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Breakthrough of Organic Electroluminescence Efficiency of Photoluminescence in Frequency Domain

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In this paper, a new way is proposed to confirm that the organic electroluminescence efficiency can exceed the 25 % limitation of that of photoluminescence in frequency domain. In present experiment, the spectra shows two characteristic emission bands and the high and low energy emission bands are due to singlet and triplet excited states. The triplet emission has longer lifetime than that of singlet emission and the emission intensity of short lifetime changes (increase and decrease) more dramatic than that of long lifetime with the changing frequency. So, it may be concluded that the 25 % limitation is not perfect and can be exceeded in the frequency domain at a given frequency.

Key Words: Frequency domain, 25 % Limitation, Triplet, Singlet.

INTRODUCTION

It is generally believed that the electroluminescence efficiency is limited to 25 % of that of photoluminescence based on the statistics of spin multiplicity. It is to say, for recombination of a pair of electron and hole (both spin 1/2), there are four microstates in total, with three triplet states and one singlet state. But recent reports have indicated that the ratio between the electroluminescence and photoluminescence quantum yields can exceed this limitation[1-8] and the reason for this is under investigation. In reference[9,10], they found a remarkable dependence of the ratio on the applied electric field. While from Wilson *et al.*[5], the ratio is almost independent of the external electric field. Theoretically, several models have been employed to explain why the ratio is not fixed at 25 %. Bittner and Kobrak[7], have simulated the intrachain collision of positive and negative polarons through a mixed quantum/classical molecular dynamics approach to illustrate that the ratio can be exceeded. Tandon *et al.*[10] observed an abrupt increase in the ratio with respect to the electric field from a quantum-dynamical calculation. Shuai *et al.*[8] have applied the Fermi-golden-rule (FGR) to calculate the matrix elements for the exciton formation process, for *p*-phenylene-vinylene (PPV), they conclude that this ratio can generally exceed the 25 % limitation. In reference[11], a correlated quantum-chemical approach coupled with a first-order perturbation is used to investigate the relationship between the ratio and the electric field. It is found that for *p*-phenylene-vinylene oligomer, the ratio increases with the electric field.

In this paper, we propose a new way in the frequency domain to illustrate that the 25 % limitation can be exceeded.

EXPERIMENTAL

The device ITO/PEDOT:PSS/PVK:Ir(ppy)2(acac)/BCP(10 nm)/Alq_3(20 nm)/Al has been fabricated. The PEDOT:PSS [poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate)] and PVK [poly-(N-vinylcarbazole)]: $Ir(ppy)_2(acac)$ [*bis*(2-phenylpyridine)(acetylacetonate)iridium(II)] were fabricated by spin-coating method with the rotation rate 2000 rpm (rotation/min). The PVK and $Ir(ppy)_2(acac)$ were dissolved in chloroform with the concentration 10 and 0.5 mg/mL, respectively. The ratio of PVK to $Ir(ppy)_2(acac)$ was 1:0.2 % in weight. The BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), Alq_3 (*tris*(8-hydroxy-quinolinato)aluminium) and Al were deposited in a vacuum chamber (the pressure was 2×10^{-6} torr) by thermal evaporation method. The typical deposition rate was about 0.03 nm/s. The thickness of layer is controlled by a quartz crystal monitor. The electroluminescence was measured using the fluolog-3 fluorescent spectrometer made by SPEX. The measurement was carried out at room temperature in ambient atmosphere.

RESULTS AND DISCUSSION

Generally, the luminescent centers which have been excited cannot be excited again and they can absorb photons again only after their de-excitation, so the luminescence lifetime and absorption rate of luminescence center have direct influence on the efficiency. The absorption rate of luminescent center can be controlled by changing the driving frequency, so the luminescence efficiency can be improved by adjusting the driving frequency. In general the lifetime of singlet is thousand time shorter than that of triplet, when the electrons still stay in the triplet, the electrons in the singlet state may give many times of luminescence. We take the lifetime of luminescence and driving frequency into consideration, the limitation of 25 % can be exceeded.

Fig. 1 is the electroluminescence spectrum of the device under different frequency. The intensity of both PVK and $Ir(ppy)_2(acac)$ emission increases with the increasing of frequency up to 100 Hz then decreases. The voltage is a constant, that is 12 V, when the frequency changes. In present experiment, the luminescence of PVK is from singlet and that of $Ir(ppy)_2(acac)$ is from triplet.

Fig. 2 is the variation of ratio $r_1 = \frac{\mathrm{PVK} : (I_x - I_{20\,Hz})}{\mathrm{Ir(ppy)_2(acac)} : (I_x - I_{20\,Hz})}$ (x = 30, 40, 60, 80 and 100 Hz) and $r_2 = \frac{\mathrm{PVK} : (I_{100\,Hz} - I_x)}{\mathrm{Ir(ppy)_2(acac)} : (I_{100\,Hz} - I_x)}$ (x = 300, 500, 1000, 2000, 5000 and 10000 Hz) with the changing frequency, here the I is the emission intensity of PVK and $Ir(ppy)_2(acac)$. It can be observed that the r_1 and r_2 increase with the increasing frequency. It is to say that the intensity of PVK emission change (increase and decrease) dramatically than that of $Ir(ppy)_2(acac)$ emission.

