

Progress Report on OLED Research :

Analysis on phosphorescence decay time of

Ir(ppy)_3 in tetrahydrofuran

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Abstract

A theoretical calculation has been done on the decay time of photoluminescence of Ir(ppy)_3 dissolved in tetrahydrofuran and its temperature dependence at 0-300K. Taking into account (1) the emitting triplet state consists of three zero-field splitting substates and (2) non-radiative phonon transition among these substates, secular equation has been solved for these substates. Three decay components are derived, where the slow component shows the variation from 145 to 2 μs with increasing temperature from 1.2 to 300 K. A good agreement has been obtained for the temperature dependence between the calculated slow decay component and the observed decay time.

1. Introduction

One way to improve the photoluminescence and electroluminescence quantum efficiency of organic light emitting diodes (OLEDs) is the usage of phosphorescent materials. In conventional organic emitting molecules, phosphorescent decay is suppressed because of long lifetime of the spin-triplet excitation. Thus most materials such as DCM and Alq_3 show fluorescence primarily from singlet excited states. As the ratio between fluorescent singlet and phosphorescent triplet states is 1:3, the harvesting of triplets is expected to increase the quantum efficiency if the materials have strong spin-orbit coupling.

The OLEDs using phosphorescent materials are interested and important because several transition metal complexes like Ir(ppy)_3 and PtOEP certainly show a relatively high quantum efficiency [1-3]. For example, Ir(ppy)_3 doped in TAZ shows a phosphorescent quantum efficiency of 80% [4], while PtOEP doped in polystyrene shows a 50% efficiency [5]. The emitting triplet state in phosphorescent OLED has been attributed to the metal-to-ligand-charge-transfer triplet state ($^3\text{MLCT}$). The detailed analysis is not yet available for the triplet state and the

radiative processes in the triplet state. The investigation of transient response after optical excitation with pulsed light helps to clarify the radiative processes. One can obtain the information of the transient process from the measurement of luminescence decay time.

Recently Finkenzeller and Yersin measured the luminescence decay times of $\text{Ir}(\text{ppy})_3$ dissolved in tetrahydrofuran (THF) at various temperatures between 1.2 and 135 K [3,6,7]. A 337.1 nm pulsed N_2 laser was used for the excitation. The 337.1 nm light can excite the metal-to-ligand-charge-transfer singlet state $^1\text{MLCT}$ of $\text{Ir}(\text{ppy})_3$. The emitting triplet state consists of three zero-field splitting substates 1, 2 and 3. The substates 2 and 3 are located at 13.5 and 83.5 cm^{-1} above the lowest-energy substate 1 for $\text{Ir}(\text{ppy})_3$ in THF, respectively, and the decay times of the substates 1, 2 and 3 are estimated as 145, 11 and 0.75 μs [3]. In the estimation, the depopulation of average total numbers of the three excited states are taken into account. In this paper we analyse the radiative processes in the triplet state of $\text{Ir}(\text{ppy})_3$ theoretically using another model and try to explain the temperature dependence of the observed decay time reported in [3,6].

2. Rate equations

Explanation of the luminescence decay time using the energy transfer from host material to $\text{Ir}(\text{ppy})_3$ guest is conceivable. In fact the energy transfer from the host to guest and back energy transfer from the guest to host gives a double exponential decay [8]. Most samples containing phosphorescent material such as $\text{Ir}(\text{ppy})_3$ shows a single exponential luminescence decay, but some samples do not [4,9,10]. Not only the double exponential decay [11,12] but also triple exponential decay has been observed (see e. g. Refs. [2,3,6,13-16]). Therefore we do not use the model of energy transfer to explain the observed luminescence decay time. The energy transfer is important during the triplet emitter is relaxed to the final triplet state, but it is suggested that, after the emitter is relaxed to the lowest-energy triplet state, the relaxation process in the substates of the lowest triplet state determines the luminescence decay time.

