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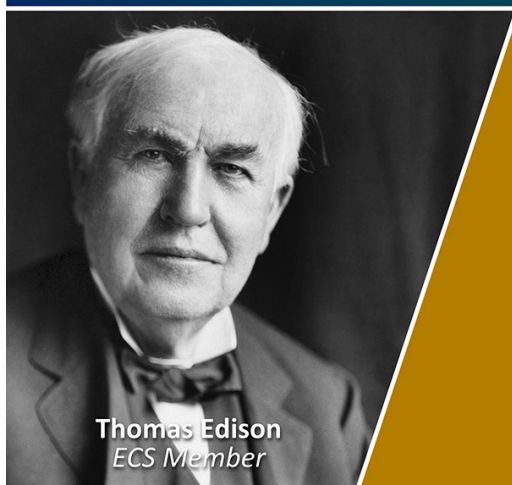
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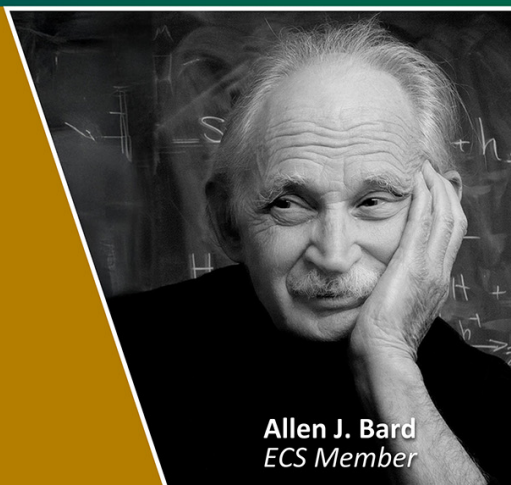


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Unusual Phosphorescence Characteristics of Ir(ppy)₃ in a Solid Matrix at Low Temperatures

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We observed unusual radiative decay characteristics of a (*fac*-tris(2-phenylpyridine)iridium [Ir(ppy)₃]) triplet-excited state doped into 4, 4'-N, N'-dicarbazole-biphenyl (CBP) and polymethylmethacrylate (PMMA) host matrices. From a measurement of the temperature dependence on the phosphorescence intensity and the lifetime of Ir(ppy)₃ in these hosts, we observed that phosphorescence intensities are independent of temperature, while the lifetimes significantly increase at temperatures below $T \sim 50$ K. These results lead us to conclude that the non-radiative transition rate (k_{nr}) from the triplet excited state is very small compared with the radiative transition rate (k_r) and that the phosphorescence quantum yield (ϕ_{PH}) is nearly 100% even at room temperature. Based on our experimental results, we propose a possible decay mechanism to rationalize the characteristic temperature dependence on the transient phosphorescence. [DOI: 10.1143/JJAP.43.L937]

KEYWORDS: phosphorescence, Ir(ppy)₃, OLED, electroluminescence, MLCT, triplet, lifetime

Organic light emitting diodes (OLEDs) using organic phosphors as an emitter have led to high efficiency electrophosphorescence from triplet-excited states. In particular, OLEDs using iridium (Ir) complexes ((2-phenylpyridine)iridium derivatives) have demonstrated very high internal quantum efficiencies approaching 100%.^{1–6} These iridium complexes form metal to ligand charge transfer (MLCT) excited states.⁷ They are due to resonance between the d-orbital of the central iridium atom and the π^* orbital of ligand molecules. A strong coupling of iridium and ligands leads to a mixing of singlet and triplet states, which in turn leads to a nearly 100% conversion of the inter-system crossing (ISC) from singlet to triplet excited states and allows for a strong radiative transition from triplet to singlet ground states. Therefore, very strong phosphorescence with a short radiative lifetime (τ) of $\sim 2 \mu\text{s}$ is possible even at room temperatures.⁸

In addition to OLED applications, the unique electronic and optical characteristics of organic phosphors have been recognized as being applicable to other organic semiconductor devices. In particular, organic phosphors have been applied to organic solar cells and have demonstrated high conversion efficiency.^{9,10} Thus, the understanding of optical and electrical properties of the organic phosphors is a significant subject in organic solid-state photo-physics.

