

Enhancement of Phosphorescence from Organic Fluorescent Materials Bebq₂ and Alq₃ by Sensitization

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Abstract

Monomer and aggregate of Bebq₂ give fluorescence at 492 and 511 nm at 12 K, respectively. Intense T₁ emission with vibronic structure was observed from Bebq₂ and Alq₃ below 70 K by heavily doping with phosphorescent Ir(ppy)₃. Energy transfer from Ir(ppy)₃ was clarified by photoluminescence excitation spectra.

1. Introduction

Electronic transition probability from the excited triplet T₁ state to the ground state S₀ is much smaller for organic fluorescent materials than the probability from the singlet S₁ state. Therefore, phosphorescence intensity is much lower than fluorescence or nearly zero. If we could enhance phosphorescence from the fluorescent materials, it would be useful as new emitter for organic light emitting diodes (OLEDs).

One way to enhance the T₁ emission is to use the energy transfer from the highly populated T₁ state of phosphor to the T₁ state of the fluorescent material. Such a sensitization by phosphor was observed for tris(8-hydroxyquinoline) aluminum (Alq₃) using tris(2-phenylpyridine) iridium [Ir(ppy)₃] [1] and for 4,4'-N,N'-dicarbazole-biphenyl (CBP) using iridium bis [(4,6-difluorophenyl)-pyridinato-N, N²] picolinate (FIrpic) [2].

Another fluorescent material, bis(10-hydroxybenzo [h] quinolinato)-beryllium (Bebq₂), is known as efficient electron transport material [3], green emitter [4,5] and host material for a red emitter tris(1-phenylisoquinoline) iridium [Ir(piQ)₃] [6] in OLEDs.

Here we present the enhancement of the T₁ emissions from of Bebq₂ and Alq₃. We use Ir(ppy)₃ as a sensitizer because its T₁ energy is higher than the T₁ energies of Bebq₂ and Alq₃.

2. Experimental

Thin films of Bebq₂(5 wt %):polystyrene (PS) (95

wt %), Bebq₂(60 wt %):NPB(40 wt %), Bebq₂(60 wt %):Ir(ppy)₃(40 wt %), neat Bebq₂ and Alq₃(60 wt %):Ir(ppy)₃(40 wt %) films were thermally evaporated on silica plate, where NPB means N,N-di(naphthalene-1-yl)-N,N-diphenyl-benzidine.

The film thickness is 100 nm. Absorption spectra were measured with a Shimadzu UV3100 spectrophotometer. The photoluminescence (PL) and PL excitation (PLE) spectra were measured with a Spex Fluorolog-3 spectrofluorimeter at 12-296 K.

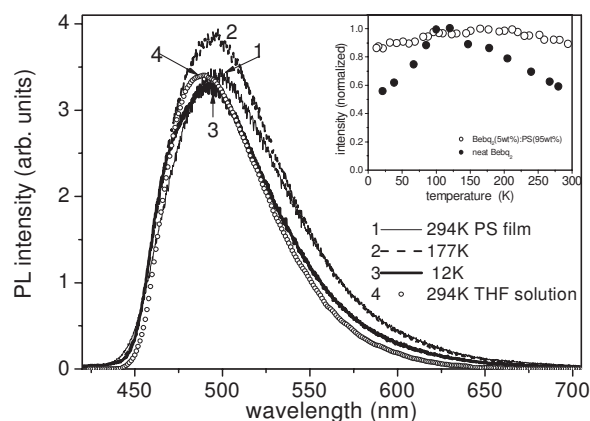


Fig. 1. PL spectra of Bebq₂(5 wt %):PS(95 wt %) film at 294, 177 and 12 K, excited at 340 nm, and Bebq₂ in THF solution, excited at 406 nm (curve 4). The PL band intensity is plotted against temperature in inset, compared with the PL intensity of neat Bebq₂ film.

3. Results and discussion

3.1. Optical characteristics of Bebq₂

A single PL band of Bebq₂ is observed at 496 and 489 nm at 294 K in the 5wt% Bebq₂-doped PS film and 10⁻³ M Bebq₂-doped tetrahydrofuran (THF)

solution, respectively (Fig. 1). This PL peak shifts to 492 nm at 12 K in the film. A vibronic sideband appears at about 474 nm below about 100 K. The PL intensity increases with decreasing temperature from 294 K to about 180 K and then decreases on going to 12 K (inset of Fig. 1). The 489 nm band observed in THF is consistent with a PL band observed at 492 nm in N,N-dimethylformamide (DMF) solution [7], indicating that the lightly doped PS film exhibits the emission from isolated Bebq_2 molecule (i.e., monomer).

