

Phosphorescence Properties of Neat FIrpic Films

Noh Soo Han, So Hyeong Sohn, Seung Min Park, and Jae Kyu Song*

Department of Chemistry, Kyung Hee University, Seoul 130-701, Korea. *E-mail: jaeksong@khu.ac.kr
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The organic phosphorescent materials accomplish higher electroluminescence quantum efficiency up to four times, due to the strong spin-orbit coupling induced by heavy atoms, than the organic fluorescent ones.¹⁻³ Thus organo-transition metal compounds have been extensively studied for applications to efficient light organic emitting diodes (OLEDs) because these compounds allow harvesting both singlet and triplet excitons by the spin-orbit coupling in electroluminescence devices. Among these materials red and green emitting compounds have been investigated in detail,¹⁻⁶ whereas the highly efficient blue emitters are still demanded for the full color operation of OLEDs. For blue emitters, iridium(III)bis[2-(4',6'-difluorophenyl)pyridinato-N,C^{2'}]-picolinate (Ir(4,6-dFppy)₂(pic), FIrpic) exhibits quantum yields of ~100% in doped films.⁷ However, luminescent properties of FIrpic are mainly examined in dilute solution (1×10^{-5} M) or thin films with a low doping ratio (< 1 wt %),⁷⁻⁹ which may not be appropriate for device applications. In this Note, we investigate luminescence of neat FIrpic films using temperature- and time-dependent spectroscopy. Triplet substates were found to be responsible for temperature- and time-dependent phosphorescence and the contribution of each substate in neat films was different from that in solution possibly due to the modification of intermolecular interactions and environments.

Figure 1(a) shows the time-integrated photoluminescence (TIPL) spectrum of neat FIrpic films at 300 K. The luminescence peaks were hardly resolved, which were different from those of FIrpic molecules in solution.⁸ The luminescence of neat films was also obtained at low temperatures because the vibronic fine structure was expected to be more resolved by the suppression of the thermal population of high-lying vibrational levels.¹⁰ However, the luminescence peaks were not well resolved even at 10 K, although the full width at half maximum (FWHM) of the luminescence was slightly reduced at the low temperature (114 nm at 300 K to 101 nm at 10 K).

To explain the luminescence difference between the neat films and dilute solution the photodynamics was investigated because the emitting states could be distinguished by the peak positions in time-resolved photoluminescence (TRPL) spectra.¹¹ The TRPL spectra at the early time (average in the range of 0-5 ns) were obtained at several temperatures. Figure 1(b) shows that two peaks (475 and 500 nm) were discernible in the TRPL spectrum at 10 K. The shoulder at