In this study, we focus on the phosphorescence decay processes of *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)₃]^{11–14} in solid state matrices. To understand the energy dissipating processes of Ir(ppy)₃ in solid matrices, we investigated the time resolved phosphorescence spectrum of Ir(ppy)₃ in both 4, 4'-N, N'-dicarbazole-biphenyl (CBP) and polymethylmethacrylate (PMMA) hosts and observed unusual phosphorescence decay characteristics.

6-wt%-Ir(ppy)₃ doped CBP films were deposited by high vacuum ($\sim 10^{-3}$ Pa) thermal evaporation onto a clean silicon substrate, and 6-wt%-Ir(ppy)₃ doped PMMA films were spin-coated from 1, 2-dichloroethane solutions containing Ir(ppy)₃ and PMMA onto a pre-cleaned silicon substrate. The thickness of the organic layers was fixed at 50 nm. These films were set in a cryostat (NAGASE Co., Model PS24). Applying an InGa alloy as a glue ensured thermal conductivity between the silicon substrate and the sample holder. Phosphorescence transient decays were obtained using a streak camera (Hamamatsu C4334). A nitrogen gas

laser (LTB, N200) with a wavelength of $\lambda = 337$ nm and a pulse width of ~ 500 ps was used as the excitation source. The temperature dependence on the absorption spectra of the films from 9 to 300 K was obtained using the same cryostat set as in a conventional absorption spectrometer (Shimadzu UV-2400PL). We investigated the temperature dependence on the radiative decay rate (k_r) of the triplet excited state of Ir(ppy)₃ by measuring the temperature dependence on the MLCT triplet absorbance.

Figure 1 shows the temperature dependence on the phosphorescence intensity and the lifetime of Ir(ppy)₃ in the 6-wt%-Ir(ppy)₃ CBP film. While the integrated phosphorescence intensity showed no temperature dependence, the lifetime increased significantly at temperatures of less than $T \sim 50$ K. We fitted the decay curves with a single exponential decay model as a first approximation. The behavior observed is quite unusual compared with the temperature dependences on fluorescence and phosphorescence of conventional organic molecules. Also, the characteristic temperature dependences of Ir(ppy)₃ in the solid film is quite different compared with that in a solution. Yersin reported that the PL intensity of Ir(ppy)₃ in a THF solution showed large temperature dependence, although the lifetime in the solution showed the similar temperature depend-

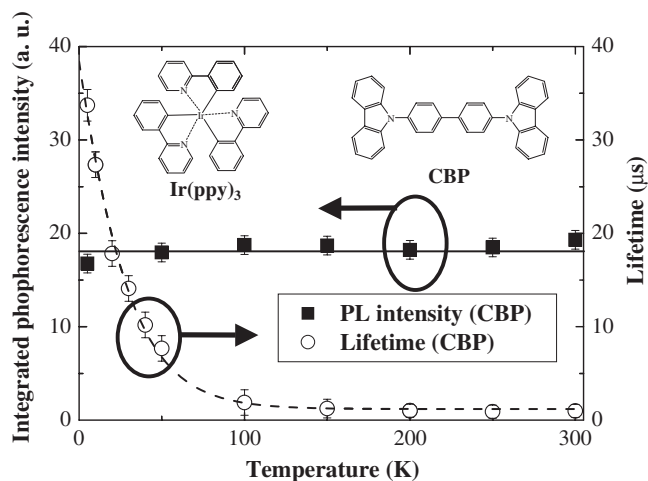


Fig. 1. Temperature dependences on integrated phosphorescence intensity and lifetime for Ir(ppy)₃ in 6-wt%-Ir(ppy)₃ CBP films. Also shown is the chemical structures of Ir(ppy)₃ and CBP.