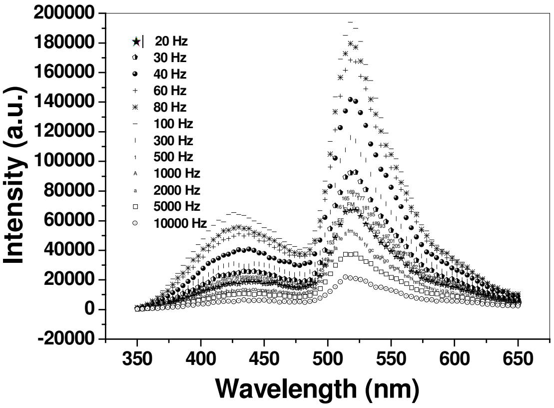

Fig. 1. Electroluminescence spectrum of the device under different frequency

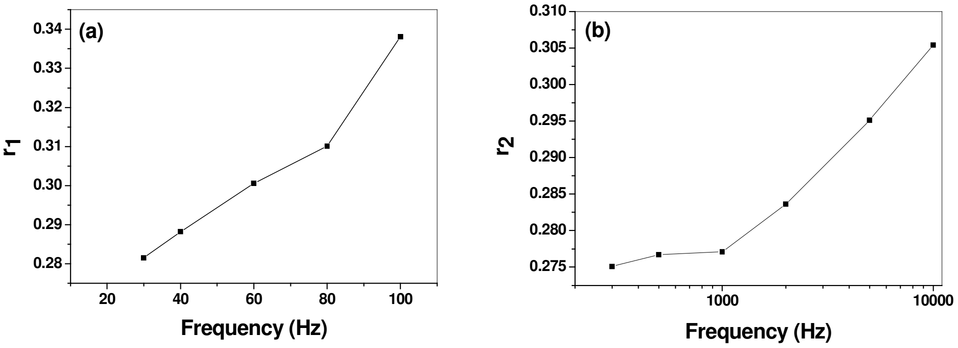

Fig. 2. Variation of r_1 (a) and r_2 (b) with frequency

In low-voltage cathodoluminescence, the decay time of green phosphors $SrGa_2S_4:Eu^{2+}$, ZnS:Cu, Al and $Gd_2O_2S:Tb^{3+}$ is 490 ns, 20 and 500 µs, respectively. In reference[12-14], the efficiency of $SrGa_2S_4:Eu^{2+}$ is higher than the other two phosphors at a given current density. The luminescence efficiency of low voltage phosphors can be greatly improved by choosing phosphors with a fast decay time that is considerably less than the excitation dwell time. This indicates that the short luminescence lifetime is in favour of improving luminescence efficiency.

In the electroluminescence of ZnS:Ce, Nd, the result is that the ratio of the emission intensity Ce^{3+}-Nd^{3+} is almost linearly increasing with the increasing excitation frequency (Fig. 3). The luminescence of Ce^{3+} is I_1:5d(^{2}D)-4f($^2F_{7/2}$) and I_2:5d(^{2}D)-4f($^2F_{5/2}$). The luminescence of Nd^{3+} is I_3:$^4G_{7/2}$-$^4I_{9/2}$, I_4:$^4G_{5/2}$-$^4I_{9/2}$ and I_5:$^4H_{11/2}$-$^4I_{9/2}$. From the slopes of these lines: $K(I_1:I_3) > K(I_1:I_5) > K(I_1:I_4)$, $K(I_2:I_3) > K(I_2:I_5) > K(I_2:I_4)$, $K(I_1:I_3) > K(I_2:I_3)$, $K(I_1:I_5) > K(I_2:I_5)$ and $K(I_1:I_4) > K(I_2:I_4)$. τ_1, τ_2, τ_3, τ_4 and τ_5 are the lifetimes of luminescence I_1, I_2, I_3, I_4 and I_5. Here τ_1 and τ_2 are about 30-100 ns. τ_3, τ_4 and τ_5 are 3.2, 4.8 and 4.2 us, respectively. It can be conclude that the increasing excitation frequency benefit the emission of short lifetime more than those of long lifetime. The reason is that for the short lifetime of Ce^{3+} τ_1 will be saturated at large frequency than that of long lifetime. This result is obtained under the condition that the period of excitation is longer than the lifetime. This indicates that the luminescence of short lifetime is prior to that of long lifetime with increasing frequency[15].

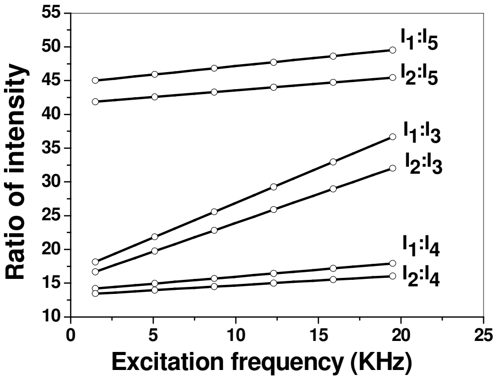

Fig. 3. Ratio of emission intensity Ce^{3+}-Nd^{3+}

In the experiment, the PVK singlet emission has short lifetime and the $Ir(ppy)_2(acac)$ triplet emission has long lifetime. From Fig. 2(a) the increasing intensity of singlet emission is larger than that of triplet emission with the increasing frequency. So the efficiency can be improved by adjusting the driving frequency and the 25 % limitation can be exceeded in frequency domain.

Conclusion

In summary, it is concluded that the 25 % limitation can be exceeded in frequency domain at a given frequency, because the different luminescence lifetime has different luminescence efficiency at a given frequency and the short lifetime luminescence is more benefit to the luminescence efficiency.

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