

SYNTHESIS OF NEW IRIIDIUM (III) PHENYLPYRIDINE COMPLEX AND ITS OLED APPLICATION

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Abstract

*A new Iridium(III)bis[2-phenylpyridinato- N,C^2']-[1-(4-fluorophenyl)-3-(4-methoxyphenyl)propane-1,3-dionate], (ppy)₂Ir(fmtdbm) was synthesized and identified by ¹H NMR and elemental analysis. In this study we present the photophysical and electrochemical properties of the new complex and investigate the possibility of its application as a dopant (0 – 10 w%) in the hole transporting layer (HTL) of the simplest organic light emitting diode (OLED) structure: Anode/HTL/ETL/Cathode. Here as a HTL we used *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine (TPD), incorporated in Poly(*N*-vinylcarbazole) (PVK) matrix, as an electron-transporting layer (ETL) - Tris-(8-hydroxyquinoline) aluminum (Alq₃), as anode - indium tin oxide (ITO) and aluminium -as cathode. We established that at different concentrations of the dopant OLED emitted green-orange light in different tunes. It was found that the lightly-doped (around 1.5 wt%) samples had better luminescence efficiency in all region of applied voltages, in comparison with undoped device.*

Key words: OLED, PhOLEDs, Iridium complexes

1. INTRODUCTION

Phosphorescent organic light-emitting diodes (PhOLEDs) offer an intriguing future for the next generation of flat-panel displays and lighting techniques because of their high quantum efficiencies relative to fluorescent OLEDs. That's why in the recent years extensive investigations of new phosphorescent materials focused on heavy metal complexes of Os(II), Pt(II) and Ir(III) have been made. The high efficiencies at these complexes are result of efficient intersystem crossing caused by heavy metal ions which removes the spin-forbidden nature of the radiative relaxation of the triplet excited state and thus both singlet and triplet electro generated excited states contribute to light emission (Kappaun, Slugovc & List 2008). The choice of iridium metal is of special interest and is based on the fact that its atom has a quasi-octahedral geometry, permitting the introduction of specific ligands through an easy and controlled manner, providing an opportunity for fine tuning of the photophysical and electrochemical properties of the complexes (Holzer, Penzkofer & Tsuboi 2005, Han et al. 2015). To date, efficient red- and green-emitting iridium (III) complexes have been well developed through inventive ligands modification (Liang et al. 2006, Sasabe et al. 2008, Lu et al. 2011). Tris[2-phenylpyridinato- C^2,N]iridium(III) (Ir(ppy)₃) is one of the most important materials for phosphorescent OLED as its emission color (at $\lambda_{max} = 514$ nm) matches well to the Commission Internationale d'Eclairage coordinates (CIE(x/y)) for green color (0.3;0.6), that makes it very suitable for use in the production of full color displays (Kawamura et al. 2005, Gong et al. 2003). Moreover, the color of light emitted by the complex can be easily changed by simple modifying of the basic (ppy) ligand or by its replacement with another auxiliary ligand.

All mention above, motivated us to focus on the synthesis of new Ir (III) complex, with two (ppy) basic ligands and one β -diketone auxiliary ligand. In this work, we report our investigation on photophysical and electroluminescent properties of new compound and discuss the possibility of its use as a phosphorescent dopant in OLED.

2. EXPERIMENTAL

2.1. Synthesis of Iridium complex

2.1.1. Synthesis of μ -chloro-bridged iridium dimer (2).

Cyclometalated Ir(III) μ -chloro-bridged dimer (2) $(ppy)_2Ir(\mu-Cl)_2Ir(ppy)_2$ was synthesized according a method reported by Nonoyama (1974) (Fig. 1). 2-phenylpyridine (1) (2.2 equiv), iridium trichloride hydrate (1 equiv), dissolved in 2-ethoxyethanol: water = 3:1 were stirred for 20 h at 110 °C under argon atmosphere. After cooling to the room temperature, the reaction mixture was filtrated. Then the precipitate was washed with ethanol and hexane several times, and dried at room temperature.