ence.¹⁵ In general, because the non-radiative decay rate (k_{nr}) of the singlet excited state is gradually suppressed with a temperature decrease due to a suppression of molecular vibrations at low temperatures, fluorescence intensity and the lifetime of the fluorescence decay of many typical organic solid states proportionally increases as temperature decreases.¹⁶ Here, the phosphorescence quantum efficiency (ϕ_p) is given by

$$\phi_p = \phi_{isc} \frac{k_{rp}}{k_{rp} + k_{nrp} + k_{trp}} = \phi_{isc} k_{rp} \tau_p, \quad (1)$$

where k_{rp} is the radiative decay rate from T_1 , k_{nrp} is the non-radiative decay rate from T_1 , k_{trp} is the energy transfer rate to an adjoined molecule, ϕ_{isc} is the inter-system crossing probability, and τ_p is the radiative lifetime of phosphorescence. Because we observed no fluorescence component from Ir(ppy)₃, we can assume that the intersystem crossing rate from S_1 to T_1 (k_{isc}) is very large and that ϕ_{isc} of Ir(ppy)₃ is nearly 100%. Also, since ϕ_p is independent of temperature, k_{nrp} must be very small compared with k_{rp} , even at room temperature, leading to $\phi_p \sim 100\%$. In fact, in a separate experiment, we determined that the absolute photoluminescence (PL) efficiency of Ir(ppy)₃ in a CBP host matrix is nearly 100%.¹⁷

One possibility for the unusual phosphorescence characteristics at low temperatures can be ascribed to the presence of energy transfer between the CBP host and Ir(ppy)₃. This is because the triplet energy of CBP ($E_T = 2.56$ eV) is competitive with that of Ir(ppy)₃ ($E_T = 2.42$ eV). We can explain the unusual phosphorescence characteristics if triplet excitons are transferred to an adjacent CBP, migrate between CBP molecules, and finally decay radiatively at Ir(ppy)₃. The energy transfer between Ir(ppy)₃ and CBP may be a thermally activated process that may change the transfer rate at low temperatures. However, this hypothesis does not explain the temperature dependence on phosphorescence with a PMMA host matrix. Figure 2 shows the temperature dependence on the phosphorescence intensity and the lifetime of Ir(ppy)₃ in the PMMA host with the PL spectra at $T = 5$ and 300 K. Here, we used a 2-wt%-Ir(ppy)₃ PMMA

film for transient phosphorescence measurement to completely exclude the energy transfer process because PMMA is optically transparent and because we are assured no energy transfer between Ir(ppy)₃ and PMMA ($k_{trp} \sim 0$). Thus, Ir(ppy)₃ is directly excited by the nitrogen gas laser, and the isolated molecular characteristics of Ir(ppy)₃ can be obtained. Very similar phosphorescence transient behavior was observed to that in the CBP host. Thus, we conclude that unusual phosphorescence characteristics are due to the internal energy dissipation characteristics of Ir(ppy)₃. These results suggest that the radiative decay rate from the triplet excited state (T_1) to the ground state (S_0) or the intersystem crossing (ISC) process from the singlet (S_1) to triplet excited state (T_1) must be temperature dependent. Here, because we observed no fluorescence from Ir(ppy)₃ even at low temperatures, the ISC rate must be very large, and the ISC cannot be a rate-determining process.

To determine the roll-off characteristics of Ir(ppy)₃ lifetime at the lowest temperatures, we first investigated the temperature dependence on the radiative decay rate of T_1 to S_0 (k_{rp}) in Ir(ppy)₃. We investigated the temperature dependence on ³MLCT absorption because the radiative decay rate from T_1 to S_0 is proportional to the MLCT absorbance ($S_0 \rightarrow T_1$).¹⁵ Figure 3 shows the temperature dependences on absorbance for Ir(ppy)₃ in 2-wt%-Ir(ppy)₃ PMMA films. The absorbance of ¹MLCT (singlet) and ³MLCT (triplet) was assigned to 385 and 450 nm, respectively.⁸ Because the absorbance of ³MLCT shows no temperature dependence from $T = 9$ to 300 K, we conclude that the radiative decay rate from T_1 to S_0 (k_{rp}) is temperature independent.

