

Analysis on Phosphorescence Decay Time of Ir(ppy)₃ in Tetrahydrofuran under Magnetic Field

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Abstract

The photoluminescence (PL) lifetime of *fac* tris(2-phenylpyridine) iridium (Ir(ppy)₃) in tetrahydrofuran has been observed to decrease from 145 to 47 μ s at 1.5 K with increasing the magnetic field B from 0 to 10 T. A numerical analysis has been done to explain the magnetic field dependence of the PL lifetime. We use a model of three substates 1, 2 and 3 for the emitting ³MLCT triplet states, where non-radiative one-phonon relaxation is undertaken, and assume the magnetic interaction between the low-energy substates 1 and 2 and neglect the interaction with the upper substates 3. Three PL lifetimes are derived. Good agreement is obtained between the observed PL lifetime and the calculated longest PL lifetime, including the deviation from the B² dependence observed above about 6 T. The field dependence is also calculated at various temperatures up to 300 K. Unlike the case of 1.5 K, the PL lifetimes change little at high temperatures.

1. Introduction

Organic light emitting diodes (OLEDs) using phosphorescent materials are interested and important because several transition metal complexes like *fac* tris(2-phenylpyridine) iridium (Ir(ppy)₃) and platinum octaethyl porphine (PtOEP) certainly show a relatively high quantum efficiency¹⁻³⁾. For example, Ir(ppy)₃ doped in 3-(4-biphenyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ) shows a phosphorescent quantum efficiency of 80%⁴⁾, while PtOEP doped in polystyrene shows an efficiency of 50%⁵⁾. The emitting triplet state in phosphorescent OLED has been attributed to the metal-to-ligand-charge-transfer triplet state (³MLCT). It is important to clarify the radiative processes in the triplet state to find new emitters which are suitable for the actual OLEDs. One of the methods is to investigate the optical properties under the external fields such as magnetic field, static electric field and hydrostatic pressure.

Compared with the studies under non-external fields, few studies have been undertaken except the studies by Matsumura group and by Yersin group. The former group studied the electroluminescence of polymer under the magnetic field and clarified the field effect on the exciton recombination and triplet-triplet annihilation⁶⁾. On the other hand, the lat-

ter group studied the photoluminescence (PL) and its decay times of various phosphorescent organic materials under the high magnetic fields^{3,7-10}.

Recently, Finkenzeller and Yersin measured the PL decay times (i.e. PL lifetime) of Ir(ppy)₃ dissolved in tetrahydrofuran (THF) at various temperatures between 1.2 and 145 K^{3,7}. A 337.1 nm pulsed N₂ laser was used for the excitation. They also measured the lifetime under the magnetic fields up to 10 Tesla (T) at 1.5K³. The lifetime has been observed to decrease from 145 to 47 μ s with increasing the magnetic field from 0 to 10 T. It is interesting to find the reason why the PL lifetime decreases with increasing magnetic field. In this paper we analyze the radiative processes in the triplet state of Ir(ppy)₃ in THF under the magnetic field and try to explain the observed field dependence of the PL lifetime.

2. Three zero-field splitting substates responsible for the phosphorescence

Theoretical studies on the ground state and excited electronic states of Ir(ppy)₃ have been carried out using time-dependent density functional theory (TDDFT)¹¹. There are ten ³MLCT triplet states located below the ¹MLCT singlet states. When the Ir(ppy)₃ molecules are excited with the 337.1 nm photons, the excitation is transferred from the ¹MLCT singlet state to the ³MLCT triplet states by excited-state internal conversion and intersystem crossing, and subsequently to the lowest triplet state at 2.59 eV. Two triplet states are at 2.60 eV and another triplet state is at 2.79 eV. The 2.60 eV state is quite close to the lowest 2.59 eV state, while the 2.79 eV state is separated by 1614 cm⁻¹ from the lowest state. Therefore it is suggested that a strong relaxation process is undertaken between the relaxed 2.59 eV state and the nearby doubly degenerated 2.60 eV state, but little interaction with the 2.79 eV state at low temperatures such as 300 K because of wide gap between the 2.59 and 2.79 eV states. As a result we can suggest both the 2.60 and 2.59 eV states are responsible for the phosphorescence at temperature range of 1.2–145 K where the PL measurement has undertaken.

