

Phosphorescence Properties of Ir(ppy)₃ Films

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The pioneering investigations by Thompson and Forrest introduced *fac*-tris(2-phenyl pyridine)iridium (Ir(ppy)₃) as a highly efficient phosphorescent material because the green emission of Ir(ppy)₃ takes advantage of both electrically generated singlet and triplet excitons.^{1,2} The luminescence efficiency can be increased to a quantum yield of up to ~100%,¹⁻⁶ which suggests emission-related applications. In general, emission from triplet to singlet states is forbidden but the electrons of Ir(III) can induce a quantum mechanical effect, such as spin-orbit coupling, and allow a phosphorescent transition.¹⁻⁶ In this regard, most studies have focused on monomeric Ir(ppy)₃ in dilute solution (1×10^{-5} M) or thin films with a low doping ratio (< 1 wt%), whereas there is little information on the intermolecular interactions of Ir(ppy)₃ molecules.^{2,3} This Note reports the luminescent properties of neat Ir(ppy)₃ films investigated by temperature- and time-dependent spectroscopy. Three triplet substates were found to be responsible for the phosphorescence. Moreover, energy transfer between Ir(ppy)₃ molecules was observed due to the physical proximity in neat films.

The photoluminescence (PL) spectrum of a typical neat Ir(ppy)₃ film at 300 K is shown in Figure 1(a). The emission peak was observed at 509 nm, which is similar to the phosphorescence of Ir(ppy)₃ in solution,^{4,6} suggesting that the triplet states are the emitting states, even in the neat film. The quantum yield is related to the strength of spin-orbit coupling because the phosphorescence is allowed due to the influence of spin-orbit coupling induced by the heavy center ion, Ir(III). In other words, the triplet state with a large extent of metal-to-ligand charge-transfer (MLCT) state, which involves the 5d orbitals of Ir(III) (the highest occupied molecular orbitals, HOMOs) and the π^* orbitals of 2-phenylpyridine (the lowest unoccupied molecular orbitals, LUMOs),⁴ would show efficient phosphorescence. The contribution of the MLCT character can be estimated by several ways. One of them is the magnitude of zero-field splitting because it is determined by the strength of spin-orbit coupling. The triplet states of Ir(ppy)₃ have a zero-field splitting value of 170 cm^{-1} in the CH₂Cl₂ solution,⁴ suggesting a large MLCT character. The rigidochromism of the emitting states is another explanation. A blue-shift of emission was observed for a transition of the MLCT state in a rigid condition^{5,7} because a charge-transfer transition state was

less relaxed by dipolar interactions of the solvents in the rigid condition. An emission peak in the neat film was observed at 509 nm, which was blue-shifted by ~10 nm compared to that in the CH₂Cl₂ solution,⁴ indicating the MLCT character in the emitting triplet states of the neat Ir(ppy)₃ film. The MLCT character was also distinguished by a broad and unstructured spectral shape of the phosphorescence spectrum,⁷⁻⁹ whereas the ligand-centered (LC) transitions exhibited vibronic fine structures.⁷⁻¹⁰ The PL spectrum at 300 K revealed another band at 537 nm. The energy of this band was ~1000 cm^{-1} lower than the peak at 509 nm, suggesting some overlap of the vibrational satellites.

The PL spectrum of the Ir(ppy)₃ film was obtained at 10 K because the vibronic fine structure was expected to be more resolved at low temperatures by the suppression of the thermal population of high-lying vibrational levels.^{10,11} However, the expected fine structure was not observed at 10 K. Instead, a drastic change in the spectral shape was observed, suggesting that the emitting triplet state was not a single state but more than two states, which were occupied differently as a function of temperature. In crystalline form, Ir(ppy)₃ has C₃ symmetry, which is usually lowered in an amorphous film. Therefore, the lowest triplet states of Ir(ppy)₃ related to a ³A term are split into three triplet substates by spin-orbit coupling. The zero-field splitting between the lowest substate (I) and the highest substate (III) was 170 cm^{-1} in the CH₂Cl₂ solution and 125 cm^{-1} in poly(methyl methacrylate) (PMMA).⁴ The transition from substate I holds the smallest transition dipole moment among three substates because it has the largest energy separation from higher-lying singlet states and thus the smallest coupling with the singlet states, such as the ¹MLCT state. The second lowest substate II lies above substate I, e.g., by 12 cm^{-1} in PMMA, which has a 10 times larger transition dipole moment than substate I.⁴ The highest substate III, which lies 125 cm^{-1} above substate I, has a 500 times larger transition dipole moment than substate I because the small energy separation from the singlet states induces large coupling.