Next, we plot the transient data as $\ln(1/\tau_p)$ vs $1/T$ to confirm the existence of an activation process. Figure 4 shows $\ln(10^6/\tau_p)$ vs $1/T$ from Fig. 2. It can be well fitted to a model with two activation energies,

$$\frac{1}{\tau_p} = C_1 \exp\left(-\frac{\Delta E_1}{kT}\right) + C_2 \exp\left(-\frac{\Delta E_2}{kT}\right), \quad (2)$$

where $C_{1,2}$ is a constant, $\Delta E_{1,2}$ are the activation energy, and k is the Boltzmann constant. With $\Delta E_1 = 11.6$ meV, $\Delta E_2 = 0.0379$ meV, $C_1 = 1.11 \times 10^6$, and $C_2 = 2.75 \times 10^4$, we

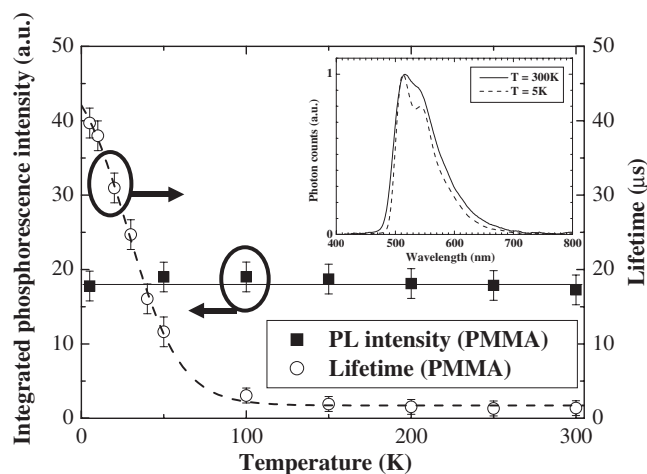


Fig. 2. Temperature dependences on integrated phosphorescence intensity and lifetime for Ir(ppy)₃ in 2-wt%-Ir(ppy)₃ PMMA films. (Inset) Normalized photoluminescence spectra of 6-wt%-Ir(ppy)₃ PMMA films at $T = 300$ K and $T = 5$ K

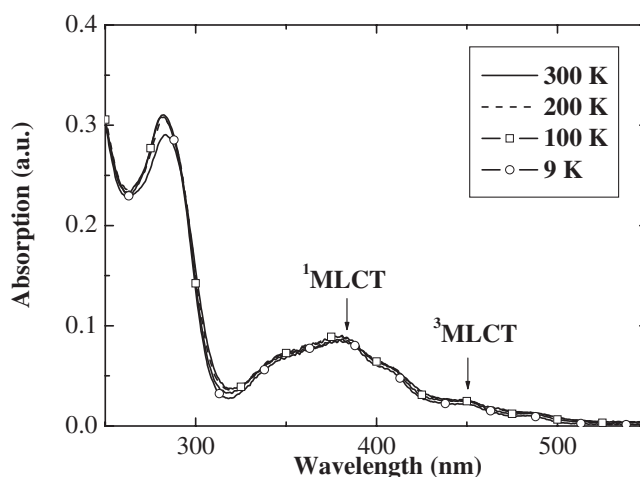


Fig. 3. Temperature dependences on absorbance for Ir(ppy)₃ in 2-wt%-Ir(ppy)₃ PMMA films.