Finkenzeller and Yersin have suggested that the emitting triplet state of Ir(ppy)₃ consists of three zero-field splitting substates 1, 2 and 3, and the substates 2 and 3 are located at 13.5 and 83.5 cm⁻¹ above the lowest-energy substate 1 for Ir(ppy)₃ in THF, respectively, i.e. E₂₁ = 13.5 cm⁻¹ and E₃₁ = 83.5 cm⁻¹^{3,7}. These values were derived from the analysis of temperature dependence of PL lifetime observed at 1.2–135 K using the thermal equilibrium approximation. Here we use the three level model to explain the magnetic field dependence of the PL lifetime.

Figure 1 shows the schematic energy level diagram of the triplet state which is responsible for the emission of phosphorescence from Ir(ppy)₃. In this figure are shown the radiative transition rates k_1 , k_2 and k_3 from the 1, 2 and 3 substates to the singlet ground state, respectively, the non-radiative transition rate k_{21} from the 2 to 1 substate, and the reverse non-radiative transition rate k_{12} from the 1 to 2 substates, etc. In the present paper we extend the three-substate model to analyze the temperature dependence of PL lifetime under the magnetic field. We assume that the non-radiative relaxation between the substates

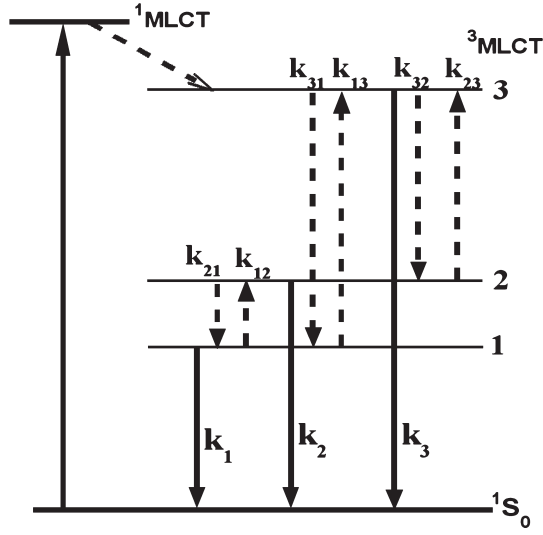


Fig. 1 Schematic energy level diagram for the emitting triplet substates 1, 2 and 3. Broken arrow indicates the non-radiative transition.

is undertaken through one-phonon process, so that for example the transition rate k_{12} is given by $k_{12} = K_1 n$, where n is the occupancy number of the effective phonon modes, K_1 is a coupling constant which reflects the interaction and energy distance between the substates 1 and 2¹²⁾.

The rate equations for the populations $N_j(t)$ ($j = 1, 2, 3$) of the substates at time t at temperature T are given by

$$\begin{aligned}
 \frac{dN_3(t)}{dt} &= -(k_3 + k_{32} + k_{31})N_3(t) + k_{23}N_2(t) + k_{13}N_1(t) \\
 \frac{dN_2(t)}{dt} &= k_{32}N_3(t) - (k_2 + k_{23} + k_{21})N_2(t) + k_{12}N_1(t) \\
 \frac{dN_1(t)}{dt} &= k_{31}N_3(t) + k_{21}N_2(t) - (k_1 + k_{12} + k_{13})N_1(t)
 \end{aligned} \tag{1}$$

Since the radiative transition from each of the three substates to the ground state is assumed (Fig.1), the PL lifetime τ is derived from the following secular equation

$$\begin{vmatrix}
 \frac{1}{\tau} - (k_3 + k_{32} + k_{31}) & k_{23} & k_{13} \\
 k_{32} & \frac{1}{\tau} - (k_2 + k_{23} + k_{21}) & k_{12} \\
 k_{31} & k_{21} & \frac{1}{\tau} - (k_1 + k_{12} + k_{13})
 \end{vmatrix} = 0 \tag{2}$$

