

Photoluminescence characteristics of Ir(ppy)₃ and PtOEP doped in TPD host material

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Abstract

Thin films of triphenylamine dimer, *N,N'*-bis(3-methylphenyl)-*N,N'*-bis(phenyl)-benzidine (TPD), *fac* tris(2-phenylpyridine) iridium (Ir(ppy)₃) doped TPD, and platinum octaethyl porphine (PtOEP) doped TPD have been characterized by photoluminescence measurements at several excitation wavelengths in the temperature range from 10 K to room temperature. The investigated doped films are phosphorescent OLED materials whereby TPD acts as triplet reservoir for Ir(ppy)₃ (endothermic transfer system) and as pathway intermediate for PtOEP (exothermic transfer system). At low temperature, phosphorescence of TPD was observed. At short-wavelength excitation, where TPD is absorbing, Förster-type energy transfer to Ir(ppy)₃ and PtOEP was resolved. The temperature-dependent phosphorescence studies revealed Dexter-type triplet–triplet forth and back excitation transfer between Ir(ppy)₃ and TPD and are compatible with Dexter-type triplet–triplet forward excitation transfer from TPD to PtOEP.

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1. Introduction

Organic phosphorescent materials are used to improve the electroluminescence (EL) 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) certainly show high quantum efficiency in OLED devices. These phosphorescent materials are doped into host materials to avoid self-quenching of photoluminescence in neat films. Special organic host materials enhance the quantum efficiency by excitation transfer from host molecules to guest molecules such as Ir(ppy)₃ and PtOEP. For triplet emitting systems, there are existing – depending on the position of the lowest triplet levels – two kinds of energy transfer: one forms an endothermic energy transfer system where the T₁ level of the host is lower than the T₁ level of the guest, the other forms an exothermic system where the T₁ level of the host is higher than the T₁ level of the guest [1–3]. The study of the

influence of the host on the emission of the phosphorescent materials gives important information on the development of phosphorescent OLEDs.

The lowest triplet state of *N,N'*-bis(3-methylphenyl)-*N,N'*-bis(phenyl)-benzidine (TPD) locates at lower energy (≈ 0.08 eV) than that of Ir(ppy)₃, while it locates at considerably higher energy (≈ 0.44 eV) than that of PtOEP as shown in Fig. 1 where the energy levels are taken from [1–3]. Ir(ppy)₃ doped in TPD forms an endothermic system, while PtOEP in TPD presents an exothermic system. Here, we study the temperature dependence of the photoluminescence (PL) of a neat TPD film (host material), of a TPD film doped with Ir(ppy)₃ (endothermic emitter system), and of a TPD film doped with PtOEP (exothermic emitter system) in order to explore the excitation transfer mechanisms towards the development of efficient OLED devices.

2. Experimental procedure

Three kinds of TPD (3-methyl-TPD) thin films were formed by dissolving materials in toluene and spin-coating

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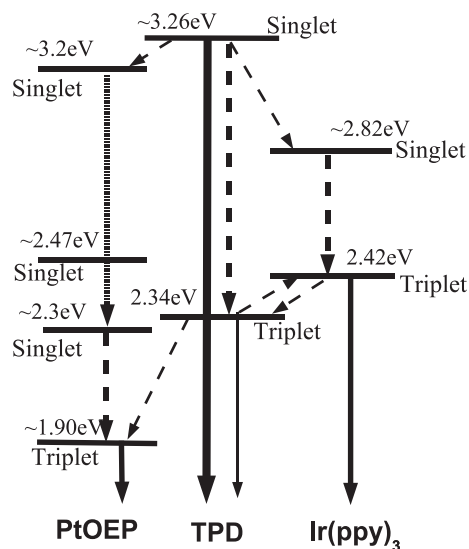


Fig. 1. Schematic energy level diagram and optical processes. Solid, thin broken, and thick broken arrows mean radiative transition, energy transfer, and inter-system crossing, respectively. Broken arrow from the upper singlet state to the lower singlet state in PtOEP indicates internal conversion.

the solutions on glass plates. The first film (called #A) is a 91 nm thick neat film of TPD, the second (called #B) is a 60 nm thick film of TPD containing 5 wt.% of Ir(ppy)₃, and the third (called #C) is a 61 nm thick TPD film containing 5 wt.% of Ir(ppy)₃. For the spin-coating, toluene solutions of TPD (20 mg/ml), Ir(ppy)₃ (20 mg/ml), and PtOEP (10 mg/ml) were prepared and mixed appropriately.

