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Letter

Sensitized infrared electrophosphorescence based on divalent copper complex by an iridium(III) complex

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ABSTRACT

We demonstrate enhanced near-infrared (NIR) electroluminescence (EL) of copper phthalocyanine (CuPc) phosphor doped organic light emitting diodes (OLED) by introducing a red phosphor, bis(1-phenylisoquinolinato) iridium(III) acetylacetonate (Ir(piq)$_2$acac). For the codoped device, due to presence of Ir(piq)$_2$acac, the NIR emission peaked at 1120 nm of CuPc was increased by 15 times comparing with the CuPc monodoped device. The enhancement of NIR emission of CuPc emitter was principally attributed to an energy transfer from Ir(piq)$_2$acac to CuPc, and the sensitized mechanism was also discussed in detail.

The organic light emitting diodes (OLEDs) that emit visible light have been considerably investigated [1–3]. The studies on electroluminescence (EL) at near-infrared (NIR) spectral region also attract increasing attentions due to the applications in optical communication networks such as low-cost NIR light sources and IR amplifiers and so on [4–6]. The NIR EL emissions of either rare earth (RE)-complex [7–9] or the noble metal-complexes [5,10,11] have been reported, but they all behave low EL intensity. Therefore, how to enhance the NIR EL emission of the organic phosphors would be very critical for their actual applications.

Recently, Cheng et al. fabricated an copper phthalocyanine (CuPc) doped device with 4,4′-N,N′-dicarbazole-biphenyl (CBP) as the host and NIR EL band peaks at about 1.1 μm was observed, however, its irradiation intensity was weak [12]. How to enhance the EL intensity of CuPc phosphor doped device would be an interesting study project. By determining absorption spectra of CuPc phosphor film we found that there were two absorption peaks [12], which overlap the emission spectrum of a red emitting (peak at 620 nm) transition metal-complex, bis(1-phenylisoquinolinato) iridium(III) acetylacetonate (Ir(piq)$_2$acac) [13]. Ir(piq)$_2$acac is a high EL efficiency red material with a

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long excited triplet lifetime of 1.29 μs. Therefore it could be conjecture that the interaction between CuPc and Ir(piq)$_2$acac phosphors would occur by codoping the two phosphors into the same host in EL device. In terms of above arguments it is speculated that the interaction should be an energy transfer from the red emitting Ir-comlex to CuPc phosphor. In this letter, we fabricate CuPc and Ir(piq)$_2$acac codoped device with CBP as host to enhance the NIR emission of CuPc. By optimize the device structure the NIR emission intensity of CuPc was enhanced by factors of about fifteen compared with the reference device without the Ir-complex codopant.

All the chemicals were commercially available. Organic films and Al cathode were deposited on indium tin oxide (ITO) glass substrate with a sheet resistance of 25 Ω/□ by thermal evaporation in a vacuum chamber with a base pressure $<3.0 \times 10^{-4}$ Pa. Various OLEDs with an active area of 2×3 mm^2 were fabricated and encapsulated under drying N_2 atmosphere for device analysis. The NIR EL signals were focused into a monochromator and detected with a liquid-nitrogen-cooled Ge detector, using standard lock-in techniques, and the NIR photoluminescence (PL) signals were detected by spectrophotometer with a InGaAs photodiode with a boxcar averager. The transient decays of Ir(piq)$_2$acac were measured by a spectrophotometer with a Spex 1403 photomultiplier with a boxcar averager, under excitation by Nd:YAG laser at a wavelength of 355 nm with 10 ns pulse width. The absorption spectrum of neat CuPc film were recorded at a UV–Vis–NIR scanning spectrophotometer UV3101 (SHIMADZU), and The PL spectrum of Ir(piq)$_2$acac film determined by Hitachi F-4500 spectrophotometer equipped with a continuous 150 W Xe-arc lamp. The electrode work functions, the data of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of m-MTDATA, TPD, CBP, Ir(piq)$_2$acac, and TPBI were cited from literatures [14,15].