The radiative lifetimes of the substates 1, 2 and 3 have been estimated as 145, 11 and 0.75 μs , respectively³⁾. This indicates that the radiative transition rates k_1 , k_2 and k_3 are given by $k_1 = 1/(145 \times 10^{-6}) \text{ s}^{-1}$, $k_2 = 1/(11 \times 10^{-6}) \text{ s}^{-1}$, $k_3 = 1/(750 \times 10^{-9}) \text{ s}^{-1}$. Regarding the

coupling constant K_1 between the substates 1 and 2, K_2 between the substates 1 and 3, and K_3 between the substates 2 and 3, we use $K_1 = K_2 = 10K_3 = 2.09 \times 10^6 \text{ s}^{-1}$ which have been obtained from the fitting of the calculated PL lifetime to the measured lifetime at zero field¹²⁾.

3. Magnetic interaction between the substates 1 and 2

We assume that the magnetic field interaction H_{mag} between the substates 1 and 2 is given by pB , i.e.

$$\langle 2 | H_{\text{mag}} | 1 \rangle = pB$$

where B is magnetic field and p is a coupling constant. We neglect the magnetic field interaction between the substates 3 and 1 (also 2) because the separation between the substates 3 and 1 (also 2) is much larger than the separation between the substates 1 and 2. Thus the following two-dimensional magnetic field interaction Hamiltonian matrix is derived for the substates 1 and 2 ,

	$ 1\rangle$	$ 2\rangle$
$\langle 1 $	0	pB
$\langle 2 $	pB	E_{21}

From this Hamiltonian, we obtain the eigenstates $a_1|1\rangle + b_1|2\rangle$ and $a_2|1\rangle + b_2|2\rangle$ with eigenvalues of $W_1 = (E_{21} - E(B))/2$ and $W_2 = (E_{21} + E(B))/2$, respectively, where $a_1^2 + b_1^2 = 1$, $a_2^2 + b_2^2 = 1$ and $E(B) = (E_{21}^2 + 4p^2B^2)^{1/2}$.

The secular equation of Eq. (2) under the magnetic field was solved after the k_1 and k_2 are substituted by the radiative transition rates under the magnetic field, $k_1'(B)$ and $k_2'(B)$, in Eq.(2), respectively, where $k_1'(B)$ and $k_2'(B)$ are approximated by $k_1'(B) = a_1^2k_1 + b_1^2k_2$, $k_2'(B) = a_2^2k_1 + b_2^2k_2$. First we estimate the p value by solving the secular equation using the experimentally obtained $\tau = 130 \text{ } \mu\text{s}$ at $B = 2 \text{ T}$. The estimated p value is $p = 0.666 \text{ cm}^{-1}/\text{T}$.

Figure 2 shows the energy level diagram of the emitting triplet substates of Ir(ppy)₃ in THF under the magnetic field. The substates 1 and 2 repel from each other with increasing field. The separation induced by the field is proportional to the square of field at low fields up to about 4 T, but it deviates from the B^2 dependence above about 4 T as seen in the right side of Fig.2. A blue shift has been observed in the emission spectrum at 10 T when compared with the emission spectrum at zero field³⁾. Such a blue shift is understood from the left figure of Fig. 2, because the energy of the substate 2 increases with increasing magnetic field by the enhancement of the mixing of the wavefunction with the substate 1.