Photoluminescence spectra were measured at various temperatures between 10 K and 300 K with a Spex Fluorolog-3 fluorophotometer. The excitation source was a 450 W Xe-lamp. Corrections were made for the luminescence spectrum wavelength sensitivity. Filters were used to avoid the half and second harmonics of the exciting light. Optical transmission spectra were measured with a Beckman type ACTA M-IV spectrophotometer at room temperature. The absorption cross-section spectra, $\sigma_a(\lambda)$, were derived from the transmission measurements.

3. Experimental results and discussion

3.1. Absorption spectra

The spectra shown in Fig. 2 were obtained by measuring the absorption cross-sections of the constituents and calculating appropriate compositions. For TPD a neat film was measured for wavelength $\lambda < 420$ nm, and a 0.039 molar solution in toluene in a 5 cm long cell was used for $\lambda > 420$ nm. Ir(ppy)₃ was measured in tetrahydrofuran, and PtOEP was measured in toluene. In Fig. 2a, the complete spectra are displayed, while in Fig. 2b, the contributions, $\chi_i \sigma_{a,i}$, of TPD, Ir(ppy)₃, and PtOEP in the host-guest films are shown (χ_i is mole-fraction of component i).

The absorption tail of TPD (Film #A) out to about 550 nm is thought to be due to singlet ground state to triplet absorption. The S_0-T_1 absorption at 540 nm ($\sigma_a \approx 2 \times 10^{-23} \text{ cm}^2$) is about a factor of 10^7 smaller than the S_0-S_1 absorption at 360 nm. The T_1-S_0 radiative lifetime is expected to be in the 0.1 s region, i.e., a factor of 10^7 longer than the S_1-S_0 radiative lifetime. The phosphorescence lifetime of TPD at room temperature was reported to be about 200 μs [1]. The long-wavelength absorption of the Ir(ppy)₃-doped TPD film (Film #B) at 490 nm ($\sigma_a \approx 2 \times 10^{-19}$) is due to S_0-T_1 absorption of Ir(ppy)₃ [4].

Intense absorption bands are observed in PtOEP at a spectral range of $\lambda < 550$ nm (Fig. 2b), which are consistent with the previous results [5,6]. These bands are attributed to transitions from the singlet ground state to excited singlet states. Absorption bands associated with the triplet states have not been observed for PtOEP. A weak absorption peak is found for PtOEP at 642 nm ($\sigma_a \approx 6.5 \times 10^{-21} \text{ cm}^2$) clearly in the present work (see Fig. 2). This band is attributed to the S_0-T_1 transition of PtOEP.

3.2. TPD without Ir(ppy)₃ and PtOEP

When Film #A is excited with UV light at 230 nm ($\approx 5.4 \text{ eV}$), TPD shows an intense PL band with peaks at

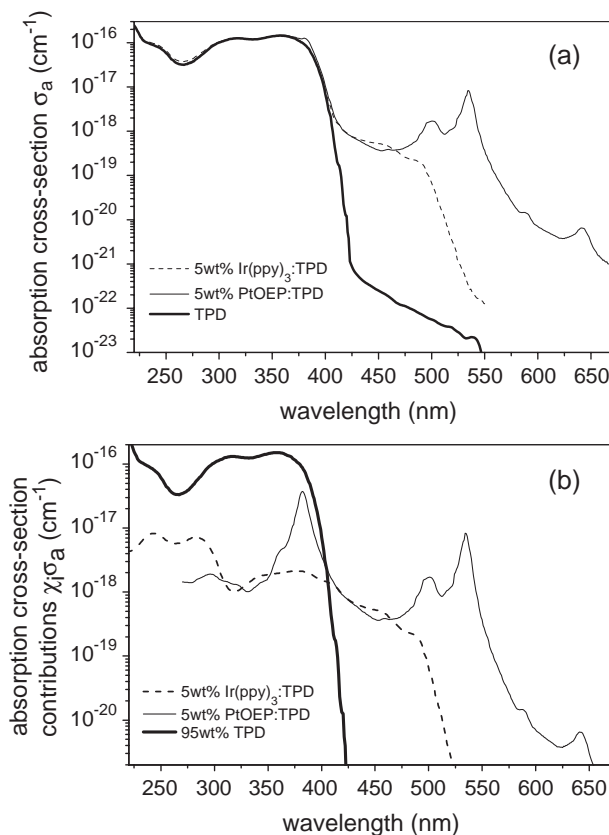


Fig. 2. (a) Composed absorption cross-section spectra of TPD (Film #A), 5 wt.% Ir(ppy)₃ doped in TPD (Film #B), and 5 wt.% PtOEP doped in TPD (Film #C) at room temperature. (b) Absorption cross-section contributions of TPD, Ir(ppy)₃, and PtOEP in the doped films.

