

Energy transfer between Ir(ppy)₃ dopant and TPD host observed from the photoluminescence intensity and lifetime of Ir(ppy)₃

Taiju Tsuboi and Nadeer Aljaroudi

Faculty of Engineering, Kyoto Sangyo University, Kamigamo, Kyoto 603-8555, Japan

Numerical calculation has been undertaken on the temperature dependence of photoluminescence (PL) intensity and PL lifetime of *fac* tris(2-phenylpyridine) iridium (Ir(ppy)₃) phosphorescent material doped in 4,4'-bis[N-(p-tolyl)-N-phenyl-amino] biphenyl (TPD) and compared with the experimental result. Good agreement is obtained between the observed and calculated PL intensities and lifetimes. Calculation is also made for the PL intensity and lifetime of the emission from the triplet state of TPD.

OCIS codes: 310.6860, 160.2540, 160.4760, 160.4890, 300.6500.

Organic light emitting diodes (OLEDs) are made from two types of light emitting molecules, fluorescent and phosphorescent. Organic phosphorescent materials are used to improve the photoluminescence (PL) and electroluminescence quantum efficiency of organic light emitting diodes (OLEDs). Several transition metal complexes like *fac* tris(2-phenylpyridine) iridium (Ir(ppy)₃) and platinum octaethyl porphine (PtOEP) show a relatively high quantum efficiency in OLED devices since the heavy metals enhance the spin-orbit coupling^[1–5]. The spin-orbit coupling induces mixing of the spin-allowed singlet state into the spin-forbidden triplet state, resulting in the increase of the radiative transition probability from the triplet state to the singlet ground state.

Recently a detailed measurement of the phosphorescence lifetime and intensity was done for Ir-compounds by the photoexcitation at wide temperature range of 5–300 K, e.g., for iridium (III) bis[(4,6-difluorophenyl)pyridinato-N, C^{2'}] picolinate (FIrpic) doped in 4,4'-N,N'-dicarbazole-biphenyl (CBP) and in N,N'-dicarbazolyl-3,5-benzene (mCP)^[6], for Ir(ppy)₃ in 1,1-bis[(di-4-tolylamino) phenyl] cyclohexane (TAPC) and 4,4'-bis[N-(P-tolyl)-N-phenyl-amino] biphenyl (TPD)^[7], and for Ir(ppy)₃ in polymethyl methacrylate (PMMA) and CBP^[8].

Unlike the cases of Ir(ppy)₃ doped in CBP, PMMA, and TAPC, curious temperature dependence has been observed in the cases of Ir(ppy)₃ in TPD and FIrpic in CBP, i.e., the PL intensity of Ir(ppy)₃ increases with increasing temperature from 5 to about 200 K^[6,7]. It is suggested that such a temperature dependence is due to the endothermic energy transfer from the lowest triplet state of the host to the triplet state of Ir(ppy)₃ dopant because the triplet state energy of the host is lower than the lowest triplet state energy of the Ir(ppy)₃ dopant^[6,7,9,10].

Another curious temperature dependence has been observed in the PL lifetime by the excitation with 337.1-nm N₂ laser, i.e., the lifetime of Ir(ppy)₃ in TPD increases with decreasing temperature from 300 K and shows maximum lifetime at 100 K, and then decreases to below 50 K^[7]. No numerical explanation has been suggested for the behavior of lifetime. In the present study we try to explain quantitatively the temperature dependences of PL intensity and lifetime of Ir(ppy)₃ in TPD.

