

Transient process in the triplet states of phosphorescent Ir(ppy)₃ material doped in organic materials: peak shift of the emission band in polycarbonate

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Red shift of green-emission band has been observed for *fac* tris(2-phenylpyridine) iridium (Ir(ppy)₃) doped in polycarbonate at 8 K during time evolution after 355-nm laser of 1-ns pulse width. We explain the peak shift and vibronic structure of the emission band using the Franck-Condon principle and the model of (1) three zero-field splitting substates of the triplet state, (2) relaxation processes among the three substates, and (3) different Huang-Rhys factors for these substates. Good agreement was obtained between the calculated and measured emission spectra at various delay times.

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Phosphorescent materials have been used as the emitters for organic light emitting diodes (OLEDs) because the population of phosphorescent triplet state is three times higher than that of fluorescent singlet state^[1,2]. In fact, some materials such as *fac* tris(2-phenylpyridine) iridium (Ir(ppy)₃) show a high phosphorescence quantum yield of nearly 100%^[3]. To tailor optimal performance of OLEDs, it is essential to investigate various optical properties of phosphors including the temporal response of phosphorescence experimentally and to explain the optical processes quantitatively.

Recently time-resolved phosphorescence spectra were measured for green-emitting Ir(ppy)₃ and for red-emitting bis[2-(2'-benzothienyl)pyridinato-N,C^{3'}] (acetylacetonate) iridium (Btp₂Ir(acac)) doped in polycarbonate (PC) by Tanaka *et al.*^[3]. The emission of Ir(ppy)₃ consists of three decay components and shifts to low energy at 8 K after excitation with 355 nm laser of 1 ns pulse width but the emission band of Btp₂Ir(acac) does not show the peak shift. The peak wavelengths of the Ir(ppy)₃ emission band are about 513, 517, 520, 522, 523 and 525 nm at delay times of 0, 5, 20, 40, 60 and 100 μs, respectively, which estimated from Ref. [3]. This experimental result has been explained neither qualitatively nor quantitatively.

It might be considered that the peak shift is caused by the energy transfer between the Ir(ppy)₃ dopant and PC host. The lowest triplet state of PC is at about 2.9 eV, while the relaxed excited triplet state of Ir(ppy)₃, from which the phosphorescence is generated, is 2.42 eV^[3]. The energy level of host is at about 0.48 eV (3872 cm⁻¹) above the dopant energy level. This indicates that such a large energy difference does not allow energy transfer from the triplet state of Ir(ppy)₃ to PC by thermal excitation even at room temperature. Therefore we abandon the idea that the host is responsible for the peak shift. Recently we explained the presence of three decay components and their temperature dependences observed for Ir(ppy)₃ doped in PC by the relaxation processes in the triplet state of Ir(ppy)₃^[4,5]. Here we try to explain the peak shift by the relaxation in the triplet state as an extension of our recent study.

The Ir(ppy)₃ emission is due to the transition from the metal-to-ligand-charge-transfer triplet state (³MLCT) to

the singlet ground state^[1,2,6]. Finkenzeller *et al.*^[6] have suggested that (1) the lowest-energy triplet state consists of three zero-field splitting substates (called substates 1, 2, and 3 in order of increasing energy, hereafter), and (2) all of these substates are responsible for the green emission of Ir(ppy)₃. They estimated the energy separations between the substates 1 and 2 to be $E_{21}=13.5$ cm⁻¹, and the separation between the substates 1 and 3 to be $E_{31}=83.5$ cm⁻¹ using the thermal equilibrium model. We also used this model and obtained a good fitting using $E_{21}=11.8$ cm⁻¹ and $E_{31}=86.2$ cm⁻¹, which are close to the values estimated in Ref. [6]. In this paper, we use the values ($E_{21}=11.8$ cm⁻¹, $E_{32}=74.4$ cm⁻¹, $E_{31}=86.2$ cm⁻¹) in the analysis of time-resolved emission spectra observed for Ir(ppy)₃ in PC.