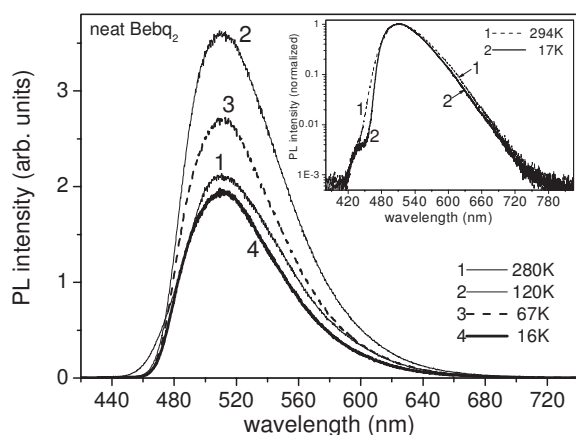


Fig. 2. PL spectra of neat Bebq_2 film at various temperatures, excited at 400 nm. Spectra at 294 and 17 K are plotted in logarithmic scale in inset.

The neat Bebq_2 film gives a PL band at 511 nm (Fig. 2). The PL intensity increases largely with decreasing temperature from 294 to about 110 K and then decreases on going down to 12 K (inset of Fig. 1). A weak shoulder due to monomer is clearly found at about 460 nm at 12 K (inset of Fig. 2). This is understood as follows. Aggregate (probably, dimer) of Bebq_2 molecules are formed in the neat film and gives rise to the PL band at 511 nm. The monomer still remains in the neat film although its amount is much smaller than the aggregate. A peak shift from 414 nm to 420 nm is observed in the absorption spectra on going from lightly Bebq_2 -doped film to neat film. This is consistent with the low-energy 511 nm PL band is attributed to the aggregate and high-energy 496 nm band to the monomer.

Taking into account the results of lightly Bebq_2 -doped PS film and neat Bebq_2 film, the 484 nm band is attributed to monomer, while the 511 nm band to

aggregate of Bebq_2 .

From the present results of lightly- and heavily-doped films and neat film, it is understood that the EL band at 516 or 518 nm observed in [4,5] is due to not monomer but aggregate because the neat Bebq_2 film was used in the OLEDs.

3.2. T_1 emission of Bebq_2

Fig. 3 shows PL spectra of Bebq_2 (40 wt %): Ir(ppy)_3 (40 wt %) film. An emission band is observed at about 516 nm at 294 K and at about 511 nm at 14 K, which is similar to the band observed in the neat film. A shoulder is also observed at about 485 nm, which is due to the monomer emission of Bebq_2 . When temperature is decreased from 294K to 12 K, a Gaussian-shape band at 604 nm increases and disappears above 120 K, while emission band with two peaks at 573 and 617 nm and a shoulder at about 665 nm appears and enhances on going down to 12 K.

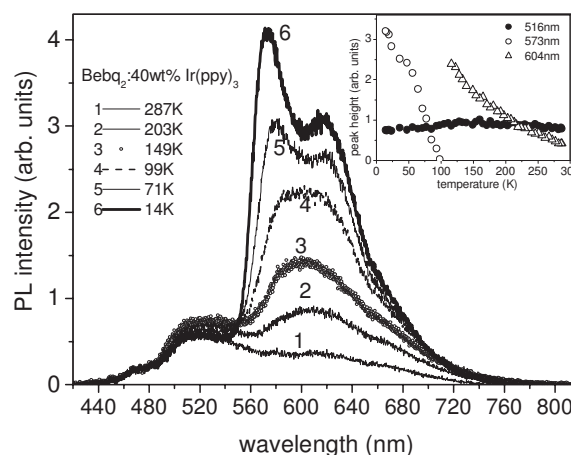


Fig. 3. PL spectra of Bebq_2 (60 wt %): Ir(ppy)_3 (40 wt %) film at various temperatures, excited at 350 nm. The PL intensities of the 516, 573 and 6034 nm bands are plotted against temperature in inset.

Unlike the 604 and 573 nm bands, the 516 nm PL band intensity is almost constant between 294 and 12 K (inset of Fig. 3). The 573 and 617 nm peaks and the 665 nm shoulder increase at the same rate with decreasing temperature, indicating that they arise from the same origin. This is confirmed from similarity of the PLE spectra for these emissions.

Different PLE spectra were obtained for the 570-760 nm red emission and the 500-540 nm green

emission. It is noted that the red emission is generated by excitation even at wavelength longer than 475 nm, but the green emission is not generated. When we compare PLE spectra with absorption spectra of the neat Ir(ppy)₃ and Beq₂ films (Fig. 4), we found that the PLE spectrum for the green emission is similar to the absorption spectrum of Beq₂, while the PLE spectrum for the red emission is composed of the absorption spectra of not only Ir(ppy)₃ but also Beq₂.