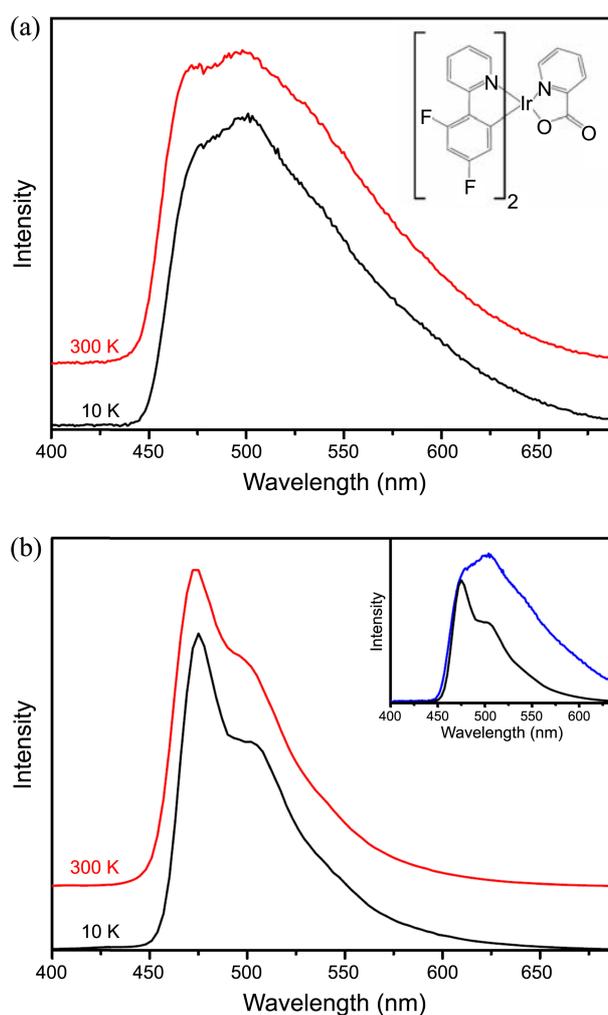


Figure 1. (a) Time-integrated photoluminescence (TIPL) spectra of a neat FIrpic film at room temperature (300 K) and a low temperature (10 K). The luminescence peaks were hardly resolved at both temperatures, although FWHM of the luminescence was slightly reduced at 10 K. The intensities were normalized and offset for better comparison. The inset shows the chemical structure of FIrpic. (b) Time-resolved photoluminescence (TRPL) spectra of a neat FIrpic film averaged at the early time (0-5 ns) at room temperature (300 K) and a low temperature (10 K). The peak wavelengths were observed to be 475 and 500 nm at both temperatures. The intensities were normalized and offset for better comparison. The relative intensities of two peaks were changed and two peaks were better resolved at 10 K. The inset shows the comparison of TIPL and TRPL spectra at 10 K, where the intensities were adjusted for better contrast.

500 nm was $\sim 1000\text{ cm}^{-1}$ lower in energy than the maximum peak at 475 nm, which suggested some overlap of the vibrational satellites.¹⁰ The spectral shape of TRPL spectrum at 300 K was similar to that at 10 K. It is also noted that the TRPL spectra at this early time were quite similar to the TIPL spectra of FIrpic in solution.⁸

The main luminescence of FIrpic is known as phosphorescence from triplet states. The heavy center ion, Ir(III), can induce strong spin-orbit coupling, which allows the intersystem crossing to triplet states and luminescence from triplet states, otherwise forbidden transitions. The intersystem crossing from the excited singlet states takes place fast within subpicosecond due to strong spin-orbit coupling.¹⁰ The emitting triplet states of FIrpic are assigned as the metal-to-ligand charge-transfer (³MLCT) states, which involve the 5d orbitals of Ir(III) and the π^* orbitals of dFppy.¹⁰ Indeed, the MLCT character has been supported by broad phosphorescence spectra because the ligand-centered transition expects vibronic fine structures. The triplet states, which are degenerated in the C_3 symmetry, are split into three substates in the lowered symmetry of FIrpic because FIrpic has two kinds of ligand groups, *i.e.*, two ligands (dFppy) involved in emitting process and the other (pic) served as an ancillary ligand. In addition, the zero-field splitting between the lowest and highest substate is affected by environments such as solvation. In the solid states, such as low temperature solutions, the different numbers and/or geometries of solvent molecules change the solvation effects, which induce the zero-field splitting in the range of $39\text{--}76\text{ cm}^{-1}$ even with the same solvent molecules.¹⁰ The transition from the lowest-lying 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. The highest-lying substate III has the largest transition dipole moment because the small energy separation from the singlet states induces large coupling. Thus the radiative rate of substate III is more than 100 times higher than that of substate I.¹⁰