2.1.2. Synthesis of iridium complex (3), $(ppy)_2Ir(fmtdbm)$.

Dimer (2), 1-(4-fluorophenyl)-3-(4-methoxyphenyl)propane-1,3-dione (2.5 equiv) and Na_2CO_3 (5 equiv) were stirred for 20 h at 110 °C in 2-ethoxyethanol under argon. After cooling to the room temperature, the obtained product was filtrated. Then the precipitate was washed with water, ethanol, and hexane several times. Finally, the crude product was purified using liquid chromatography (silica gel, dichloromethane) and dried. The final product was identified by ^1H NMR and elemental analysis wich showed:

^1H NMR (500 MHz, $CDCl_3$) δ 16.99 (s, 1H), 8.12 – 7.58 (m, 12H), 7.14 – 6.57 (m, 12H), 3.88 (s, 3H).
Anal. Found C 60.75, H 4.48, N 4.09, Ir 25.54; Calc: C 59.13, H 3.63, N 3.64, Ir 24.90.

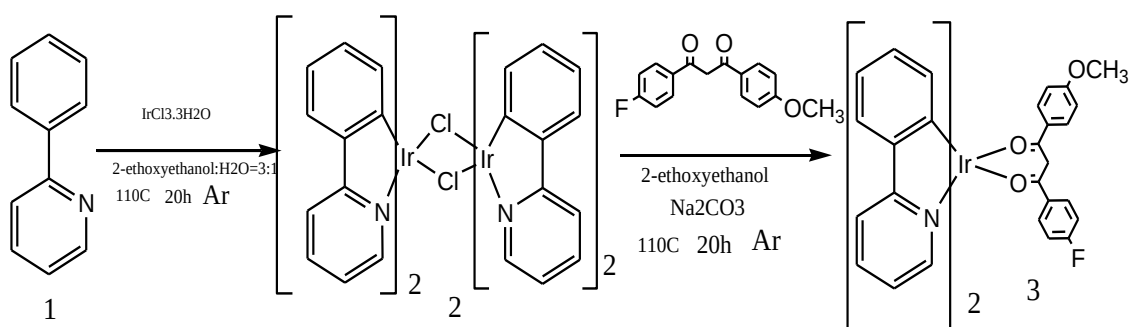


Fig. 1. Synthesis of iridium complex $(ppy)_2Ir(fmtdbm)$.

2.2. OLED fabrication

The newly synthesized complex has been studied as a dopant in the simplest OLED structure: ITO/doped-HTL/ETL/M (fig. 2), where ITO was a transparent anode of $In_2O_3:SnO_2$, M - a metallic Al cathode, HTL - N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) incorporated in poly(N-vinylcarbazole) (PVK) matrix and ETL - electron-transporting layer of Tris-(8-hydroxyquinoline) aluminum (Alq_3).

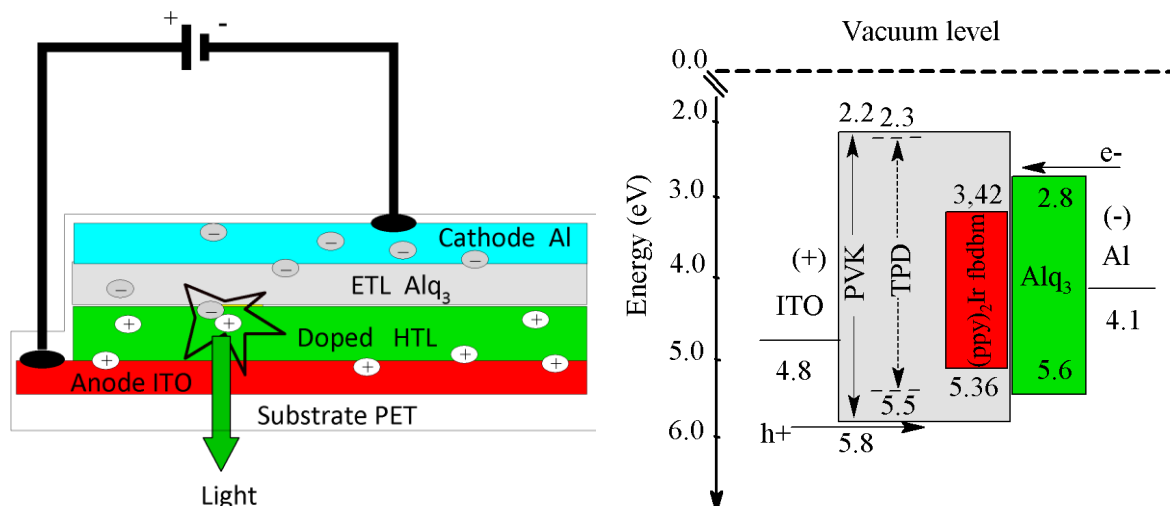


Fig. 2. OLED architecture and energy diagram.

