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Sensitized photo- and electroluminescence from Er complexes mixed with Ir complex

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We investigated the sensitized effect of *fac*-tris(2-phenylpyridine) iridium [Ir(ppy)₃] on tris-(dibenzoylmethanato)-mono-(bathophenanthroline) erbium (Er-DB) for 1.5 μm near-infrared emission. Compared with the neat Er-DB film, the blend film composed of Er-DB and Ir(ppy)₃ with a 1:1 of the weight ratio shows 20 times and 4 times enhancement on intensity of photoluminescence (PL) and electroluminescence (EL), respectively. The improvement in both PL and EL intensities was conjectured to be the result of the energy transfer from Ir(ppy)₃ to Er-DB complex, and the detailed mechanisms of the enhancement were also discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2889473]

The organic light emitting diodes (OLEDs) emitting visible light have been investigated considerably.^{1–3} The electroluminescence (EL) of OLEDs at near-infrared (NIR) region also attracts increasing attention because of its applications in optical communication networks, low-cost NIR light sources, IR amplifiers, etc.^{4–7} The NIR emissions from trivalent Nd, Yb, Er, and Pr complexes have been reported in both photoluminescence (PL) and EL cases.^{8–11} Among these NIR emissions, the 1.5 μm emission was particularly attractive for its good agreement with the efficient working window of a quartz fiber.^{12,13} Therefore, the development of materials operating at 1.5 μm , for example, the EL emission from Er-complex based OLEDs,¹² has become an interesting subject. Unfortunately, the NIR EL emission still behaves weak, that is, it can only be obtained at high driving bias voltage.^{11,12} Therefore, it is necessary to select a method to sensitize the NIR emission from Er³⁺ ion in its complex. A potentially and a more versatile approach with clear advantages uses transition-metal chromophores, which strongly absorbs, as antenna. A transition metal complex, *fac*-tris(2-phenylpyridine) iridium [Ir(ppy)₃] has very strong charge-transfer absorptions at a range of wavelengths that span the visible region with extinction coefficients of the order of 10⁴ M⁻¹ cm⁻¹ and can offer 510 nm emission.^{14,15} We can expect that the increasing NIR emission from Er complex can be attained if a feasible sensitized luminescent systems of PL and EL could be design.

In this letter, we demonstrate the improvements of the PL and EL intensities of Er³⁺ ion in tris-(dibenzoylmethanato)-mono-(bathophenanthroline) erbium (Er-DB) blended with the phosphor, i.e., *fac*-tris(2-phenylpyridine) iridium [Ir(ppy)₃] (called blend film, hereafter), at different mixing ratios. As a result, in comparison with the Er-DB based neat film and its device, the maximum NIR PL and EL intensities at 1.5 μm from Er³⁺ ion of the

corresponding blend film with 1:1 weight ratio increase by 20 and 4 times, respectively.

Er-DB was synthesized in our laboratory, while other chemicals were obtained from chemical companies. A series of blend films with different mixed ratios was deposited on cleaned quartz substrates by thermal evaporation and all of the films were kept to have a thickness of 100 nm in order to determine the PL spectra. For the device, organic films and Al cathode were deposited on indium tin oxide (ITO) glass substrate with a sheet resistance of 25 Ω/\square by thermal evaporation in a vacuum chamber with a base pressure of $<5.0 \times 10^{-4}$ Pa. The evaporating rate was kept at 2–3 $\text{\AA}/\text{s}$ for organic layers and 10 $\text{\AA}/\text{s}$ for alloy cathode, respectively. The made-up devices were encapsulated in dried nitrogen ambient. NIR (700–1600 nm) and visible (400–750 nm) spectra were measured on a Biorad PL-9000FT spectrometer equipped with a liquid-nitrogen-cooled Ge detector and a Hitach-4000 fluorescence spectrophotometer at room temperature, respectively. For the PL measurement in the NIR range, a 488 nm Ar-ion laser with an incident energy density of 30 mW/cm² was used as the excitation source.

Firstly, the PL spectrum of the blend films with different mixed ratios were determined under 480 nm laser excitation, as indicated in Fig. 1. We can note that the relative emission intensity of Er³⁺ ions at around 1.5 μm , which was ascribed to the ⁴I_{13/2} to ⁴I_{15/2} transition,¹⁶ increases with increasing Ir(ppy)₃ content until the concentration exceeds that of Er-DB. The maximum relative intensity occurs in the blend film with 1:1 weight ratio. Meanwhile, the neat Er-complex film only offers weak EL emission, as shown in inset of Fig. 1.

