

Energy-transfer dynamics of blue-phosphorescent iridium and rhodium complexes doped in fluorescent molecules

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Abstract — The temperature-dependent photoluminescence features of polycarbonate thin films doped with blue-phosphorescent molecules, either bis[(4,6-difluorophenyl)-pyridinato- $N,C2'$] (picolinate) iridium (Flrpic) or bis(2-phenylpyridinato- $N,C2'$) (acetylacetonate) rhodium [(ppy)₂Rh(acac)], which have an equivalent triplet energy of 2.64 eV, have been studied. The photoluminescence intensity of the Flrpic-doped polycarbonate thin film did not show any dependence on temperature. On the other hand, as for the (ppy)₂Rh(acac)-doped polycarbonate thin film, decreasing photoluminescence intensity with increasing temperature (especially above 100K) was clearly visible. These results reflect that the internal heavy-atom effect of (ppy)₂Rh(acac) is weaker than that of Flrpic. Furthermore, the steady-state and time-resolved photoluminescence spectra of tris(8-hydroxyquinoline) aluminum (Alq₃) thin films heavily doped with Flrpic or (ppy)₂Rh(acac) (50 wt.%) at 8K was studied. It was found that the enhanced phosphorescence from Alq₃ is mainly due not to the external heavy-atom effect by doping with the phosphorescent molecule but to the exothermic triplet energy transfer from the phosphorescent molecule to Alq₃.

Keywords — Organic light-emitting device, photoluminescence, phosphorescence, heavy-ion effect, Forster energy transfer, Dexter energy transfer, iridium, rhodium.

1 Introduction

The strong spin-orbit coupling induced by heavy atoms (*i.e.*, atoms of large atomic number) allows for fast and efficient intersystem crossing (ISC) from the singlet states to the triplet ones, known as the heavy-atom effect.¹ Using heavy-metal complexes as the triplet emitter has dramatically improved the emission efficiency of organic light-emitting devices (OLEDs).² A large number of studies have been carried out on phosphorescent OLEDs since the first report by Baldo *et al.*³ In particular, cyclometalated iridium complexes such as *fac* tris(2-phenylpyridine) iridium [Ir(ppy)₃] are promising candidates for phosphorescent dopants⁴ because they exhibit highly efficient emission from the triplet metal-to-ligand charge-transfer (³MLCT) states even at room temperature.^{5–8} According to the recent theoretical study by Nozaki,⁹ the phosphorescent states of Ir(ppy)₃ have been characterized by a mixture of 40% ³MLCT and 58% intra- and inter-ligand ³ π – π^* with charge distribution being partially localized to a single ligand. From the viewpoint of OLED performance, the studies on the energy-transfer and light-emission mechanisms in heavy-metal complexes other than platinum or iridium complexes have been superficial.

In our previous study, we demonstrated that the phosphorescence emission from fluorescent molecules used for OLEDs, tris(8-hydroxyquinoline) aluminum (Alq₃)^{10,11} and

bis(2-methyl-8-quinolino)-4-phenylphenolate aluminum (BALq)¹² is drastically enhanced by doping with the phosphorescent molecule, Ir(ppy)₃. Moreover, we found that the lowest triplet-excited (T₁) states of Alq₃ and BALq locate at 0.4 and 0.2 eV lower energy than the T₁ states of Ir(ppy)₃, respectively. The triplet energies of Alq₃ and BALq were evaluated to be 2.03 and 2.18 eV, respectively. The host ISC rate is usually assumed as a constant even when the metal complexes are doped into the organic semiconductor host. This is because the host excitons are separated from the metal ion by the ligands. We concluded that the exothermic triplet energy transfers from the phosphorescent molecule [Ir(ppy)₃] to the fluorescent one (Alq₃ and BALq) result in the phosphorescence enhancement.^{10–12} Another possible origin of the enhancement is attributed to the external heavy-atom effect by Ir(ppy)₃ doping. Very recently, Liao *et al.* reported photo-induced absorption measurements that show the ISC rate of polyfluorene is made remarkably efficient by doping with tris[2-(4-tolyl)phenylpyridine] iridium [Ir(mppy)₃].¹³ To understand the enhanced-phosphorescence origin and the mechanism more precisely, further studies of photoluminescence (PL) properties of the fluorescent molecules doped with phosphorescent molecules (which have core metals with various atomic numbers and triplet energies) are needed.

