

Bright green phosphorescent organic light-emitting diode with doped hole transporting layer

P. Ivanov*, P. Petrova, R. Tomova

*Institute of Optical Materials and Technologies "Acad. J. Malinowski",
Bulgarian Academy of Sciences, Acad. G. Bonchev str. bl. 109, 1113 Sofia, Bulgaria*

Received October 10, 2016; Revised November 20, 2016

The application of green phosphorescent complex Tris[2-phenylpyridinato- C^{2},N]iridium(III) - Ir(ppy)₃ as a dopant in the hole transporting layer (HTL) of Organic light emitting diode (OLED) structure: HTL/EIL/ETL has been studied. We have found that devices containing from 4 wt.% - 6 wt.% Ir(ppy)₃ emit pure green light with CIE (x;y) chromaticity coordinates 0.2969; 0.4860 - 0.3184; 0.4905 very close to these of the ideal green color 0.3; 0.6, which is recommended at the displays manufacturing.

Keywords: Phosphorescent OLED, Cyclometalated iridium complexes, Tris[2-phenylpyridinato- C^{2},N]iridium(III) (Ir(ppy)₃)

INTRODUCTION

Since Baldo et al. reported the first example of electrophosphorescence at room temperature, phosphorescent materials have attracted much attention due to their high external quantum efficiencies in organic light emitting diodes (OLEDs) [1, 2]. Extensive investigations of phosphorescent materials have focused on d^6 and d^8 heavy metal complexes such as Os(II) [3], Ir(III) [4, 5] and Pt(II) [6]. OLEDs based on those phosphorescent materials can significantly improve electroluminescent performances because both singlet and triplet excitons can be harvested for light emission by strong spin-orbit coupling. The internal quantum efficiency of phosphorescent emitters can theoretically approach 100%, and the external quantum efficiency can approach 20% [7, 8, 9]. Due to their strong spin-orbit coupling, these complexes can burrow intensity from the singlet metal-to-ligand-charge-transfer (¹MLCT) state and emit effectively from their triplet ³MLCT states. Among all phosphorescent complexes these based on iridium recently are the subject of intensive studying, because Ir atom owns intense phosphorescence at room temperature, stable and accessible oxidation and reduction states and quasi-octahedral geometry, permitting introducing of specific ligands in a controlled manner [1, 10, 11].

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 λ_{\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 [12-15]. The high efficiency devices with Ir(ppy)₃ doped with electroluminescent layer is based on (i) the high cross-section for formation of electron-hole pairs (singlet and triplet excitons) on Ir(ppy)₃ in matrix materials, (ii) a fast intersystem crossing from the excited singlet to the emitting triplet states, and (iii) on the high emission quantum yield of about 40% of the triplet sub-states at ambient temperature [11]. Usually as a host matrix for Ir(ppy)₃ guest are preferred materials with wide band gap: small molecule compounds as 4,4'-N,N'-Dicarbazolylbiphenyl (CBP) [16-19]; 4,4',4''-tri(N-carbazolyl) triphenylamine (TCTA) [20] used in multilayered OLEDs obtained by thermal evaporation, and Poly(9-vinylcarbazole) (PVK) in monolayer electrophosphorescent polymer light-emitting diodes (PLED) produced by spin coating or spin casting. PVK is one of the widely used polymers because in addition to its large HOMO-LUMO separation, owns relatively high value of the lowest triplet state T¹ (about 2.5 eV) preventing back crossing of the triplet exciton from the phosphor to the host triplet state [21-23]. The main advantage of using a polymer matrix as a host material in comparison with such based on small molecule compound is the easy manner of control

* To whom all correspondence should be sent:
E-mail: ivanov.petar@mail.bg

of the dopant concentration. That is why, in recent years high-performance devices fabricated by employing $\text{Ir}(\text{ppy})_3$ incorporated in conjugated and non-conjugated polymer hosts were reported [12, 24] although PLEDs are less efficient than small molecule type devices.

In this paper we present the results obtained for OLED structure with $\text{Ir}(\text{ppy})_3$ doped composite hole transporting layer (HTL) of PVK:TPD in effort to obtain appropriate for display application device emitting pure and stable green light with CIE coordinates close to these of the ideal green color (0.3;0.6).

