New cyclometalated Iridium(III) beta-dicetone complex as phosphorescent dopant in Organic light emitting devices

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Abstract. A new Bis[4-(benzothiazolato-N,C2′-2-yl)-N,N-dimethylaniline]Iridium(III) acetylacetonate (Me2N-bt) 2Ir(acac) was synthesized and identified by 1H NMR and elemental analysis. The application of the new compound as a dopant in the hole transporting layer (HTL) of Organic light emitting diode (OLED) structure: HTL/EL/ETL, where HTL was N,N′-bis(3-methylphenyl)-N,N′-diphenylbenzidine (TPD), incorporated in Poly(N-vinylcarbazole) (PVK) matrix, EL - electroluminescent layer of Bis(8-hydroxy-2-methylquinoline)-(4-phenylphenoxy)aluminum (BAIQ) and ETL - electron-transporting layer of Tris-(8-hydroxyquinoline) aluminum (Alq) or Bis[2-(2-benzothiazolyl)phenolato]zinc (Zn(btz)2). We established that the electroluminescent spectra of OLEDs at different concentrations of the dopant was basically the sum of the greenish-blue emission of BAlq and yellowish-green emission of Ir complex. It was found that with increasing of the dopant concentration the relative electroluminescent intensity of Iridium complex emission increased and this of BAlq decreased and as a result the fine tuning of OLED color was observed.

1. Introduction

During the past decade, intense research efforts have been devoted to the design of new emitting materials for organic light emitting devices (OLEDs). Phosphorescent OLEDs (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 [1-2]. Among all emitters that have been investigated to date, phosphorescent complexes have attracted more attention than the fluorescent ones due to their capability of achieving 100% internal quantum efficiency [2-4]. Extensive investigations of this materials have focused on heavy metal complexes of Os(II), Pt(II) and Ir(III) [3, 4]. Mixing of the singlet and triplet excited states of these d6 complexes via spin-orbit coupling, removes the spin-forbidden nature of the radiative relaxation of the triplet state, leading to high phosphorescence efficiencies [5]. The choice of iridium metal is of special interest because its stable and accessible oxidation and reduction states and quasi-octahedral geometry permitted introducing of specific ligands in a controlled manner. Varying the respective set of ligands on the iridium(III) center permits a variety of efficient emission wavelengths, such as blue, green, yellow or red, which can be used in color tuning and full-color applications [6-8].
2. Experimental

2.1 Instruments and measurements

$^1$H-NMR (600 MHz) spectra were recorded on a Bruker Avance II+ 600 at room temperature. The $^1$H-NMR spectra were referenced to internal standard tetramethylsilane (TMS). The elemental analyses were made on Elementar Vario EL III. The UV and fluorescent spectra of the complexes in solutions were recorded on a Thermo Spectronic Unicam 500 spectrophotometer and a Varian Cary Eclipse fluorescence spectrophotometer, respectively. All measurements of OLED structures were performed at room temperature and under ambient atmosphere, without any encapsulation. The electroluminescent spectra (EL) and CIE (Commission internationale de l'éclairage) coordinates were obtained by Ocean Optics HR2000+ spectrometer. The current-voltage (I-V) curves were measured by programmable with Labview power supply. The luminescence (L) was determined in DC (direct current) mode and the light output was detected using a calibrated Hamamatsu silicon photodiode S2281-01. The electroluminescent efficiency ($\eta_{EL}$) were calculated by equations (1) and used for quantifying the properties of the OLEDs.

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

where L is the luminescence (in cd/m$^2$), I is current density (in A/m$^2$).

2.2. Synthesis of Iridium complex

Ligand 1 (figure 1) was obtained according procedure reported in [9]. The other initial reagents and solvents were purchased from Merck and used without any purification. Synthesis of μ-chloro-bridged iridium dimer (2).

Cyclometalated Ir(III) μ-chloro-bridged dimer (Me$_2$N-bt)$_2$Ir(μ-Cl)$_2$Ir(Me$_2$N-bt)$_2$ was synthesized according a method reported by Nonoyama [10]. 2-(4-dimethylaniline)benzo[d]thiazole (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. After cooling to the room temperature, the reaction mixture was filtrated, and the orange-yellow precipitate was obtained. Then the precipitate was washed with ethanol and hexane several times, and dried at room temperature.

![Figure 1. Synthesis of iridium acetylacetonate complex (Me$_2$N-bt)$_2$Ir(acac).](image)

2.2.2. Synthesis of iridium acetylacetonate complex (3), (Me$_2$N-bt)$_2$Ir(acac).

Dimmer (2), 2,4-pentanediione (2.5 equiv) and Na$_2$CO$_3$ (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 giving an orange-yellow precipitate. 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.