In our present work, we studied the steady-state (CW) PL properties of blue phosphorescent molecules, namely,

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bis[(4,6-difluorophenyl)-pyridinato-N,C^{2'}] (picolate) iridium (FIrpic) and bis(2-phenylpyridinato-N,C^{2'}) (acetylacetonate) rhodium [(ppy)₂Rh(acac)], doped in polycarbonate (PC) over the wide temperature range from 8 to 295 K. PC is a stable and optically non-activated host polymer with a high triplet energy of about 2.9 eV.¹⁴ The atomic number of the core metal of FIrpic, iridium (⁷⁷Ir), is much larger than that of (ppy)₂Rh(acac), rhodium (⁴⁵Rh). This indicates that the internal heavy-atom effect of (ppy)₂Rh(acac) is weaker than that of FIrpic, which reflects the difference in the temperature-dependent PL behaviors. In contrast, the triplet energies of FIrpic and (ppy)₂Rh(acac) have been equivalent and have been estimated to be 2.64 eV from the highest energy peak of the phosphorescence emission. To confirm whether the enhanced phosphorescence from the fluorescent molecule by doping with the phosphorescent molecule which have the higher triplet energy is due to the energy transfers or the external heavy-atom effect, we characterized the transient PL properties of the Alq₃ thin films doped with a blue phosphorescent molecule, either FIrpic or (ppy)₂Rh(acac).

2 Experimental

The chemical structures of the phosphorescent-guest and fluorescent-host molecules used in this study are shown in Fig. 1. PC-based thin films were spin-coated from chloroform solutions containing FIrpic or (ppy)₂Rh(acac) and PC onto a pre-cleaned quartz substrate (with an area of 20 × 20 mm and a thickness of 0.5 mm) in a nitrogen atmosphere. Alq₃-based thin films were deposited by high-vacuum thermal evaporation onto the pre-cleaned quartz substrate. The thicknesses of the prepared PC- and Alq₃-based thin films were 100 and 50 nm, respectively. Since the phosphores-

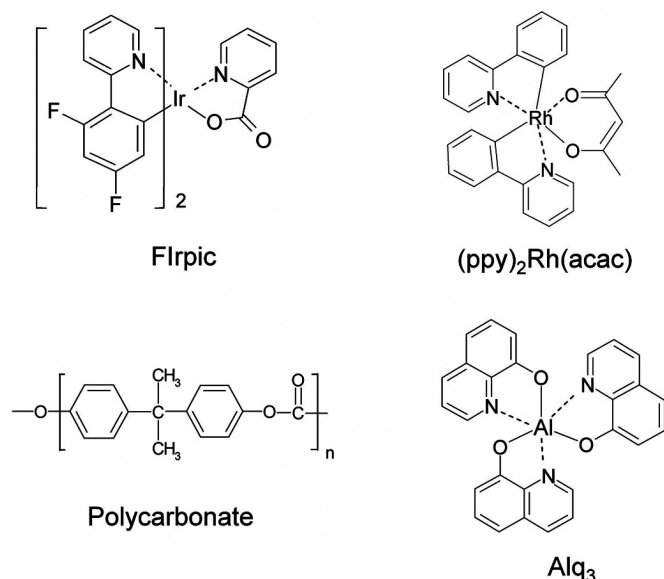


FIGURE 1 — Chemical structures of the phosphorescent-guest and fluorescent-host molecules used in this study.

cence emission is affected by oxygen, the thin films used for the PL characteristics were encapsulated in a nitrogen atmosphere by using a glass cap with ultraviolet-epoxy adhesive.

The samples were held in a contact-type cryostat (Daikin Industries, UV202CLS). The sample temperature was adjusted from 8 to 295 K. The photo-excitation was done with a diode-pumped passively Q-switched neodymium-doped yttrium–aluminum garnet laser (Crystal GmbH, FTSS355-Q) with a wavelength of 355 nm. For the cw PL measurements, the typical power density at the sample's surface was about 1 W/cm². For the time-resolved PL measurements, the power density was about 0.1 mJ/cm², and the pulse width was about 1 nsec. A nitrogen laser (Laser Photonics, LN120C) with a wavelength of 337 nm and a pulse width of 300 psec was used for the transient PL measurements at a delay time less than 200 nsec. The CW and time-resolved phosphorescence spectra were obtained, respectively, by using a photomultiplier tube (Hamamatsu Photonics, R955) and a streak camera (Hamamatsu Photonics, C4334) through a monochromator. The absorption spectra at room temperature were measured with a Shimadzu UV-3100 spectrometer.