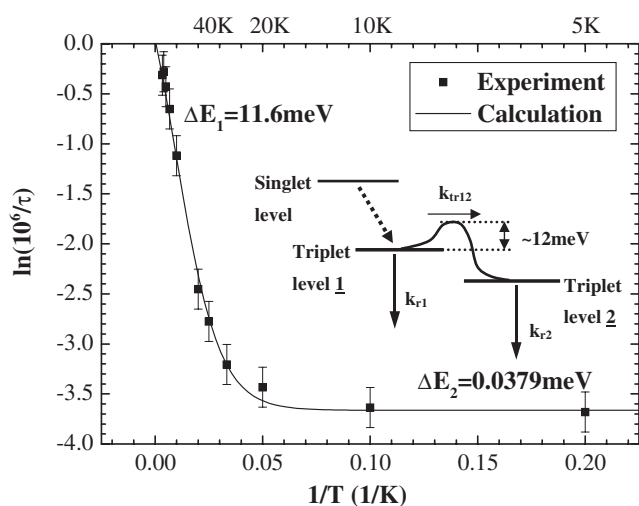


Fig. 4. $\ln(10^6/\tau) - 1/T$ characteristics of 2-wt%-Ir(ppy)₃ PMMA film. The theoretical fitting of eq. (2) is shown as a solid line. (Inset) Schematic model of energy transfer between level 1 and level 2.

obtained excellent coincidence between the experimental values and the eq. (2). Here, we mention that the activation energy of ΔE_2 is much smaller than that of ΔE_1 and that there is virtually no activation energy in ΔE_2 . Thus, this fitting leads us that there are mainly two processes for the transient decay. Here, we explain our two level model. In the inset of Fig. 4, we show our model of two triplet levels that has a characteristic potential barrier of ~ 12 meV from level 1 to level 2 and radiative decay rates of k_{r1} and k_{r2} . Here, we assume that singlet excited energy primarily decays to level 1 and that k_{r2} is larger than k_{r1} ($k_{r2} \gg k_{r1}$). At high temperatures ($T > \sim 100$ K), an energy transfer from level 1 to level 2 with a transfer rate of k_{tr12} actively occurs due to the slow k_{r1} ($k_{tr12} > k_{r1}$). Therefore, because the transfer rate of k_{tr12} is proportional to $\exp(-\Delta E_1/kT)$, the resulting lifetime is controlled by k_{tr12} with the activation energy of ΔE_1 . However, because overcoming the energy barrier from level 1 to level 2 is difficult at low temperatures ($T < \sim 50$ K), the excited energy decays mostly at level 1 with a temperature independent radiative decay rate of k_{r1} . The observed temperature independency of the radiative decay rate from T_1 to S_0 as shown in Fig. 3 is consistent with this consideration because k_{r1} and k_{r2} are temperature independent and only k_{tr12} is temperature dependent in our model.

Our explanation for the energy activation model can be related to the degenerate nature of the triplet state. In principle, three different triplet levels (T_+ , T_- , and T_0) form triplet sub-levels that should display their individual properties for the behavior of the emission and that should have characteristic activation energies to transfer between these levels. Assuming that the emission comes from the lower sub-levels at high temperatures and from the higher sub-levels at low temperatures, we can explain the change in lifetimes while keeping the phosphorescence intensity

constant. In fact, the presence of sub-levels with different emission lifetimes in some heavy-metal complexes has been reported in special solid matrices.^{15,18,19} Finally, in addition to energy transfer between the multiple MLCT triplet levels, the energy transfer between triplet $\pi-\pi^*$ (ligand) and MLCT levels is another possibility that explains our model.

In summary, we observed unusual luminescence characteristics of Ir(ppy)₃ at low temperatures using CBP and PMMA host matrices. While phosphorescence intensity is temperature independent, the lifetimes are significantly changed at low temperatures. The temperature independency of phosphorescence intensity clearly demonstrates that the internal quantum efficiency (ϕ_{int}) of Ir(ppy)₃ is nearly 100%. We discussed a possible mechanism to explain the temperature dependence of the lifetimes. The two activation models explained the experimental results well. Further support for this conclusion will come from a lifetime analysis of Ir(ppy)₃ in special solid matrices^{18,19} and a theoretical calculation of the excited state.²⁰

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