

## Bis(2-phenylbenzothiazolato) (acetylacetonate) iridium complex as phosphorescent dopant for White Organic Light Emitting Diodes

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In this article we demonstrate White Organic Light Emitting Diodes (WOLEDs) using yellow-emitting iridium complex bis(2-phenylbenzothiazolato) (acetyl-acetonate)iridium(III) ( $\text{Ir}(\text{bt})_2\text{acac}$ ), as a dopant in the hole-transporting layer (composed of N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) dispersed in poly(N-vinylcarbazole) (PVK) matrix. Bis(8-hydroxy-2-methylquinoline)-(4-phenylphenoxy)aluminum (BALq) and bis(2-(2-hydroxyphenyl) benzothiazolato)zinc ( $\text{Zn}(\text{btz})_2$ ) were used as electroluminescent and electron-transporting materials. It was found that OLED with 2.5 wt %  $\text{Ir}(\text{bt})_2\text{acac}$  irradiated a white light which CIE coordinates changed from bluish-white (0.28, 0.30) at 8 V, to yellowish-white (0.35, 0.40) at 20 V.

**Keywords:** WOLEDs,  $\text{Ir}(\text{bt})_2\text{acac}$ , BALq,  $\text{Zn}(\text{btz})_2$

### INTRODUCTION

WOLEDs have attracted great attention due to their potential applications such as full color displays, backlight units for LCD displays and solid-state light sources for interior and exterior general illumination. WOLEDs can be classified into three types according to the emitters used: fluorescent devices (F-WOLEDs), phosphorescent devices (P-WOLEDs) and hybrid devices employing both fluorescent and phosphorescent emitters (F/P-WOLED) [1, 2]. It has been shown that P-WOLEDs based on heavy metal complexes (Ru, Os, Eu, Pt, particularly Ir [3-6]) can achieve an internal quantum efficiency of 100%, as compared to the theoretical value of 25% in F-WOLEDs, because they harvest both singlet and triplet emissions. Among these phosphorescent complexes, cyclometalated iridium(III) complexes are the most promising because of their good stability, high photoluminescence (PL) quantum yields, ease of spectral tuning and short triplet state lifetimes. The yellow-emitting Ir(III) complexes are of great interest in view of the fact that in combination with blue emitters, they can be used for fabrication of white WOLEDs [7, 8].

The typical orange phosphorescent emitter Bis(2-phenylbenzothiazolato)-

N,C<sup>2</sup>)iridium(acetylacetonate) [ $(\text{bt})_2\text{Ir}(\text{acac})$ ] [9] and its derivatives have been widely investigated mainly as dopants in different electroluminescent hosts materials for: “small molecule“ OLED (SMOLED), obtained by vacuum evaporation and “polymer“ OLED (POLED), obtained by spin coating [10-12]. The frequently used host for SMOLED is CBP (4,4'-N,N'-dicarbazole-biphenyl) independently [3, 13] or mixed with NPB (N,N'-Di(naphthalen-1-yl)-N,N'-diphenyl-benzidine) [14] or UGH3 (m-bis-(triphenylsilyl)benzene [5] and for POLED - PVK (poly(N-vinylcarbazole). The electroluminescent properties of developed devices are still very unsatisfactory that motivated us to investigate the possibility of application of  $(\text{bt})_2\text{Ir}(\text{acac})$  as a dopant in the hole transporting layer (HTL) of OLED.

### EXPERIMENTAL DETAILS

We investigated the device structure: PET/ITO/doped-HTL/EL/ETL/M, where ITO was a transparent anode of  $\text{In}_2\text{O}_3:\text{SnO}_2$ , doped-HTL was doped with  $\text{Ir}(\text{bt})_2\text{acac}$  HTL or incorporated in PVK matrix N, N'-bis(3-methylphenyl)-N, N'-diphenylbenzidine (TPD), EL - electroluminescent layer of Bis(8-hydroxy-2-methylquinoline)-(4-phenylphenoxy) aluminum (BALq), ETL - electron-transporting layer of Bis[2-(2-benzothiazoly) phenolato]zinc(II) ( $\text{Zn}(\text{btz})_2$ ) and M - a metallic Al cathode.