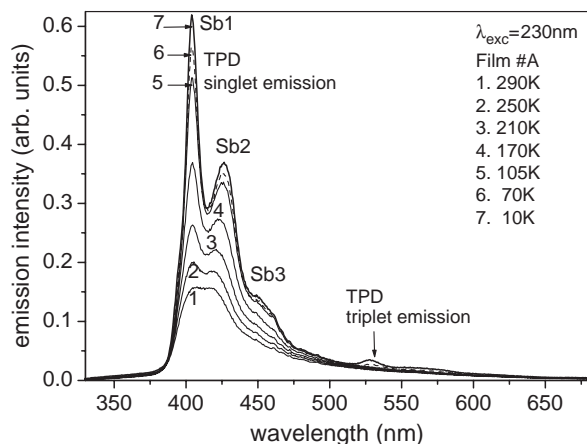


Fig. 3. Emission spectra of Film #A excited with 230 nm light at various temperatures.

403.1 nm and 426.5 nm and a shoulder at 447 nm due to a vibronic progression (called Sb1, Sb2 and Sb3) as shown in Fig. 3. This emission spectrum is consistent with previous measurements using 3-methyl-TPD [7] and 4-methyl-TPD [8]. This band is due to the transition from the first excited singlet state S_1 to the ground state S_0 , i.e., the blue emission is fluorescence. Additionally a very weak PL band with peaks at 528 nm and 568 nm and a shoulder at about 608 nm is observed (called Tb1, Tb2 and Tb3, see Figs. 3 and 4). This PL is due to triplet state T_1 to ground state S_0 emission, i.e., phosphorescence [2]. The triplet PL band is not observed at high temperature such as room temperature, but it appears below about 150 K, and its intensity increases with decreasing temperatures as shown in Fig. 5 likely because of reduced non-radiative decay. The intensity of the singlet PL also increases with decreasing temperature from 290 K, but its increase stops below about 70 K when excited at 230 nm (Fig. 5). The singlet PL band intensity (i.e., integrated area) is about 50 times bigger than the triplet PL band intensity at 30 K, confirming that TPD has been classified as the fluorescent material. It was expected that the 230 nm excitation causes

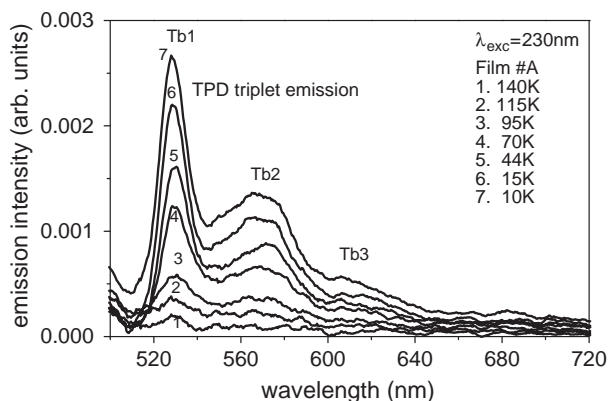


Fig. 4. Emission spectra due to triplet state of TPD at various temperatures. The background of the emission due to the singlet state of TPD is subtracted.

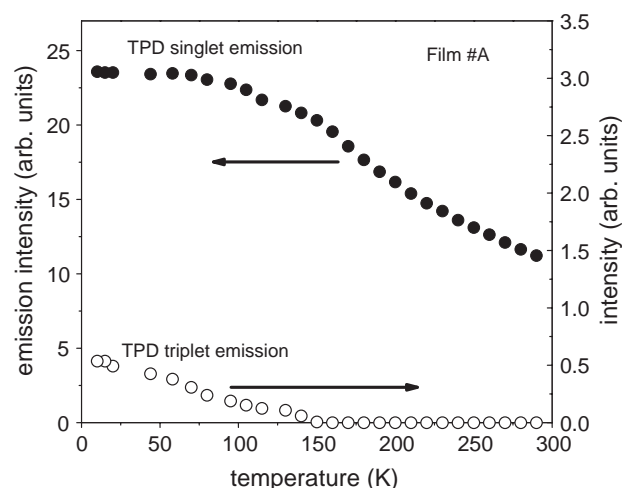


Fig. 5. Temperature dependence of integrated band areas of the singlet and triplet PL bands of TPD in Film #A which is excited with 230 nm light.

photo-degradation by photochemical reaction, but no degradation was observed after the photoexcitation.