Figure 1 shows the schematic energy level diagram of the emitting triplet state, with the non-radiative phonon relaxation process among the three substates, where k_1 , k_2 and k_3 are radiative transition probability from the 1, 2 and 3 substates to the singlet ground state, respectively, k_{21} is the non-radiative transitions from the 2 to 1 substate, and k_{12} is the reverse non-radiative transitions from the 1 to 2 substates. Assuming that one-phonon is involved in these non-radiative processes, the rate constants for these processes are described as follows :

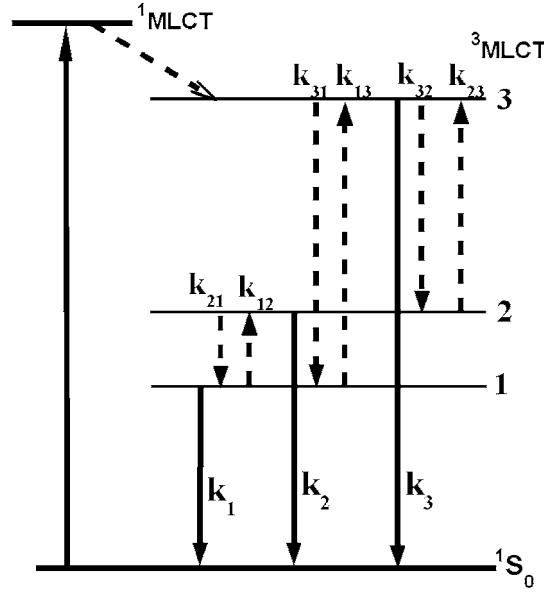


Fig. 1 Schematic energy level diagram for the excited spin-singlet and emitting triplet states and optical processes in the three substates 1, 2 and 3.

$$k_{12} = K_1 n$$

where n is the occupancy number of the effective phonon modes, K_1 is the non-radiative transition probability at 0 K, which reflects the interaction between the substates 1 and 2 [19]. Same formulae are applied to k_{23} and k_{13} ; $k_{23} = K_3 n'$, $k_{13} = K_2 n''$.

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

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

Provided that the observed emission can be represented by the superposition of three exponential decay components, the decay time is derived from the following secular equation

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

3. Temperature dependence of decay time

In a derivation of theoretical temperature dependence of decay time, we used the decay times of the substates 1, 2 and 3, which were estimated in [3], as the reciprocal values of k_1 , k_2 and k_3 , and the energy separations among the substates 1, 2 and 3 estimated in [3] as the values of E_{21} , E_{32} and E_{31} , i. e. $k_1 = 1/(145 \times 10^{-6}) \text{ s}^{-1}$, $k_2 = 1/(11 \times 10^{-6}) \text{ s}^{-1}$, $k_3 = 1/(750 \times 10^{-9}) \text{ s}^{-1}$, $E_{21} = 13.5 \text{ cm}^{-1}$, $E_{32} = 70 \text{ cm}^{-1}$ and $E_{31} = 83.5 \text{ cm}^{-1}$. We calculated decay times in various cases of the non-radiative transition probabilities K_1 , K_2 and K_3 , e. g. $K_1 = K_2 = aK_3$ ($a = 0.1, 1.0, 10, 20, 25, 50$) where we assumed $K_1 = K_2$, and assumed that K_3 is different from K_1 and K_2 because, unlike the substates 2 and 3, the transition from the substate 1 to the ground state is forbidden [3].