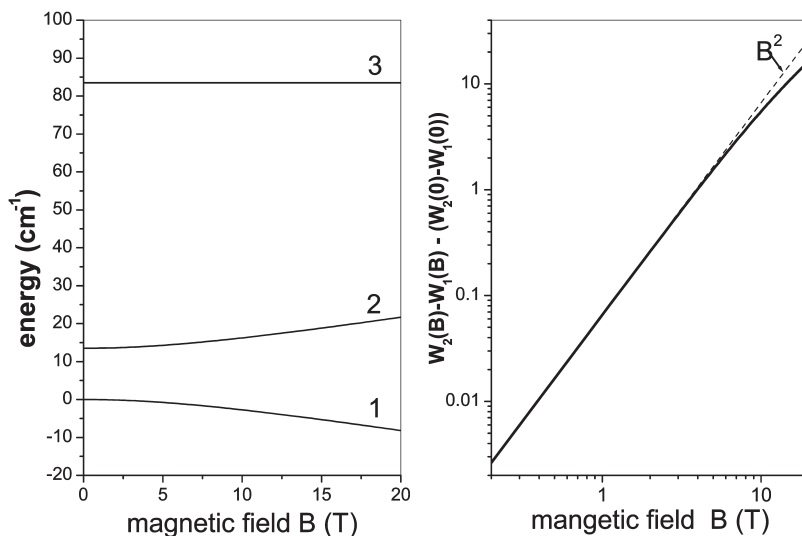


Fig. 2 Energy levels of triplet substates 1, 2 and 3 of Ir(ppy)₃ in THF at 1.5 K under the magnetic field B (left figure) and the separation of the substates 1 and 2 induced by the field (right figure). $W_1(B)$ means the energy of the substate 1 at magnetic field of B. The broken line shows a straight line of slope 2.

4. Calculated PL lifetime at magnetic field and discussion

The field-dependence of PL lifetimes is calculated by solving the secular equation Eq. (2). Three PL lifetimes τ_1 , τ_2 , τ_3 (where $\tau_1 > \tau_2 > \tau_3$) are derived. Figure 3 shows the PL lifetimes at 1.5 K. The long PL lifetime (τ_1) decreases considerably with increasing magnetic field, while the short PL lifetime τ_2 increases (Fig. 4). These results are understood by the mixing of the substate 2 of lifetime (11 μ s) with the substate 1 of much longer lifetime (145 μ s). On the other hand, the shortest PL lifetime τ_3 is 0.2748 μ s and never changes for the variation of the field (see also Fig. 4) because we have neglected the magnetic field interaction of the substate 3 with the other substates. In Fig. 3 is also plotted the PL lifetime measured at 1.5 K by Finkenzeller and Yersin³⁾. A good agreement is obtained between the experimental PL lifetime and the calculated longest PL lifetime τ_1 . This indicates that the three level model^{3,12)}, where the zero-field splitting substates 1, 2 and 3 have the radiative lifetimes of 145, 11 and 0.75 μ s, respectively, is reasonable as the emitting ³MLCT state. The calculation is undertaken by taking into account the one-phonon non-radiative relaxation between the substates 1, 2 and 3. Therefore this suggests that such a relaxation process occurs in the triplet emitter.

In Fig. 5, $(1/\tau_{1B}) - (1/\tau_{10})$ is double-log plotted against magnetic field, where τ_{1B} and τ_{10} are the PL lifetime τ_1 at magnetic field and zero-field, respectively, together with the observed PL lifetime. The experimental values seem to be proportional to B^2 as expected from the perturbation theory^{3,8-10)}, but when we look at Fig. 5 closely, we find that they have

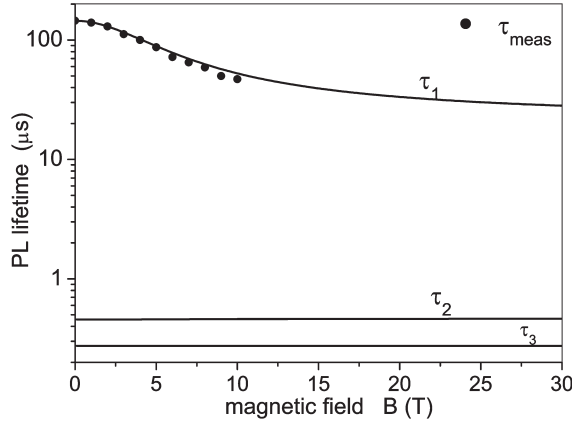


Fig. 3 Calculated and measured PL lifetimes of luminescence from Ir(ppy)_3 in THF at 1.5 K which are plotted against magnetic field. The measured lifetimes were taken from Ref. [3].