The vibronic-structured red band with peaks at about 573, 617 and 665 nm is attributed to the T₁ emission from Beq₂. The T₁ energy is estimated from the onset position of the high-energy 0-0 vibronic phosphorescence band. The onset of the 573 nm band is at 549 nm, corresponding to 2.26 eV.

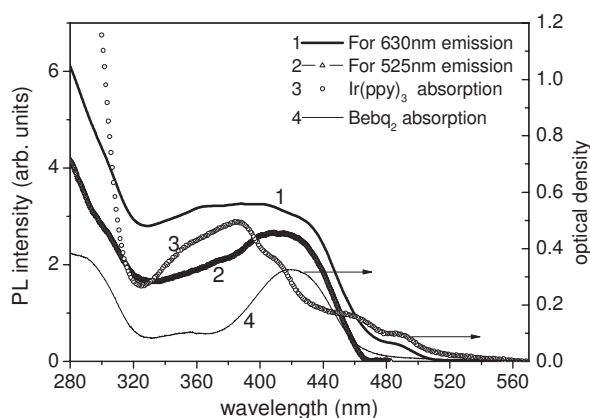


Fig. 4. PLE spectra for 630 and 525 nm emissions in Beq₂(60 wt %):Ir(ppy)₃ (40 wt %) film at 12 K, together with absorption spectra of neat Ir(ppy)₃ film at 12 K and neat Beq₂ film at 294 K.

As temperature is decreased from 296 K to 120 K, the non-structured 604 nm symmetric PL band appears before the T₁ emission appears (Fig. 7). Such a temporal appearance of Gaussian-shape band is also observed in Alq₃(60 wt %):Ir(ppy)₃(40 wt %) [1]. This is understood as follows. The Gaussian-shape band is due to a large difference of equilibrium position between the excited and ground state wide in the configuration coordinate diagram, i.e., large Huang-Rhys parameter *S* [8]. On the other hand, asymmetric vibronic-structured T₁ emission band indicates a small *S* parameter. The *S* parameter is estimated to be *S*=0.76 from the height ratio of the 617 nm one-phonon band to the 573 nm zero-phonon band. Therefore we suggest that the T₁ state takes

different potential energy relative to the ground state, depending on temperature.

From comparison of the PLE spectrum for the red T₁ emission with the absorption spectra of Ir(ppy)₃ and Beq₂ (Fig. 4), we found that the T₁ emission is generated by excitation into both Ir(ppy)₃ and Beq₂ with UV light. The irradiation with UV light, e.g., 360 nm light, excites into the singlet state of Ir(ppy)₃ and Beq₂. The excited Ir(ppy)₃ relaxes to its T₁ state, then its energy is effectively transferred to the lower-energy T₁ state of nearby Beq₂ by the Dexter-type transfer, resulting in the T₁ emission from Beq₂ and no T₁ emission from Ir(ppy)₃. On the other hand, the S₁ emission of Beq₂ is generated by excitation into not Ir(ppy)₃ but Beq₂. Thus, the excited Beq₂ relaxes to its S₁ state, and gives rise to (1) its S₁ emission and (2) energy transfer to the T₁ state of Ir(ppy)₃ by the Foerster-type transfer because the T₁ state is mixed with the S₁ state by strong spin-orbit coupling in Ir(ppy)₃. The T₁ state locates close to the S₁ state of Beq₂, resulting in efficient energy transfer (Fig. 5).

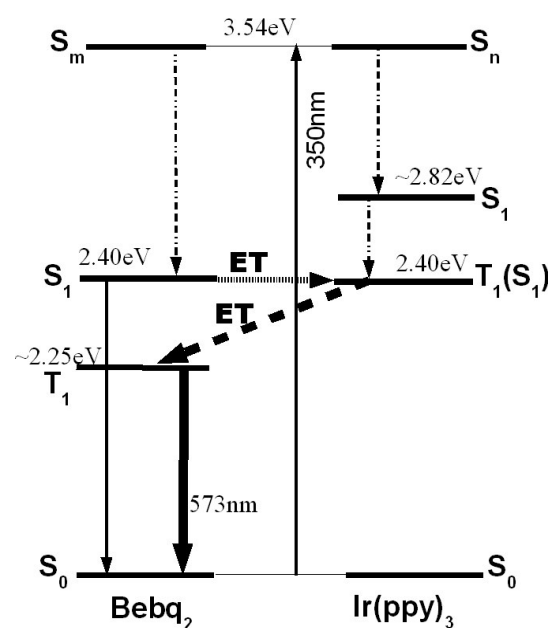


Fig. 5. Emission process in Alq₃(60 wt %) : Ir(ppy)₃ (40 wt %) film after excitation at 350 nm.