The emitting triplet state in phosphorescent OLED has

been attributed to the metal-to-ligand-charge-transfer triplet state (³MLCT)^[3,11]. The lowest-energy triplet state in the ³MLCT states consists of three zero-field splitting substates 1, 2, and 3, where the transition from the lowest-energy substate 1 (called level 1, hereafter) to the singlet ground state is forbidden, while the transitions from the levels 2 and 3 are allowed^[2,3]. Finkenzeller and Yersin have explained the temperature dependence of PL lifetime observed for Ir(ppy)₃ doped in tetrahydrofuran (THF) by the three-level model where the radiative transition occurs from each of the three substates^[3]. They obtained using thermal equilibrium approximation in the three substates that the radiative transition rates k_1 , k_2 , and k_3 from the levels 1, 2, and 3 to the singlet ground state, the energy separation E_{21} between the levels 2 and 1, and the energy separation E_{31} between the highest energy level 3 and the level 1 are $k_1 = 1/(145 \times 10^{-6}) \text{ s}^{-1}$, $k_2 = 1/(11 \times 10^{-6}) \text{ s}^{-1}$, $k_3 = 1/(0.75 \times 10^{-6}) \text{ s}^{-1}$, $E_{21} = 13.5 \text{ cm}^{-1}$, and $E_{31} = 83.5 \text{ cm}^{-1}$, respectively. In this paper we explain the experimental result of Ir(ppy)₃ doped in TPD using these values.

The triplet state energy of TPD is at 2.34 eV (18874 cm⁻¹), while the lowest energy of the triplet state of Ir(ppy)₃ (i.e., level 1) is 2.42 eV (19519 cm⁻¹), i.e., the triplet state of TPD (named level 4 hereafter) is located at 645 cm⁻¹ below the level 1 (see Fig. 1)^[7]. We assume that the energy transfer between the level 1 and level 4 takes place by the non-radiative transition through one phonon as shown in Fig. 2, where k_{41} ($=K_4 n$, n is the occupancy of the effective phonon modes, K_4 is a coupling constant between the level 1 and level 4) is the non-radiative transition rate from the level 1 to 4.

From the energy level diagram of Fig. 1, the rate equations for the populations $N_j(t)$ of the j ($= 1, 2, 3, 4$) levels at time t are given as

$$\begin{cases} \frac{dN_4(t)}{dt} = -(k_4 + k_{41})N_4(t) + k_{14}N_1(t) \\ \frac{dN_3(t)}{dt} = -(k_3 + k_{32} + k_{31})N_3(t) + k_{23}N_2(t) \\ \quad + k_{13}N_1(t) + k_{21}N_2(t) \\ \frac{dN_2(t)}{dt} = k_{32}N_3(t) - (k_2 + k_{23} + k_{21})N_2(t) \\ \quad + k_{12}N_1(t) \\ \frac{dN_1(t)}{dt} = k_{41}N_4(t) + k_{31}N_3(t) + k_{21}N_2(t) \\ \quad - (k_1 + k_{12} + k_{13} + k_{14})N_1(t) \end{cases}, \quad (1)$$

where k_4 is the radiative transition rate, i.e., radiative

transition probability of the triplet state of TPD, k_{21} is non-radiative transition rate from the level 2 to 1, and k_{12} is the reverse transition rate^[12,13]. These relaxation processes between the three zero-field splitting substates occur by one-phonon process, so that for example the transition rate k_{12} is given by $k_{12} = K_1 n$, where K_1 is a coupling constant which reflects the interaction between the levels 1 and 2. In the optical processes we have neglected the non-radiative transition from the level 1 to the ground state of Ir(ppy)₃, because it was shown from the analysis for temperature dependences of PL intensity and lifetime of Ir(ppy)₃ doped in CBP and PMMA that such a transition does not occur^[12,13].

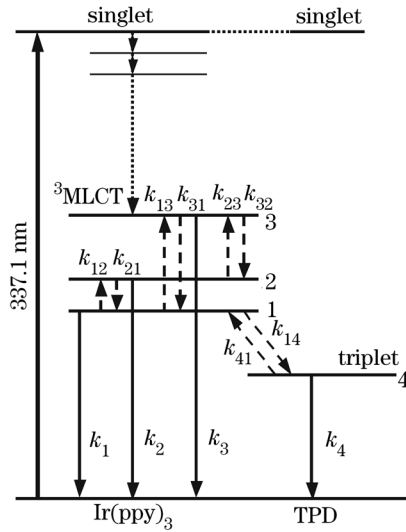


Fig. 1. Schematic energy level diagram for the excited spin-singlet and emitting triplet states 1, 2 and 3 of Ir(ppy)₃ and the lowest-energy triplet state of TPD (level 4), together with the photophosphorescence optical processes in these levels. Straight arrow indicates the radiative transition, while broken arrow indicates the non-radiative transitions.