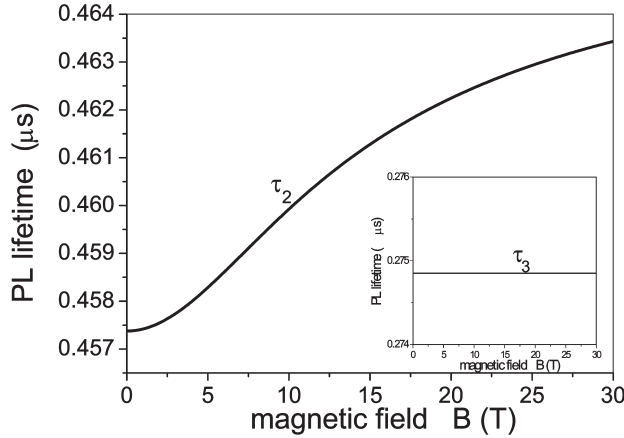


Fig. 4 Enlarged figure of Fig. 3, showing the details of the short PL lifetimes τ_2 and τ_3 at various temperatures.

a tendency to deviate from the B^2 dependence at high field above about 6 T. This is also pointed out by Finkenzeller and Yersin³⁾, and they suggested that the reason is due to a pronounced interaction with the upper-lying substate 3 at high fields.

The PL lifetime calculated using our model predicts such a deviation from the B^2 dependence at high field as seen in Fig. 5. According to our calculation, the mixing parameters a_i and b_i ($i = 1, 2$) are proportional to B at fields below about 4 T, but they deviate from the Zeeman approximation at high fields with increasing magnetic field, resulting in such a deviation of the PL lifetime from the B^2 dependence. We have neglected the magnetic interaction of the two substates 1 and 2 with the substate 3. Therefore it is suggested that, unlike the suggestion in Ref. [3], the interaction with the substate 3 is not so pronounced even at high fields such as 6–10 T.

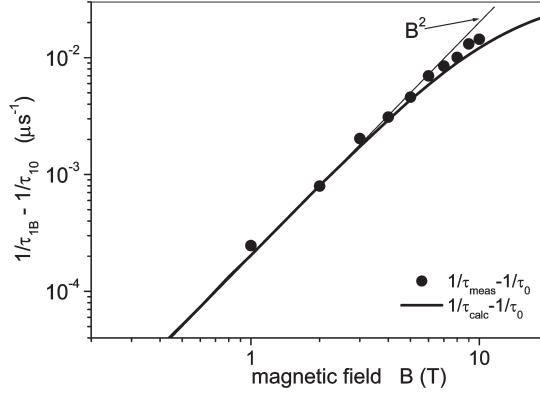


Fig. 5 Calculated and measured PL lifetimes of luminescence from Ir(ppy)₃ in THF at 1.5 K which are plotted against magnetic field. τ_{1B} and τ_{10} are the longest PL lifetime τ_1 at magnetic field and zero-field, respectively, and a broken line shows the line with a slope of 2. The measured lifetimes were taken from Ref.[3].

Our calculation predicts the presence of two additional short PL lifetimes. These PL lifetime is less than 0.47 μ s. The lifetime measurement at magnetic field was undertaken using equipment with maximum time-resolution of 300 ns³⁾. Therefore, taking into account the much weaker emission intensity of the short decay components, it seems difficult to reveal the presence of the short decay components by the measurement.

We have calculated the PL lifetime at 1.5 K to compare with the experimental result. We extend the calculation to the case of higher temperatures. Figure 6 shows the longest PL lifetime (τ_1) calculated under various magnetic fields between 0 and 30 T at various temperatures between 1 and 300 K. The THF has a phase transition at 165 K above which the THF becomes liquid phase, but we neglected the presence of the phase transition. The PL lifetime at zero field decreases with increasing temperature, in agreement with the experimentally observed lifetime³⁾. As shown in Fig. 6 it is obtained at various temperatures that the lifetime decreases with increasing magnetic field as obtained at 1.5 K. The decrement becomes small with increasing temperature. Examples of the lifetime are shown for the cases of 25, 50 and 300 K in Fig. 7. The PL lifetime decreases from 26.2 μ s to 20.6 μ s at 20 K when the magnetic field increases from 0 T to 30 T, while from 11.6 μ s to 11.0 μ s at 50 K, and from 9.88 μ s to 9.83 μ s at 300 K. Comparing with the case of 1.5 K where the lifetime decreases from 145 μ s to 28.9 μ s, we found a big difference between 1.5 K and 50 K.