EXPERIMENTAL

OLED fabrication

We investigated the multilayered OLED structure of ITO/doped-HTL/EIL/ETL/M, where ITO was a transparent anode of $\text{In}_2\text{O}_3:\text{SnO}_2$, M - a metallic Al cathode, HTL -N,N'-Bis(3-

methylphenyl)-N,N'-diphenylbenzidine (TPD) involved in poly(N-vinylcarbazole) (PVK) matrix, EIL - electroluminescent layer of Bis(8-hydroxy-2-methylquinoline)-(4-phenylphenoxy)aluminum (BALq) and ETL - electron-transporting layer of Bis[2-(2-benzothiazoly)phenolato]zinc ($\text{Zn}(\text{bt})_2$). Devices with area of 1cm^2 were prepared on commercial polyethylene terephthalate (PET) substrates coated with ITO ($40\ \Omega/\text{sq}$). The layer (30 nm) of PVK:TPD (10%(relatively to PVK) + $\text{Ir}(\text{ppy})_3$ composite films were prepared by spin-coating from 0.75% PVK solution in dichloroethane at 2000 rpm. Other organic layers BALq (40nm) and $\text{Zn}(\text{bt})_2$ (35nm), and the Al cathode (100nm) were deposited by thermal evaporation in vacuum better than 10^{-4} Pa at rates 2-5 $\text{\AA}/\text{s}$, without interrupting the vacuum. The layers thicknesses were controlled in situ with quartz crystal microbalance sensor, positioned near the PET/ITO substrate.

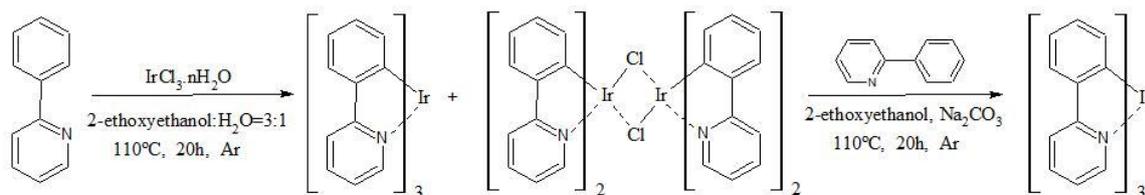


Fig. 1. Scheme of the synthesis of $\text{Ir}(\text{ppy})_3$ complex.

All materials were purchased from Sigma-Aldrich Co. LLC., except $\text{Ir}(\text{ppy})_3$ complex, which was synthesized by us according to procedure developed by King et al. [25] (Fig. 1). 2-Phenylpyridine(1) (2.2 equiv), and iridium trichloride hydrate (1 equiv) dissolved in 2-ethoxyethanol: water = 3:1 were stirred for 20 h at 110 °C under argon atmosphere. After that, the cooled to the room temperature reaction mixture was filtrated. The obtained greenish precipitate was washed with ethanol and hexane several times, and dried at room temperature.

Instruments and measurements

The photoluminescence emission (PI) spectra of PVK and TPD, electroluminescent emission (EI) spectra of OLEDs, and CIE (x;y) chromaticity coordinates of emitted light were obtained by Ocean Optics HR2000+ spectrometer. The excitation (Exc) and PI spectra of $\text{Ir}(\text{ppy})_3$ complexes were recorded on a Jobin-Yvon-Horiba Fluorolog III spectrofluorometer. The current-

voltage (I-V) curves were measured by programmable with Labview power supply. The electroluminescence (EL) 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}) was calculated by equation (1) and used for quantifying the properties of the OLEDs.

$$\eta_{\text{EL}} = \frac{EL}{I} \quad (1)$$

where EL is the electroluminescence (in cd/m^2), I is the current density (in A/m^2).

All measurements of OLED structures were performed at room temperature and under ambient conditions, without any encapsulation.

RESULTS AND DISCUSSION

Excitation and photoluminescence

The excitation spectrum, taken at $\lambda_{\text{emiss}} = 536$ nm, and photoluminescence emission spectrum, taken (at $\lambda_{\text{excit}} = 400$ nm) of $\text{Ir}(\text{ppy})_3$ in CH_2Cl_2 solution are shown in Fig. 2. It is seen that in Exc

spectrum of $\text{Ir}(\text{ppy})_3$ there are two excitation bands. The first is centered at region below 300 nm and contains bands for electronic transitions, which lead to excitations in ligands themselves, most probably due to transition to lowest singlet ligand centered (^1LC) excited state. The second band is very broad, peaked at 372 nm and is connected to singlet and triplet metal to ligand charge transfer ($^1\text{MLCT}$, $^3\text{MLCT}$). Effective spin-orbit coupling (SOC) in this complex relax the spin forbiddance and mix the singlet and triplet states making the band for resonant transition $^1\text{S}_0 \rightarrow ^3\text{MLCT}$ detectable in Exc spectrum (around 480 nm).