3 Results and discussion

3.1 Phosphorescence properties of FIrpic and (ppy)₂Rh(acac)

The PL spectra of a 5-wt.-%-FIrpic-doped PC [PC:FIrpic(5 wt. %)] thin film at 8, 150, and 295 K are shown in Fig. 2. The PC:FIrpic thin film exhibited blue emission with a peak at

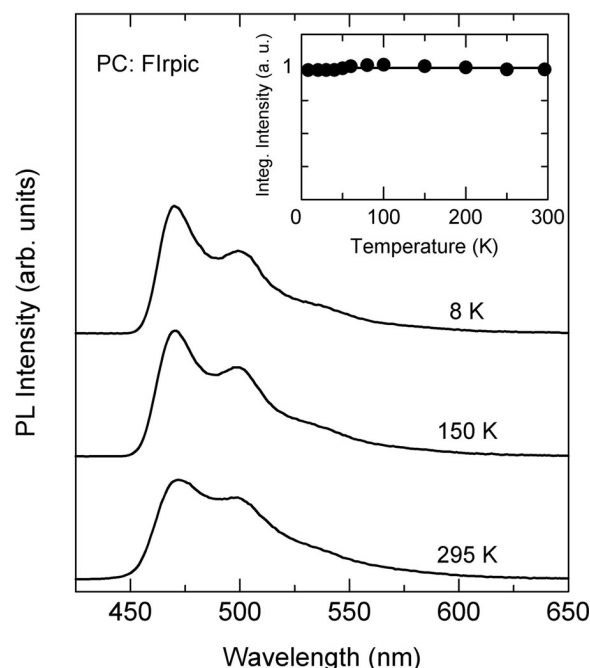


FIGURE 2 — Photoluminescence spectra of a PC:FIrpic (5 wt.%) thin film at 8, 150, and 295 K. The inset shows the temperature dependence of the integrated intensity.

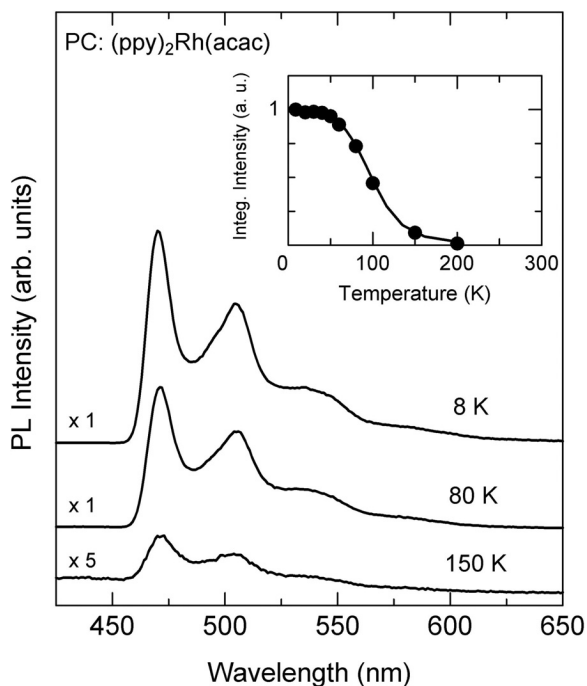


FIGURE 3 — Photoluminescence spectra of a PC:(ppy)₂Rh(acac) (5 wt.%) thin film at 8, 80, and 150 K. The inset shows the temperature dependence of the integrated intensity.

470 nm. This emission is assigned to the phosphorescence due to the ³MLCT transition of FIrpic.^{15–17} The triplet energy of FIrpic was estimated to be 2.64 eV from the highest energy peak of the phosphorescence emission. The peak intensity at 8 K was 80% that at 295 K. The PL spectrum became broader with increasing temperature. As shown in the inset of Fig. 2, similar to the results for CBP:Ir(ppy)₃^{18,19} and PC:Ir(ppy)₃,²⁰ the integrated PL intensity did not show any dependence on temperature. The independence of PL intensity on temperature results not only from the strong spin-orbit coupling due to the heavy atom (Ir) but also from the excellent confinement of the triplet energy on the FIrpic guest in the PC host. The above-mentioned PL results are consistent with the PL quantum yield of approximately 100% reported by Kawamura *et al.*¹⁷