Iridium(III)bis[4-(benzothiazolato-N,C$_2$-2-yl)-N,N-dimethylaniline]acetylacetonate, (Me$_2$N-bt)$_2$Ir(acac) : Yield: 70 %. $^1$H NMR (600 MHz, CDCl$_3$) δ[ppm]: 1.71 (s, 6H), 2.51 (s,12H), 5.08
(s, 1H), 5.58 (d, J=2.4 Hz, 2H), 6.15 (dd, J1=2.4 Hz, J2=8.4 Hz, 2H), 7.20–7.22 (m, 2H), 7.26–7.28 (m, 2H), 7.39 (d, J=9 Hz, 2H), 7.69 (dd, J1=0.6 Hz, J2=7.8 Hz, 2H), 7.96 (dd, J1=0.6 Hz, J2=8.4 Hz, 2H); C35H33N4O2S2Ir. Elemental analysis: Calc. C 52.68 %, H 4.17 %, N 7.02 %. Found: C 52.51 %, H 4.10 %, N 6.92 %.

2.3. OLED fabrication
Devices with area 1 cm² were prepared on commercial polyethylene terephthalate (PET) substrate, precoated with ITO (40 Ω/sq). The (30nm) composite films of PVK:TPD10 wt%: (Me2N-bt)2Ir(acac)x wt% (relatively to PVK) were formed by spin-coating from 0.75% PVK solution in CH2Cl2 at 2000 rpm. The films of BAlq (40nm), Zn(btz)2 (35nm) and Al cathode (120nm), were deposited in vacuum, better than 10⁻⁴ Pa, by thermal evaporation at rates 2-5 Å/s, controlled with a quartz crystal microbalance.

3. Results and discussion
3.1. UV-VIS absorption and photoluminescence
In figure 2 the normalized UV-VIS absorption spectra of complexes (bt)2Ir(acac) and (Me₂N-bt)₂Ir(acac) and photoluminescent spectra (PL) of: (bt)₂Ir(acac), (Me₂N-bt)₂Ir(acac), PVK and TPD dissolved in CH₂Cl₂ are presented. The absorption spectra of both complexes (curves 1 and 2) had almost identical shapes with peaks at 327 and 332nm (table 1), typical for that kind of complexes.

The spectra can be considered as composed of two parts. The region below 360 nm contains bands for electron transitions, which leads to excitations in the bt-ligand. Most probably, the band around 330 nm is due to the transition to lowest singlet ligand centered (1LC) excited state. This statement is in accordance with published before articles discussing similar complexes. The shoulders above 360 nm are assigned to singlet and triplet metal-to-ligand charge transfer bands (1MLCT, 3MLCT), respectively. Effective spin-orbit coupling (SOC) in this complex leads to mixing of the singlet and triplet states making the band for resonant transition 1S₀ → 3MLCT detectable in absorption spectrum (~480 nm). The band for 1MLCT transition is centered at 440 nm. The both complexes showed emission in yellowish-green region (table 1) with peaks at 558 nm for (bt)₂Ir(acac) and 563 nm for (Me₂N-bt)₂Ir(acac).
(Me₂N-bt)₂Ir(acac) and shoulders respectively at 594 and 604 nm (curves 3 and 4). It is seen that the PL spectrum of (Me₂N-bt)₂Ir(acac) was red shifted with 5 nm with respect to the PL spectrum of the unsubstituted (bt)₂Ir(acac), that is a typical for derivatives containing electron donating substituent [11, 12]. The PVK (curve 5) and TPD (curve 6) emitted a blue light with peaks at 367, 385 and 414 nm respectively. That’s why it could be expected that energy transfer from PVK and TPD to both complexes would be possible since ¹MLCT and ³MLCT absorption spectra of the dopants had a broad spectral overlap with fluorescent spectra of PVK and TPD. The PL spectra of thermal evaporated neat Zn(btz)₂ and B Alq films shown in figure 2 (curves 5 and 6) were very close to each other, with comparatively broad peaks centered at ≈ 490 nm.

Table 1. Photophysical data of (bt)₂Ir(acac) and (Me₂N-bt)₂Ir(acac) in Ar saturated CH₂Cl₂

| Complex            | Absorption λ nm, (lgε) | Emission λ max [nm] | QY  |
|--------------------|-------------------------|---------------------|-----|
| (bt)₂Ir(acac)      | 272(3.93), 315(3.86), 327(3.88), 407(3.21), 442(3.19), 489(3.03) | 558             | 0.50|
| (Me₂N-bt)₂Ir(acac) | 408 (4.41), 446 (4.08) | 563             | 0.16|

* ε is the molar absorption coefficient (molar absorptivity)

3.2. Electroluminescence

The electroluminescent spectra (EL) of various OLEDs viewed in the normal direction at a benchmark luminance of 18 V DC with structure doped HTL/[(PVK:TPD)/BAlq/Alq₃ with different concentrations of (Me₂N-bt)₂Ir(acac) are shown in figure 3. For comparison the normalized EL spectra of devices with undoped HTL and EL of BAlq, Zn(btz)₂ and BAlq/Zn(btz)₂ are presented in figure 4.