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Devices with area  $1\text{cm}^2$  were prepared on polyethylene terephthalate (PET) substrates coated with ITO ( $40\ \Omega/\text{sq}$ ). The doped HTL of PVK:TPD $_{10\text{wt}\%}$ :Ir(bt) $_2$ acac $_x$  wt% (wt% relative to PVK) composite film was formed by spin-coating from 0.75 % solutions in dichloroethane at 2000 rpm. The layers of BALq (40 nm), Zn(bt) $_2$  (35 nm) and Al cathode (80 nm) were thermal evaporated in vacuum better than  $10^{-4}$  Pa at rates 0.2 - 0.5 nm/s. The quartz crystal microbalance thickness sensor was positioned near the PET/ITO substrate for better accuracy. For each run, four samples were fabricated simultaneously without breaking the vacuum, to ensure similar deposition conditions. All materials were purchased from Aldrich, except Zn(bt) $_2$  and Ir(bt) $_2$ acac which were synthesized in the Laboratory of Organic Photochemistry Faculty of Chemistry and Pharmacy, University of Sofia "St. Kl. Ohridski".

All measurements were performed at room temperature and under ambient atmosphere, without any encapsulation. The photoluminescence (PL) and the electroluminescence (EL) spectra were taken out on Ocean Optics HR2000+ spectrometer. The current-voltage (I-V) curves were recorded by programmable with Labview power supply. The electroluminescence was measured in continuous DC mode and the light output was detected using a calibrated Hamamatsu silicon photodiode S2281-01. The current and external quantum efficiency ( $\eta_L$ ,  $\eta_{\text{EQE}}$ ) were calculated by equations (1) and (2) and used for quantifying the properties of the OLEDs.

$$\eta_L = L/I, \text{ cd/A} \quad (1)$$

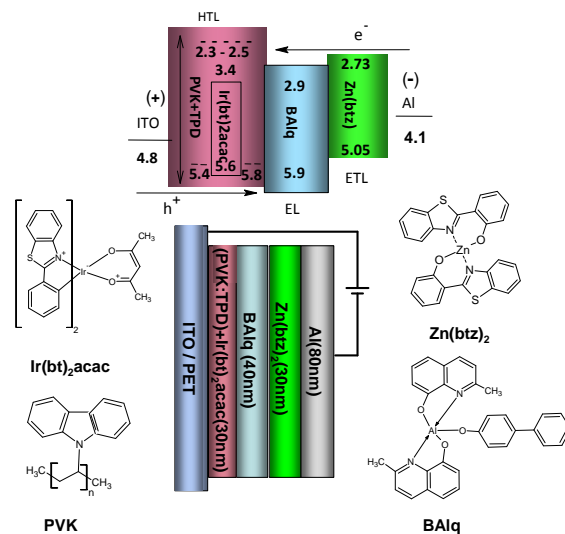
$$\eta_{\text{EQE}} = I_\phi 100/I, \% \quad (2)$$

where  $L$  is the luminescence (in  $\text{cd/m}^2$ ),  $I$  and  $I_\phi$  are the densities of current and photocurrent (in  $\text{A/m}^2$ ), respectively.

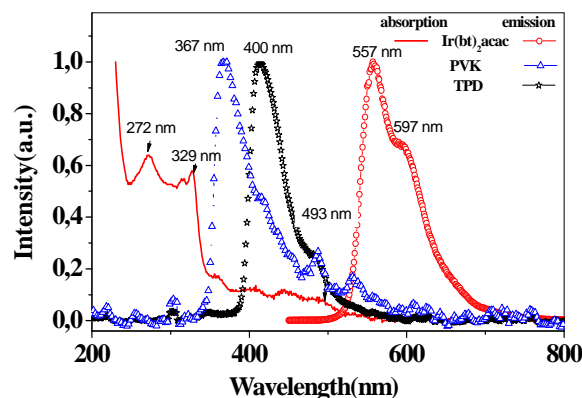
Chemical structures of used organic materials, device structure, and schematic energy level diagram of OLEDs discussed in this study, are briefly summarized in Fig. 1.