Figure 3 shows the PL spectra of the PC:(ppy)₂Rh(acac) (5 wt.%) thin film at 8, 80, and 150 K. The PC:(ppy)₂Rh(acac) thin film exhibited blue emissions with four peaks (at 470, 505, 545, and 585 nm) with vibronic fine structures. The lifetimes of these emissions were evaluated to be 43 μsec at 8 K. From the vibronic line shape²¹ and the relatively long lifetime, we believed that this emission is the phosphorescence due to the transitions from the ³π–π* ligand states. The ³π–π* transition in (ppy)₂Rh(acac) is similar to that in Rh(ppy)₃ reported by Colombo *et al.*⁶ The triplet energy of (ppy)₂Rh(acac) was estimated to be 2.64 eV from the highest energy peak, and this value is in good agreement with that for the above-discussed FIrpic. As shown in the inset of Fig. 3, decreasing PL intensity with increasing temperature (especially above 100 K) is clearly visible. Unfortunately, the PL emission could not be observed at room temperature,

indicating that the phosphorescence quantum yield of (ppy)₂Rh(acac) is negligible at room temperature. The PL properties of the PC:(ppy)₂Rh(acac) thin film are quite different from those of the PC:FIrpic thin film, reflecting that the internal heavy-atom effect of (ppy)₂Rh(acac) is weaker than that of FIrpic.

3.2 Energy transfers between FIrpic or (ppy)₂Rh(acac) and Alq₃

The CW and time-resolved PL spectra of the Alq₃ thin films heavily doped with FIrpic and (ppy)₂Rh(acac) at 50 wt.% at 8 K are shown in Fig. 4. For comparison, the CW-PL spectrum of the Alq₃:Ir(ppy)₃ (50 wt.%) thin film,^{10,11} where the triplet energy of Ir(ppy)₃ is 2.42 eV, is also shown by the broken line. The broad emission of the Alq₃:Ir(ppy)₃ (50 wt.%) thin film in the wavelength range above 600 nm is due to the phosphorescence from Alq₃. In our previous works,^{10,11} we demonstrated that Ir(ppy)₃ plays an important role as a phosphorescent sensitizer for Alq₃. Focusing on the CW PL spectra (top of Fig. 4) and the time-resolved PL spectra without delay (middle of Fig. 4), it is clear that in the Alq₃:FIrpic and Alq₃:(ppy)₂Rh(acac) thin films the green fluorescence emissions from Alq₃ are observed at around 520 nm. In the 50-μsec delayed PL spectra with 150-μsec gate width corresponding to 50–200-μsec integrated spectra (bottom of Fig. 4) for the both thin films, the main green emissions and the weakly overlapped emissions indi-

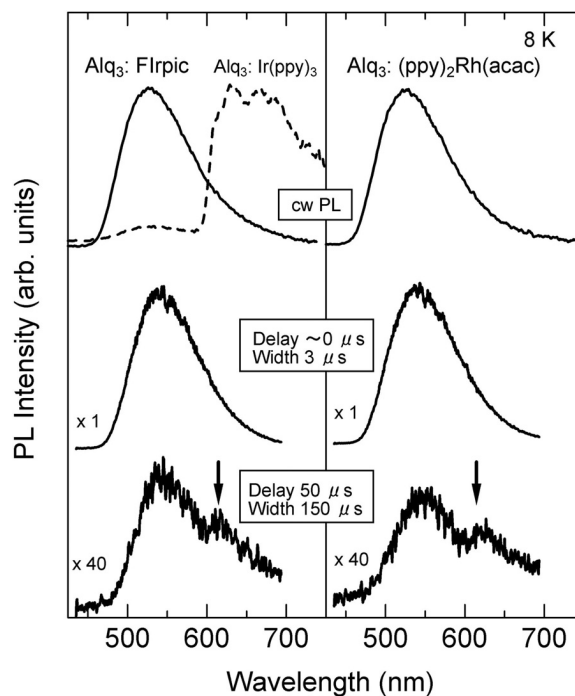


FIGURE 4 — Steady-state and time-resolved PL spectra of Alq₃:FIrpic (50 wt.%) and Alq₃:(ppy)₂Rh(acac) (50 wt.%) thin films at 8 K. The arrows indicate the enhanced phosphorescence emission from Alq₃. For comparison, the PL spectrum of a Alq₃:Ir(ppy)₃ (50 wt.%) thin film is shown by the broken line.