First we solved the secular equation using an observed decay time of $\tau = 11.5 \mu\text{s}$ at 50K under a condition of $K_1 = K_2 = aK_3$ ($a = 0.1, 1.0, 10, 20, 25, 50$), and obtained the value of K_1 . The value of K_1 was $1.16 \times 10^6 \text{ s}^{-1}$, $2.09 \times 10^6 \text{ s}^{-1}$ and $0.29 \times 10^6 \text{ s}^{-1}$ for $a = 1.0, 10$, and 50 , respectively. Then we calculated temperature dependence of three solutions $\tau(\tau_1, \tau_2, \tau_3)$, where $\tau_1 > \tau_2 > \tau_3$. Figure 2 shows the temperature dependence curves of the decay times in the cases of $a = 10, 0.1$ and 1.0 . Unlike the cases of τ_2 and τ_3 , the slowest decay time τ_1 is almost the same value for $a = 10, 0.1$ and 1.0 , therefore curve **a** in Fig. 2 shows the all cases of $a = 10, 0.1$ and 1.0 .

In Fig. 2 the experimental result of Ir(ppy)₃ obtained by Finkenzeller and Yersin [3, 6] is shown for comparison. Figure 3 shows the enlarged figure for the slow decay time. A good fit to the experiment is obtained for the slow decay component in various cases of $a = 0.1, 1.0, 10, 20, 25, 50$. We discuss later which a value of these $a = 0.1, 1.0, 10, 20, 25$ and 50 is reasonable.

4. A simple calculation using the thermal equilibrium model

A simple way to derive the decay time is to use a thermal equilibrium model for the substates 1, 2 and 3, i. e. using a model of the depopulation of average total numbers of the three

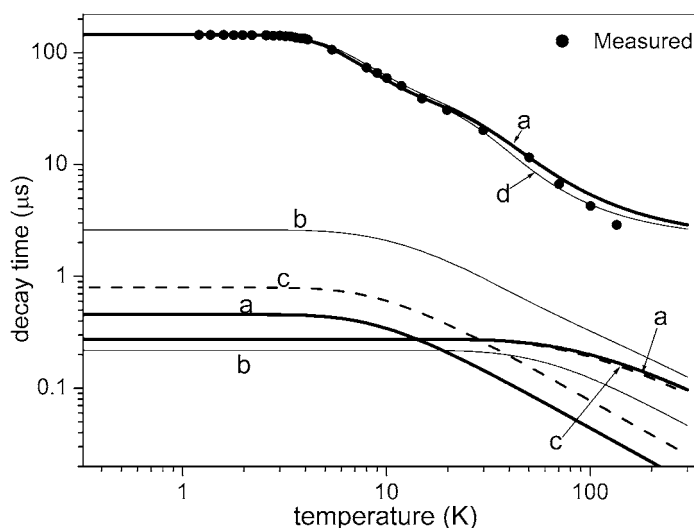


Fig. 2 A log-log plot temperature dependence of calculated emission decay times of $\text{Ir}(\text{ppy})_3$ doped in THF. Calculation is made for the cases of (a) $K_1=K_2=10K_3$, (b) $K_1=K_2=0.1K_3$, and (c) $K_1=K_2=K_3$ (see text). Curve d was obtained from the calculation using the average depopulation method. Closed circle is the observed decay time [3,6].

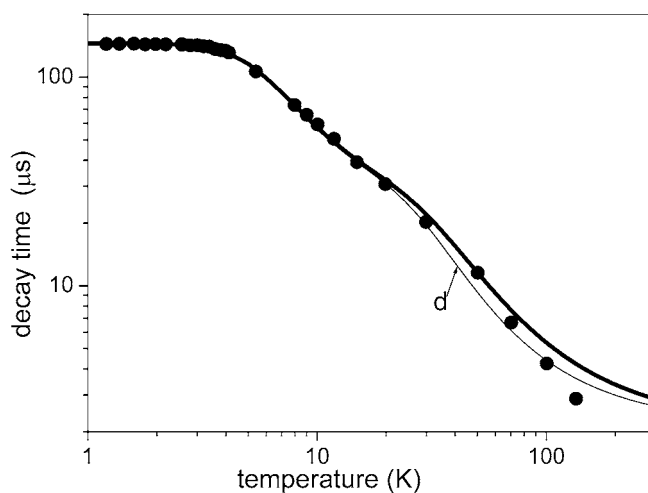


Fig. 3 Enlarged figure of Fig. 2 regarding the slow decay times. The thick solid line is obtained from the calculation with $K_1=K_2=10K_3$, the curve d is decay time calculated using the average depopulation method, and the closed circle is the observed decay time of $\text{Ir}(\text{ppy})_3$ in THF [3,6].

