I_0(t)$ would be unity at $t=0$. If the lifetime is independent of the field, $I_F(t)/I_0(t)$ would remain constant over the period. As shown in Fig. 3(c), the ratio is less than unity at $t=0$, indicating that the population of the emitting state decreased due to the presence of electric fields. With the passage of time, the ratio decreases, indicating that the lifetime becomes shorter in the presence of electric fields (Table I). Interestingly, this behavior is different from one reported so far,⁶ where the lifetime increased with application of electric fields up to 2 MV cm⁻¹ and decreased afterwards with further increasing field strength. As already reported so far,²³ the emitting state of Ir(ppy)₃ is not purely a triplet state but the PL originates from low lying spin-mixed metal-to-ligand charge transfer (CT) states; a charge-separated state is produced following photoexcitation. Then field-induced dissociation of the charge separated state i.e., migration of hole and/or electron takes place prior to their relaxation to the emitting state. The fact that the temperature did not affect the field-induced quenching implies that the quenching is independent of the vibrational relaxation.

Here, we have demonstrated that the electric-field-induced quenching of PL, has occurred in Ir(ppy)₃ doped in

a PMMA film. The quenching is independent of excitation energy and temperature. This has been attributed to decreased emitting state population and lifetime. Field-induced dissociation of $e-h$ pair might be the quenching mechanism because the electric field can increase the charge separation and slow down the $e-h$ recombination. Finally, we feel that the knowledge of field-induced quenching and the estimated fundamental parameters $\Delta\bar{\alpha}$ and $|\Delta\mu|$ of this phosphor is important for its applications in OLEDs.

M.S.M. thanks JSPS, Japan for a fellowship award (No. P07337) and Dr. T. Nakabayahshi and Dr. T. Iimori, RIES, Japan for their help in experiments, and Dr. H.C. Joshi, IPR, Gandhinagar, India for valuable comments. This work has been supported in part by a Grant-in-Aid for Scientific Research (Grant No. 20043005) from MEXT in Japan.

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¹¹See supplementary material at <http://dx.doi.org/10.1063/1.3582916> for Figs. S1, S2, and S3.

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