The population of three substates was determined by temperature according to the Boltzmann distribution because the intersystem crossing to triplet states and the thermal equilibration of triplet states occurred much faster than the decay of triplet states.¹⁰ Although the energy difference between substate I and III was not large ($< 80\text{ cm}^{-1}$),¹⁰ the population was critically affected by temperature. For example, with decrease in temperature, the thermal population of substate III changed from 30% (300 K) to 0.2% (10 K) and 26% (300 K) to 0.001% (10 K), when the zero-field splitting of three substates was assumed to be the lower value (39 cm^{-1}) and the upper value (76 cm^{-1}) in solution, respectively.¹⁰ Thus phosphorescence would be predominantly from substate III at 300 K because of its largest transition dipole moments. However, due to the low population of substate III, the contribution of the other substates would increase at 10 K. In other words, the phosphorescence at 10 K was composed of the transition from substate I (62%), substate II (38%), and substate III (0.01%), when the

transition dipole moments of the upper zero-field splitting value (76 cm^{-1}) were taken into account. Since the radiative rate of substate II is more than twice of substate I,¹⁰ phosphorescence from substate II could mainly contribute to the TRPL spectra in the initial stages at 10 K. The moderately allowed transition from substate II was also dominated by the 0-0 transition with a small intensity of Franck-Condon active vibrational satellites,¹² which suggested that the transition from substate II would show the similar shape to that from substate III in the phosphorescence spectrum. That is, the transition from substate II was not clearly distinguishable from substate III due to the intrinsically broad nature of vibrational satellites and the small energy difference between substate II and III ($< 70\text{ cm}^{-1}$). Nevertheless, the intensity of the shoulder peak at 10 K was lower than that at 300 K, which might indicate the contribution of substate II at the low temperature.

To examine the triplet substates in more detail, TRPL spectra were obtained at 10 K as a function of detection time, which is presented in Figure 2(a). The emission peak

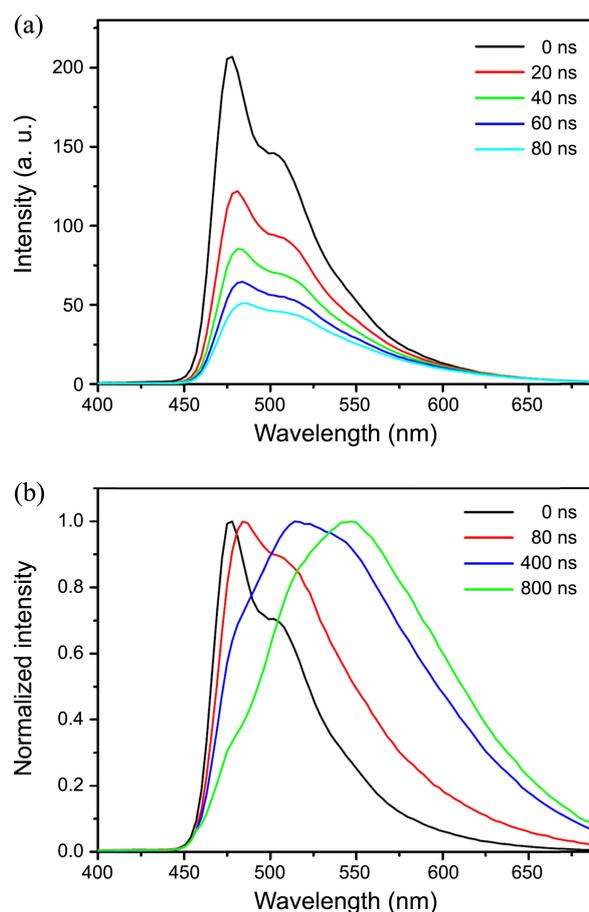


Figure 2. (a) TRPL spectra of a neat FIrpic film at 10 K as a function of detection time. The TRPL were reconstructed from the decay profiles measured at 3 nm intervals, which were obtained using the time-correlated single photon counter technique. From top to bottom, the TRPL spectra were shown with increasing detection time. (b) The red-shift of phosphorescence was observed with increasing time. The intensities were normalized for better comparison.

was significantly red-shifted with time, as clearly found in the normalized spectra in Figure 2(b). Phosphorescence from substate II contributed to the TRPL spectra in initial stages. With increase in time, on the other hand, the contribution of the other substate changed the shape of TRPL spectra. The transition from substate I was only slightly allowed, where it was aided by Herzberg-Teller coupling.¹³ 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. Therefore, the transition from substate I was responsible for the red-shift and the change in the spectral shape, as shown in Figure 3, although the energy difference between substate I and II was less than 10 cm^{-1} .¹⁰ Therefore, phosphorescence from substate I explained the spectral difference between the TIPL and TRPL spectra. Indeed, phosphorescence from substate I was estimated to be major (62%) at 10 K, which was responsible for the unstructured shape of TIPL spectra in neat films.