excited states. From Eq. (1), we obtain

$$dN/dt = -(k_3N_3 + k_2N_2 + k_1N_1),$$

where $N = N_3 + N_2 + N_1$. If we assume the Boltzmann distribution for the N_i ($i=1, 2, 3$), the following equation is derived

$$dN/dt = -(k_3f_3 + k_2f_2 + k_1f_1)N,$$

where $f_i = \exp(-E_{i1}/kT) / [1 + \exp(-E_{21}/kT) + \exp(-E_{31}/kT)]$ with the Boltzmann constant k and energy E_{i1} of the substate i relative to the lowest-energy substate 1. If the quantity $k_3f_3 + k_2f_2 + k_1f_1$ is expressed by k_{therm} , we obtain

$$dN/dt = -k_{\text{therm}}N.$$

This gives $N(t) = N_0 \exp(-k_{\text{therm}}t)$, where N_0 is total population of the three substates excited by 337.1 nm laser pulse at $t=0$.

The emission intensity I is given by $I = k_3N_3 + k_2N_2 + k_1N_1$, resulting in

$$I(t) = N_0 k_{\text{therm}} \exp(-k_{\text{therm}}t).$$

Therefore the emission intensity is given by a single exponential time dependence with decay time of $\tau = 1/k_{\text{therm}}$. We calculated this decay time using the k_1 , k_2 , k_3 , E_{21} and E_{31} values given in Sec. 3. The result is shown by curve **d** of Figs. 2 and 3. The curve **d** is the same as the curve of Fig. 5 in [3]. It is noted that the decay time derived from such a thermal equilibrium method is close to the slow decay time τ_1 calculated from the secular equation. From this result it is suggested that the τ_1 reflects the thermal equilibrium among the three substates. This indicates that the emission decay time τ_1 is determined by the lifetime of the lowest-energy substate 1 at low temperature because thermal energy is not enough to give rise to transition from the substate 1 to the upper substates 2 and 3, and the τ_1 value decreases with increasing temperature because of enhancement of thermal transitions from the substate 1 to the upper substates 2 and 3.

Like this secular equation method, the thermal equilibrium method explains the observed temperature dependence of phosphorescence decay time. A big difference between the two methods is that the former method predicts the presence of two additional fast decay times, while the latter does not. In the following we discuss which method is reasonable.

5. Why only a single exponential decay was observed ?

Two or three decay components have been observed in several phosphorescent materials, e. g. in Pd(2-thpy)₂ doped in the Shpol'skii matrices n-octane-h₁₈ and c-octane-h₁₈ [15], Pd(2-thpy)₂ doped in the Shpol'skii matrix [16], Pt(2-thpy)(CO)Cl [20], Pt(qol)₂ doped in the Shpol'skii matrix [14], PtOEP in polystyrene [11], PtOEP in ethyl cellulose [12]. Regarding Ir(ppy)₃, triple exponential decay has been observed in Ir(ppy)₃ doped in polycarbonate at 8-150 K range [17,18], while Finkenzeller and Yersin observed a single exponential decay curve for Ir(ppy)₃ doped in THF [3,6]. Why such a double or triple exponential decay was not observed for Ir(ppy)₃ doped in THF ? In the following we consider the reason.