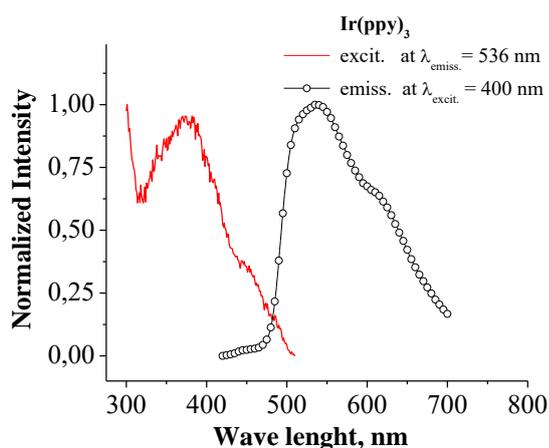


Fig. 2. Excitation (at $\lambda_{\text{emiss.}} = 536 \text{ nm}$) and photoluminescence emission (at $\lambda_{\text{excit.}} = 536 \text{ nm}$) spectra of $\text{Ir}(\text{ppy})_3$ CH_2Cl_2 solution.

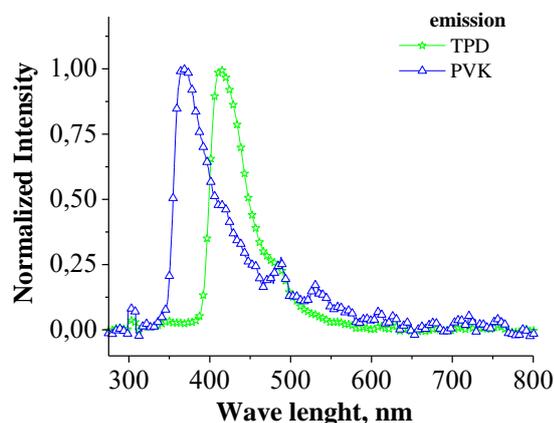


Fig. 3. Photoluminescence emission spectra of PVK and TPD in CH_2Cl_2 solution taken under excitation with tungsten halogen white light sources (LS-1, Ocean Optics Inc.).

The PL spectra of PVK and TPD in CH_2Cl_2 solution taken under excitation with tungsten halogen white light sources (LS-1, Ocean Optics Inc.) are presented in Fig. 3. As can be seen PVK and TPD emit a blue light with peaks at 367 and 415 nm respectively and exhibit good spectral

overlapping with MLCT excitation bands of $\text{Ir}(\text{ppy})_3$ ranged from 360 nm to 480 nm, which is a good prerequisite for the efficient Förster or Dexter energy transfer from the host (PVK:TPD) to the $\text{Ir}(\text{ppy})_3$ guest.

The PL emission spectrum of $\text{Ir}(\text{ppy})_3$ in non-degassed CH_2Cl_2 at room temperature obtained under excitation at 400 nm exhibited strong green phosphorescence with maximum emission peak at 533 nm and shoulder at 608 nm.

Electroluminescence

In Fig. 4 are shown the normalized EL spectra of investigated device HTL: $\text{Ir}(\text{ppy})_3(x)$ /BALq(40 nm)/ $\text{Zn}(\text{bt})_2(35\text{nm})$ at different doping concentration x (wt.%) and referent devices HTL/ $\text{Zn}(\text{bt})_2(75\text{nm})$ and HTL/BALq(75nm). For comparison the EL spectrum of OLED structure HTL/Alq₃(75), widely used for its pure green fluorescent emission, is also presented. As might be seen device with EIL of BALq emits at 496 nm, and these with $\text{Zn}(\text{bt})_2$ and Alq₃ relatively at 533nm and 528 nm. The shape of EL spectrum of OLED with consequent evaporated layers of BALq(40)/ $\text{Zn}(\text{bt})_2(35\text{nm})$ was just the same as that of OLED with BALq. In our opinion, as the HOMO level (5,05 eV) of $\text{Zn}(\text{bt})_2$ is much lower than HOMO level (5,90 eV) of BALq, the $\text{Zn}(\text{bt})_2$ cannot stop the holes and they leakage unimpeded from $\text{Zn}(\text{bt})_2$ layer. By this reason in BALq/ $\text{Zn}(\text{bt})_2$ structure $\text{Zn}(\text{bt})_2$ acts the role only of ETL.