## RESULTS AND DISCUSSION

Figure 2 shows the optical absorption spectrum of Ir(bt) $_2$ acac and PL spectra of Ir(bt) $_2$ acac, PVK and TPD in  $\text{CH}_2\text{Cl}_2$  solution at photoexcitation with PX-2 Pulsed Xenon Lamp UV (220-750 nm). The Ir(bt) $_2$ acac emitted a greenish yellow light with a peak at 557 nm and shoulder at 597 nm. The PVK

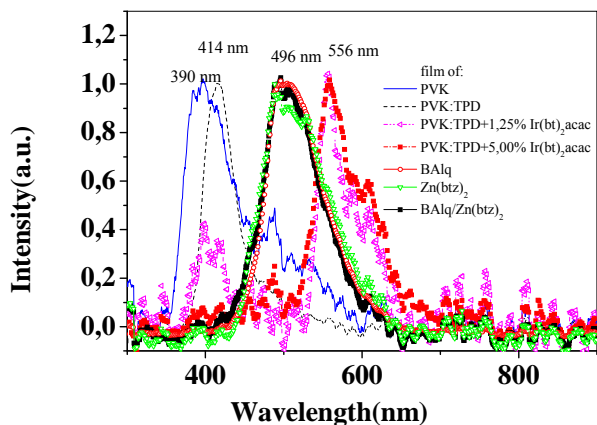


**Fig. 1.** Chemical structure of the organic materials, device structure, and schematic energy level diagram of WOLED.

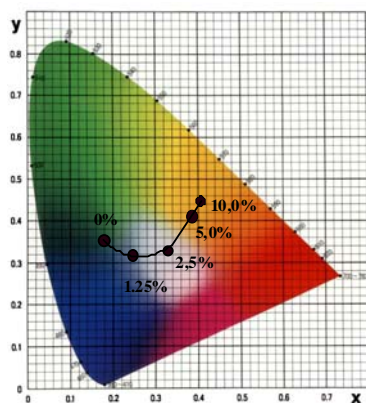
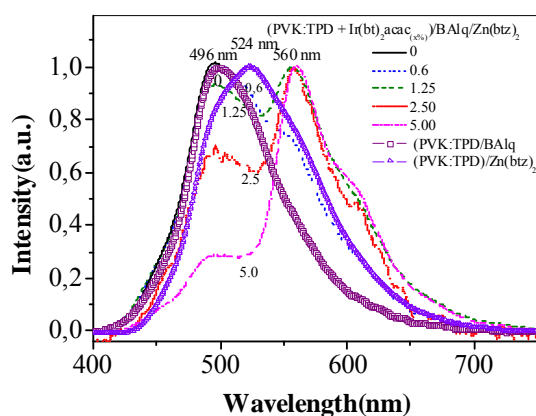


**Fig. 2.** UV-visible absorption spectrum of Ir(bt) $_2$ acac and PL emission spectra of Ir(bt) $_2$ acac, PVK and TPD in  $\text{CH}_2\text{Cl}_2$ .

and TPD emitted a blue light with peaks at 367 and 414 nm. It can be expected that the efficient either Förster or Dexter energy transfer would be possible from PVK and TPD host to Ir(bt) $_2$ acac guest, since  $^1\text{MLCT}$  and  $^3\text{MLCT}$  absorption spectra of Ir(bt) $_2$ acac has broader spectral overlap with fluorescence spectra of PVK in the range from 330 to 450 nm and of TPD from 390 to 450 nm. The PL spectra of pure and doped with Ir(bt) $_2$ acac PVK:TPD spin coated films are shown in Fig. 3. It is seen that the blue emission at  $\sim 414$  nm, attributed to PVK:TPD composite film, reduces



**Fig. 3.** PL spectra of: pure and doped with Ir(bt)<sub>2</sub>acac PVK:TPD spin coated films; neat BAq, Zn(bt)<sub>2</sub> and consequent BAq/Zn(bt)<sub>2</sub> thermal evaporated films.



**Fig. 4.** Taken at 16 V DC normalized EL spectra and CIE coordinates of OLEDs with different concentrations of the dopant.

significantly with increasing of the dopant concentration from 0 to 5 wt %, indicating that an energy transfer from PVK and TPD to Ir(bt)<sub>2</sub>acac not only takes place, but also increases with doping