The population N_i is obtained from the equilibrium condition

$$\frac{dN_i}{dt} = 0$$

in Eq.(1). Thus we obtain the following equations for N_3 and N_1 relative to N_2

$$N_3 = \frac{k_{12}k_{23} + k_{13}(k_2 + k_{23} + k_{21})}{k_{13}k_{32} + k_{12}(k_3 + k_{32} + k_{31})} N_2$$

$$N_1 = \frac{k_{32}k_{31} + k_{21}(k_2 + k_{23} + k_{21})}{k_{31}k_{12} + k_{32}(k_1 + k_{12} + k_{13})} N_2$$

The emission intensity I_i due to the radiative transition from the substate i to the ground state is given by

$$I_i = K_i N_i$$

Figure 4 shows the temperature dependence of I_1 and I_3 emission intensities relative to the I_2 emission intensity, i. e. I_1/I_2 and I_3/I_2 . The I_1 intensity is larger than the I_2 intensity below 7.5 K, while the I_3 intensity is larger than the I_2 intensity above 44.2 K. This means that the Ir(ppy)₃ emission intensity is mostly due to the I_1 emission below 7 K, the I_2 emission at about 8-44 K, and the I_3 emission above 45 K.

The observed luminescence decay time of Ir(ppy)₃ in THF is about 145 μ s at 1-5 K, decreases from 145 to 11 μ s with increasing temperature from 5 to 50 K, and then approaches about 2 μ s with increasing temperature from 50 to 300 K [3]. The experimental limit of the photoluminescence decay time measurement was 300 ns [3], i. e. photoluminescence with decay time of shorter than 300 ns was not observed clearly. Taking into account this situation, we examine

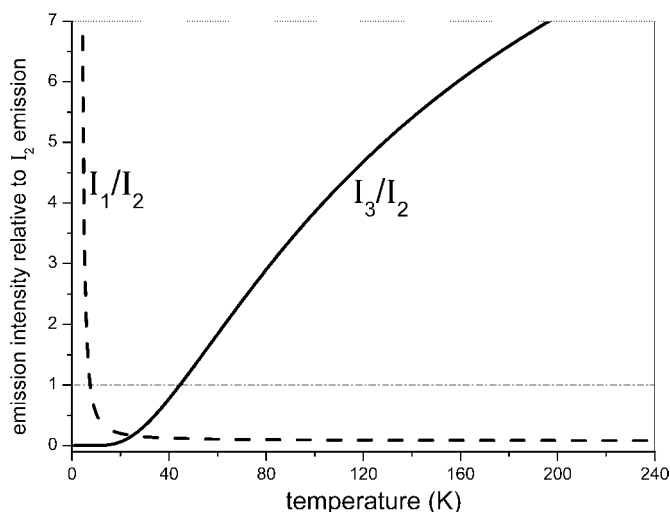


Fig. 4 Temperature dependence of the emission intensities from the triplet substates 1 and 3 relative to the intensity from the substate 2, I_1/I_2 and I_3/I_2 , respectively, in the case of $K_1=K_2=10K_3$.

which case of the relationship between K_1 and K_3 is reasonable. From the theoretical calculation for the case of $K_1=K_2=K_3$, it is expected that two decay components of 145 and 0.8 μs are observed below 8 K because the other fast component has a decay time of about 0.28 μs which is shorter than 0.3 μs . The luminescence with 145 and 0.8 μs decay time is due to the I_3 and I_2 emission, respectively. It is also expected at 8-40 K that two components (one is between 100 and 20 μs , the other is between 0.8 and 0.3 μs) are observed. At 8-40 K region, the photoluminescence with decay time of 0.8-0.3 μs is expected to appear at 8-40 K because the I_2 emission is much intense than the I_1 and I_3 emission (see Fig. 4). Similarly from the theoretical calculation for the case of $K_1=K_2=0.1K_3$, it is expected that two decay components of 145 and 2.7 μs are observed below 8 K, and two components (one is between 100 and 20 μs , the other is between 2.6 and 0.8 μs) are observed at 8-40 K. Only one decay component of about 145-25 μs , however, was experimentally observed at 1.5-40 K. This indicates that $K_1=K_2=K_3$ and $K_1=K_2=0.1K_3$ do not occur in Ir(ppy)_3 doped in THF.

