ELectronics EXpress

IEICE Electronics Express, Vol.1, No.10, 281–286

Photoluminescence lifetime of $Ir(ppy)_3$ used for organic light emitting diodes

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Abstract: We calculated temperature dependence of photoluminescence (PL) lifetime of *fac* tris(2-phenylpyridine) iridium ($Ir(ppy)_3$) doped in 4,4′-N,N′-dicarbazole-biphenyl (CBP). The emitting triplet state consists of three zero-field splitting substates. Taking into account non-radiative transitions among these substates, rate equations for the populations of the substates are solved and three PL lifetimes are derived. A good agreement has been obtained for the temperature dependence between the observed lifetime and calculated long lifetime.

Keywords: OLED, photoemission, lifetime, non-radiative transition.

Classification: New functional devices and materials.

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DOI: 10.1587/elex.1.281
Received July 01, 2004
Accepted July 26, 2004
Published August 25, 2004

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1 Introduction

Organic phosphorescent materials are used to improve the photoluminescence (PL) and electroluminescence (EL) quantum efficiency of organic light emitting diodes (OLEDs). Several transition metal complexes like *fac* tris(2-phenylpyridine) iridium ($Ir(ppy)_3$) show a relatively high quantum efficiency in OLED devices since the heavy metals enhance spin-orbit coupling [1]. The emitting triplet state in phosphorescent OLED has been attributed to the metal-to-ligand-charge-transfer triplet state (^{3}MLCT) [2, 3]. The complete analysis is not yet available for the radiative processes in the triplet state.

Recently PL lifetime was measured at wide temperature (T) range for $Ir(ppy)_3$ in tetrahydrofuran (THF) [3, 4] and in 4,4′-N,N′-dicarbazole-biphenyl (CBP) [5]. The $Ir(ppy)_3$ doped in CBP is important because the material is used for actual OLED device emitting intense green light [1, 6]. The investigation of transient response after excitation with pulsed light helps to clarify the radiative processes in the triplet state. Here we try to explain the observed T-dependence of PL lifetime of $Ir(ppy)_3$ in CBP.

2 Rate equations for populations of three triplet substates

The lowest-energy triplet state in the ^{3}MLCT states consists of three substates 1, 2 and 3 in order of increasing energy, where the transition from the substate 1 to the singlet ground state is forbidden, while the transitions from the substates 2 and 3 are allowed [2-4]. The T-dependence of PL lifetime observed for $Ir(ppy)_3$ in THF was explained using the three-level model [3]. However, the relaxation processes among the three substates are neglected. Here we extend the theoretical calculation (under the same three-level model) of [3] to more general cases.

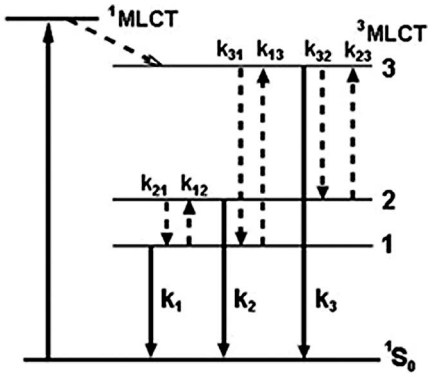

Fig. 1. Schematic energy level diagram for the emitting triplet substates 1, 2 and 3. Broken arrow indicates the non-radiative transition.

Figure 1 shows the schematic energy level diagram of the triplet state which is responsible for the emission of phosphorescence. 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

DOI: 10.1587/elex.1.281
Received July 01, 2004
Accepted July 26, 2004
Published August 25, 2004

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. We assume that the relaxation process between the substates is a 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 between the substates 1 and 2.

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

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

Since the radiative transitions from the three substates are assumed (Fig. 1), the PL lifetime τ is derived from the following secular equation

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

To estimate the energy-level separations and the radiative transition rates of $Ir(ppy)_3$, the following procedure is done. From Eq. (1), we obtain

$$dN(t)/dt=-(k_3N_3(t)+k_2N_2(t)+k_1N_1(t)), \tag{3}$$

where $N(t)=N_3(t)+N_2(t)+N_1(t)$. When all the substates are in thermal equilibrium (TE), Eq. (3) is expressed using the Boltzmann distribution for substates : $dN(t)/dt=-(k_3f_3+k_2f_2+k_1f_1)N(t)$,
where $f_j=\exp(-E_{j1}/kT)/[\exp(-E_{31}/kT)+\exp(-E_{21}/kT)+1]$ with the energy separation E_{j1} of the substate j and the substate 1.