Devices with dimension 1cm^2 were prepared on commercial polyethylene terephthalate (PET) substrate coated with ITO ($40\Omega/\text{sq}$). The 30 nm doped with Ir(III) complex, composite PVK:TPD (10 wt % in relative to PVK) film was deposited through spin-coating at 2000 rpm from 0.75% PVK solution in dichloroethane. Organic layer of Alq_3 (40nm) and Al cathode (100 nm) were obtained by thermal evaporation in vacuum better than 10^{-4} Pa at rates 2-5 $\text{\AA}/\text{s}$, without breaking vacuum. The layers thicknesses were controlled with quartz crystal microbalance sensor, positioned near the PET/ITO substrate.

2.3. Instruments and measurements

The excitation (Ex.) and photoluminescent (PL) emission spectra of Iridium complex are taken on FluoroLog3-22, Horiba JobinYvon and PL spectra of PVK and TPD are taken on Ocean Optics HR2000+ spectrophotometer by usage of LS-1 Tungsten Halogen Light Source.

OLEDs measurements were carried out on non-encapsulated devices on air at room temperature. The electroluminescence emission spectra (EL) and CIE coordinates were taken on the Ocean Optics HR2000+ spectrometer. The current-voltage (I-V) characteristics were performed using programmed via Labview Keithley 2220-30-1 power supply. The electroluminescence was determined in DC (direct current) mode and the light output was detected using a calibrated Hamamatsu silicon photodiode S2281-01. The current efficiency (η_{EL}) used for quantifying the properties of OLEDs, were calculated according equation (1).

$$\eta_{\text{EL}} = EL/I, \text{ Cd/A}, \quad (1)$$

where EL was the electroluminescence (in Cd/m^2) and I - the current density (in A/m^2).

3. RESULT AND DISCUSSION

3.1. Electrochemical properties

Cyclic voltammetric (CV) technique was employed to investigate the electrochemical behaviour of the Ir complex and estimation of its ionization potential (I_p) and electron affinity (E_a) in accordance with the theory proposed by Pommerehne et al. 1995. Measurements were provided in three electrode electrochemical cell in acetonitrile (ACN), containing 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte and using ferrocene/ferrocenium ion (Fc/Fc^+) as the internal standard.

$$I_p = E_{1/2}^{\text{ox}} + 4.8 \quad (2)$$

$$E_a = E_{1/2}^{\text{red}} + 4.8 \quad (3)$$

$$E_g = I_p - E_a, \quad (4)$$

where: $E_{1/2}^{\text{ox}}$ and $E_{1/2}^{\text{red}}$ are electrochemical potentials over ferrocenium/ferrocene (Fc^+/Fc) reference (vs. Ag/AgCl), and 4.8 eV is the value of Fc with respect to zero vacuum level. I_p and E_a may be regarded as the HOMO and the LUMO and the electrochemical gap between them as the band gap (E_g) of the complex.

The cyclic voltammograms are shown in fig. 3 and the results are summarized in table 1. As can be seen from the fig. 3, the complex exhibited two reversible oxidation and reduction waves at 0,94 and 1,00 V (vs. Ag/AgCl). As the potential of Fc^+/Fc reference at the same conditions was measured at 0,38 V, corresponding values of HOMO and LUMO levels were calculated respectively at 5,36 and 3,42 eV.

Table 1. Electrochemical data of $(\text{ppy})_2\text{Ir}(\text{fntdbm})$

$-E_{1/2}^{\text{red}}$ vs. $\text{Ag}/\text{AgCl}(\text{V})$	$-E_{1/2}^{\text{red}}$ vs. $\text{Fc}/\text{Fc}^+(\text{V})$	$E_a(\text{-LUMO})$ (eV)	$E_{1/2}^{\text{ox}}$ vs. $\text{Ag}/\text{AgCl}(\text{V})$	$E_{1/2}^{\text{ox}}$ vs. $\text{Fc}/\text{Fc}^+(\text{V})$	$I_p(\text{-HOMO})$ (eV)	E_g (eV)
1,00	1,38	3,42	0,94	0,54	5,36	1,94

The energy band gaps (E_g) of the complex, calculated at 1,94 eV, demonstrate that the complex may be potentially suitable greenish-orange emitting material. The complex has displayed excellent electrochemical properties, which are beneficial for its OLED application.