Firstly, we investigated the PL of CuPc film and Ir(piq)$_2$acac:CuPc blend film. Under an illumination of 355 nm Nd:YAG laser with energy density 30 mW/cm^2, no emission was observed from a 40 nm CuPc film. But in the 40 nm blend film Ir(piq)$_2$acac:CuPc, we observed the 1120 nm emission of CuPc. By modify the weight ratio of the two components, the Ir(piq)$_2$acac:CuPc blend film with 1:1 weight ratio emits the most intensive NIR emission from CuPc, and the intensity can be compared with that of Yb^{3+} in (dibenzoylmethanato)$_3$-(bathophenanthroline)-ytterbium which under an illumination of 532 nm Nd:YAG laser with energy density 50 mW/cm^2.

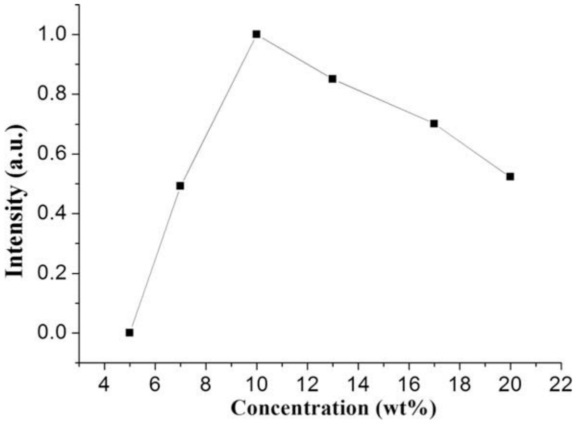

Fig. 1. CuPc EL intensity in 1.1 μm as a function of concentration of Ir(piq)$_2$acac dopant.

Based on the results of PL, we fabricated OLED devices with structures of ITO/m-MTDATA (20 nm)/TPD (20 nm)/CBP: CuPc:Ir(piq)$_2$acac (*x*, *y* wt%, 30 nm)/TPBI (40 nm)/LiF(1 nm)/Al (150 nm), here, *x* and *y* express the concentrations of Ir(piq)$_2$acac and CuPc. m-MTDATA, TPD and TPBI denote 4,4′,4″-tris[3-methyl-pheny(phenyl)-amino] triphenylamine, N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′diamine, and 2,2′,2″-(1,3,5-benzenetriyl) tris-[1-phenyl-1H-benzimidazole], respectively.

Fig. 1 shows CuPc EL intensity as a function of concentration of Ir(piq)$_2$acac dopant, and the optimal concentrations of Ir(piq)$_2$acac and CuPc locates 10 and 12 wt%, respectively. The device with the optimal concentration called optimal device, and the 12 wt% CuPc monodoped device will be called reference device. Because we adopted m-MTDATA as hole injection layer, LiF as cathode buffer layer, and TPD, a low efficient PL and EL material, as hole transport layer, the NIR emission intensity of the reference device was enhanced by about two times comparing with the reported CuPc device [12] under the same measurement condition.

Fig. 2 shows the EL spectra at the NIR spectral zone for the optimal and reference devices, respectively. It can be seen that the CuPc EL intensity was enhanced by about 15 times compared with reference device. Furthermore, in optimal device, the red emission of Ir(piq)$_2$acac was too weak to be detected, although the maximal current efficiency and luminance of the Ir(piq)$_2$acac monodoped device can offer 10.17 cd/A and 11 000 cd/m^2, respectively. Inset denotes the chemical structures of CuPc and Ir(piq)$_2$acac. In order to understand the enhanced mechanism