These results indicate that the magnetic field effect becomes weak considerably with increasing temperature. This is understood as follows. The non-radiative one-phonon transitions among the three substates enhance with increasing temperature, giving rise to the enhancement of populations of the substates 2 and 3. As a result the PL lifetime decreases because the radiative lifetime of the substates 2 and 3 are 11 μ s and 0.75 μ s, respectively³⁾, which are shorter than that of the substate 1 (145 μ s). The magnetic field also leads to increase of population of the substate 2 by the mixing of the substates 1 and 2. However the

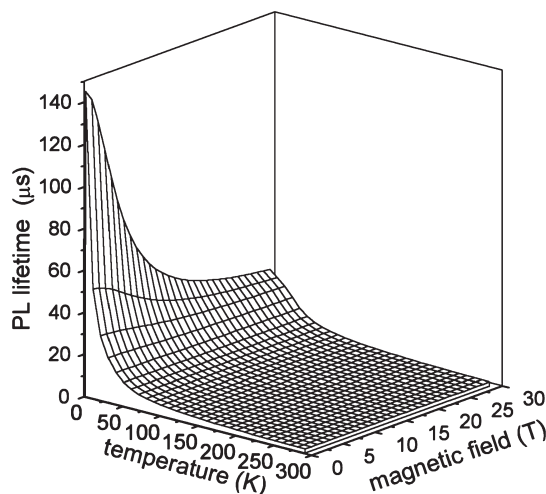


Fig. 6 The calculated photoluminescence lifetime τ_1 of Ir(ppy)₃ in THF at various magnetic fields and temperatures.

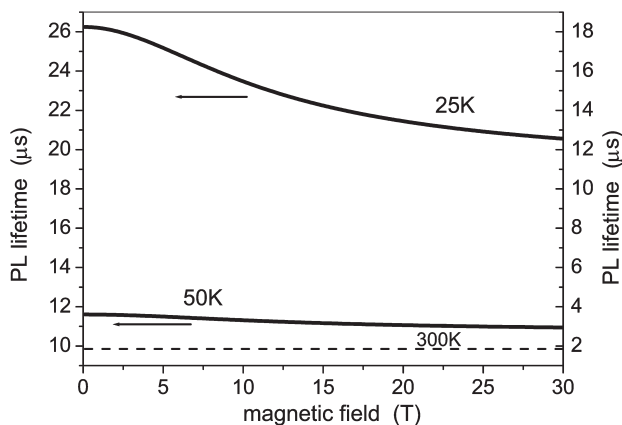


Fig. 7 The calculated magnetic field dependence of the photoluminescence lifetime τ_1 at 20, 50 and 300 K (left scale for the lifetimes at 25 and 50 K).

mixing effect is much weaker than the mixing effect by temperature.

The decay with single exponential has been observed under the magnetic field³⁾. Our model predicts decay with triple exponentials which consist of two short and a long PL lifetimes. If a careful measurement of transient response at 0–10 μ s time range would be undertaken under magnetic fields, one can check if our model is reasonable or not. Additionally the measurement would be undertaken at high temperatures such as 50 and 150 K, one can check if our model is reasonable.

Summary

The PL lifetime of Ir(ppy)₃ in THF has been observed to decrease from 145 to 47 μ s at 1.5 K with increasing the field from 0 to 10 T. A calculation has been done to explain the magnetic field dependence of the PL lifetime using the model of three substates 1, 2 and 3 for the emitting ³MLCT triplet states. We assume the magnetic field interaction between the substates 1 and 2, while we neglect the magnetic field interaction between the substates 3 and 1 (also 2) because the separation between the substates 3 and 1 (also 2) is much larger than the separation between the substates 1 and 2. The calculation is undertaken by taking into account the one-phonon non-radiative relaxation between the substates 1, 2 and 3. Three PL lifetimes are derived. A good agreement is obtained between the experimental PL lifetime and the calculated longest PL lifetime τ_1 , including the deviation from the B² dependence observed at high field above about 6 T. Calculation is made not only at 1.5 K but also various temperatures up to 300 K. Unlike the case of 1.5 K, the field dependence of the PL lifetimes becomes little with increasing temperature.

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