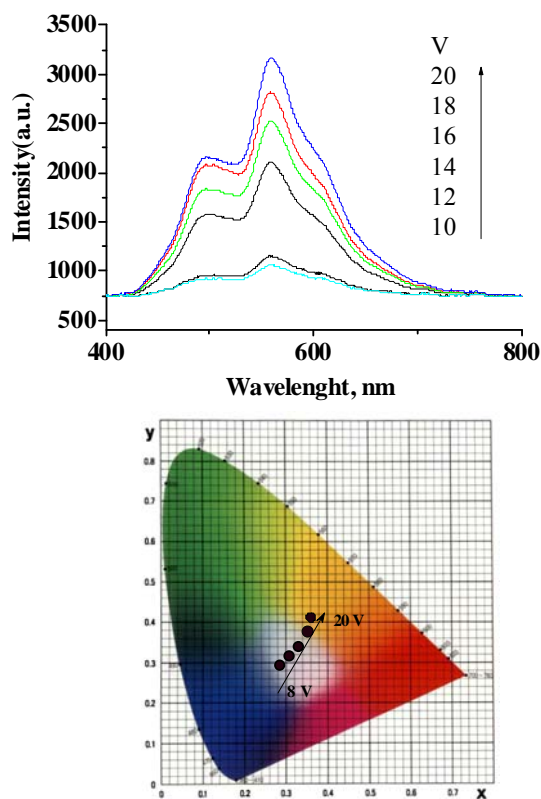
concentration and was completely brought to an end at 2.5 wt %. In the same figure the PL spectra of thermally evaporated on a quartz glass neat films of BAq and Zn(bt)<sub>2</sub> as well as consequently evaporated over BAq Zn(bt)<sub>2</sub> film are presented. It was found that neat films had similar spectra with PL maximums at 496 nm and there are not essential differences between them and consequently evaporated BAq/Zn(bt)<sub>2</sub>.

In contrast to the PL spectra of the doped with iridium complex PVK films (Fig. 3.), in the EL spectra of OLED devices (Fig. 4.), any PVK-induced emission about 400 nm was not observed, irrespective of the Ir(bt)<sub>2</sub>acac concentration. The absence of major PVK related emission features has implied a charge trapping rather than an exciton transfer mechanism. The EL spectra of doped devices did not include any Zn(bt)<sub>2</sub> emission at 529 nm too and were basically the sum of the emissions of Ir(bt)<sub>2</sub>acac (at 560 nm) and BAq (at 496 nm). With increasing Ir(bt)<sub>2</sub>acac concentration, the relative intensity of the greenish-blue emission (496 nm) decreased, while the yellow (560 nm) - increased and CIE coordinates of OLEDs shifted from blue (0.19, 0.30) at 0 wt % to yellow (0.42, 0.45) at 5 wt % of the dopant. It was established that the OLED with 2.5 wt % Ir(bt)<sub>2</sub>acac irradiated a white light which intensity increased with increasing of applied voltages and CIE coordinates changed from bluish-white (0.28, 0.30) at 8 V, to yellowish-white (0.35, 0.40) at 20 V (Fig. 5).

The L-I-V characteristics of the devices with different dopant concentration and their current and external quantum efficiencies ( $\eta_L$ ,  $\eta_{EQE}$ ) are presented in Fig. 6a and Fig. 6b. It can be seen that increasing Ir(bt)<sub>2</sub>acac concentration from 0.5 to 5 wt% decreases the driving voltage from 10.5 to 8 V and enhances electroluminescence and current density at 13 V from 100 to 400 Cd/m<sup>2</sup> and from 20 to 110 A/m<sup>2</sup>, respectively. A further increase in the dopant concentration to 10 wt% results in a weak rising of the driving voltage to 8.5 V and in materially reducing of the luminescence to 350 Cd/m<sup>2</sup> and the current density to 95 A/m<sup>2</sup>. Besides, the electroluminescent and external quantum efficiencies decrease from 6 Cd/A and 1.5% EQE for non doped device to 4 Cd/A and 1.05 % EQE for doped with 10 w% Ir(bt)<sub>2</sub>acac device. At the same time the range of current densities with maximum efficiencies at the fixed dopant concentration expands and reaches its optimal value at 5wt% Ir(bt)<sub>2</sub>acac.

The obtained results can be explained with energy level diagram of studied device, shown in