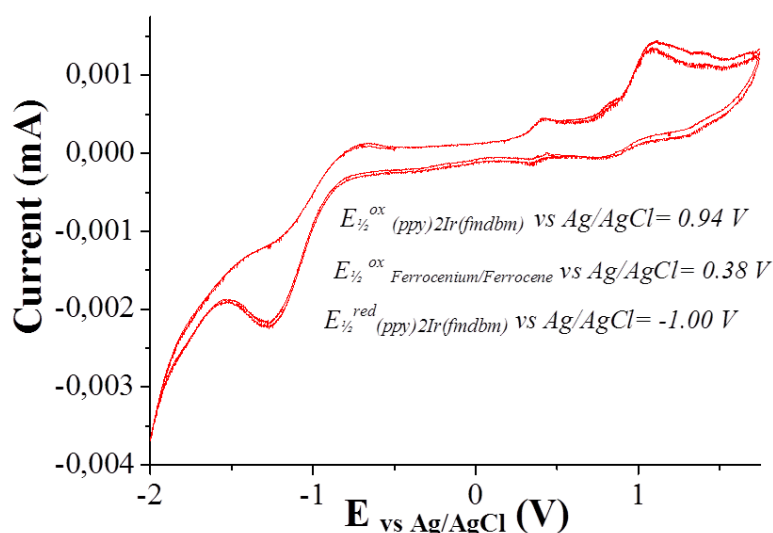


Fig. 3. CV waves of 0.001 M $(\text{ppy})_2\text{Ir}(\text{fntdbm})$ and Ferrocene in acetonitrile and 0.1 M TBAPC, at scan rate 100 mV/min.

3.2. UV-VIS absorption and photoluminescence.

The excitation of Ir(III) complex and photoluminescent spectra of Ir(III) complex, TPD and PVK in CH_2Cl_2 , measured under ambient conditions, are shown in fig. 4.

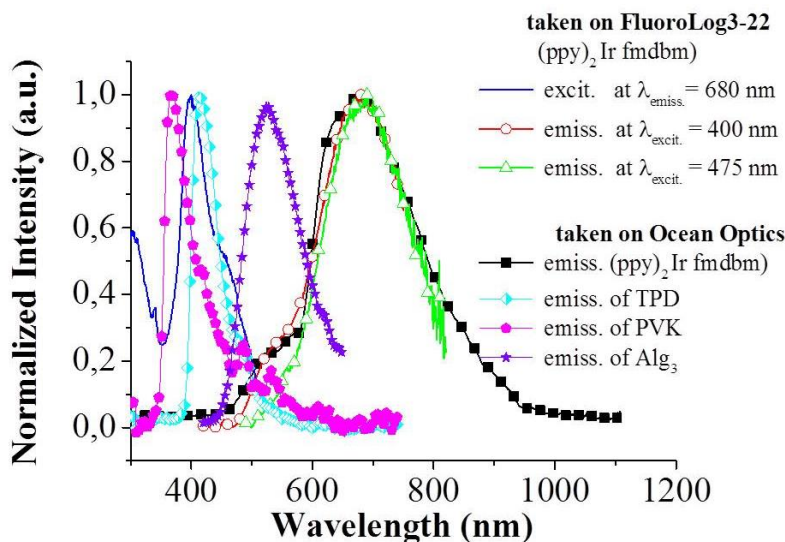


Fig. 4. The excitation and photoluminescent spectra in CH_2Cl_2 of $(\text{ppy})_2\text{Ir}(\text{fmdbm})$, taken on FluoroLog3-22, and PL emission spectra of $(\text{ppy})_2\text{Ir}(\text{fmdbm})$, PVK, TPD and Alq_3 in CH_2Cl_2 , taken on Ocean Optics spectrophotometers.