Next we observe the PL spectra of the Film #A under the 360 nm (≈ 3.43 eV) excitation. The 360 nm illumination gives rise to excitation into the singlet S_1 state of TPD. We observed the same PL spectra as observed under the 230 nm excitation, but the temperature dependence was different. Fig. 6 shows the temperature dependence of the TPD emission intensities when excited with 360 nm. The singlet emission intensity increases with decreasing temperature down to 150 K, but below 100 K, the emission intensity decreases slightly with decreasing temperature. The 360 nm light excites directly into the first excited singlet state S_1 of TPD, while the 230 nm light excites a higher excited singlet state of TPD. The low excess energy in the case of 360 nm excitation may allow the formation of trapped states at low temperatures which reduces the fluorescence efficiency. Regarding the weak phosphorescence band at 520–650 nm, the temperature dependence is the same as the case of the 230 nm excitation (see Figs. 5 and 6).

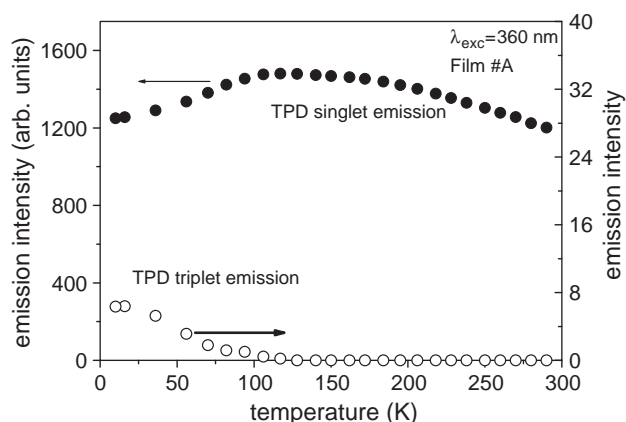


Fig. 6. Temperature dependence of integrated band areas of the singlet and triplet PL bands of TPD in Film #A which is excited with 360 nm light.

It is found from Fig. 3 that the Sb1 peak position does not change with temperature, while the Sb2 peak shifts to shorter wavelength with rising temperature. Probably with rising temperature emission from thermally populated levels gains importance. At 10 K, the Sb2 peak height is roughly a half of the Sb1 peak height. At 290 K, the Sb1 and Sb2 peaks have about the same height. The peaks broaden with rising temperature. The two peaks Sb1 and Sb2 convolve towards a new peak in the middle because of spectral broadening.

3.3. TPD with Ir(ppy)₃

In Film #B, not only the PL band of TPD host but also PL band of the guest Ir(ppy)₃ (with a peak at 505 nm and a shoulder at 541 nm) is observed by excitation with 360 nm light as is shown in Fig. 7. In Fig. 8, the temperature dependence of the emission band intensities (integrated areas) of TPD and Ir(ppy)₃ is shown. The 360 nm light illumination gives rise to excitation of the TPD host predominantly (see absorption contributions of Fig. 2b). The strong Ir(ppy)₃ phosphorescence is thought to be mainly due to Förster-type energy transfer from TPD S₁ state to the Ir(ppy)₃ singlet system and subsequent intersystem crossing to the Ir(ppy)₃ triplet system [9], since the Ir(ppy)₃ phosphorescence signal is larger than the TPD fluorescence signal despite the fact that the absorption efficiency of TPD is about a factor of 70 larger than that of Ir(ppy)₃.