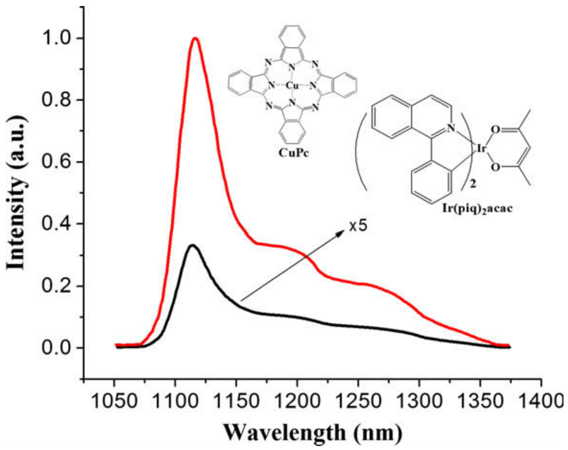

Fig. 2. The NIR EL spectra of CuPc in the optimized device (red) and reference device (black). (The absolute emission intensity is not referred to in this work purely because of the difficulty for our testing system.). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the NIR emission of CuPc, we determined the absorption spectrum of CuPc film and emission spectrum of Ir(piq)$_2$acac film. It is found that there is a markedly overlapping between the two spectral bands, as indicated in Fig. 3, which implies that the energy transfer from the Ir-complex to CuPc in device would occur. Besides we also measured the photoluminescence transient decays in the 50 nm thick CBP: Ir(piq)$_2$acac (10 wt%), and CBP: Ir(piq)$_2$acac: CuPc (10, 12 wt%) mixing film, respectively. It is found that the excited triplet lifetime of Ir(piq)$_2$acac in the CBP: Ir(piq)$_2$acac mixing film is 1.29 μs, while in the codoped films it was shortened to 0.82 μs. Basing on the above-mentioned spectral overlapping and the shortened excited triplet lifetime of Ir(piq)$_2$acac phosphor, we can deduce that the improvement in NIR EL intensity is mainly attributed to the primarily energy transfer to CuPc from the red emitting Ir-complex.

To further prove the energy transfer from the red Ir-complex to CuPc in the codoped devices, we also fabricated other two series of OLED devices. Series A: ITO/m-MTDATA (20 nm)/TPD (20 nm)/CBP: CuPc (*x* wt% 30 nm)/CBP: Ir(piq)$_2$acac (*y* wt% 30 nm)/TPBI (40 nm)/LiF(1 nm)/Al (150 nm); Series B: ITO/m-MTDATA (20 nm)/TPD (20 nm)/CBP: Ir(piq)$_2$acac (*y* wt% 30 nm)/CBP: CuPc (*x* wt% 30 nm)/TPBI (40 nm)/LiF(1 nm)/Al (150 nm). We have taken any values of x and y in the two series devices, but the NIR emission enhancement was not as much as the optimal device. The reasons could be understood as follow. In CuPc and Ir(piq)$_2$acac codoped device the intermolecular contact between two dopants are more close and behaves more favorite for Dexter energy transfer. For the other two series devices, the two dopants distribute in two layers separately, so the probable energy transfer process is only the Förster mechanism, which leads to lower efficiency process comparing with the codoping system. Therefore we conclude that the two phosphors codoped device provides more favorite surroundings for the sensitization of CuPc emission by the red Ir-complex than other device system.

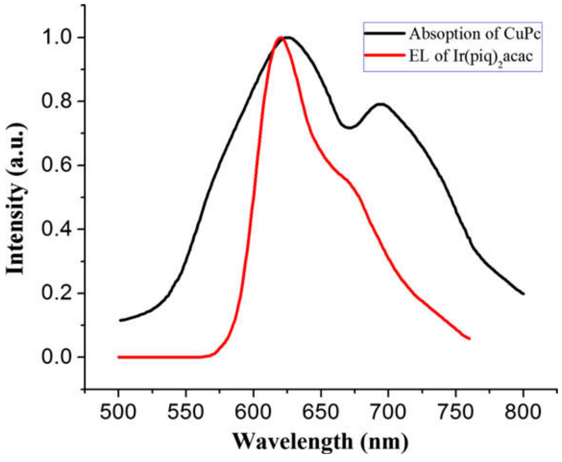

Fig. 3. The absorption spectrum of neat CuPc film and PL spectrum of Ir(piq)$_2$acac. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