cated by the arrows are observed. The former delayed green emissions are due to the so-called “P-type” delayed fluorescence from Alq₃. The delayed fluorescence occurs as a result of the annihilation of two triplet excitons, namely, triplet–triplet (T–T) annihilation and is therefore a bimolecular process.²² The latter weak red emissions at around 610 nm show a long lifetime in the order of milliseconds. It is concluded from the spectral line shape and the long lifetime that the red emissions are due to the phosphorescence from Alq₃. The enhancement of the Alq₃ phosphorescence by FIrpic doping is similar to that by (ppy)₂Rh(acac) doping in spite of the difference in the heavy-atom effects of the two complexes. However, it should be noted in the top of Fig. 4 that the degree of enhancement by doping with the blue-phosphorescent complex, either FIrpic or (ppy)₂Rh(acac) (triplet energy, $E_T = 2.64$ eV), is much less than that by doping with Ir(ppy)₃ ($E_T = 2.42$ eV). This suggests that the phosphorescence enhancement in the Alq₃:FIrpic and Alq₃:(ppy)₂Rh(acac) thin films with the doping concentrations of 50 wt.% is not attributed to the external heavy-atom effect by doping with a heavy-metal complex.

The absorption and PL spectra of Alq₃, FIrpic, and (ppy)₂Rh(acac) are shown in Fig. 5. The measurements were carried out at 295K, except for the PL spectrum of (ppy)₂Rh(acac) at 8K. A chloroform solution was used for the absorption measurements. The deposited thin film (Alq₃) and the PC-based thin films [FIrpic and (ppy)₂Rh(acac)] were used for the PL measurements. Figure 5 shows that the spectral overlap between the absorption band of the blue-phosphorescent molecule and the PL band of Alq₃ and that between the absorption band of Alq₃ and the PL band

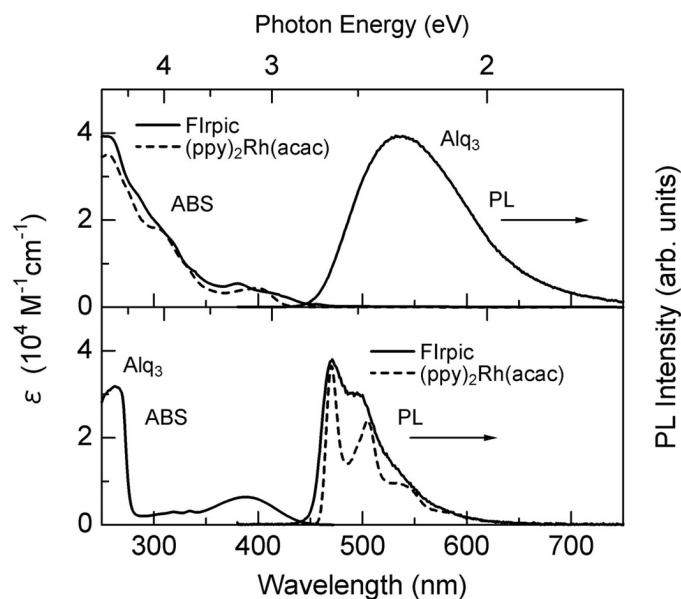


FIGURE 5 — Absorption and PL spectra of Alq₃, FIrpic, and (ppy)₂Rh(acac) at 295K, except for the PL spectrum of (ppy)₂Rh(acac) at 8K. A chloroform solution was used for the absorption measurements. The deposited Alq₃ thin film and the PC-based thin films [FIrpic and (ppy)₂Rh(acac)] were used for the PL measurements.

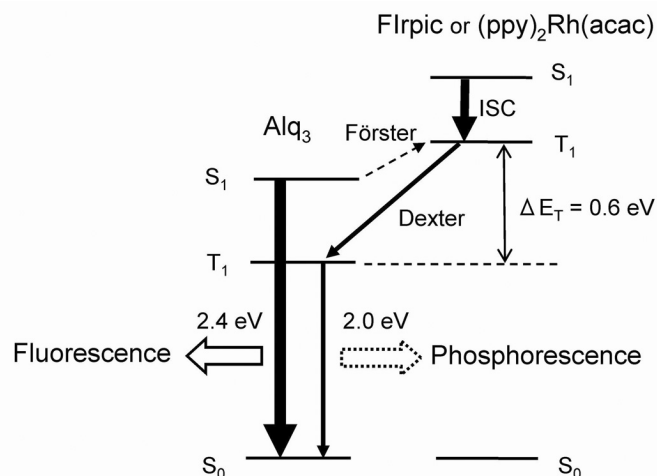


FIGURE 6 — Schematic energy-level alignment of singlet-excited state (S_1), triplet-excited states (T_1), and singlet-ground states (S_0) in Alq₃ and FIrpic, and (ppy)₂Rh(acac). The energy-transfer and light-emission processes are shown by the arrows.