The enhancement mechanism in NIR emission from Er³⁺ ion by the blended Ir complex can be understood as follows. Under 488 nm laser excitation, 1.5 μm emission of Er³⁺ ion in Er-DB neat film was well known to be directly excited to the *f-f* absorption rather than to the ligand due to the ligand absorption band located at high energy region. However, the *f-f* transition is forbidden,¹⁶ therefore, the neat Er-complex film only emits weak NIR emission at 1.5 μm . In order to explore the enhancement mechanism, we determined the ab-

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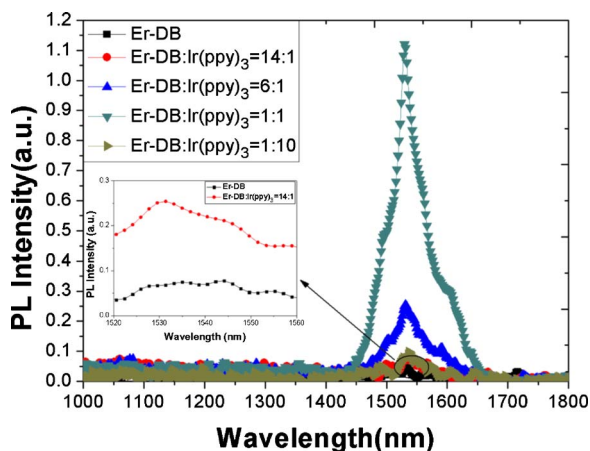


FIG. 1. (Color online) The PL spectrum of neat Er-DB and blend films with different mixed ratios. Inset: the partial PL spectrum of neat and blend film with 14:1 mixed ratio.

sorption spectrum of Er-DM and Ir(ppy)₃ in the chloroform solution at room temperature. The absorption spectra display that the former has a stronger absorption but the latter has no absorption in the 400–500 nm region, as indicated in Fig. 2. We also measured the excitation spectrum of the chloroform solutions of Ir complex for its 510 nm emission, which also exhibits an obvious overlapping between excitation band and the excitation light of 488 nm laser, as shown in inset of Fig. 2. This shows that the Ir complex must be efficiently excited by 480 nm light of the laser. The ³MLCT ($19.9 \times 10^3 \text{ cm}^{-1}$)¹⁵ of the Ir complex belongs to allow absorption transition due to the strong spin-orbit coupling on Ir, giving the formally spin-forbidden ³MLCT an intensity comparable to the allowed ¹MLCT,^{17,18} which is much larger than that of *f-f* absorption transition in RE³⁺-complex. Namely, under excitation of 488 nm laser, corresponding to an energy of $20.5 \times 10^3 \text{ cm}^{-1}$, the Ir(ppy)₃ with the lower ³MLCT was intensively excited and then relaxed via fast interconversion from $20.5 \times 10^3 \text{ cm}^{-1}$ to ³MLCT level. The energy on ³MLCT can be transferred to the triplet level of the first ligand of Er-DB (*T*₁ of DBM) via intermolecular energy transfer (endothermic reaction).^{19,20} The energy on *T*₁ of DBM is transferred to the higher level (²*H*_{11/2}) of the Er³⁺

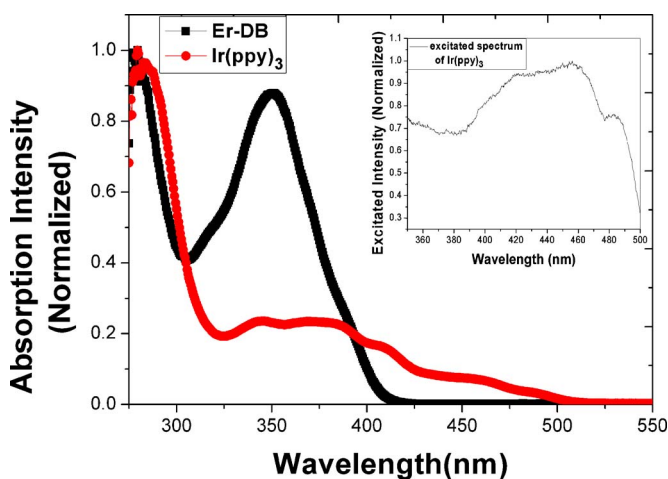


FIG. 2. (Color online) The absorption spectra of Er-DB and Ir(ppy)₃. Inset: the excited spectrum of Ir(ppy)₃ for 514 nm. All spectra are measured in chloroform solution at room temperature.