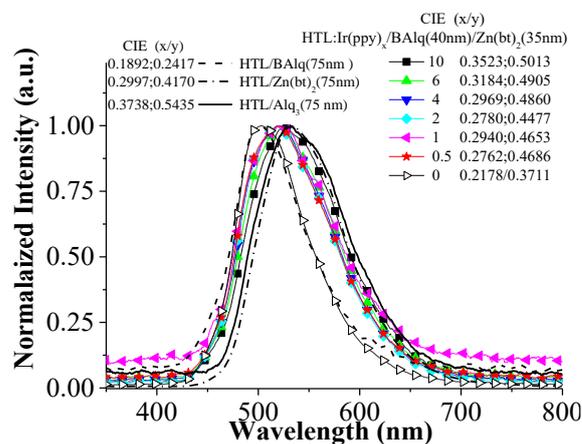


Fig. 4. Normalized electroluminescence spectra of devices HTL/BALq(75nm), HTL/ $\text{Zn}(\text{bt})_2(75\text{nm})$, HTL/Alq₃(75nm), and HTL: $\text{Ir}(\text{ppy})_3(x)$ /BALq(40)/ $\text{Zn}(\text{bt})_2(35\text{nm})$ (at different concentrations x), viewed in the normal direction at a benchmark of 18 V DC, and their CIE (x;y) chromaticity coordinates.

The EL spectra of doped devices did not include any PVK and TPD emissions that points out the effective charge trapping on the $\text{Ir}(\text{ppy})_3$ and/or

effective energy transfer from host to the complex guest. The increasing of the dopant concentration x caused a decreasing of the relative intensity of the bluish-green emission of BAQ at 496 nm, and red shifting of λ_{\max} and CIE (x;y) coordinates from 504 nm and 0,2178;0, 3711 (bluish-green) for undoped device to 525 nm and 0,3523; 0,5013 (greenish-yellow) for device doped with 10 wt.% of Ir(ppy)₃. Devices doped with 4 wt.% $\leq x \leq 6$ wt.% demonstrated CIE (x;y) coordinates in the range from 0.2969; 0.4860 to 0.3184; 0.4905 which were a lot closer to these of the ideal green color 0.3; 0.6 in comparison with these (0.3738; 0.5435) displayed by OLED with EIL of Alq₃.

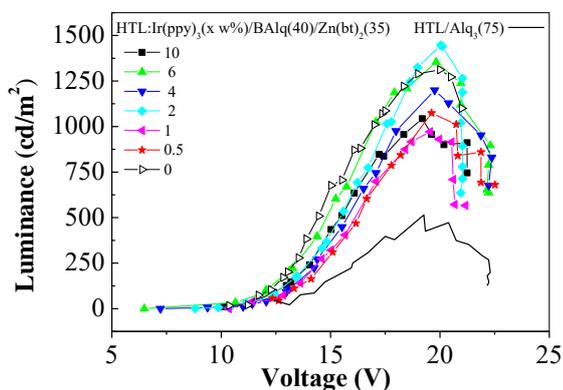


Fig. 5. Electroluminescence – voltage characteristics of devices HTL:Ir(ppy)₃ (x wt.%) / BAQ(40nm) / Zn(bt)₂ (35nm) and HTL/Alq₃(75nm).

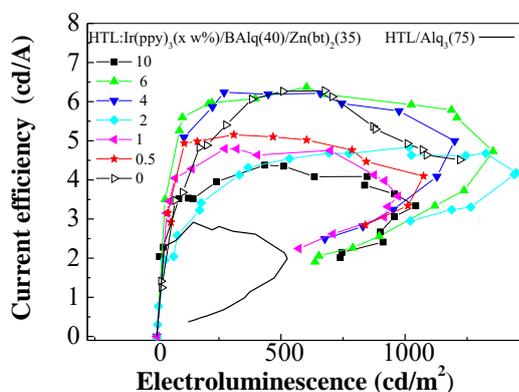


Fig. 6. Current efficiency as a function of electroluminescence of devices HTL:Ir(ppy)₃ (x wt.%) / BAQ(40nm) / Zn(bt)₂ (35nm) and HTL/Alq₃(75nm).

