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Photodynamics of OLED Triplet Emitters Ir(ppy)$_3$ and PtOEP

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The absorption behaviour and the emission dynamics of the triplet emitters Ir(ppy)$_3$ and PtOEP in the singlet emitters, polystyrene (PS) and dicarbazole-biphenyl (CBP), are studied. Thin films are prepared by spin-coating. The host (PS, CBP) – guest (Ir(ppy)$_3$, PtOEP) interaction is investigated. The luminescence behaviour in the case of guest excitation (the excitation frequency in the transparency region of hosts) is compared with the luminescence behaviour in the case of host excitation (the excitation frequency in the absorption region of hosts). The efficient host-to-guest energy transfer is observed. Additionally, the excitation transfer from PS to CBP and TPD (triphenylamine dimer) is studied.

Keywords: emission dynamics; host-guest systems; triplet emitters

INTRODUCTION

Organic light emitting diodes play an important role in displays [1,2]. They are prominent candidates to replace conventional light sources [3]. Phosphorescent organic light emitting diodes (PHOLEDs) using a phosphorescent emitter give a higher electroluminescence quantum efficiency than singlet OLEDs [4]. In organic materials, one quarter of electrons is excited to the singlet system, and three quarters are excited

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21

to the triplet system by electrical pumping. In phosphorescent materials, the strong intersystem-crossing transfers the singlet excited molecules to the triplet system, resulting in an accumulation of all excited molecules in the triplet system. In the group of organometallic complexes, especially porphyrin platinum complexes such as platinum octaethylporphyrin (PtOEP) [5–7] and phenylpyridine iridium complexes such as $Ir(ppy)_3$ [8–10] are the most widely used OLED materials.

Phosphorescent materials are doped into host materials to avoid the self-quenching of phosphorescence in neat films. In doped bulk solids or liquids, the photo-excitation has to occur into their transparent region in order that the excitation penetrate into the volume and be absorbed by doped molecules (guests, solute molecules). In thin films as applied in OLEDs, generally only a part of the excitation light is absorbed by the guests in the transparency region of the hosts. In this case, the excitation into the absorption region of the host allows the efficient absorption of a pump light which is transferred to the emitting guests by excitation transfer [11–13]. In the case of host singlet state excitation, the energy transfer may occur by the singlet host to singlet guest Förster-type energy transfer [14] followed by the guest intersystem crossing [15,16]. From the triplet system of the host, the excitation transfer to the triplet system of the guest may occur by the Dexter-type energy transfer [17], either by endothermic transfer if the T_1 level of the host is lower than the T_1 level of the guest, or by exothermic transfer if the T_1 level of the host is higher than the T_1 level of the guest [11–13].

Previously, we studied the absorption and emission spectroscopic characterization of $Ir(ppy)_3$ [10] and PtOEP [7] in liquid solutions (tetrahydrofuran, toluene, chloroform), doped films (PS, CBP), and neat films. The photoluminescence characteristics of $Ir(ppy)_3$ and PtOEP doped into TPD (triphenylamine dimer, N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)-bezidine) were studied in [15], and the energy transfer in a thin film of TPD doped with PtOEP and $Ir(ppy)_3$ simultaneously was studied in [16]. Here, the photoluminescence of thin films of PS and CBP doped with $Ir(ppy)_3$ and PtOEP with excitation into the host absorption region and into the host transparency region is studied. Additionally, the emission behaviour of PS films doped with the singlet emitters CBP and TPD is investigated.

EXPERIMENTAL

The metal complex $Ir(ppy)_3$ was purchased from W. Sands Corp., Jupiter, Fl, USA. The metal complex PtOEP was bought from Frontier Scientific, Logan, Utah, USA. Polystyrene (PS, molar mass

$100\,000\,\mathrm{g\,mol^{-1}}$) was got from Aldrich Co., Germany. CBP and TPD were delivered by Syntec GmbH, Wolfen, Germany. All compounds were used as supplied without further purification.