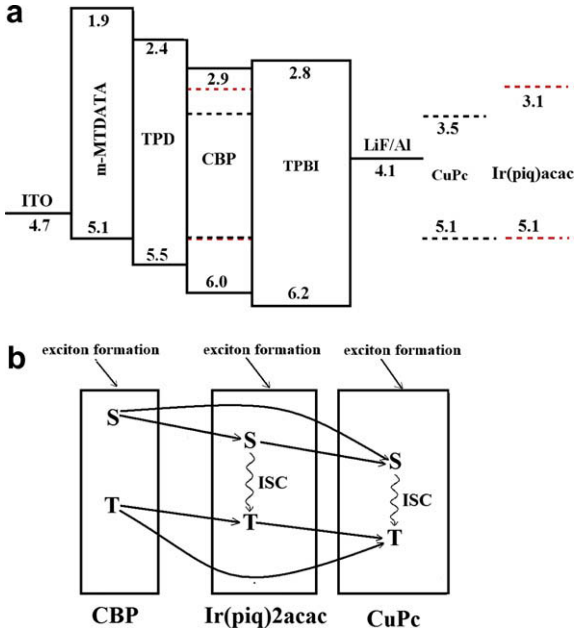

Fig. 4. The schematic energy diagram of the codoped drvice (a) and the energy transfer processes in the codoped system (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In term of the codoped device structure, here we show the schematic energy diagram, as in Fig. 4. Under the energy diagram, the improvement of NIR emission of CuPc was also understood as follows. Under excitation of the electrical field, the excitons are firstly formed on CBP molecules with the singlet-to-triplet ratio of 1/3. On the other hand, triplet excitons can be formed directly on the phosphor centers by trapping both the injected holes and electrons. The singlet energy of CBP can be directly transferred to that of both Ir(piq)$_2$acac and CuPc via Förster process, while the triplet of CBP can be directly transferred to the triplet states of Ir(piq)$_2$acac and CuPc by Dexter process. The singlet energy of the two phosphors may rapid converted to their triplet states by intersystem crossing (ISC) due to strong spin orbit coupling. Due to the efficient ISC of Ir(piq)$_2$acac, energy transfer from the singlet of Ir(piq)$_2$acac to CuPc is less and hence can be ignored. Because the triplet energy level of Ir(piq)$_2$acac is about 0.6 eV lower than that of CBP, which restricts the back energy transfer from Ir(piq)$_2$acac to CBP, thus, there are two probable pathways to relaxation of Ir(piq)$_2$acac triplet, i.e., one is radiating to its ground states and another is transferring to CuPc triplet. Weak emission of Ir(piq)$_2$acac in the two phosphors codoped EL device indicates that the fraction of the radiation of Ir(piq)$_2$acac should be small. The shorter excited lifetime of CuPc (<50 ns) [16] comparing with Ir(piq)$_2$acac (1.29 μs) is another essential conditions for the energy transfer from Ir(piq)$_2$acac to CuPc. Thus, nearly all the exciton energies could be transferred to the CuPc triplet, as a result the NIR emission of CuPc increased.

Curry and Gillin have reported the NIR EL emission from erbium (III) tris(8-hydroxyquinolate) (ErQ) based device with structure of Si/NPB (40 nm)/ErQ (50 nm)/Al (200 nm), and a internal quantum efficiency of ~0.01% was obtained [17]. We have fabricated the similar EL device using ITO rather than Si as the anode substrate. By comparing the heights of EL emission peaks which origin from Er^{3+} in ErQ device and CuPc in our sensitized device under the same determining condition, the internal quantum efficiency of the sensitized emission of CuPc was estimated roughly. Basing on the estimation, our sensitized CuPc device with the red Ir-phosphor offers an internal quantum efficiency of about 0.1%, which is little higher than that of CuPc reported by Rosenow et al. [18].

In summary, the NIR emission of CuPc was enhanced by $Ir(piq)_2acac$ in codoped device system. The improvement was attributed to the intermolecular energy transfer from $Ir(piq)_2acac$ to CuPc in the same host (CBP). The observation of the enhanced NIR emission of the CuPc would inspire us to design and develop other new type of sensitized phosphorescent OLEDs by intermolecular energy transfer processes. The concept can also be used for the application in efficient organic photovoltaic cells with new triplet materials.

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