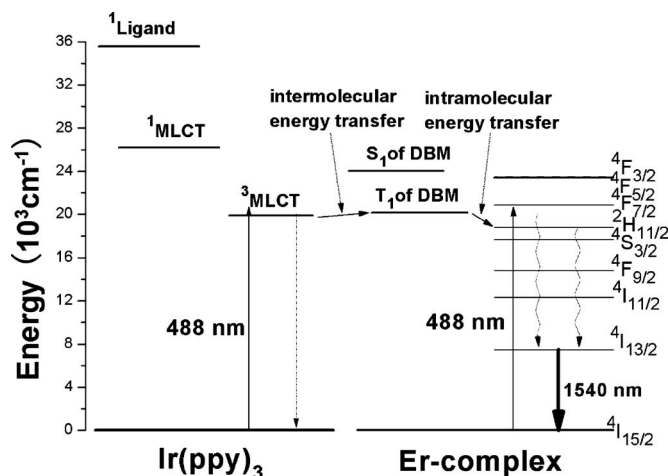


FIG. 3. The energy level scheme of Er-DB and that of Ir(ppy)₃ accompanied with the proposed PL process.

ion emitting level (⁴*I*_{13/2}) via intramolecular energy transfer in succession. Finally, the energy at ²*H*_{11/2} level experiences a fast nonradiative decay, i.e., interconversion, to the ⁴*I*_{13/2} level, then it decays to the ground state by emitting NIR light at 1540 nm, as shown in Fig. 3.

Due to the maximum emission of Er³⁺ ion that was achieved in the blend film with 1:1 mix ratio, as shown in Fig. 1, indicating that the NIR intensity is sensitive to the distance between donor and acceptor, we speculate that the energy transfer from Ir(ppy)₃ to the *T*₁ of DBM appears to be Dexter energy transfer mechanism.²¹ To confirm our speculation, another blend film mixed Er-DB with tris(8-hydroxy-quinoline) aluminum (1:1), which have a similar PL spectrum to Ir(ppy)₃, was made and measured in the same run, but no enhancement at 1.5 μm emission was observed (the result is not shown here). In other words, under 488 nm laser excitation, the highly absorbing Ir(ppy)₃ would be excited so that Dexter energy transfer to the *T*₁ of DBM occurs, which is in favor of the Er³⁺ ion emission, but Forster energy transfer²² that depends on the overlapping between donor emission and acceptor absorption can be ignored.

In terms of the improvement in PL, the EL enhancement of Er³⁺ ion emission from Er-DB mixed with Ir(ppy)₃ was also explored. We constructed the devices with structure of ITO/*m*-MTDATA (10 nm)/NPB (30 nm)/Er-DB:Ir(ppy)₃ (*x* wt %, 40 nm) / Bath (30 nm) / LiF (1 nm) / Al (120 nm), here *m*-MTDATA, NPB, and Bath denote 4,4',4''-tris[3-methyl-phenyl(phenyl)-amino] triphenyl-amine, 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]-biphenyl, and 4,7-diphenyl-1,10-phenanthroline, respectively, which work as the hole injection, hole transporting, and the hole blocking/electron transfer layers, respectively, as well *x*=0 and 50, respectively. The devices with *x*=0 and 50 were called as the reference and optimal device, respectively. Due to the fact that the optimal mass ratio in the PL of blend film is 1:1, the same mass ratio was also used for the fabrication of the optimized device. Figure 4 indicates the NIR EL emission spectra of the device with *x*=0 and 50. In the same manner as PL, the optimal device with blend film as EML exhibits four times higher EL intensity at 1.5 μm than that of the reference device, as shown in Fig. 4. This finding should be ascribed to the sensitization by the Ir complex. On the other hand, weak visible green emission from Ir(ppy)₃ can be

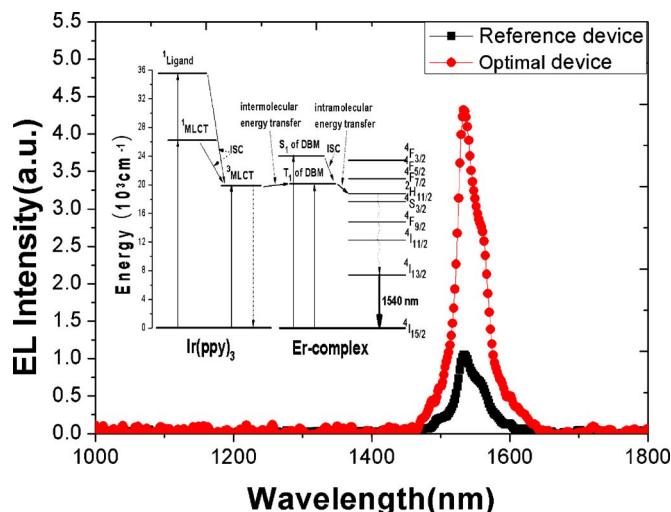


FIG. 4. (Color online) The EL spectra of reference and optimal devices at 16 V. Inset: the proposed EL energy transfer process in optimal device. Under electrical excitation, the S_1 and T_1 levels of the first ligand of Er-DB, as well as S_1 , $^1\text{MLCT}$, and $^3\text{MLCT}$ levels of the $\text{Ir}(\text{ppy})_3$ were possibly excited. Then, $S_1 \rightarrow T_1$ in Er-DB and S_1 , $^1\text{MLCT} \rightarrow ^3\text{MLCT}$ in $\text{Ir}(\text{ppy})_3$ occur via ISC, respectively. The energy on $^3\text{MLCT}$ of $\text{Ir}(\text{ppy})_3$ was transferred to T_1 of DBM by intermolecular energy transfer in succession. Then, $^2H_{11/2}$ level was firstly excited via intramolecular energy transfer from T_1 of DBM because of the favorable energy alignment between them. Finally, the internal conversion from $^2H_{11/2}$ to $^4I_{13/2}$ levels, followed by relaxation to the ground state were created, and the enhanced NIR emission at 1540 nm was achieved.