The films were prepared by dissolving the compounds in tetrahydrofuran (THF) and the spin-coating solutions as described in [7,10]. The absolute intrinsic luminescence spectra, $E_L(\lambda)$, were determined with a self-assembled fluorimeter in front-face collection arrangement [18]. The samples were excited with a 200-W high-pressure mercury lamp ($\lambda_{exc} = 311$, 365, 407, and 526 nm) or a 450-W xenon lamp ($\lambda_{exc} = 260$ nm, FWHM $= 30$ nm). For the absolute quantum yield calibration, the dyes {quinine sulphate dihydrate in $1\,\mathrm{N}$ aqueous H_2SO_4 (fluorescence quantum yield $\phi_F = 0.546$ [19]), rhodamine $6\,\mathrm{G}$ in methanol ($\phi_F = 0.94$ [20]), and cresyl violet in methanol ($\phi_F = 0.54$ [21])} were used as reference ones. The luminescence lifetime measurements, $S_L(t)$, were carried out with a mode-locked and frequency-doubled ruby laser (the wavelength $\lambda_{exc} = 347.15$ nm, duration 35 ps), and the emission detection with a fast micro-channel-plate photomultiplier (Hamamatsu type R1564U-01) and a fast real-time digital oscilloscope (LeCroy type WaveRunner 6050 A).
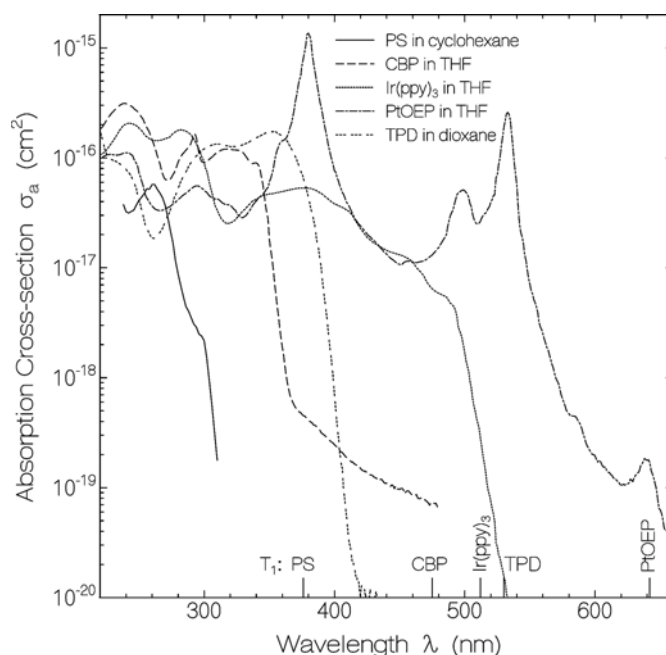

FIGURE 1 Absorption cross-section spectra.

RESULTS

The absorption cross-section spectra of the investigated samples are shown in Figure 1. The long-wavelength absorption tails of CBP, $Ir(ppy)_3$, and PtOEP belong to singlet-triplet absorption. The T_1 level positions of the samples are indicated along the abscissa. They were obtained from phosphorescence spectra for PS [22], CBP [12], TPD [12], $Ir(ppy)_3$ [12], and PtOEP [12]. For the metal complexes PtOEP [7] and $Ir(ppy)_3$ [10,23], the singlet-triplet absorption is strong due to the heavy atom effect, and the position of the lowest triplet level, T_1, is seen by the long-wavelength edge of the absorption spectrum.