Taking into account (1) three zero-field splitting substates in the lowest-energy triplet state and (2) relaxations among these substates, we calculated the temperature dependence of the three decay times. Good agreement has been obtained between the calculated PL lifetimes and the observed ones using values of $k_1=1/(33.7 \times 10^{-6})$ s⁻¹, $k_2=1/(14.3 \times 10^{-6})$ s⁻¹, $k_3=1/(0.3 \times 10^{-6})$ s⁻¹, $K_1=589$ s⁻¹, $K_2=1.19 \times 10^6$ s⁻¹, and $K_3=1.61 \times 10^6$ s⁻¹, where k_1 , k_2 , and k_3 are radiative transition rates from the substates 1, 2, and 3 to the singlet ground state, respectively, k_{21} is non-radiative transition rate from the substate 2 to 1, and k_{12} is the reverse non-radiative transition rate from the substates 1 to 2 (see Fig. 1)^[4,5]. We assumed 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, and K_1 is a coupling constant which reflects the electron-phonon interaction between the substates 1 and 2, while K_2 and K_3 are coupling constants between the substates 1 and 3 and between the substates 2 and 3, respectively.

A vibronic progression is seen in the PL emission band for various organic materials. The emission band of Ir(ppy)₃ doped in PC has a shoulder at the low energy side of the main band as shown in Fig. 2. The main band and shoulder are attributed to the 0-0 and 0-1 vibronic lines, respectively. They are due to the transitions from the vibrational level $n=0$ of the excited state to the vibrational levels $n=0$ and 1 of the ground state, where n is the vibrational quantum number. The emission band

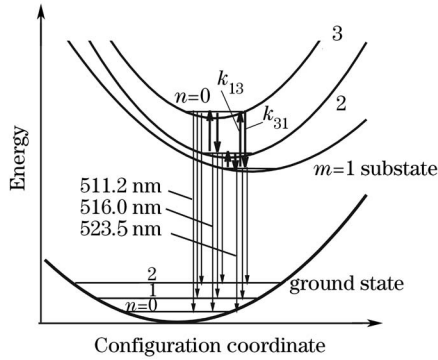


Fig. 1. Schematic Franck-Condon energy level diagram for the ground state and three zero-field splitting substates $m=1, 2,$ and 3 in the triplet state of $\text{Ir}(\text{ppy})_3$. Straight arrow indicates the radiative transition from the $n=0$ vibrational level to the $n=0, 1, 2$ levels of the ground state, while thick arrow indicates the relaxation via phonon transitions in the triplet state.

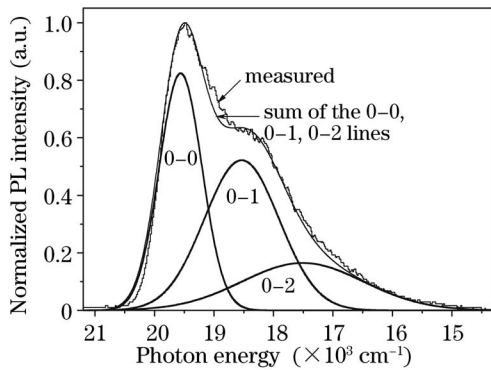


Fig. 2. Measured and calculated PL spectra of $\text{Ir}(\text{ppy})_3$ in polycarbonate at 8 K at zero delay time. The calculated line shape was obtained by sum of the line shapes due to the zero (0-0), one (0-1) and two (0-2) phonon transitions. The measured spectrum was obtained from Ref. [3].

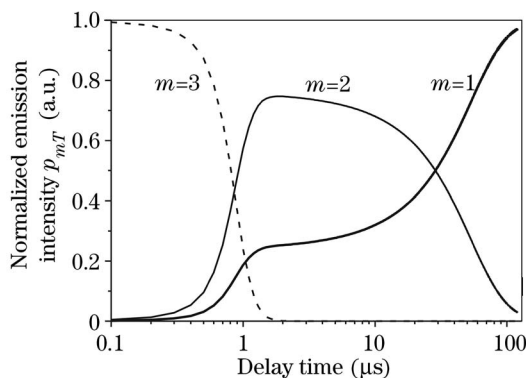


Fig. 3. Delay time dependence of the calculated $p_{mT}(t)$ ($m=1, 2, 3; T=8$) emission intensities due to the triplet substates $m=1, 2,$ and 3 of $\text{Ir}(\text{ppy})_3$ at 8 K.

with vibronic structure is analyzed by the Franck-Condon principle^[7-9]. The relative transition probability W_{0n} of the 0-th vibrational level of the excited state to the

n -th vibrational level of the ground state is given by $W_{0n} = \exp(-S)S^n/n!$ at 0 K using the Huang-Rhys factor S . The non-zero factor S is caused by displacement of the excited-state vibronic potential from the ground state potential. Its magnitude is proportional to the difference in the electron-phonon coupling constant between the ground and excited states. This W_{0n} is replaced by the modified Bessel function for the probability at temperatures above 0 K^[7]. The probability ratios of the 0-1 line to the 0-0 line are 0.6321, 0.6321, and 0.6359 at 0, 8, and 290 K, respectively, for the case of $S=0.6322$. The probability is almost the same among these temperatures. Therefore we use W_{0n} (at 0 K) for the spectra at 8 K.