of the blue-phosphorescent molecule are extremely small. This result indicates that Förster energy transfers²³ by dipole–dipole coupling in both the Alq₃:FIrpic and Alq₃:(ppy)₂Rh(acac) systems are not efficient.

The energy-transfer and light-emission mechanisms are discussed hereafter. Figure 6 shows the schematic energy-level alignment of the lowest singlet-excited (S_1) states, the T_1 states, and the singlet-ground (S_0) states in Alq₃, FIrpic, and (ppy)₂Rh(acac). After photoexcitation, both the S_1 states in Alq₃ and the S_1 states in FIrpic or (ppy)₂Rh(acac) are generated. The prompt fluorescence emission from Alq₃ consequently occurs. Moreover, as discussed above, delayed fluorescence with a longer lifetime should be considered. For FIrpic and (ppy)₂Rh(acac), the rapid ISC from the S_1 states to the T_1 states might occur because of strong spin-orbit coupling. The phosphorescence emissions from FIrpic and (ppy)₂Rh(acac) were not observed in the Alq₃:FIrpic (50 wt.%) and Alq₃:(ppy)₂Rh(acac) (50 wt.%) thin films, indicating faster energy transfer from the T_1 states in FIrpic or (ppy)₂Rh(acac) to the T_1 states in Alq₃. In addition, the concentration quenching due to the highly doping with FIrpic and (ppy)₂Rh(acac) might be considered.^{17,24} This exothermic triplet energy transfer is ascribed to the short-range process of Dexter energy transfer,²⁵ which requires an overlap of the molecular orbital of adjacent molecules. It is noted that the triplet-energy difference (ΔE_T) between FIrpic or (ppy)₂Rh(acac) and Alq₃ is 0.6 eV, which is 1.5 times larger than that between Ir(ppy)₃ and Alq₃. The rate of Dexter energy transfer depends not only on the donor–acceptor distance but also on spectral overlap between donor emission and acceptor absorption.²⁵ The smaller enhancement of the phosphorescence from Alq₃ in the Alq₃:FIrpic and Alq₃:(ppy)₂Rh(acac) thin films is attributed to the smaller spectral overlap due to the large ΔE_T .

Finally, we discuss the energy-dissipative processes from the S_1 states in Alq₃. Figure 7 shows the decay profiles detected at the prompt fluorescence peaks (520 nm) of the

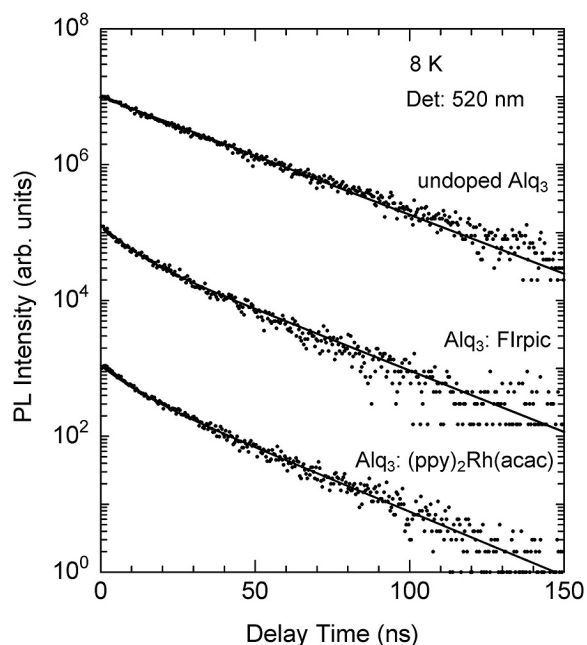


FIGURE 7 — Decay profiles detected at the prompt fluorescence peaks (520 nm) of the Alq₃, Alq₃:FIrpic (50 wt.%), and Alq₃:(ppy)₂Rh(acac) (50 wt.%) thin films at 8K.