The fluorescence quantum distributions, $E_F(\lambda)$, of the neat films of PS (thickness $d_f = 97\,nm$) and CBP ($d_f = 190\,nm$), together with the guests CBP in PS (concentration $2\,wt.\%$, $d_f = 3.5\,\mu m$) and TPD in PS ($4\,wt.\%$, $d_f = 240\,nm$) are shown in Figure 2. For the guests, two fluorescence spectra are shown: the thin curves belong to the excitation in the transparency region of the host, and the thick curves belong to the excitation in the absorption region of the host. In both
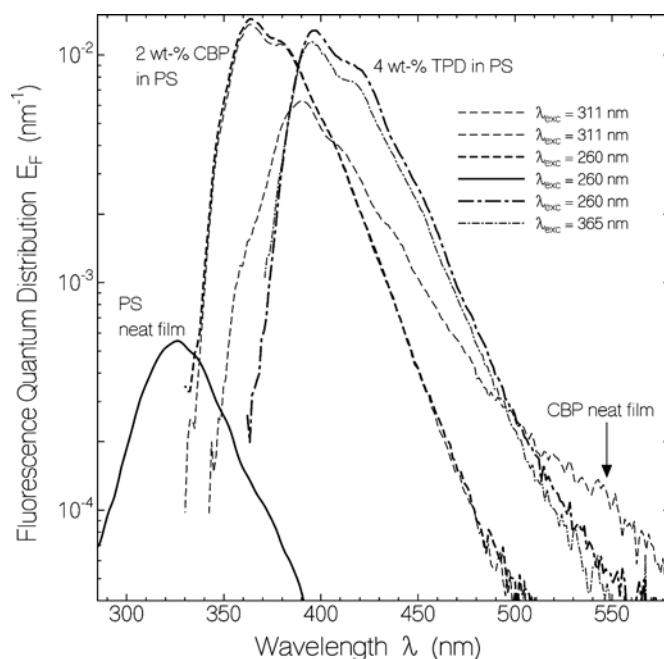

FIGURE 2 Fluorescence quantum distributions of PS and CBP neat films, and of CBP and TPD in PS with excitation in the PS absorption region and transparency region.

cases, the fluorescence quantum distributions are quite similar, despite the fact that, in the case of the excitation into the absorption band of PS, most of the light is absorbed by PS. This indicates the efficient excitation transfer from a host to a guest. The obtained fluorescence quantum yields, $\phi_F = \int E_F(\lambda)d\lambda$, are listed in Table 1.

The guest phosphorescence quantum distributions, $E_P(\lambda)$, of 4 wt.% Ir(ppy)$_3$ in the hosts PS and CBP together with remaining small host fluorescence quantum distributions, $E_F(\lambda)$, are shown in Figures 3a and 3b, respectively. The phosphorescence quantum distributions are nearly independent of the excitation wavelength in the transparency or absorption region of the hosts. This indicates the efficient excitation transfer from the host system to the guest system. The phosphorescence quantum yields, $\phi_P = \int E_P(\lambda)d\lambda$, are rather high in the 60–90% region. They are listed in Table 1.

The guest phosphorescence quantum distributions and the remaining host fluorescence quantum distributions of 4 wt.% PtOEP in the hosts PS and CBP are shown in Figures 4a and 4b, respectively. Again the phosphorescence quantum distributions are nearly independent of the

TABLE 1 Emission Spectroscopic Data of the Investigated Thin Films

Host guest	PS				
	neat film	2 wt.% CBP	4 wt.% TPD	4 wt.% Ir(ppy)$_3$	4 wt.% PtOEP
ϕ_F	0.029	0.67 @ 260 nm 0.65 @ 311 nm	0.61 @ 260 nm 0.54 @ 365 nm		
ϕ_P				0.91 @ 254 nm 0.86 @ 407 nm	0.10 @ 260 nm 0.11 @ 526 nm
$\tau_{F,1/e}$ (ns)		3.2	0.60		
$\tau_{P,1/e}$ (μs)				1.0	10
$\tau_{rad,F}$ (ns)		≈4.8	≈1.0		
$\tau_{rad,p}$ (μs)				≈1.1	≈100

