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,C′] (picolinate) iridium (FIrpic) or bis(2-phenylpyridinato-N,C′) (acetylacetonate) rhodium [(ppy)2Rh(acac)], which have an equivalent triplet energy of 2.64 eV, have been studied. The photoluminescence intensity of the FIrpic-doped polycarbonate thin film did not show any dependence on temperature. On the other hand, 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 FIrpic. Furthermore, the steady-state and time-resolved photoluminescence spectra of tris(8-hydroxyquinoline) aluminum (Alq3) thin films heavily doped with FIrpic or (ppy)2Rh(acac) (50 wt.%) at 8K was studied. It was found that the enhanced phosphorescence from Alq3 is mainly due 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 3π–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-quinolinato)-4-phenylphenolate aluminum (BAIq)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 BAIq 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 BAIq 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 BAIq) 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,
bis[(4,6-difluorophenyl)-pyridinato-N,C\textsubscript{2}] (picolinate) iridium (FIrpic) and bis(2-phenylpyridinato-N,C\textsubscript{2}) (acetylacetone) rhodium [(ppy)\textsubscript{2}Rh(acac)], doped in polycarbonate (PC) over the wide temperature range from 8 to 295K. PC is a stable and optically non-activated host polymer with a high triplet energy of about 2.9 eV.\textsuperscript{14} The atomic number of the core metal of FIrpic, iridium (77Ir), is much larger than that of (ppy)\textsubscript{2}Rh(acac), rhodium (45Rh). This indicates that the internal heavy-atom effect of (ppy)\textsubscript{2}Rh(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)\textsubscript{2}Rh(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 Alq\textsubscript{3} thin films doped with a blue phosphorescent molecule, either FIrpic or (ppy)\textsubscript{2}Rh(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)\textsubscript{2}Rh(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. Alq\textsubscript{3}-based thin films were deposited by high-vacuum thermal evaporation onto the pre-cleaned quartz substrate. The thicknesses of the prepared PC- and Alq\textsubscript{3}-based thin films were 100 and 50 nm, respectively. Since the phosphorescence 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 295K. 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/cm\textsuperscript{2}. For the time-resolved PL measurements, the power density was about 0.1 mJ/cm\textsuperscript{2}, 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)\textsubscript{2}Rh(acac)

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

![FIGURE 1 — Chemical structures of the phosphorescent-guest and fluorescent-host molecules used in this study.](image1)

![FIGURE 2 — Photoluminescence spectra of a PC:FIrpic (5 wt.%) thin film at 8, 150, and 295K. The inset shows the temperature dependence of the integrated intensity.](image2)
470 nm. This emission is assigned to the phosphorescence due to the $^3\text{MLCT}$ transition of FIrpic.\textsuperscript{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 8K was 80% that at 295K. The PL spectrum became broader with increasing temperature. As shown in the inset of Fig. 2, similar to the results for CBP:Ir(ppy)$_3$\textsuperscript{18,19} and PC:Ir(ppy)$_3$\textsuperscript{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.\textsuperscript{17}

Figure 3 shows the PL spectra of the PC:(ppy)$_2$Rh(acac) (5 wt.%) thin film at 8, 80, and 150K. The PC:(ppy)$_2$Rh(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 $\mu$s at 8K. From the vibronic line shape\textsuperscript{21} and the relatively long lifetime, we believed that this emission is the phosphorescence due to the transitions from the $^3\pi-\pi^*$ ligand states. The $^3\pi-\pi^*$ transition in (ppy)$_2$Rh(acac) is similar to that in Rh(ppy)$_3$ reported by Colombo et al.\textsuperscript{6} The triplet energy of (ppy)$_2$Rh(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 100K) is clearly visible. Unfortunately, the PL emission could not be observed at room temperature, indicating that the phosphorescence quantum yield of (ppy)$_2$Rh(acac) is negligible at room temperature. The PL properties of the PC:(ppy)$_2$Rh(acac) thin film are quite different from those of the PC:FIrpic thin film, reflecting that the internal heavy-atom effect of (ppy)$_2$Rh(acac) is weaker than that of FIrpic.