determined although the energy transfer from $^3\text{MLCT}$ of $\text{Ir}(\text{ppy})_3$ to Er complex presents. Unlike the PL process, under electrical driving, the singlet and triplet of Er complex and Ir complex would be excited simultaneously, then their energies were transferred to Er^{3+} ion via different paths, but the final $1.5 \mu\text{m}$ emission from Er^{3+} ion results from the same resonant level as the above-mentioned PL emission. More detailed process is under study.

In summary, we demonstrate the PL and EL improvement on $1.5 \mu\text{m}$ emission from Er^{3+} ion in Er-DB complex mixed with $\text{Ir}(\text{ppy})_3$. In the blend film with 1:1 weight ratio and the related device, 20 and 4 times PL and EL relative intensity enhancements compared with that in the neat Er-DB film were achieved, respectively. These enhancements were attributed to the intermolecular energy transfer from

$\text{Ir}(\text{ppy})_3$ to the T_1 of DBM. It is expected that the device design discussed in this work could also be useful for developing highly efficient RE^{3+} complex device using other phosphor materials. Besides, the sensitized NIR emission under excitation of a visible light will be applied for luminescent mark of some certificates.

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- ¹C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- ²B. W. D'Andrade, J. Brooks, M. E. Thompson, and S. R. Forrest, *Adv. Mater. (Weinheim, Ger.)* **14**, 147 (2002).
- ³Y. R. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, and S. R. Forrest, *Nature (London)* **440**, 908 (2006).
- ⁴H. Kajii, T. Taneda, and Y. Ohmori, *Thin Solid Films* **438**, 334 (2003).
- ⁵E. L. Williams, J. Li, and G. E. Jabbour, *Appl. Phys. Lett.* **89**, 083506 (2006).
- ⁶F. Meinardi, N. Colombi, S. Destri, W. Porzio, S. Blumstengel, M. Cerninara, and R. Tubino, *Synth. Met.* **137**, 959 (2003).
- ⁷L. H. Slooff, A. van Blaaderen, A. Polman, G. A. Hebbink, S. I. Klink, F. C. J. M. van Veggel, D. N. Reinhoudt, and J. W. Hofstraat, *J. Appl. Phys.* **91**, 3955 (2002).
- ⁸Y. Kawamura, Y. Wada, Y. Hasegawa, M. Iwamuro, T. Kitamura, and S. Yanagida, *Appl. Phys. Lett.* **74**, 3245 (1999).
- ⁹Y. Kawamura, Y. Wada, M. Iwamuro, T. Kitamura, and S. Yanagida, *Chem. Lett.* **2000**, 280.
- ¹⁰Y. Hasegawa, Y. Kimura, K. Murakoshi, Y. Wada, J. Kim, N. Na-Kashima, T. Yamanaka, and S. Yanagida, *J. Phys. Chem.* **100**, 10201 (1996).
- ¹¹R. J. Curry and W. P. Gillin, *Appl. Phys. Lett.* **75**, 1380 (1999).
- ¹²R. J. Mears and S. R. Baker, *Opt. Quantum Electron.* **24**, 517 (1992).
- ¹³E. Desurvire, *Phys. Today* **97**, 20 (1994).
- ¹⁴N. M. Shavaleev, L. P. Moorcraft, S. J. A. Pope, Z. R. Bell, S. Faulkner, and M. D. Ward, *Chem.-Eur. J.* **9**, 5283 (2003).
- ¹⁵C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **77**, 904 (2000).
- ¹⁶G. A. Crosby, R. E. Whan, and R. M. Alire, *J. Chem. Phys.* **34**, 743 (1961).
- ¹⁷S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Rezzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest, and M. E. Thompson, *J. Am. Chem. Soc.* **123**, 4304 (2001).
- ¹⁸S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Rezzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, and M. E. Thompson, *Inorg. Chem.* **40**, 1704 (2001).
- ¹⁹M. A. Baldo and S. R. Forrest, *Phys. Rev. B* **62**, 10958 (2000).
- ²⁰C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **79**, 2082 (2001).
- ²¹D. L. Dexter, *J. Chem. Phys.* **21**, 836 (1953).
- ²²T. Förster, *Discuss. Faraday Soc.* **27**, 7 (1959).