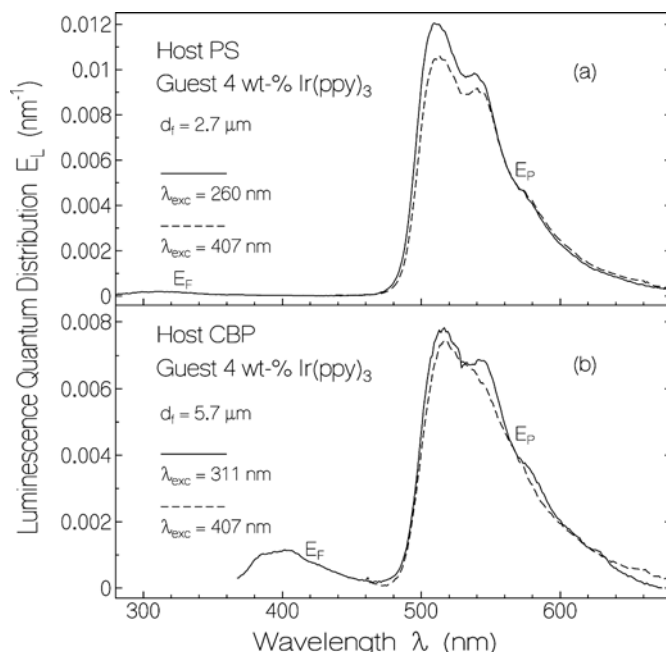| Host guest	CBP			TPD
	neat film	4 wt-% Ir(ppy)$_3$	4 wt-% PtOEP	neat film
ϕ_F	0.345			0.40[a]
ϕ_P		0.70 @ 311 nm 0.62 @ 407 nm	0.158 @ 311 nm 0.153 @ 526 nm	
$\tau_{F,1/e}$ (ns)	0.72			0.44[a]
$\tau_{P,1/e}$ (μs)		0.37	16	
$\tau_{rad,F}$ (ns)	≈2.1			≈1.1
$\tau_{rad,p}$ (μs)			≈100	

[a]From [24].

FIGURE 3 Luminescence quantum distribution of Ir(ppy)$_3$ in PS and CBP hosts. Samples were excited in the host absorption and transparency region.

excitation in the transparency region or absorption region of the hosts. The phosphorescence quantum yields are from 10% to 16% (see Table 1). The phosphorescence efficiency of PtOEP in the films is reduced by oxygen quenching under ambient conditions [7]. Higher phosphorescence quantum yields were obtained in [7] under vacuum conditions.

The temporal phosphorescence traces of 4 wt.% Ir(ppy)$_3$ (a) and 4 wt.% PtOEP (b) in PS and CBP are displayed in Figure 5. The 1/e-lifetimes (time period within which luminescence decreased to 1/e of its peak value) are listed in Table 1. The samples were excited at $\lambda_{exc} = 347.17$ nm with laser pulses of 35 ps in duration. In the case of PS host, the excitation is in the host transparency region; in the case of CBP host, the excitation is dominantly absorbed by the host. The phosphorescence decay of Ir(ppy)$_3$ in CBP is non-exponential. This behaviour is likely due to the triplet-triplet annihilation because of a high excitation energy density [10,12]. The phosphorescence lifetime of Ir(ppy)$_3$ is more than a factor of 10 shorter than the phosphorescence lifetime of PtOEP showing the stronger spin-orbit coupling of Ir(ppy)$_3$ as compared to PtOEP. Estimates of the radiative
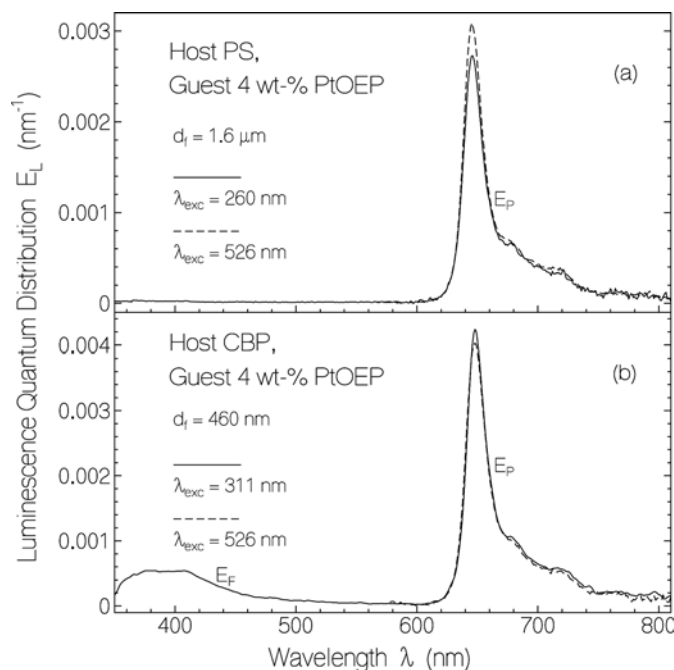
FIGURE 4 Luminescence quantum distribution of PtOEP in PS and CBP hosts. Samples were excited in the host absorption and transparency region.

phosphorescence lifetimes are included in Table 1. They are obtained by the relation $\tau_{rad,P} = \tau_{P,1/e}/\phi_P$.