With rising temperature, the TPD singlet emission reduces, while for neat TPD, it was only weakly temperature-dependent (see Fig. 6). The Förster-type singlet energy transfer from TPD to Ir(ppy)₃, i.e., S₁(TPD) + S₀(Ir(ppy)₃) → S₀(TPD) + S₁(Ir(ppy)₃) [9] is thought to be improved with rising temperature due to enlargement of the Franck–Condon overlap integrals. The Ir(ppy)₃ phosphorescence rises slightly in lowering the temperature from room temperature to 200 K probably due to reduction of non-

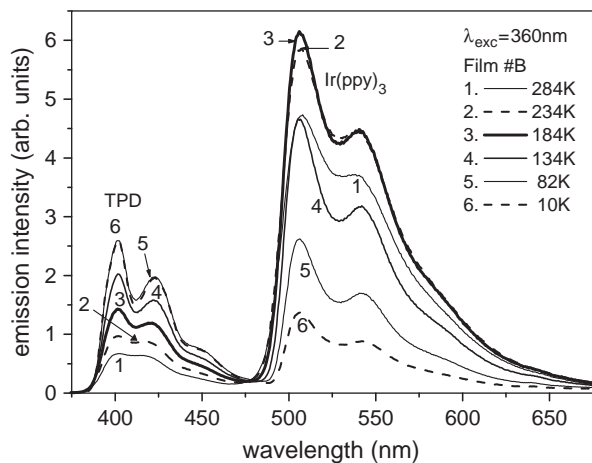


Fig. 7. Emission spectra of Film #B excited with 360 nm light at various temperatures.

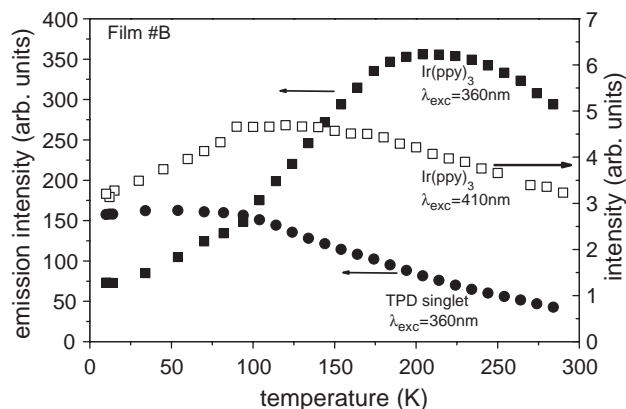


Fig. 8. Temperature dependence of integrated band areas of Ir(ppy)₃ and TPD in Film #B which is excited with 360 nm light (left scale), together with emission band of Ir(ppy)₃ excited with 410 nm light (right scale).

radiative pathways. Below 200 K, the Ir(ppy)₃ phosphorescence reduces with decreasing temperature because of Dexter-type energy transfer from triplet Ir(ppy)₃ to triplet TPD according to T₁(Ir(ppy)₃) + S₀(TPD) → S₀(Ir(ppy)₃) + T₁(TPD) and reduced thermally activated back-transfer from the T₁ state of TPD to the T₁ state of Ir(ppy)₃ [T₁(TPD) + S₀(Ir(ppy)₃) → S₀(TPD) + T₁(Ir(ppy)₃)] since the TPD T₁ level is lower than the Ir(ppy)₃ T₁ level (endothermic system) [1–3,9]. The phosphorescence reduction from 200 K to 10 K is only slightly more than a factor of four since the difficulty of thermally overcoming the energy barrier is partly compensated by the elongation of the T₁ state lifetime of TPD at low temperature (stronger population accumulation in the T₁ state of TPD, because the T₁ state lifetime is likely of the order of 0.1 s at 10 K).

The endothermic energy transfer dynamics of Ir(ppy)₃ in TPD was studied in detail in [1–3,9]. A similar endothermic system consisting of iridium (III) bis [(4,6-difluorophenyl)pyridinato-*N*, C²] picolinate (FIrpic) guest and 4,4'-*N,N'*-dicarbazole-biphenyl (CBP) host was investigated in [10] and a quite similar temperature dependence of PL efficiency (with a maximum at about 200 K) was found as in our case of Ir(ppy)₃ doped in TPD. In Ref. [3], the intensity of the luminescence emission of Ir(ppy)₃ doped in TPD was measured at 5, 50, 100, 150, 200, 250 and 300 K by 337.1 nm excitation. There the film was fabricated by high-vacuum thermal evaporation, which is different from our fabrication by spin-coating. The temperature dependence of the luminescence of our Ir(ppy)₃:TPD Film #B, when excited with 360 nm light (Fig. 8), is similar to that found in Ref. [3].