The basic excitation bands taken at emission 680 nm were observed at 303, 400 and 475 nm. The first one can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene and the second and third can be assigned to singlet and triplet metal-to-ligand charge transfer ($^1\text{MLCT}$, $^3\text{MLCT}$). Under 400 and 475 nm light excitation of $(\text{ppy})_2\text{Ir}(\text{fmdbm})$ complex exhibited strong yellow-orange phosphorescence with maximum emission peak at 680 nm, which could be attributed to predominantly $^3\text{MLCT}$ state. It was also found that at irradiation with tungsten halogen light source the complex had just the same spectrum and Alq_3 emitted green light with peak at 521 nm.

Furthermore as can be seen in fig. 4 PVK and TPD emitted a blue light with peaks at 367 and 415 nm respectively, that provides a good spectral overlapping with MLCT absorption bands of Ir(III) complexes ranged from 303 – 480 nm, and is a good prerequisite for Förster or Dexter energy transfer (Gong et al. 2003) from the host (PVK:TPD) to the guest of $(\text{ppy})_2\text{Ir}(\text{fmdbm})$.

3.3. Electroluminescence

The EL spectra and CIE coordinates of doped with different concentrations of $(\text{ppy})_2\text{Ir}(\text{fmdbm})$ devices, taken at 16 V DC, are presented in fig. 5. All devices emitted in green-orange color and their light was slightly shifted toward the red end of the spectrum with increasing of the dopant concentration. The position of EL max of the spectrum and CIE (x/y) coordinates of emitted light were moved from 529 nm and 0,3479/0,5505 at 0,5 wt % to 535 nm and 0,3815/0,5514 at 10 wt %. As can be seen at the EL spectra of devices any emission from PVK and TPD were not observed, that confirms the transfer of energy from host to the guest.

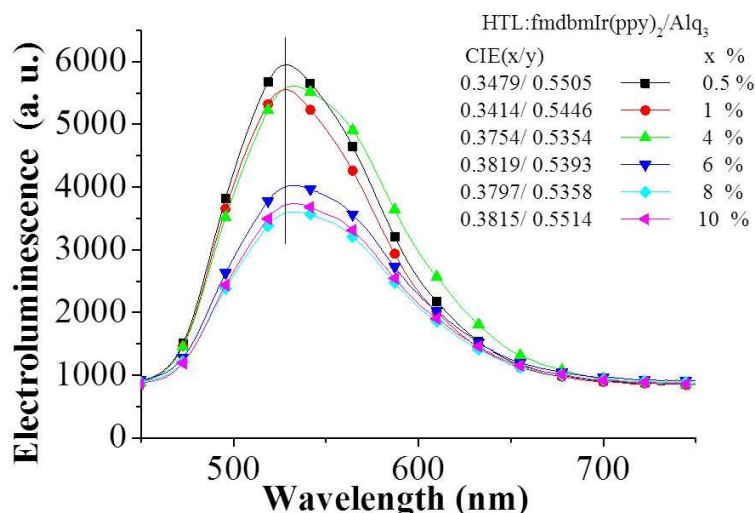


Fig. 5. El spectra and CIE coordinates of doped with different concentrations of $(ppy)_2Ir(fmtdbm)$ devices, taken at 16 V DC.

The luminescence-voltage characteristics of OLEDs are shown in fig. 6, their external current efficiencies (η_{EL}) are presented in fig. 7. All electroluminescent data are summarized in table 2. All devices became visible between 10 - 12 V depending on the doping concentration. It was found that with increasing of the dopant concentration the threshold voltage increased from 8.74 to 11.47 V (fig. 6.). At the same time the electroluminescence and power efficiency initially increased respectively from 521 Cd/m^2 ; 0.87 Lm/W to 600 Cd/m^2 ; 0.94 Lm/W in the range from 0 to 2 wt %, then decreased to 180 Cd/m^2 ; 0.58 Lm/W at 8.0 wt % and over 8.0 wt % again started to increase (table 2).