The determined 1/e fluorescence lifetimes of CBP neat film, TPD neat film (from [24]), CBP in PS, and TPD in PS are included in Table 1. They are in the nanosecond to sub-nanosecond range. Approximate radiative fluorescence lifetimes were obtained by the relation $\tau_{rad,F} = \tau_{F,1/e}/\phi_F$.

DISCUSSION

The energy level schemes with the first excited singlet state and the lowest triplet state are shown in Figure 6. The photo-excitation of PS, CBP, or TPD by singlet-singlet absorption at room temperature results in the $S_1 - S_0$ fluorescence emission. Phosphorescence is not observed at room temperature. The photo-excitation of Ir(ppy)$_3$ and PtOEP by singlet-singlet absorption at room temperature results in the $T_1 - S_0$ phosphorescence emission. The singlet-triplet intersystem-crossing is very efficient due to the strong spin-orbit coupling by
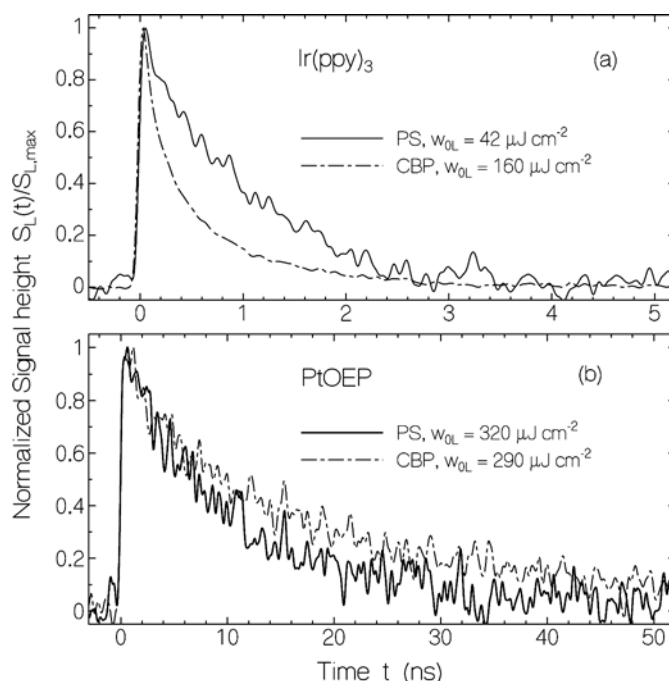
FIGURE 5 Phosphorescence signal traces for $Ir(ppy)_3$ (a) and PtOEP (b) in PS and CBP (excitation wavelength 347.15 nm).