Our model for the emission process is shown in Fig. 1. The emission band is due to the transitions from the $n=0$ levels of the three excited substates $m=1, 2,$ and 3 to the $n=0, 1,$ and 2 levels of the ground state. Two kinds of line shapes, Gaussian and Lorentzian, have been used for analysis of the vibronic spectra^[8,9]. We used the Lorentzian line shape, but we could not obtain good agreement between the observed and calculated line shapes. Using Gaussian model, the emission line shape is given

$$\text{by } \sum_{n=0}^2 \sum_{m=1}^3 p_{mT}(t) \exp(-S) \frac{S^n}{n!} \exp\left(\frac{-4(E - (E_{m0} - nh\nu))^2}{w_n^2}\right),$$

where E_{m0} , $h\nu$, and w_n are peak photon energy of the emission band due to the 0-0 transition from the substate m to the ground state, vibrational energy coupled with the ground state, and half width of the line shape due to the 0- n transition, respectively. The vibrational energy and Huang-Rhys factor are estimated to be $h\nu=1026 \text{ cm}^{-1}$ and $S=0.63$ from the separation and intensity ratio of the observed 0-0 and 0-1 lines.

$p_{mT}(t)$ is related with the emission intensity due to the transition from the substate m to the ground state at the delay time t at temperature T , which is given by $p_{mT}(t) = k_m N_{mT}(t) / [k_3 N_{3T}(t) + k_2 N_{2T}(t) + k_1 N_{1T}(t)]$, where $N_{mT}(t)$ means the population of the substate m . The populations $N_{mT}(t)$ ($m=1, 2, 3$) of the substates 1, 2, and 3 at time t are given by^[4,5]

$$\begin{aligned} dN_{3T}(t)/dt &= -(k_3 + k_{32} + k_{31})N_{3T}(t) + k_{23}N_{2T}(t) + k_{13}N_{1T}(t); \\ dN_{2T}(t)/dt &= k_{32}N_{3T}(t) - (k_2 + k_{23} + k_{21})N_{2T}(t) + k_{12}N_{1T}(t); \\ dN_{1T}(t)/dt &= k_{31}N_{3T}(t) + k_{21}N_{2T}(t) - (k_1 + k_{12} + k_{13})N_{1T}(t). \end{aligned}$$

Figure 3 shows the time dependence of $p_{mT}(t)$ calculated for the substates $m=1, 2,$ and 3 . This figure indicates that the emission from the upper substate $m=3$ dominates over emission from the lower substates at short delay times less than $1 \mu\text{s}$, but it does not appear after about $2 \mu\text{s}$, and emission from the substate $m=2$ becomes more intense than emission from the substate $m=1$ until about $30 \mu\text{s}$, and then emission from the substate $m=1$ dominates after about $60 \mu\text{s}$.

We calculated the line shape of the emission band by changing the E_{m0} and w_n values variously. Good fitting to the observed emission band shapes were obtained by choosing 19102 cm^{-1} (523.5 nm), 19380 cm^{-1} (516.0 nm) and 19562 cm^{-1} (511.2 nm) for E_{10} , E_{20} , and E_{30} (see Fig. 1), respectively, and 1012, 1786 and 2893 cm^{-1} for w_1 , w_2 , and w_3 as shown in Fig. 2 for the case of zero delay time. Figure 2 is the calculated 0-0, 0-1, and 0-3 vibrational lines. It is suggested that the observed emission band consists of these three components.

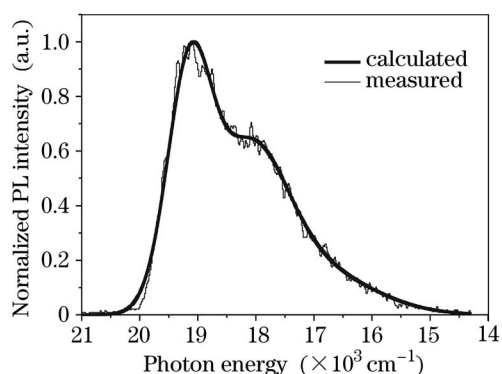


Fig. 4. Measured and calculated PL spectra of Ir(ppy)₃ in polycarbonate at 8 K at delay time of 60 μ s. The measured spectrum was obtained from Ref. [3].