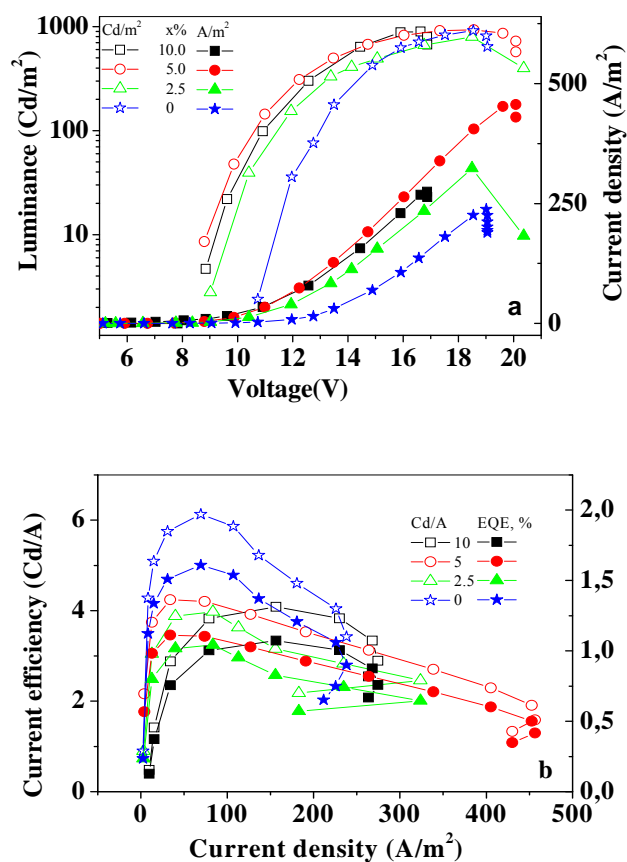
Fig. 1. According to this diagram, most probably the observed yellow emission (except Förster or Dexter energy transfer from PVK:TPD composite film to the dopant) appears as a result of the direct recombination of injected carriers at the Ir(bt)<sub>2</sub>acac sites.



**Fig. 5.** EL intensity of the device with 2.5 % Ir(bt)<sub>2</sub>acac and its CIE coordinates at different bias voltages.

In undoped device excitons generate at the PVK:TPD/BAIq interface and recombine in the BAIq layer irradiating a blue light. The introduction of Ir(bt)<sub>2</sub>acac in PVK:TPD matrix causes trapping of some carriers on HOMO and LUMO levels of the dopant (-5.6 and -3.4 eV), located within HOMO and LUMO level of the host composite film (-5.8 and -2.5 eV). Later the formed excitons decay radiatively emitting a red light. For that reason the increasing of dopant concentration or the applied voltage lead to a red shift of the CIE coordinates. Charge trapping within the dopant material can be explained by the distribution of dopant molecules within the host. At the low concentration of dopant in the host matrix, the mobility limitation of a charge from one dopant site

to another will lead to a higher driving voltage [6]. However, when the doping concentration increases, the charge mobility increases since the distance



**Fig. 6.** Electroluminescence–current and density–voltage characteristics (a); Current and external quantum efficiencies of devices with different dopant concentrations (b).

between the Ir(bt)<sub>2</sub>acac molecules decreases. Such a transport characteristic causes effective decreasing of the driving voltage and increasing of the current density and the light intensity. The fact that current and external quantum efficiencies decrease notwithstanding the increase of light intensity also confirms charge trapping mechanism.

## CONCLUSIONS

It was established that the incorporation of Ir(bt)<sub>2</sub>acac in HTL of the investigated devices tunes the light emission allowing the successful development of WOLED.

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## BIS(2-PHENYLBENZOTHAZOLATO) (АСЕТЫЛАСЕТОНАТЕ) ИРИДИЕВ КОМПЛЕКС КАТО ФОСФОРЕСЦЕНТЕН ДОПАНТ ЗА БЕЛИ ОРГАНИЧНИ СВЕТОИЗЛЪЧВАЩИ ДИОДИ

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(Резюме)

В тази статия са представени резултатите от разработването на бели органични светоизлъчващи диоди (WOLEDs), в които като допант в транспортиращия дупки композитен слой от диспергиран в матрица от poly(N-vinylcarbazole) (PVK) - N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) е използван излъчващия жълта светлина иридиев комплекс bis(2-phenylbenzothiazolato) (acetyl-acetonate)iridium(III) (Ir(bt)<sub>2</sub>acac) Като електролуминесцентен и електрон транспортен слой в WOLED са използвани Bis(8-hydroxy-2-methylquinoline)-(4-phenylphenoxy)aluminum (BALq) и bis(2-(2-hydroxyphenyl) benzothiazolate)zinc (Zn(bt)<sub>2</sub>). Установено е, че устройствата с 2.5 тегловни % Ir(bt)<sub>2</sub>acac излъчват бяла светлина със CIE координати, променящи се от студено бяло (0.28, 0.30) при напрежение 8 V до топло бяло (0.35, 0.40) при напрежение 20 V.