When the zero-field splitting in neat amorphous films is assumed to be similar to that in PMMA, the thermal population of the three substates is I = 40%, II = 38%, and III = 22% at 300 K according to the Boltzmann distribution.

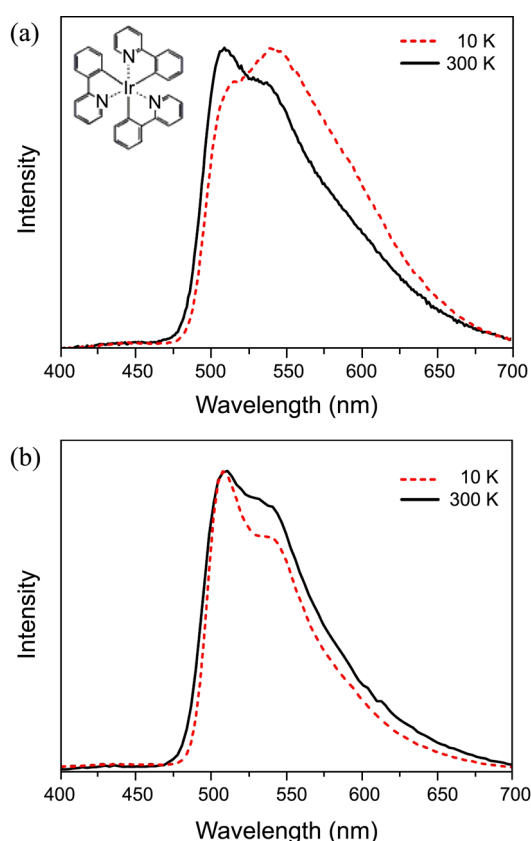


Figure 1. (a) Time-integrated photoluminescence spectra of a neat Ir(ppy)₃ film at room temperature (300 K) and a low temperature (10 K). The peak wavelength of 509 nm was observed at 300 K, whereas a shoulder peak of 512 nm was observed at 10 K. The intensities were normalized for comparison. The inset shows the chemical structure of Ir(ppy)₃. (b) Time-resolved photoluminescence spectra of a neat Ir(ppy)₃ film integrated at the early time (0-5 ns). The intensities were normalized for comparison.

As the equilibration between the triplet substates is faster than radiative decay,⁶ the phosphorescence from substate III would be predominant owing to its large transition dipole moment. For example, the phosphorescence from substate III was ~96% of the total emission assuming that the transition dipole moments were also identical to those in PMMA. This suggests that the emission observed at 300 K originates mainly from the phosphorescence of substate III, despite its low population (22%).

On the other hand, three substates were differently populated at 10 K, I = 85%, II = 15%, and III = 1.3×10^{-6} %. Due to the extremely low population, the phosphorescence from substate III was virtually negligible, whereas the estimated emission from substates II and I was 64 and 36%, respectively. The moderately allowed transition from substate II was dominated by the 0-0 transition with a small intensity of Franck-Condon active vibrational satellites. On the other hand, the transition from substate I was only slightly allowed, where it could be aided by Herzberg-Teller coupling.^{4,12} This vibronic coupling was associated with higher-lying vibrational states, which resulted in the occurrence of many vibrational satellites and even smeared out

electronic 0-0 transitions.⁴ Therefore, the transition from substate I is responsible for the change in the spectral shape at low temperatures, where substate I is more important according to the Boltzmann distribution. The change in the main emitting triplet state is supported by the shoulder peak of 512 nm at 10 K, which was shifted from the peak of 509 nm at 300 K. This red-shift is unusual, because a blue-shift has been reported at low temperatures due to the rigidochromism related to the phase transition of solvents from fluid to crystalline.^{5,7} However, the phase transition was not expected in the Ir(ppy)₃ film, which explains the absence of the blue-shift. Moreover, the red-shift of ~3 nm agrees with the energy difference between substates III and II, suggesting the phosphorescence from substate II.