These results on the one hand and the absence of any PVK and TPD emission in El spectra of doped devices - on the other, show the charge trapping in the Ir complex, rather than the energy transfer, as the dominant mechanism in investigated OLEDs. At the low concentration of the dopant in host matrix the mobility limitation of a charge from one dopant site to another appears due to deep traps, caused by the big difference between HOMO/LUMO levels of the host and the guest (see energy diagram in fig. 2). Deep traps catch up the electric charges in the guest molecules and in this way cause rising of the threshold voltage of device. Further increasing of dopant concentration increases the charges mobility since the distance between the molecules of the dopant decreases and the threshold voltage start to fall. However, when the concentration of the dopant increases above a certain value, its molecules start to aggregate which causes the degradation of device performance again.

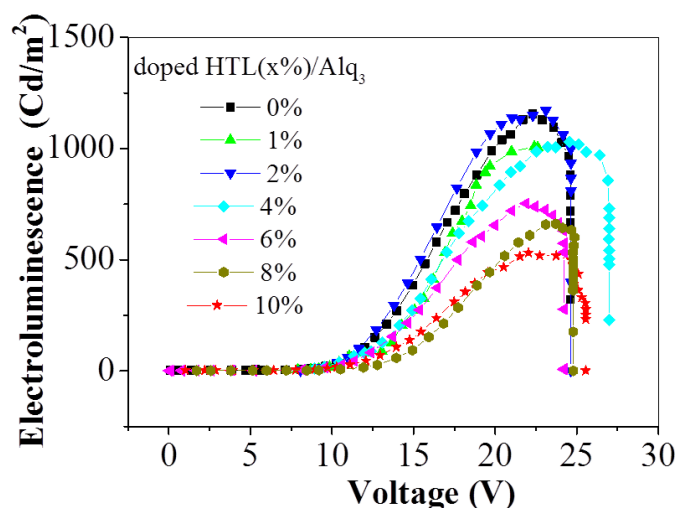


Fig. 6. Electroluminescence-voltage characteristics of OLEDs doped with different concentrations of $(ppy)_2Ir(fmtdbm)$.

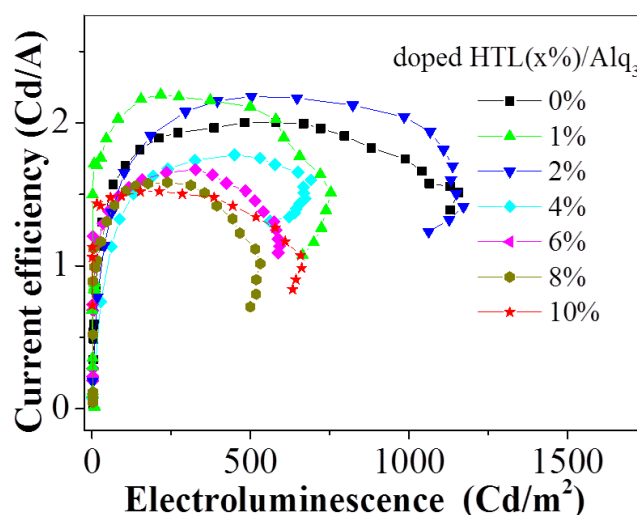


Fig. 7. External current efficiencies of OLEDs doped with different concentrations of $(ppy)_2Ir(fmtdbm)$.

Table 2. Electroluminescence data of doped OLEDs.

Dopant (wt %)	Current efficiency ^a (Cd/A)	Power efficiency ^a (Lm/W)	Threshold voltage (V)	Electroluminescence ^b (Cd/m ²)
0	2.45	0.87	8.74	521
1	2.12	0.89	9.05	410
2	2.01	0.94	9.27	600
4	1.69	0.90	9.35	420
6	1.64	0.68	10.40	340
8	1.59	0.58	11.13	195
10	1.51	0.60	11.47	210

^a Data was obtained at brightness 250 Cd/m²

^b Data was measured at 16 V DC

The best performance had device doped with 2 wt % of (ppy)₂Ir(fmtdbm). It demonstrated stable current efficiency of 2.0 – 2.25 Cd/A in the range of 150 to 1200 Cd/m² of electroluminescence.

4. CONCLUSION

New yellow-orange iridium complex (ppy)₂Ir(fmtdbm) has been synthesized and applied as a dopant in OLEDs. It was found that devices at different dopant concentrations emitted green-orange light in different tunes. We established that the lightly-doped 2 wt % samples had better luminescence efficiency in all region of applied voltages, in comparison with undoped device.

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