The influence of the dopant concentration on intensity of electroluminescence as a function of applied voltage and on current efficiency as a function of electroluminescence are shown in Fig. 5. and Fig. 6. We established that with increasing of the dopant concentration from 0 to 1.0 wt.% the threshold voltage of all devices initially increased

from 10.2 to 11.4 V and then decreased to 8 V at 10 wt.% (Fig. 5.). At the same time the electroluminescence (at one and same voltage) (Fig. 5.) and current efficiency (at one and the same electroluminescence) (Fig. 6.) had just the opposite behavior: initially decreased from 0 to 1.0 wt.%, then increased from 1.0 wt.% to 6.0 wt.% and over 6.0 wt.% again decreased.

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 that leads to a rise of the threshold voltage. Further increasing of dopant concentration increases the charges mobility since the distance between the Ir(ppy)₃ molecules decreases. When the dopant concentration falls beyond a certain value, its molecules start to aggregate which causes the degradation of device performance again.

The best performance had devices doped in the range of 4 to 6 wt.% of Ir(ppy)₃ with their electroluminescence of 1200 – 1350 cd/m² at 18 V DC and current efficiency of nearly 6.25 cd/A in the range of 100 to 1200 cd/m² of electroluminescence. For comparison the device with EIL of Alq₃ demonstrated two times lower EL (485 cd/m²) and current efficiency (2.75 cd/A) at the same conditions.

CONCLUSION

In summary we propose the OLED structure: HTL/BAQ/Zn(bt)₂ hole transporting layer doped with green phosphorescent complex Ir(ppy)₃. Devices containing from 4 wt.% - 6 wt.% Ir(ppy)₃ emit pure green light with intensity 1200 – 1350 cd/m² (at 18 V DC) and 6.25 cd/A current efficiency in wide range of electroluminescence (100 - 1200 cd/m²). The CIE coordinates of emitted light in these concentration limits are in the range of 0.2969; 0.4860 - 0.3184; 0.4905 and they are very close to these of the ideal green color 0.3; 0.6, which is recommended for the display's manufacturing.

Acknowledgement: This research was done with the financial support of the "Program for career development of young scientists" of the Bulgarian Academy of Sciences.

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ЯРКО ЗЕЛЕН ФОСФОРЕСЦЕНТЕН ОРГАНИЧЕН СВЕТО ДИОД С ДОТИРАН ТРАНСПОРТИРАЩ ПОЛОЖИТЕЛНИТЕ ЗАРЯДИ СЛОЙ

П. Иванов, П. Петрова, Р. Томова

Институт по Оптически Материали и Технологии "Акад. Йордан Малиновски"
Българска Академия на Науките, ул. Акад. Г. Бончев, бл.109, 1113, София, България

Постъпила на 10 октомври 2016 г.; коригирана на 20 ноември, 2016 г.

(Резюме)

Разработена е структура на органичен свето диод (ОЛЕД) HTL/BAIq/Zn(bt)₂, в която слоят осигуряващ придвижването на положителните заряди (HTL) е дотиран с фосфоресцентния иридиев комплекс Tris[2-phenylpyridinato-C²,N]iridium(III) - Ir(ppy)₃. Изследвано е влиянието на концентрацията на допанта върху запалващото напрежение, силата на тока, интензитета и цвета на излъчваната светлина. Установено е, че при концентрации на Ir(ppy)₃ от 4 до 6 тегл.% ОЛЕДите излъчват светлина с интензитет 1200 – 1350 cd/m² (при напрежение 18 V) и демонстрират стабилна токова ефективност от 6.25 cd/A в широк диапазон от стойности на интензитета на светлината 100 - 1200 cd/m². В тези концентрационни граници цветът на излъчваната светлина е с CIE (x;y) координати 0.2969; 0.4860 - 0.3184; 0.4905, които са много близки до тези на идеалния зелен цвят 0.3; 0.6, препоръчван за производството на дисплеи. Това прави предлаганата ОЛЕД структура обещаваща за приложение в това направление.