The emission intensity $I_T(t)$ at time t at temperature T is given by

$$I_T(t)=k_3N_{3T}(t)+k_2N_{2T}(t)+k_1N_{1T}(t), \tag{4}$$

resulting in $I_T(t)=N_0k_{therm}\exp(-k_{therm}t)$, where $k_{therm}=k_3f_3+k_2f_2+k_1f_1$ and N_0 is total population of the three substates at $t=0$. Therefore the emission intensity is given by a single exponential with emission lifetime of $\tau=1/k_{therm}$, i.e.

$$\frac{1}{\tau}=\frac{k_3\exp(-E_{31}/kT)+k_2\exp(-E_{21}/kT)+k_1}{\exp(-E_{31}/kT)+\exp(-E_{21}/kT)+1}. \tag{5}$$

A T-dependence of PL lifetime has been measured for $Ir(ppy)_3$ in THF, especially at 1.2-10 K in detail [3, 4]. The PL lifetime at about 0 K is necessary to estimate the reliable values of the energy separation among the substates and the radiative transition rates. These values are obtained by fitting of Eq. (5) to the observed PL lifetime. Good fitting was obtained with $k_1=1/(145\times10^{-6})$ s^{-1}, $k_2=1/(13.5\times10^{-6})$ s^{-1}, $k_3=1/(0.65\times10^{-6})$ s^{-1}, $E_{21}=11.8$

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Received July 01, 2004
Accepted July 26, 2004
Published August 25, 2004

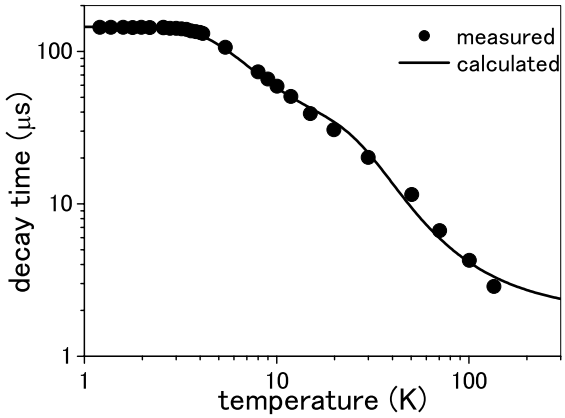

Fig. 2. Double logarithmic plotted temperature dependence of measured and calculated emission lifetimes of $Ir(ppy)_3$ doped in THF.

cm^{-1}, $E_{31}=86.2\ cm^{-1}$ as shown in Fig. 2, where the measured lifetimes were obtained from [3, 4].

In a derivation of theoretical T-dependence of PL lifetimes for $Ir(ppy)_3$ in CBP, we use the same energy separation among the three substates ($E_{21}=11.8\ cm^{-1}$, $E_{31}=86.2\ cm^{-1}$), i.e. we assume that the energy separation in the triplet substates of $Ir(ppy)_3$ does not depend on host material. Additionally we simply assume $K_1=K_2=K_3$ for the coupling constants at this moment because it is difficult to estimate these values exactly, where K_2 is the coupling constants between the substates 1 and 3, and K_3 is the coupling constants between the substates 2 and 3.

3 PL lifetime of Ir(ppy)3 in CBP

First we determine the radiative transition rates by fitting of the PL lifetime calculated under the TE approximation (Eq. (5)) to the lifetime observed for $Ir(ppy)_3$ in CBP. We obtained $k_1=1/(38\times10^{-6})\ s^{-1}$, $k_2=1/(11\times10^{-6})\ s^{-1}$ and $k_3=1/(0.30\times10^{-6})\ s^{-1}$. The coupling constant $K_1(=K_2=K_3)$ was determined by solving the secular equation. The K_1 value, which fits to the observed PL lifetimes, is $K_1=2.53\times10^6\ s^{-1}$.

Using these k_1, k_2, k_3, E_{21}, E_{31} and $K_1(=K_2=K_3)$ values, we obtained the T-dependence of three lifetimes τ_1, τ_2, τ_3, where $\tau_1>\tau_2>\tau_3$. Figure 3 shows the T-dependence of the calculated lifetimes (solid lines) for $Ir(ppy)_3$ in CBP, together with the measured PL lifetime (closed circles [5]). The double logarithmic plot is used to show the fitting and appearance of two short lifetimes clearly. A good fitting is obtained between the calculated lifetime τ_1 and the observed lifetime. Broken line of Fig. 3 shows the best fitted T-dependence of lifetime, which was calculated by the TE model.

Next we calculate the PL lifetimes by another method, i.e. from the transient response curves $I_T(t)$ of Eq. (4) at various temperatures by solving the rate equations Eq. (1). We assume that at $t=0$ (i.e. when the excitation laser pulse is applied) the relative populations are $N_3(t=0)=1$ and $N_1(t=0)=N_2(t=0)=0$ for the substates, because it is believed that the

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Received July 01, 2004
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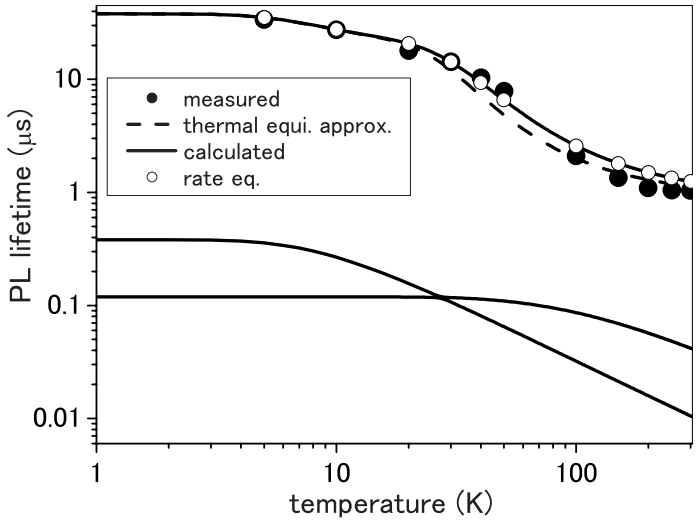

Fig. 3. The calculated and measured PL lifetimes for $Ir(ppy)_3$ in CBP.