Alq₃, Alq₃:FIrpic (50 wt.%), and Alq₃:(ppy)₂Rh(acac) (50 wt.%) thin films at 8K. The observed delay-time range is less than 150 nsec, which indicates that the delayed fluorescence with a long lifetime is out of range in Fig. 7. The undoped Alq₃ thin film exhibits a mono-exponential decay profile, and its lifetime is estimated to be 25 nsec. On the other hand, the PL decay profiles of the Alq₃:FIrpic and Alq₃:(ppy)₂Rh(acac) thin films were fitted by a double-exponential model:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \quad (1)$$

where τ_1 and τ_2 are decay times. The fitted PL-decay times are listed in Table 1. Remarkable change of decay profiles was not observed by doping with FIrpic and (ppy)₂Rh(acac). Furthermore, the Alq₃:FIrpic and Alq₃:(ppy)₂Rh(acac) thin films showed nearly identical decay profiles. The slight change of decay profiles by doping might be due to the weak Förster energy transfer from the S₁ states in Alq₃ to the T₁ states in FIrpic or

TABLE 1 — Photoluminescence-decay times detected at the prompt fluorescence peak (520 nm) of Alq₃, Alq₃:FIrpic (50 wt.%), and Alq₃:(ppy)₂Rh(acac) (50 wt.%) thin films at 8K. The decay times are estimated on the basis of the double-exponential model expressed by Eq. (1).

	τ_1 (nsec)	τ_2 (nsec)
Alq ₃	—	25
Alq ₃ :FIrpic	7	24
Alq ₃ :(ppy) ₂ Rh(acac)	8	23

(ppy)₂Rh(acac), which is indicated by the broken arrow in Fig. 6. Although the S₁ → T₁ transition is naturally forbidden, the strong spin-orbit coupling of the phosphorescent molecule might allow the energy transfer from the S₁ states in Alq₃ to the T₁ states in the phosphorescent molecule. In our previous study,¹⁰ we reported the remarkable shortening of the fluorescence lifetime of Alq₃ by Ir(ppy)₃ doping; *i.e.*, from 25 nsec (for the undoped Alq₃) to 4 nsec [for the Alq₃:Ir(ppy)₃ (50 wt.%)]. These decay profiles indicate that the energy transfer from the S₁ states in Alq₃ to the T₁ states in the phosphorescent molecule for both the Alq₃:FIrpic and Alq₃:(ppy)₂Rh(acac) thin films is not as efficient as that for the Alq₃:Ir(ppy)₃ thin film. Therefore, the reason for the smaller enhancement of phosphorescence than that in the Alq₃:Ir(ppy)₃ thin film is due to the weaker energy transfer of the T₁[FIrpic or (ppy)₂Rh(acac)] → T₁(Alq₃) and T₁(Alq₃) → S₁[FIrpic or (ppy)₂Rh(acac)] transitions. These transient PL properties suggest that in the phosphorescent molecule doped Alq₃ system with the doping concentration less than 50 wt.% the enhancement of phosphorescence is mainly due to the exothermic triplet energy transfer from the phosphorescent molecule to Alq₃.

4 Summary

We have measured the PL spectra of the PC:FIrpic (5 wt.%) and PC:(ppy)₂Rh(acac) (5 wt.%) thin films, where FIrpic and (ppy)₂Rh(acac) have an equivalent triplet energy of 2.64 eV, over the wide temperature range 8–295K. The integrated PL intensity of the PC:FIrpic thin film did not show any dependence on temperature. On the other hand, for the PC:(ppy)₂Rh(acac) thin film, decreasing PL intensity with increasing temperature (especially above 100K) was clearly visible. This difference in the PL properties reflects that the internal heavy-metal effect of (ppy)₂Rh(acac) is weaker than that of FIrpic. Furthermore, to study the origin of the enhanced phosphorescence from fluorescent Alq₃ by doping with the phosphorescent molecule, the PL properties of the Alq₃:FIrpic (50 wt.%) and Alq₃:(ppy)₂Rh(acac) (50 wt.%) thin films were characterized. Subsequently, it was concluded from the CW and time-resolved PL results that the enhancement of phosphorescence in the case of the doping concentration less than 50 wt.% is mainly due not to the external heavy-metal effects by doping with the phosphorescent molecule but to the exothermic triplet energy transfer from phosphorescent molecules to Alq₃. This finding will be helpful in the development of new phosphorescent guest molecules and host molecules and in understanding of device tailoring for highly efficient phosphorescent OLEDs.

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