Non-radiative transitions in the emitting spin-triplet states
in phosphorescent organic material

Taiju Tsuboi and Nadeer Aljaroudi
Faculty of Engineering, Kyoto Sangyo University,
Kamigamo, Kita-ku, Kyoto 603-8555, Japan

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 triplet excitation. Thus most materials such as 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 because some transition metal complexes like $Ir(ppy)_3$ certainly show a high quantum efficiency. For example, $Ir(ppy)_3$ in TAZ shows a quantum efficiency of 80%. The emitting triplet state in phosphorescent OLED has been attributed to metal-to-ligand-charge-transfer (^{3}MLCT). The detailed analysis is not yet available for the radiative processes in the triplet state.

Recently Finkenzeller and Yersin measured the luminescence decay times and intensities of $Ir(ppy)_3$ dissolved in tetrahydrofuran (THF) at 1.2-300 K in detail [1]. A 337.1 nm N_2 laser was used for the excitation in the singlet state ^{1}MLCT of $Ir(ppy)_3$. Here we try to explain the temperature dependences observed.
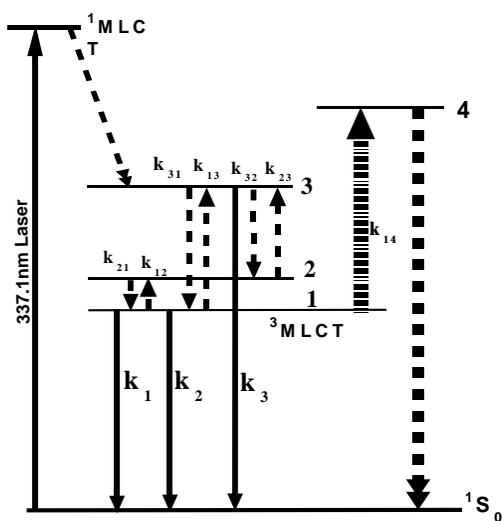
Fig.1 Schematic energy level diagram showing the optical processes after excitation. k_{31} means the non-radiative transition probability from the substate 3 to the substate 1, while k_1 means the radiative transition probability.

The emitting triplet state 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 substate 1 for $Ir(ppy)_3$ in THF, respectively [1]. Taking into account the one-phonon non-radiative transitions among the three substates and also taking into account the non-radiative transition from the lowest-energy substate 1 to a crossing

point (named level 4) of the configuration coordinate (CC) curve of the substate 1 and the CC curve of the singlet ground state (see Fig.1), we solve the rate equations and secular equation for the populations of the three substates.
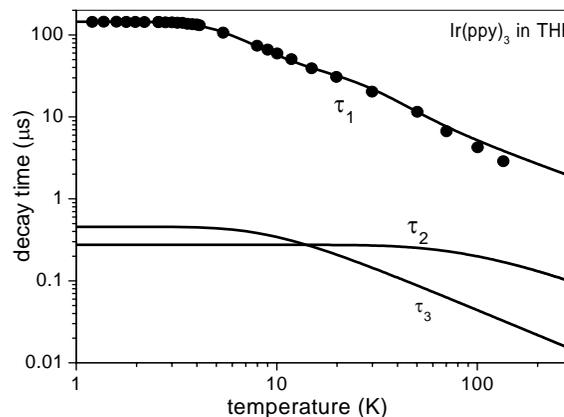
Fig.2 Calculated decay times plotted against temperature, compared with the observed decay times (closed circles).

Three decay times τ_1, τ_2, τ_3 (where $\tau_1 > \tau_2 > \tau_3$) are derived, which are shown in Fig.2. In the calculation the radiative transition probabilities from the substates 1, 2 and 3 were used those estimated in [1]. A good agreement is obtained between the calculated longest decay time τ_1 and measured decay time. Our calculation predicts two additional decay times which are less than 0.5 µs. Such fast decay components will be found if experiment is done using equipment with high time-resolution.

Figure 3 shows the temperature dependence of calculated emission intensity and observed intensity. A good agreement is also obtained between the two intensities. The best fit to the experiment was obtained when we assume that the level 4 is at 350 cm^{-1} above the substate 1. Thus it is concluded that the phosphorescence characteristics are determined by the non-radiatve processes in the three zero-field splitting substates.
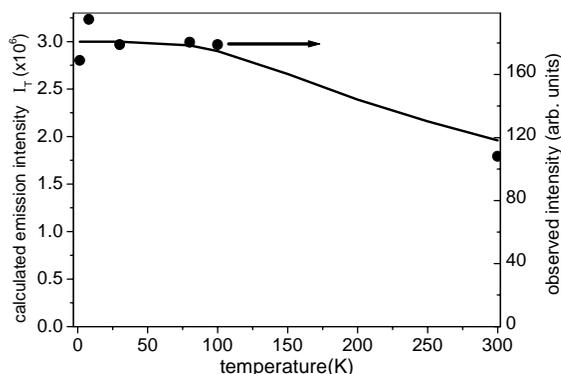
Fig.3 Calculated emission intensity plotted against temperature, compared with the experimentally obtained intensities (closed circles, which were estimated from [1]).

Reference
[1] W.J. Finkenzeller and H. Yersin, Chem. Phys. Lett. **377** (2003) 299.