When the Film #B is excited with 410 nm light (3.03 eV), only the emission of Ir(ppy)₃ is observed but no emission of TPD is observed (curve not shown). At this wavelength, the absorption efficiency of TPD is approximately a factor of 4.5 lower than that of Ir(ppy)₃ (see Fig. 2b). Fig. 8 includes the temperature dependence of the emission of Ir(ppy)₃ excited with 410 nm. The Ir(ppy)₃ emission has a maximum intensity at about 120 K. The

phosphorescence signal is reduced a factor of 100 compared to the case of 360 nm excitation showing the strong influence of the TPD to Ir(ppy)₃ energy transfer when TPD is excited. The same temperature dependence of the Ir(ppy)₃ emission was observed in the case of 440 nm excitation (2.82 eV) as in the case of 410 nm excitation (curve not shown). The Ir(ppy)₃ phosphorescence quenching at low temperature due to triplet transfer from T₁(Ir(ppy)₃) to T₁(TPD) is not so pronounced for 410 nm or 440 nm excitation than for 360 nm excitation.

Fig. 9 shows the excitation spectra for the 450 nm emission of TPD at 10 K and for the 540 nm emission of Ir(ppy)₃ at 10 K. The two emissions have the same excitation bands at 360, 320, 288 and 240 nm. These excitation bands are attributed to the singlet excited states of TPD [7,8], suggesting that energy transfer from the TPD host to the Ir(ppy)₃ guest occurs.

3.4. TPD with PtOEP

Fig. 10 shows the emission spectra of Film #C (TPD doped with PtOEP) excited with 360 nm light at various temperatures. The 360 nm irradiation predominantly excites TPD (see Fig. 2b), resulting in emission of TPD. Besides the TPD emission, a very weak emission band due to PtOEP is observed at 640 nm. Unlike the case of Film #A, no TPD triplet emission (with peaks at 525, 555 and 570 nm) was observed as seen in Fig. 10. The lowest triplet state of TPD is located at higher energy than the lowest triplet state of PtOEP as shown in Fig. 1. Exothermic ³TPD to ³PtOEP by Dexter-type triplet–triplet transfer seems to depopulate the TPD triplet system and thereby reduces the TPD phosphorescence.

At 360 nm, the absorption efficiency of TPD is a nearly a factor of 30 larger than the absorption efficiency of PtOEP (see Fig. 2b). Therefore, it is thought that TPD sensitized PtOEP emission dominates over the directly excited PtOEP emission at 640 nm. Likely Förster-type singlet–singlet energy transfer from TPD to PtOEP takes place

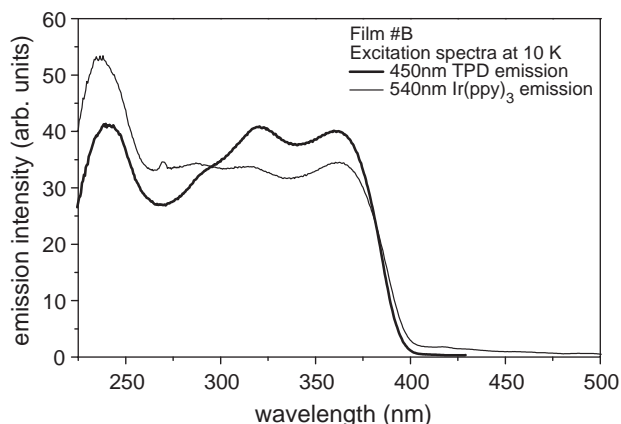


Fig. 9. Excitation spectra for the 450 nm emission of TPD and for the 540 nm emission of Ir(ppy)₃ in Film #B at 10 K.

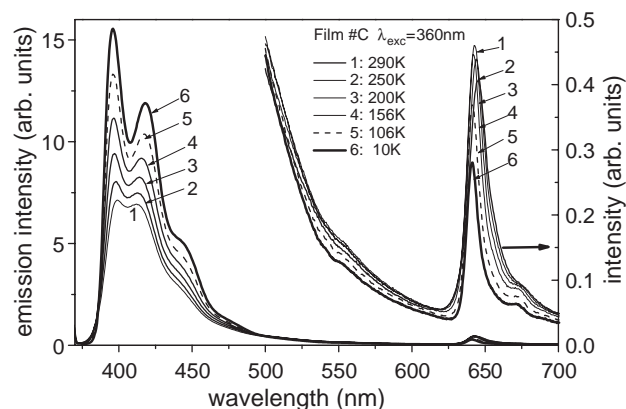


Fig. 10. Emission spectra of Film #C excited with 360 nm light at various temperatures.