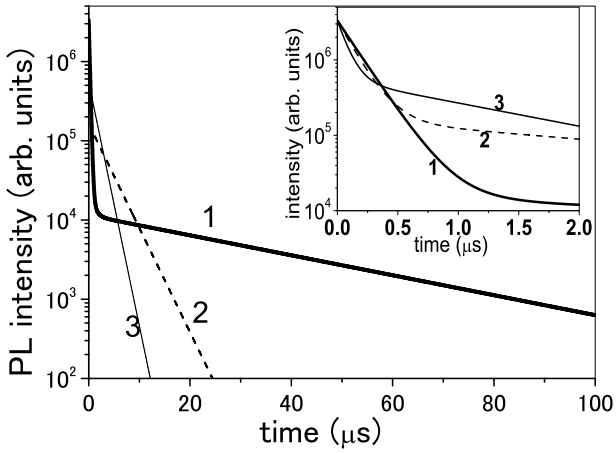

Fig. 4. Time dependence of the calculated PL intensity $I_T(t)$ for $Ir(ppy)_3$ in CBP at 5 K (1), 150 K (2) and 300 K (3). Inset shows the intensity at 0-2 μs.

excited $Ir(ppy)_3$ molecules are relaxed into the upper substate 3 from the singlet state immediately (in less than sub-μs) after the excitation.

Figure 4 shows examples of the calculated curves at 5, 100 and 300 K. The PL decay consists of at least two exponentials from which we can estimate the PL lifetimes τ_1 and τ_3 easily. To estimate the middle lifetime τ_2, we have to enlarge the PL curve where the two exponentials overlap with each other. The estimated long lifetime τ_1 is shown by open circles in Fig. 3. The estimated lifetimes are almost same as those calculated using the secular equation. Good agreement is obtained between the estimated and measured PL lifetimes.

Additionally we calculated the emission intensity at various temperature between 1-300 K using Eq. (4). We obtained the T-independent intensity, which agrees with the observation [5].

DOI: 10.1587/elex.1.281
Received July 01, 2004
Accepted July 26, 2004
Published August 25, 2004

4 Discussion

Theoretical studies on the electronic states of $Ir(ppy)_3$ have been carried out using time-dependent density functional theory (TDDFT) [7]. According to the theoretical calculation, the lowest-energy triplet state is at 2.59 eV, and the first, second and third excited triplet state is at 2.60, 2.60 and 2.79 eV, respectively. Taking into account the calculation error regarding the energy values, it is suggested that e.g. the first excited state locates between 2.595 eV and 2.604 eV. Therefore the first and second excited triplet states are expected to locate between 8 cm^{-1} and 153 cm^{-1} above the lowest triplet state. This expectation is consistent with our result that the substates 2 and 3 are at 11.8 and 86.2 cm^{-1}, respectively. Thus, the presence of three substates is confirmed by the TDDFT calculation.

Although a single lifetime of 1-40 μs has been observed for $Ir(ppy)_3$ in CBP, our calculation predicts additional PL lifetimes which are much shorter than the observed lifetime. In several phosphorescent materials including $Ir(ppy)_3$ in polycarbonate, PL decay with two or three lifetimes has been observed [2, 8]. Recently we measured lifetime of the 525 nm PL by undoped $Ir(ppy)_3$ film at 288 K, which is encapsulated to avoid oxygen and water, and we obtained three lifetimes (1.70 μs, 0.171 μs and 5 ns) from the triple exponential decay curve [9]. The measurement was done with a Jobin Yvon FluoroCube and a 370 nm LED of 1.3 ns pulse width. The observed lifetimes are close to the lifetimes predicted for $Ir(ppy)_3$ doped in CBP (Fig. 3). This result gives a support for the present calculation.

5 Conclusion

Theoretical calculation is done on the PL lifetime of $Ir(ppy)_3$ in CBP at 0-300 K. The emitting triplet state consists of three zero-field splitting substates. The energies and radiative transition rates of these substates are derived from the TE model. The level energies are consistent with the TDDFT calculation. Taking into account non-radiative transitions among these substates, the rate equations are obtained for the populations of these substates. Three PL lifetimes are derived by solving the rate equations. A good agreement is obtained for the T-dependence between the calculated long lifetime and the observed one for $Ir(ppy)_3$ in CBP. The TE model explains the observed T-dependence of phosphorescence lifetime. However, unlike our model, this model cannot predict the presence of two additional short lifetimes. The three predicted lifetimes are consistent with our observation of three PL lifetimes using an undoped $Ir(ppy)_3$ film.

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Received July 01, 2004
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Published August 25, 2004