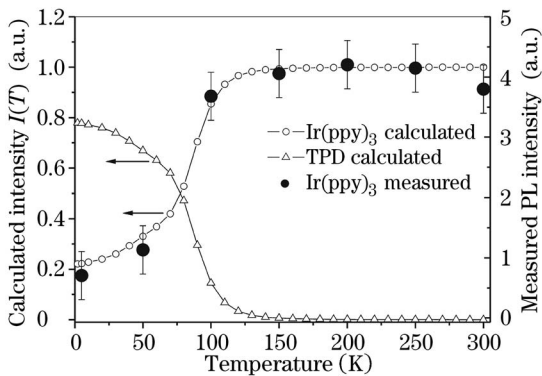


Fig. 2. Temperature dependence of the calculated $I(T)$ for emission from Ir(ppy)₃ doped in TPD (open circle), compared with the measured intensity (closed circles with error bar, right scale) which were obtained from Ref. [7]. Calculation is made using values of $E_{21} = 13.5 \text{ cm}^{-1}$, $E_{31} = 83.5 \text{ cm}^{-1}$, $E_{14} = 645 \text{ cm}^{-1}$, $K_1 = K_2 = K_3 = 6.2 \times 10^6 \text{ s}^{-1}$, $K_4 = 1.5 \times 10^6 \text{ s}^{-1}$, $k_1 = 1/(145 \times 10^{-6}) \text{ s}^{-1}$, $k_2 = 1/(11 \times 10^{-6}) \text{ s}^{-1}$, $k_3 = 1/(0.75 \times 10^{-6}) \text{ s}^{-1}$, $k_4 = 1/(50 \times 10^{-3}) \text{ s}^{-1}$. Calculation is also made for the temperature dependence of emission from the triplet state of TPD (open triangle) under assumption that no triplet-triplet annihilation occurs in the TPD emission.

We make the following assumption regarding the coupling constant. $K_1 = K_2 = K_3$ (where K_2 is the coupling constant between the levels 1 and 3, and K_3 is the coupling constant between the levels 2 and 3) but K_4 is different from the other coupling constants, i.e., the coupling constant is the same for the transitions between the energy levels in the same molecule but different for the transition between the different molecules.

The emission intensity of Ir(ppy)₃ at time t is proportional to $I(t)E_{\text{photon}}$ where $I(t)$ is given by

$$I(t) = k_3 N_3(t) + k_2 N_2(t) + k_1 N_1(t), \quad (2)$$

and E_{photon} is photon energy of luminescence. The emission intensity of Ir(ppy)₃ at temperature T is proportional to $I(T)$ which is derived by integrating Eq. (2) in time range from zero to infinity. We calculate the temperature dependence of $I(T)$ by changing the K_1 , K_4 and k_4 values variously under $k_1 = 1/(145 \times 10^{-6}) \text{ s}^{-1}$, $k_2 = 1/(11 \times 10^{-6}) \text{ s}^{-1}$, $k_3 = 1/(0.75 \times 10^{-6}) \text{ s}^{-1}$, $E_{21} = 13.5 \text{ cm}^{-1}$, $E_{31} = 83.5 \text{ cm}^{-1}$ and $E_{14} = 645 \text{ cm}^{-1}$, and then compare with the experimental result.

Good fitness to the experimental result was obtained at $K_4 = 1.5 \times 10^6 \text{ s}^{-1}$ and $K_1 = K_2 = K_3 = 6.2 \times 10^6 \text{ s}^{-1}$ as shown in Fig. 2.

We calculated the time dependence of $I(t) (= k_3 N_3(t) + k_2 N_2(t) + k_1 N_1(t))$, which reflects the PL intensity of Ir(ppy)₃ in TPD, using the rate equations (1) at various temperatures. Figure 3 shows $I(t)$ in a time range of 0–0.1 ms.