From the theoretical calculation for the case of $K_1=K_2=10K_3$, it is expected that three decay components of 145, 0.47 and 0.28 μs are observed below 8 K, and similarly three decay components are also observed at 8-40 K where the slow one is between 100 and 20 μs depending on temperature, the middle one is between 0.4 and 0.28 μs , and the fast one is less than 0.28 μs .

The luminescence with decay time of $0.47 \mu\text{s}$ below 8 K is difficult to be observed because the corresponding I_2 emission intensity is much weaker than the I_3 emission with decay time of $145 \mu\text{s}$ below 8K (see Fig. 4). On the other hand, the luminescence with decay time of $0.4 \mu\text{s}$ is difficult to be observed using the equipment with measurement limit of $0.3 \mu\text{s}$. Therefore the decay time calculation in case of $K_1=K_2=10K_3$ predicts observation of only one decay component, which agrees with the experimental result for $\text{Ir}(\text{ppy})_3$ doped in THF. Thus we can suggest that the case of $K_1=K_2=10K_3$ is applicable to the $\text{Ir}(\text{ppy})_3$. In this way we understand the reason why only the single exponential decay curve was obtained in Refs. 3 and 6.

6. Calculated photoluminescence transient response

We calculate the time response of luminescence of $\text{Ir}(\text{ppy})_3$ in THF generated by excitation with the 337.1 nm N_2 pulsed laser. We solved Eq.(1) by neglecting the non-radiative transitions from the lower substate to upper substate, i. e. $k_{23}=k_{13}=k_{12}=0$ (see Fig. 5). Such a case is applicable for $\text{Ir}(\text{ppy})_3$ at very low temperature such as 1.2 K since thermal energy is not enough to excite from the lower substate 1 to upper substates 2 and 3 and also transition from the substate 2 to substate 3. We assume that at $t=0$ (i. e. when the excitation laser pulse is applied) the relative populations are 0, 0 and 1 for the substates 1, 2 and 3, respectively because

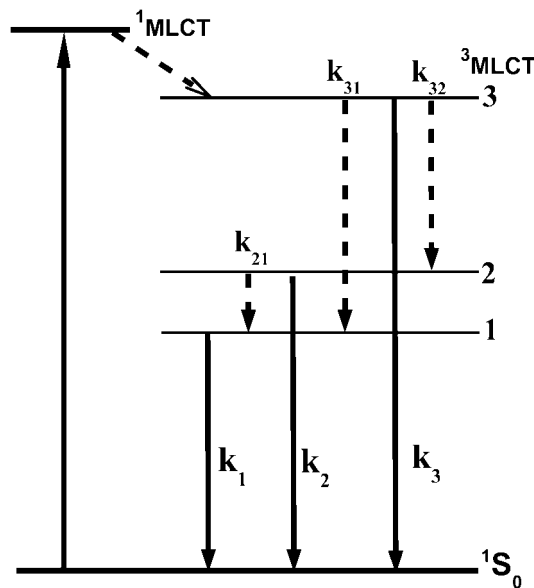


Fig. 5 Schematic energy level diagram for the excited spin-singlet and emitting triplet states and optical processes in the three substates 1, 2 and 3 at 1.2 K.