(¹TPD* + ¹PtOEP → ¹TPD + ¹PtOEP*) with subsequent ¹PtOEP* → ³PtOEP intersystem crossing. ³PtOEP population may also proceed from ¹TPD* to ³TPD by intersystem crossing and from ³TPD to ³PtOEP by Dexter-type triplet–triplet transfer. This population pathway is important in electroluminescence [1]. The two pathways may be distinguished by time-dependent luminescence measurements since the ³TPD to ³PtOEP channel is thought to be slow (long ³TPD lifetime) while the ¹TPD* to ³PtOEP channel via ¹PtOEP* is fast (short ¹TPD* lifetime, time-dependent measurements are outside the scope of this paper).

In the case of 360 nm excitation, the absorption behavior of PtOEP in TPD (Film #C) is similar to the absorption behavior of Ir(ppy)₃ in TPD (Film #B). But the luminescence of PtOEP is considerably weaker than the luminescence of Ir(ppy)₃. There seems to be stronger phosphorescence quenching for PtOEP in TPD than for Ir(ppy)₃ in TPD. It should be noted that the singlet–triplet absorption strength of PtOEP is lower than that of Ir(ppy)₃, and therefore, the radiative lifetime of the lowest triplet state of PtOEP is long than the radiative lifetime of the lowest triplet state of Ir(ppy)₃ (the same non-radiative rate results in a smaller luminescence signal for PtOEP than for Ir(ppy)₃).

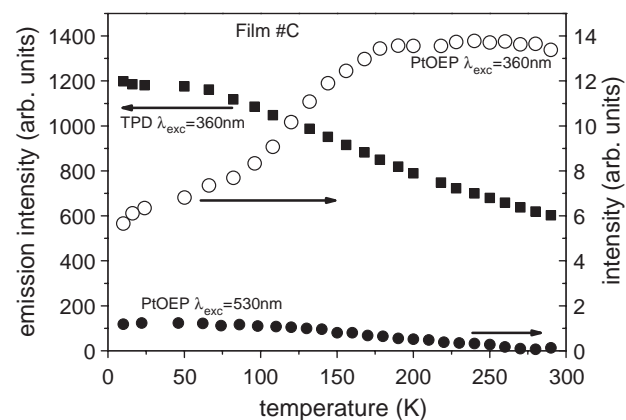


Fig. 11. Temperature dependence of integrated luminescence band areas of PtOEP and TPD in Film #C which is excited with 360 nm light, together with emission band of PtOEP excited with 530 nm light.

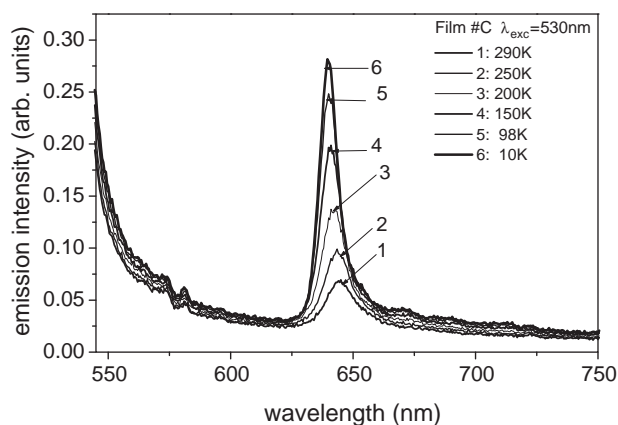


Fig. 12. Emission spectra of PtOEP in Film #C excited with 530 nm light at various temperatures.

Fig. 11 shows the temperature dependence of the intensities (integrated areas) of the TPD and PtOEP emission bands. The TPD emission intensity increases with decreasing temperature from 300 K, and it saturates below about 70 K. Unlike the case of TPD emission, the PtOEP emission intensity decreases with decreasing temperature from 300 K. It is thought that the singlet–singlet energy transfer efficiency from TPD to PtOEP rises somewhat with temperature.

A different temperature dependence was observed for the PtOEP emission when it was excited with 530 nm (≈ 2.34 eV) light (see Figs. 11 and 12), which excites only PtOEP because PtOEP has an absorption band at 530 nm but TPD does not (see Fig. 2b). The PtOEP emission intensity increases with decreasing temperature from 300 K and it saturates below about 100 K. The PL quantum efficiency reduces with rising temperature. At room temperature, the photoluminescence in the case of 360 nm excitation is a factor of about 50 larger than at 530 nm excitation. The TPD to PtOEP energy transfer in the case of 360 nm excitation enhances the phosphorescence. Dexter-type back energy transfer from $^3\text{PtOEP}$ to ^3TPD (exothermic system) plays no role since the energy level difference between $T_1(\text{TPD})$ and $T_1(\text{PtOEP})$ is too large.