The PL decay consists of four exponentials with PL lifetimes $\tau_1, \tau_2, \tau_3, \tau_4$ where $\tau_4 > \tau_1 > \tau_2 > \tau_3$. Figure 3 shows the PL components due to the longer lifetimes τ_4 and τ_1 . The longest component τ_4 increases with decreasing temperature from 300 to 100 K. The τ_4 value, however, does not change below about 80 K. Figure 4 shows the temperature dependence of the calculated $\tau_1, \tau_2, \tau_3, \tau_4$ lifetimes, which are compared with the PL lifetime measured by Goushi et al.^[7]. A good fit was obtained for the longest lifetime τ_4 at temperature range of 100–300 K. The lifetimes measured at 5 and 50 K, however, deviate from the calculated τ_4 .

We calculated the time dependence of intensity of emission from the triplet state of TPD, i.e., emission intensity from the level 4, using the same values that used above. The emission intensity at temperature T is proportional to $I_{\text{TPD}}(T)$ which is derived by integrating

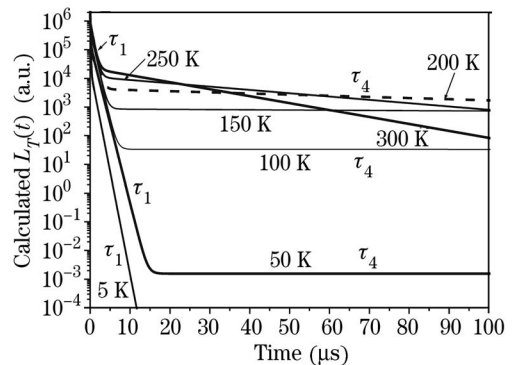


Fig. 3. Time dependence of the calculated $I(t)$ for Ir(ppy)₃ in TPD at various temperatures.

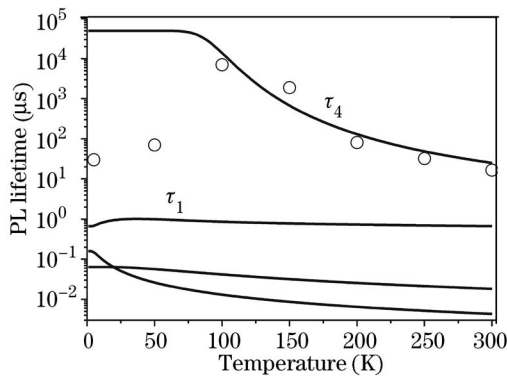


Fig. 4. Temperature dependence of the calculated PL lifetime for Ir(ppy)₃ in TPD, compared with the measured PL lifetime (open circle) which were obtained from Ref. [7].

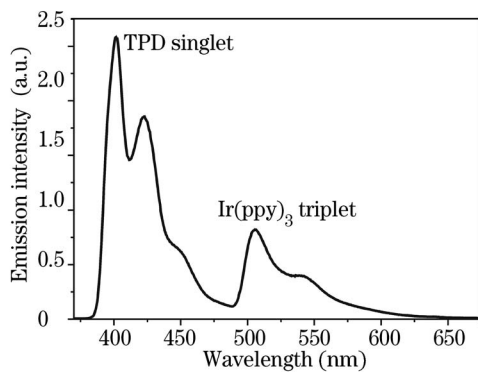


Fig. 5. PL spectrum of a thin film of TPD doped with 5 wt.-% Ir(ppy)₃, which was excited with 360-nm light at 10 K.