The T₁ emission of Beq₂ was never observed in film of Beq₂(60 wt %):NPB(40 wt %). Only a single PL peak was observed at 507 nm at 296 K, which shifts to 484 nm at 12 K. The NPB is a fluorescent material, i.e., its T₁ state is less populated. Therefore energy transfer to the T₁ state of Beq₂ is impossible

although the T_1 state of Bebq_2 is lower than that of NPB at 2.30 eV. This indicates that the T_1 emission of fluorescent material is enhanced by the energy transfer from the phosphorescent material.

3.3. T_1 emission of Alq_3

Fig. 6 shows the temperature dependence of the PL spectra from $\text{Alq}_3(60 \text{ wt } \%):\text{Ir}(\text{ppy})_3(40 \text{ wt } \%)$ film which was excited at 350 nm. When temperature is decreased from 300 K to 12 K, intense S_1 emission of Alq_3 increases, but decreases below 200 K (inset of Fig. 6). The highest band peak is observed at about 500 nm at 12 K. This emission shows the vibronic structure at low temperatures. The vibronic peaks are observed at 427, 439, 451, 471 and 483 nm at 12 K. The onset appears at 424 nm. This structure is quite similar to the PL spectrum observed for δ -phase Alq_3 crystal at 1.3 K [9].

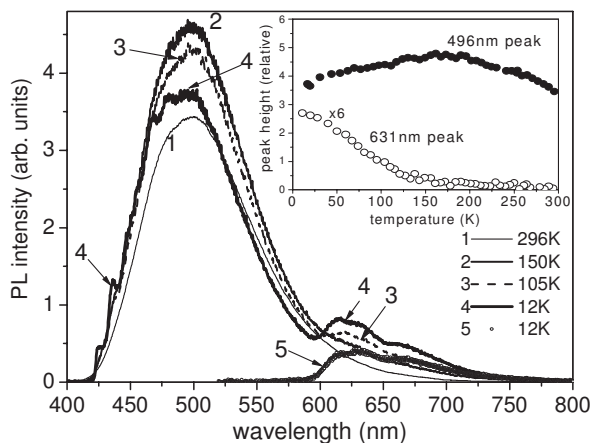


Fig. 6. Temperature dependence of PL spectra of $\text{Alq}_3(60 \text{ wt } \%):\text{Ir}(\text{ppy})_3(40 \text{ wt } \%)$ film excited at 350 nm. Intensity is plotted in inset.

A weak emission band with vibronic structure at about 619, 631 and 663 nm appears below about 150 K. These intensities increase at the same rate with decreasing temperature from about 150 K, while the green PL intensity decreases (inset of Fig. 6). When subtracted the background of the superimposing green emission, the 631 nm component is higher than the other components (curve 5 of Fig. 6). The 619, 631 and 663 nm components are attributed to the 0-0, 0-1 and 0-2 vibronic bands, respectively. This vibronic

spectrum is similar to the delayed PL spectrum of δ -phase Alq_3 crystal [10]. From the S_1 and T_1 emission spectra, it is suggested that δ -phase Alq_3 structure is formed in the present film. Presence of δ -phase is confirmed from vibronic structure appeared in the PLE spectrum for the S_1 emission of Alq_3 .

The PLE spectra indicate that the T_1 emission of Alq_3 is generated by excitation into $\text{Ir}(\text{ppy})_3$ predominantly, while the S_1 emission of Alq_3 by excitation into not $\text{Ir}(\text{ppy})_3$ but Alq_3 . This is quite similar to the case of $\text{Bebq}_2(40 \text{ wt } \%):\text{Ir}(\text{ppy})_3(40 \text{ wt } \%)$.

4. Summary

The PL characteristics of Bebq_2 are studied using films of lightly Bebq_2 -doped polystyrene, neat Bebq_2 , and heavily $\text{Ir}(\text{ppy})_3$ -doped Bebq_2 . Monomer and aggregate of Bebq_2 give fluorescence bands at 492 and 511 nm at 12 K, respectively. Intense T_1 emission band with asymmetric vibronic structure is observed from Bebq_2 below 70 K by heavily doping with $\text{Ir}(\text{ppy})_3$. The T_1 energy is estimated to be 2.26 eV. It is found from the PLE spectra that the T_1 emissions of fluorescent materials Bebq_2 and Alq_3 are enhanced by energy transfer from the T_1 state of nearby $\text{Ir}(\text{ppy})_3$ which was highly populated by (1) relaxation from the photo-excited singlet state in $\text{Ir}(\text{ppy})_3$ and (2) energy transfer from the S_1 state of Bebq_2 and Alq_3 .

5. References

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