The photodynamics was investigated to examine the substates because an emissive state could be distinguished by the peak position and a time constant in the time-resolved photoluminescence (TRPL) spectra.^{13,14} Figure 1(b) shows that the TRPL spectra at the early time (0-5 ns). The electronic 0-0 transition was dominant at both 10 and 300 K, which is in contrast to the time-integrated PL spectra. The highest-lying substate III has the largest radiative rate because of the largest transition dipole moment. This means that the phosphorescence from substate III contributed mainly to the TRPL spectra in the initial stages, which explains the similar spectral shapes at 10 and 300 K. However, the population of substate III, which was estimated to be 1.3×10^{-6} % at 10 K, appeared to contradict the dominating phosphorescence from substate III, even in the initial stages. The enhanced contribution of substate III could be due to the excess energy of the excitation (355 nm), which was ~9000 cm⁻¹ larger than the triplet states. When the excess energy was distributed over all vibrational modes, the temperature of Ir(ppy)₃ could increase up to 80 K. However, the temperature might be much lower than 80 K, because excess energy was also transferred to the nearby Ir(ppy)₃ molecules,⁶ which served as solvents estimated to be over 90% of Ir(ppy)₃ molecules. Nevertheless, the population of substate III could increase to be non-negligible in the initial stages, when the large radiative rate is considered. On the other hand, the difference in the spectral shape between TRPL at the early time (0-5 ns) and the time-integrated PL (0-1 μs) spectra was not significant at 300 K. A minor change was observed in that the latter exhibited a slightly larger intensity at ~600 nm than the former because substates I and II contributed to the latter.

To study the substates in more detail, the TRPL spectra were obtained at 10 K as a function of the detection time (Fig. 2(a)). The emission peak in the TRPL spectra showed a significant red-shift with time. In other words, the emission in the initial stages was dominated by structured emission, which changed to broad emission peaking at 540 nm at 80 ns, supporting the existence of more than one state for phosphorescence. The main emitting substate in the initial stages was substate III owing to its large radiative rate. After the fast decay of substate III, substates I or II would be the main emitting state. When the zero-field splitting and transi-

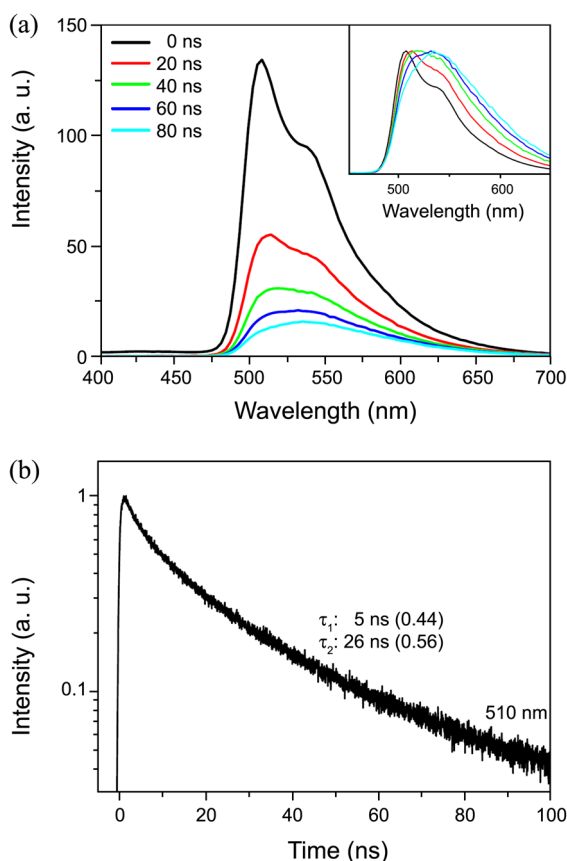


Figure 2. (a) Time-resolved photoluminescence spectra of a neat Ir(ppy)₃ film at 10 K as a function of the detection time. The time-resolved photoluminescence spectra were reconstructed from the decay profiles measured at 2 nm intervals, which were obtained using the time-correlated single photon counter technique. From top to bottom, the photoluminescence spectra were shown with increasing detection times. The inset shows a red-shift of photoluminescence with increasing time. The intensities were normalized for comparison. (b) A typical decay profile of the phosphorescence at 510 nm. The time constants were obtained by fitting, and the numbers in parentheses represent the relative contributions of the time components.

tion dipole moments were assumed to be similar to the PMMA condition, the intensity from substate II was almost double that from substate I.