the heavy atom effects of Ir and Pt. In host-guest systems, it is necessary that the long-wavelength absorption edge of the guest be at longer wavelength than the long-wavelength absorption edge of the guest if the efficient emission from the guest is wanted. In the investigated host-guest systems, the excitation into the transparency region of the host does not involve the host system in the absorption and emission dynamics. The excitation into the absorption band of the host causes the guest excitation partially by the direct absorption of the guest (determined by the absorption coefficient contribution of the guest at the excitation wavelength) and partially by the excitation transfer from the host to the guest. In the singlet-emitter guest-host systems CBP in PS and TPD in PS, the excitation into the PS absorption region causes the Förster-type energy transfer [14] from the excited singlet system of the host to the excited singlet system of the guests $[S_1(host) + S_0(guest) \rightarrow S_0(host) + S_1(guest)]$ with the subsequent guest fluorescence emission. In the triplet-emitter guest host systems $Ir(ppy)_3$ and PtOEP in either PS or CBP, the excitation into the host absorption region causes again the Förster-type energy
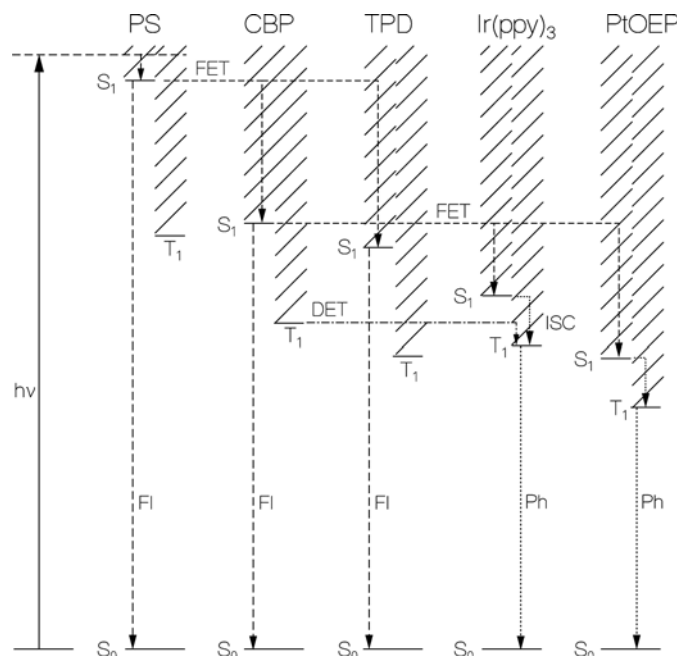
FIGURE 6 Singlet and triplet level schemes of PS, CBP, TPD, Ir(ppy)$_3$, and PtOEP together with most important transitions. FET: Förster-type energy transfer. DET: Dexter-type energy transfer. ISC: intersystem crossing.

transfer from the excited singlet system of the hosts to the excited singlet system of the guests followed by the singlet-triplet intersystem-crossing in the guest systems and the subsequent guest phosphorescence emission. For Ir(ppy)$_3$ and PtOEP in either PS or CBP, the T_1 triplet levels of the hosts are energetically higher than the triplet levels of the guests. An exothermic Dexter-type excitation transfer [17] from the host triplet system to the guest triplet system [T_1(host) + S_0(guest) → S_0(host) + T_1(guest)] is possible. But, at room temperature, this excitation transfer contribution is thought to be negligible since the quantum yield of the host triplet population is moderate (the quantum yield of the intersystem-crossing of styrene is ϕ_{isc} = 0.395 [25], $\phi_{\text{isc}}(\text{CBP}) < 1 - \phi_{\text{F}}(\text{CBP}) = 0.65$), and the triplet state population is quenched in a nonradiative way (short phosphorescence lifetime, no detectable phosphorescence).

At low temperatures, the exothermic Dexter-type excitation transfer from triplet PS and CBP to triplet Ir(ppy)$_3$ and PtOEP may be important because the host triplet state lifetime should become

long (approaching the triplet state radiative lifetime). In the host-guest system TPD doped with Ir(ppy)$_3$, the T$_1$ energy levels of TPD (2.34 eV) and Ir(ppy)$_3$ (2.42 eV) are near together, and the endothermic energy transfer from a host to a guest and the exothermic energy transfer from a guest to a host play an important role [11–13], especially at low temperatures [15,16].

The excitation transfer efficiency, β_{ET}, may be estimated by the ratio of the guest luminescence quantum yield in the case of the excitation into the host absorption region, $\phi_{L,guest}(\lambda_{exc,host})$, to the guest fluorescence quantum yield in the case of the excitation into the host transparency region $\phi_{L,guest}(\lambda_{exc,guest})$ if the guest absorption in the host absorption region is neglected, i.e., $\beta_{ET} \approx \phi_{L,guest}(\lambda_{exc,host})/\phi_{L,guest}(\lambda_{exc,guest})$. For all guest-host systems studied here, we find $\beta_{ET} \approx 1$ indicating the efficient host-to-guest excitation transfer.

CONCLUSIONS

The emission spectroscopic behaviour of the triplet emitters Ir(ppy)$_3$ and PtOEP in the hosts PS and CBP was studied. The highly efficient Förster-type excitation transfer from a host to a guest was observed in thin films. The high phosphorescence efficiency of the guests ($\phi_P \approx 0.6 - 0.9$ for Ir(ppy)$_3$ and $\phi_P \approx 0.1 - 0.16$ for PtOEP) under ambient conditions verify their potential as emitters in phosphorescent OLED devices.

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