On the other hand, the spectral difference in the inset of Figure 1(b) seemed to suggest more enhanced phosphorescence from substate I in neat films. The difference in ligand groups of FIrpic (dFppy and pic) could change the effects of the solvent coordination. For example, different solvation environments of FIrpic in rigid conditions revealed the different values of the zero-field splitting even in the same solvent, where the values changed almost twice (39 to 76 cm^{-1}).¹⁰ This indicated that the triplet states with large MLCT characters were differently relaxed in the rigid conditions by inhomogeneous dipolar interactions of solvents. Consequently, the zero-field splitting influenced by the environment and the resulting transition dipole moment of the substates could be spread over wide ranges in the neat films and the contribution of the substates in the neat films was different from that in relatively homogeneous environments such as solution and low doped matrix. In other words, phosphorescence from substate I gained more intensity in the neat films than homogeneous environments presumably because many

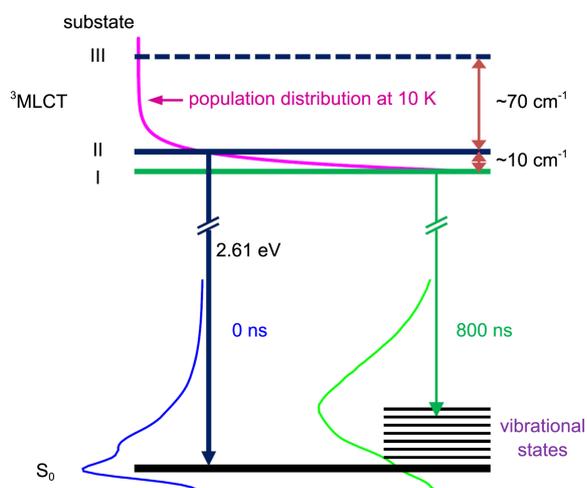


Figure 3. Schematic diagram of the phosphorescence dynamics of neat FIrpic films at 10 K.

dopant ensemble environments contributed differently to phosphorescence in neat films. Therefore, the unexpected shape in TIPL spectra at 10 K was also related to the inhomogeneous environments of the neat films, which reduced the transition dipole moment difference between the substates. The detailed dynamics and temperature dependence of the substate distributions are currently under investigation to better understand the phosphorescence from each substate.

In summary, luminescence properties of neat FIrpic films were examined by temperature- and time-dependent spectroscopy. Three triplet substates were responsible for the temperature- and time-dependent change of phosphorescence in the neat films. The contribution of the substates in the neat films was found to be different from that in solution due to the unique environments of the neat films.

Experimental Sections

FIrpic thin films were amorphously deposited onto glass substrates with a thickness of $\sim 100\text{ nm}$. The vacuum evaporation technique was used to deposit thin films in a pressure of $\sim 1 \times 10^{-7}$ Torr. FIrpic was purchased from Luminescence Technology Corp. and used without further purifications. The thin films were mounted on a cold finger in a cryostat, which could change the temperature of the thin films from 10 to 300 K. The thin films in a cryostat were excited by the second harmonic (355 nm) of a cavity-dumped oscillator (Mira/PulseSwitch, Coherent, 1 MHz, 150 fs). The emission was collected using a series of lens, resolved spectrally using a monochromator, and detected using a photomultiplier tube to obtain the TIPL spectra. The detected emission was also recorded using a time-correlated single photon counter (TimeHarp, PicoQuant) to obtain the TRPL spectra.^{14,15}

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