Figure 2(b) shows a typical decay profile of the phosphorescence at 10 K. The decay profile of 510 nm was fitted by a double-exponential model.

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

where $I(t)$ is intensity, τ_1 and τ_2 are the decay times, and A_1 and A_2 are the relative magnitudes. The decay profile showed two time constants (5 and 26 ns) with relevant relative magnitudes (0.44 and 0.56). The fast time constant might indicate the lifetime of substate III, which was much smaller than that in dilute solution (> 200 ns).⁴ In general, energy transfer between Ir(ppy)₃ does not occur at low Ir(ppy)₃ concentrations in solution (for example, 1×10^{-5} M). However, the energy transfer process becomes important in neat films due to the physical proximity between the

Ir(ppy)₃ molecules. The efficiency of Förster energy transfer is strongly dependent on the intermolecular distance and spectral overlap between the donor emission and acceptor absorption.^{3,4,15,16} Almost complete quenching of the donor emission was observed when the spectral overlap between the donor and acceptor complexes was well matched.¹⁶ This efficient energy transfer reduced the lifetime of the donor Ir(III) complexes to 25 ns in PMMA films, even though the lifetime was 1.4 μ s in a dilute solution. In addition, even when the spectral overlap was nearly absent, the lifetime of the Ir(III) complexes was reduced to 270 ns due to their physical proximity.¹⁶ This could be explained by Dexter-type energy transfer,^{2,3,17} even though Förster-type energy transfer was more efficient judging from the lifetime changes. In this regard, owing to the small Stokes shift of Ir(ppy)₃ (~ 10 nm), Förster-type energy transfer to the Ir(ppy)₃ solvent molecules is quite probable in the neat film, where Dexter-type transfer was also enhanced significantly. Hence, the lifetime of substate III (τ_{III}) is affected by the energy transfer rate (k_{ET}) as well as radiative decay (k_r) and nonradiative decay (k_{nr}).

$$\tau_{III} = \frac{1}{k_r + k_{nr} + k_{ET}} \quad (2)$$

Since k_r and k_{nr} might not change drastically in the films, k_{ET} is responsible for the change in τ_{III} . In addition, τ_{III} is determined mainly by k_{ET} because k_{ET} was much larger than k_r and k_{nr} . Therefore, the short lifetime of substate III originated from the enhanced Förster- and Dexter-type energy transfer in thin films.

Finally, a slow time constant (26 ns) was also observed with a meaningful magnitude (0.56). Similar multi-exponential behaviors have been reported for Ir(ppy)₃ and other Ir(III) complexes in solution.^{4,11} Indeed, the lifetimes of the triplet states could be distributed inhomogeneously because Ir(III) complexes are affected by non-identical environments. In other words, the superposition of the lifetimes related to the different sites was fitted by a double-exponential model, whereas the contribution of substates I and II could not be ruled out, even in the initial stages.

In summary, the emissive properties of Ir(ppy)₃ films were examined by temperature- and time-dependent spectroscopy. Three triplet substates were responsible for the temperature- and time-dependent change in phosphorescence in the neat films. Dexter-type as well as Förster-type energy transfer between Ir(ppy)₃ molecules induced the unique lifetime of the emissive triplet substate in the neat films.

Experimental Section

Amorphous Ir(ppy)₃ thin films (100 nm thick) were deposited onto a precleaned glass substrate by the vacuum evaporation technique under a pressure of $\sim 1 \times 10^{-7}$ Torr. The deposition rate was 1.0 $\text{\AA}/\text{sec}$. Glass substrates were cleaned by sonication in isopropylalcohol, rinsing in deionized water, and irradiation in a UV-ozone chamber. Ir(ppy)₃ was purchased from Luminescence Technology Corp. and used

as received. The temperature of the thin films held in a cryostat was adjusted from 10 to 300 K. For TRPL spectroscopy, the thin films were excited by the second harmonic (355 nm) of a cavity-dumped oscillator (Mira/PulseSwitch, Coherent, 1 MHz, 150 fs). The collected photoluminescence was resolved spectrally using a monochromator, detected using a photomultiplier, and recorded using a time-correlated single photon counter (TimeHarp, PicoQuant).

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