4. Summary

The triplet behavior of a neat film of TPD, of an Ir(ppy)_3 :TPD thin film, and of a PtOEP:TPD thin film was investigated by temperature and excitation wavelength-dependent spectral photoluminescence measurements. The presented absorption cross-section spectra at their long-wavelength part show strong singlet ground state to triplet absorption for Ir(ppy)_3 (Ir ligand heavy-atom effect), medium singlet–triplet absorption for PtOEP (Pt coordination heavy-atom effect), and weak singlet–triplet absorption for TPD. Ir(ppy)_3 :TPD films and PtOEP:TPD films are important electroluminescent materials in OLEDs,

because electrical pumping populates singlet and triplet states, the singlet excited electrons intersystematically cross to the triplet systems, and the lowest triplet to singlet ground state phosphorescence is highly efficient in these materials [1–4]. Besides the strong fluorescence of TPD neat films [7,8], phosphorescence was detected at low temperature (<150 K). In the Ir(ppy)_3 and PtOEP guest-TPD host systems, excitation into the host absorption bands resulted in Förster-type singlet–singlet energy transfer to the guests which relaxed to the triplet emitting states by intersystem crossing. The position of the lowest triplet state of the host relative to the lowest triplet state of the guest is sensitive to the guest phosphorescence [1–3,9,10]. For the weakly endothermic Ir(ppy)_3 :TPD guest–host system, the temperature-dependent phosphorescence of Ir(ppy)_3 revealed Dexter-type forward triplet–triplet Ir(ppy)_3 to TPD excitation transfer (nearly temperature independent) and Dexter-type backward triplet–triplet TPD to Ir(ppy)_3 excitation transfer (strongly temperature-dependent) which makes delayed phosphorescence by uphill excitation transfer possible because of the long lifetime in the T_1 state of TPD. For the strongly exothermic PtOEP:TPD guest–host system, the temperature-dependent PtOEP phosphorescence is compatible with Dexter-type forward triplet–triplet TPD to PtOEP excitation transfer (nearly temperature-independent) and negligible Dexter-type backward triplet–triplet PtOEP to TPD excitation transfer (too high energy barrier).

The phosphorescence studies here were restricted to spectral measurements. The presented interpretation of the observed temperature and excitation wavelength-dependent photodynamics is in good agreement with the conclusions drawn from time-resolved electroluminescence and photoluminescence studies [1–3,9,10]. The obtained insights may support the development of efficient phosphorescent organic light-emitting diodes.

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References

- [1] M.A. Baldo, M. Segal, Phys. Status Solidi, A 201 (2004) 1205.
- [2] M.A. Baldo, S.R. Forrest, Phys. Rev., B 62 (2000) 10958.
- [3] K. Goushi, R. Kwong, J.J. Brown, H. Sasabe, C. Adachi, J. Appl. Phys. 95 (2004) 7798.
- [4] W. Holzer, A. Penzkofer, T. Tsuboi, Chem. Phys. 308 (2005) 93.
- [5] P.A. Lane, L.C. Palilis, D.F. O'Brien, C. Giebeler, A.J. Cadby, W. Blau, D.D.C. Bradley, Phys. Rev., B 63 (2001) 235206.

- [6] T. Tsuboi, M. Tanigawa, *Thin Solid Films* 438–439 (2003) 301.
- [7] W. Holzer, A. Penzkofer, H.-H. Hoerhold, *Synth. Met.* 113 (2000) 281.
- [8] R. Philip, W. Holzer, A. Penzkofer, H. Tillmann, H.-H. Hoerhold, *Synth. Met.* 132 (2003) 297.
- [9] J. Kalinowski, W. Stamor, M. Cocchi, D. Virgili, V. Fattori, P. Di Marco, *Chem. Phys.* 297 (2004) 39.
- [10] R.J. Holmes, S.R. Forrest, Y.-J. Tung, R.C. Kwong, J.J. Brown, S. Garon, M.E. Thompson, *Appl. Phys. Lett.* 82 (2003) 2422.