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Phosphorescence Decay Time of $Ir(ppy)_3$ in Tetrahydrofuran at Magnetic Field

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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}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 clear 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 $Ir(ppy)_3$ dissolved in tetrahydrofuran (THF) at various temperatures between 1.2 and 300 K [3,6]. 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}MLCT of $Ir(ppy)_3$. They also measured the decay time at 1.5 K under the magnetic fields up to 10 Tesla (T) [3]. The decay time has been observed to decrease from 145 to 47 μs with increasing the field from 0 to 10 T. Finkenzeller and Yersin have suggested from their measurement that the emitting triplet state consists of three zero-field splitting substates I, II and III, and the substates II and III are located at 13.5 and 83.5 cm^{-1} above the lowest-energy substate I for $Ir(ppy)_3$ in THF, respectively [3,6].

In this paper we analyze the radiative processes in the triplet state of $Ir(ppy)_3$ in THF under the magnetic field theoretically and try to explain the observed field dependence of the decay time. Taking into account the non-radiative transitions in the singlet and triplet states, we solve the rate equations at 1.5 K under the magnetic field.

Three decay times τ_1, τ_2, τ_3 (where $\tau_1 > \tau_2 > \tau_3$) are derived, which are shown in Fig.1. The slow decay time largely depends on magnetic field, the fast decay time τ_2 is a slightly depending on the field, while the fastest decay

time τ_3 is 0.2748 μs and never changes for the variation of the field. This τ_3 value is very close to the fast decay time (0.290 μs) obtained from the calculated transient response of emission intensity.

In Fig.1 is also plotted the decay time measured at 1.5 K by Finkenzeller and Yersin [3]. A good agreement is obtained between the experimental decay time and the calculated slowest decay time τ_1.
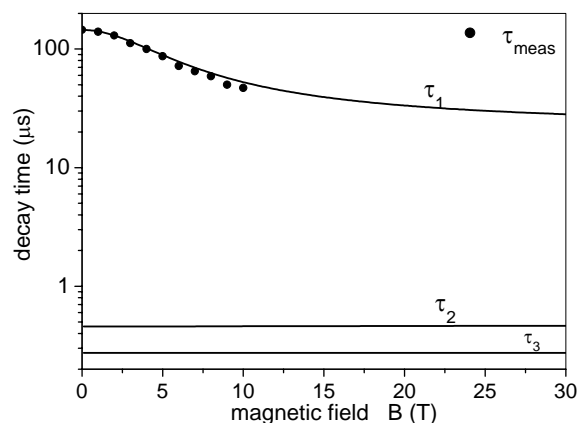

Fig.1 Calculated and measured decay times of luminescence from $Ir(ppy)_3$ in THF at 1.5 K which are plotted against magnetic field. The measured decay times were obtained from Ref.[3].

In Fig.2, $(1/\tau_{1B})-(1/\tau_{10})$ is double-log plotted against magnetic field B, where τ_{1B} and τ_{10} are the decay time τ_1 at magnetic field and zero-field, respectively, together with the observed decay time. A good agreement is obtained between the calculated and experimental decay times. When we look at Fig.2 closely, we find that the experimental $(1/\tau_{1B})-(1/\tau_{10})$ values seem to be proportional to square of magnetic field B^2 as expected from the first order perturbation theory [3], but the experimental values have a tendency to deviate from the B^2 dependence at high field above about 6 T. The calculation using the first order perturbation theory indicates the B^2 dependence even at high magnetic fields [3], while our calculation predicts deviation from the B^2 dependence above about 6 T for the slowest decay time τ_1, which is consistent with the experimental result.

Additionally, unlike the calculation by Finkenzeller and Yersin [3], our theoretical calculation predicts the presence of two additional fast decay times. These decay

time is less than 0.47 µs. The photoluminescence decay time measurement at magnetic field was undertaken using equipment with maximum time-resolution of 300 ns [3]. Therefore, taking into account the much weaker emission intensity of the fast decay components, it seems difficult to reveal the presence of the fast decay components by the measurement. We expect that this prediction would be confirmed if the measurement is made using a highly sensitive and resolved transient response equipment.
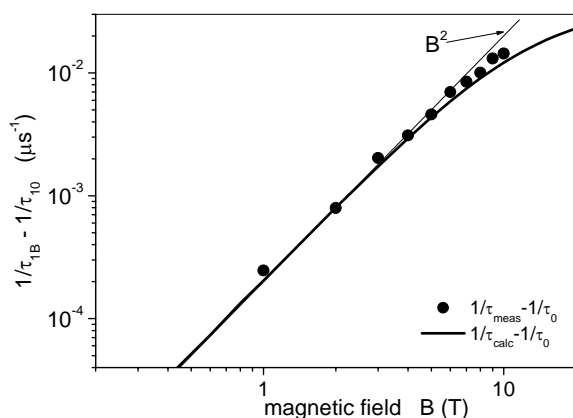

Fig.2 Calculated and measured decay times of luminescence from Ir(ppy)$_3$ in THF at 1.5 K which are plotted against magnetic field. τ_{1B} and τ_{10} are the slow decay time τ_1 at magnetic field and zero-field, respectively, and a straight line shows line with a slope of 2. The measured decay times were obtained from Ref.[3].

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