$k_4 N_4(t) (= I_{\text{TPD}}(t))$ in time range from zero to infinity. The calculated $I_{\text{TPD}}(T)$ is shown by triangles in Fig. 2. The TPD intensity is 3.5 times as large as the Ir(ppy)₃ intensity at 10 K. It decreases with increasing temperature and it is almost zero above 150 K. Such a large intensity at 10 K is caused by a much higher population of level 4, N_4 , than the populations of levels 1, 2, and 3. It was found that 1) the population N_4 is much higher in a calculated temperature range of 1–300 K than the populations N_1 , N_2 and N_3 , and 2) the ratio of N_4 to N_1 is almost constant at 1–50 K but decreases rapidly with increasing temperature from about 50 K, e.g., the ratio is 80000 at 10 K and 21 at 300 K. The decrease of N_4 is due to the endothermic energy transfer from the level 4 to level 1. Calculation was also made for the PL lifetime of the TPD emission. The lifetime was the same as the the longest PL lifetime (τ_4) estimated for Ir(ppy)₃ which is shown in Fig. 4, leading to confirmation of energy transfer between these dopant and host.

The triplet emission of TPD appears in a range of 520–650 nm with a sharp peak at 528 nm and a broad band with peak at about 570 nm^[7,14]. The emission appears at low temperatures below about 150 K and its intensity is about 0.026 times as large as the emission due to the singlet state of TPD at 10 K, which was observed using

a thin film of TPD^[14]. The calculated $I_{\text{TPD}}(T)$ predicts considerable enhancement of the triplet emission at 10 K in the case of TPD doped with Ir(ppy)₃ because of the non-radiative transition from the level 1. Figure 5 shows the photoluminescence spectrum of a thin film of TPD doped with 5 wt.-% Ir(ppy)₃, which was excited with 360-nm light at 10 K^[14]. Intense emission band due to the singlet state of TPD is observed at 395–480 nm, together with the green emission band due to Ir(ppy)₃ which is superimposed on the tail of the TPD emission band. The emission due to the triplet TPD is not seen in Fig. 5. This does not agree with the calculated result which predicts the triplet TPD emission more intense than the Ir(ppy)₃ emission. The disagreement is explained as follows. We have neglected the triplet-triplet annihilation in TPD. The radiative lifetime of the level 4 is 50 ms. Such a very long lifetime induces the triplet-triplet annihilation in TPD, resulting in strong depression of the triplet emission. Therefore, from the result of calculation for TPD emission shown in Fig. 5, we suggest the importance of the triplet-triplet annihilation in TPD.

The present work was partly supported by the Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (No. 15550165). T. Tsuboi's e-mail address is tsuboi@cc.kyoto-au.ac.jp.

References

1. M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Pure Appl. Chem.* **71**, 2095 (1999)
2. H. Yersin, W. Humbs, and J. Strasser, *Topics in Current Chemistry*, H. Yersin (ed.) (Springer-Verlag, Berlin, 1997) p.154.
3. W. J. Finkenzeller and H. Yersin, *Chem. Phys. Lett.* **377**, 299 (2003).
4. J. Shinar and V. Savvateev, *Organic Light-Emitting Devices*, J. Shinar (ed.) (Springer-Verlag, Berlin, 2004) chap.1.
5. L. S. Hung and C. H. Chen, *Mater. Sci. Eng.* **R39**, 143 (2002).
6. R. J. Holmes, S. R. Forrest, Y.-J. Tung, R. C. Kwong, J. J. Brown, S. Garon, and M. E. Thompson, *Appl. Phys. Lett.* **82**, 2422 (2003).
7. K. Goushi, R. Kwong, J. J. Brown, H. Sasabe, and C. Adachi, *J. Appl. Phys.* **95**, 7798 (2004).
8. K. Goushi, Y. Kawamura, H. Sasabe, and C. Adachi, *Jpn. J. Appl. Phys.* **43**, L937 (2004).
9. M. A. Baldo and S. R. Forrest, *Phys. Rev. B* **62**, 10958 (2000).
10. M. A. Baldo and M. Segal, *Phys. Stat. Sol. (a)* **201**, 1205 (2004).
11. P. J. Hay, *J. Phys. Chem. A* **106**, 1634 (2002).
12. T. Tsuboi and N. Aljaroudi, *IEICE Trans. Electron. E* **87-C**, 2028 (2004).
13. T. Tsuboi and N. Aljaroudi, *Jpn. J. Appl. Phys.* **44**, 591 (2005).
14. T. Tsuboi, H. Murayama, and A. Penzkofer, *Thin Solid Films* (to be published) (2005).