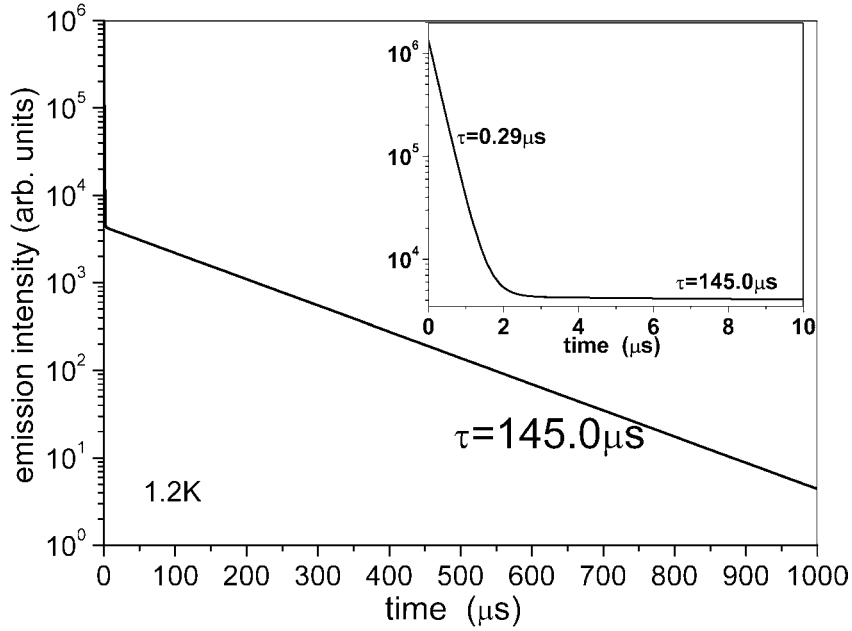


Fig. 6 Time dependence of the calculated emission intensity $I_T(t)$ at 1.2 K, which was obtained under a condition of $K_1=K_2=10K_3$.

the excited Ir(ppy)₃ molecules are relaxed immediately (in pico-seconds) to the upper substate 3 from the singlet state. The 337.1 nm laser gives rise to excitation in the singlet state because the absorption band due to the ¹MLCT singlet state locates at 325-425 nm [21]. The solutions of the rate equations are expressed in the following forms

$$N_3(t) = A_{33}\exp(-a_3t) + A_{32}\exp(-a_2t) + A_{31}\exp(-a_1t)$$

$$N_2(t) = A_{23}\exp(-a_3t) + A_{22}\exp(-a_2t) + A_{21}\exp(-a_1t)$$

$$N_1(t) = A_{13}\exp(-a_3t) + A_{12}\exp(-a_2t) + A_{11}\exp(-a_1t)$$

where $a_3=k_3+k_{32}+k_{31}$, $a_2=k_2+k_{21}$, $a_1=k_1$.

The transient luminescence intensity $I_T(t)$ is given by $I_T(t) = k_3N_3(t) + k_2N_2(t) + k_1N_1(t)$.

Figure 6 shows the time dependence of the calculated $I_T(t)$ at 1.2 K, which was obtained under a condition of $K_1=K_2=10K_3$. Single exponential decay curve is seen from the figure, with the decay time of 145.0 μ s. This value is quite close to the observed one at 1.2 K [3]. This indicates that our assumption is reasonable at 1.2 K. When we look at the curve at 0-15 μ s closely, we found an additional exponential with decay time of 0.29 μ s as shown in inset of Fig.

5, i. e. Ir(ppy)_3 doped in THF shows a double-exponential-like decay curve with a fast $0.29 \mu\text{s}$ components and a slow $145.0 \mu\text{s}$ component. Finkenzeller and Yersin used an equipment which is difficult to observe luminescence with decay time of faster than $0.3 \mu\text{s}$ clearly [3], therefore they could not find this fast $0.29 \mu\text{s}$ component. Like this, we certainly understand their observation of single exponential decay curve at 1.2 K [6].

7. Summary

Theoretical calculation has been done on the decay time of photoluminescence of Ir(ppy)_3 dissolved in tetrahydrofuran and its temperature dependence at $0\text{--}300\text{K}$. Taking into account (1) the emitting triplet state consists of three zero-field splitting substates and (2) non-radiative phonon transition among these substates, secular equation has been solved for these substates. Three decay components are derived, where the slow component shows the variation from 145 to $2 \mu\text{s}$ with increasing temperature from 1.2 to 300 K . A good agreement has been obtained for the temperature dependence between the calculated slow decay component and the observed decay time. The present method using the secular equation predicts presence of two additional fast decay times.

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