### 3.2 Energy transfers between FIrpic or (ppy)$_2$Rh(acac) and Alq$_3$

The CW and time-resolved PL spectra of the Alq$_3$ thin films heavily doped with FIrpic and (ppy)$_2$Rh(acac) at 50 wt.% at 8K are shown in Fig. 4. For comparison, the CW-PL spectrum of the Alq$_3$:Ir(ppy)$_3$(50 wt.%) thin film,\textsuperscript{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 Alq$_3$:Ir(ppy)$_3$ (50 wt.%) thin film in the wavelength range above 600 nm is due to the phosphorescence from Alq$_3$. In our previous works,\textsuperscript{10,11} we demonstrated that Ir(ppy)$_3$ plays an important role as a phosphorescent sensitizer for Alq$_3$. 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 Alq$_3$:FIrpic and Alq$_3$: (ppy)$_2$Rh(acac) thin films the green fluorescence emissions from Alq$_3$ are observed at around 520 nm. In the 50-$\mu$s delayed PL spectra with 150-$\mu$s gate width corresponding to 50–200-$\mu$s integrated spectra (bottom of Fig. 4) for the both thin films, the main green emissions and the weakly overlapped emissions indi-
ated 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 Alq$_3$:FIrpic and Alq$_3$: (ppy)$_2$Rh(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)$_2$Rh(acac) are shown in Fig. 5. The measurements were carried out at 295K, except for the PL spectrum of (ppy)$_2$Rh(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)$_2$Rh(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 of the blue-phosphorescent molecule are extremely small. This result indicates that Förster energy transfers$^{23}$ by dipole–dipole coupling in both the Alq$_3$:FIrpic and Alq$_3$: (ppy)$_2$Rh(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 ($S_1$), triplet-excited states ($T_1$), and singlet-ground states ($S_0$) in Alq3, FIrpic, and (ppy)$_2$Rh(acac). After photoexcitation, both the $S_1$ states in Alq3 and the $S_1$ states in FIrpic or (ppy)$_2$Rh(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)$_2$Rh(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)$_2$Rh(acac) were not observed in the Alq$_3$:FIrpic and Alq$_3$: (ppy)$_2$Rh(acac) thin films, indicating faster energy transfer from the $T_1$ states in FIrpic or (ppy)$_2$Rh(acac) to the $T_1$ states in Alq3. In addition, the concentration quenching due to the highly doping with FIrpic and (ppy)$_2$Rh(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 ($\Delta E_T$) between FIrpic or (ppy)$_2$Rh(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 Alq$_3$:FIrpic and Alq$_3$: (ppy)$_2$Rh(acac) thin films is attributed to the smaller spectral overlap due to the large $\Delta E_T$.

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
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:

\[ I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \]

where \( \tau_1 \) and \( \tau_2 \) are decay times. The fitted PL decay times are listed in Table I. 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 \( S_1 \) states in Alq3 to the \( T_1 \) states in FIrpic or (ppy)2Rh(acac), which is indicated by the broken arrow in Fig. 6. Although the \( S_1 \rightarrow T_1 \) transition is naturally forbidden, the strong spin-orbit coupling of the phosphorescent molecule might allow the energy transfer from the \( S_1 \) states in Alq3 to the \( T_1 \) states in the phosphorescent molecule. In our previous study, 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 \( S_1 \) states in Alq3 to the \( T_1 \) 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 in the Alq3:Ir(ppy)3 thin film is due to the weaker energy transfer of the \( T_1(FIrpic \text{ or (ppy)}_2\text{Rh(acac)}) \rightarrow T_1(Alq3) \text{ and } T_1(Alq3) \rightarrow S_1(FIrpic \text{ or (ppy)}_2\text{Rh(acac)}) \) 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.

### 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 phosphorescent molecules, 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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References


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