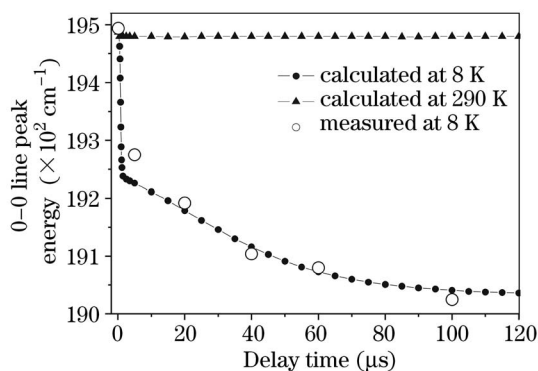


Fig. 5. Delay time dependence of the measured and calculated PL peak energies of Ir(ppy)₃ in polycarbonate (open circles and closed circles, respectively) at 8 K. The calculated PL peak energies at 290 K are shown by closed triangles. The measured peak energies were estimated from Ref. [3].

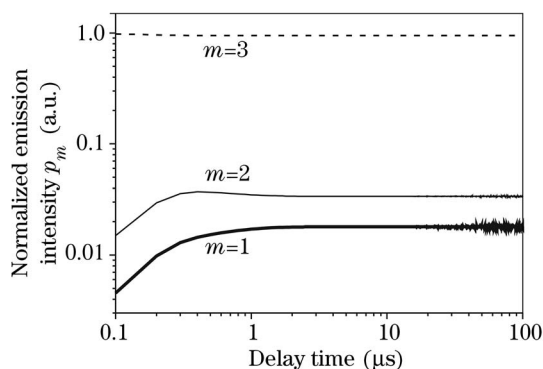


Fig. 6. Log-log plotted delay-time dependence of the calculated p_m emission intensities due to the triplet substates $m=1$, 2, and 3 of Ir(ppy)₃ at 290 K.

The same calculation was done for various delay times. We also obtained good agreement with the observed emission bands as seen in Fig. 4, which shows the PL spectra at delay time of 60 μ s. Figure 5 plots the calculated peak energy of the main band (i.e., 0-0 line) at 8 K against the delay time and compared with the observed peak energy. A good agreement is obtained between the calculated and

measured peak energies. From these results, it is suggested that the present calculation method is reasonable.

We also calculated the emission line shape at 290 K. The calculated peak wavelength of the main 0-0 line is 513.1 nm (19489 cm^{-1}) and, unlike the case at 8 K, it does not change with the delay time as shown in Fig. 5. At high temperature such as 290 K, the emission is mainly due to emission from the upper substate $m=3$ by thermal excitation from the two lower substates. This is confirmed from the delay time dependence of $p_m(t)$ calculated at 290 K (Fig. 6). No report has been given on the time-resolved emission spectra at room temperature. We expect that no peak shift would be observed at high temperatures such as 290 K.

We assumed the peak wavelengths of the emission bands due to the 0-0 transition from the substates $m=1$, 2, and 3 to the ground state are 523.5, 516.0, and 511.2 nm, respectively, as mentioned above. The energy difference between the $m=1$ and the $m=3$ bands is about 460 cm^{-1} . This seems to be inconsistent with the separation of the $m=1$ and $m=3$ energy levels $E_{31}=86.2 \text{ cm}^{-1}$. The 523.5 nm emission peak means that the energy separation between the substate $m=1$ and ground state. Therefore, taking into account that the Huang-Rhys factor S is different among the three substates as shown in Fig. 1, it is not unreasonable that the 460 cm^{-1} separation of the $m=1$ and $m=2$ emission peaks is largely different from the separation $E_{31}=86.2 \text{ cm}^{-1}$.

In conclusion, we have calculated the time-dependent peak shift and vibronic structure for the green-emission band of Ir(ppy)₃ doped in PC under the Franck-Condon principle using (1) three zero-field splitting substates of the triplet state which give rise to emission bands with different peak energies, (2) relaxation processes among the three substates, and (3) different Huang-Rhys factors for the substates. Good agreement was obtained between the calculated and measured emission spectra at various delay times.

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