Figure 3. EL spectra of devices with structure: doped HTL/[(PVK:TPD)/BAlq/Alq₃ with different concentrations of (Me₂N-bt)₂Ir(acac), viewed in the normal direction at a benchmark of 18 V DC.

Figure 4. EL spectra of devices: HTL/BAlq; HTL/Zn(btz)₂ and doped HTL/[(PVK:TPD)/BAlq/Zn(btz)₂ with 1 and 10 wt% of (Me₂N-bt)₂Ir(acac) and (bt)₂Ir(acac) devices, viewed in the normal direction at a benchmark of 18 V DC.

It is seen that device with EL of BAlq irradiated at λ max 496 nm and with Zn(btz)₂ – at 524 nm (figures 4). The shape of EL of OLED with consequent evaporated layers of BAlq/Zn(btz)₂ was just
the same as that of OLED with EL of BAQ. In our opinion, it is due to the fact that in the both cases the recombination zone is near to the HTL/BAQ interface. As the HOMO$_{Zn(btz)}$ level (5.05 eV) was lower than HOMO$_{BAQ}$ (5.90 eV) level, Zn(btz)$_2$ didn’t stop the holes, which flowed unimpeded from Zn(btz)$_2$ layer. By this reason in BAQ/Zn(btz)$_2$ structure Zn(btz)$_2$, acted the role only of ETL. The EL spectra of doped devices did not include any Zn(btz)$_2$, PVK and TPD emissions and were basically the sum of emissions of (Me$_2$N-bt)$_2$Ir(acac) and BAQ. The absence of any emission peaks of PVK and TPD pointed out the effective charge trapping on the Ir(III) complexes and/or effective energy transfer to the Ir(III) complexes.

Increasing of the (Me$_2$N-bt)$_2$Ir(acac) concentration caused decreasing of the relative intensity of the greenish-blue emission (496 nm) and increasing of the yellow emission (559 nm) of devices that suggests that the exciton recombination zone migrates from HTL/BAQ interface deeper in the doped HTL layer. The Commission Internationale de L’Eclairage CIE (x/y) coordinates of OLEDs shown in figure 3 were red shifted from yellow green 0.2699/0.4373 for undoped device structure: doped HTL/BAQ/Alq to orange - 0.3562/0.4224 at 10 wt% of (Me$_2$N-bt)$_2$Ir(acac).

As can be seen in figure 4 at one and the same concentrations of the dopants the Full width at half maximum (FWHM) of EL spectra of devices with (Me$_2$N-bt)$_2$Ir(acac) were broader with 42 nm in comparison with FWHM of devices doped with (bt)$_2$Ir(acac) due to more intensive and widely red shifted with 35 nm shoulder. Obviously the replacement of an H atom in the 2-phenylbenzothiazole ligand with a dimethylamine radical leads to a strong red shifting of the emitted light which is typical for electron donating groups.

The influence of the dopant concentration on electroluminescent performance of the OLED structure HTL: (Me$_2$N-bt)$_2$Ir(acac) are presented in figure 5. We established that with increasing of the dopant concentration at one and the same voltage the current density decreased while the luminescence initially increased and then decreased (figure 5 a). This shows that a small amount of dopant improves the current efficiency of device due to enhancing of the carrier mobility as can be seen in figure 5 b. As the dopant concentration goes beyond a certain value, the dopant tend to aggregate and the aggregations degrade the device performance [2]. The best performance had device doped with 1 wt% (Me$_2$N-bt)$_2$Ir(acac) with its 533 Cd/m$^2$ luminescence; 95 A/m$^2$ current density and 5.69 Cd/A current efficiency demonstrated at 16 V DC in comparison with undoped device with its 253 Cd/m$^2$;70 A/m$^2$ and 3.51 Cd/A at the same voltage.

Figure 5. a) L-V-I and b) $\eta_{EL}$ –I characteristics of devices with structure: doped HTL/BAQ/Alq$_3$ at different concentrations of (Me$_2$N-bt)$_2$Ir(acac), viewed in the normal direction.

The electroluminescence in PhOLEDs comes either from the energy transfer from the host to the guest molecules, as described previously, or from the charge trapping by the guest molecules, where the dopant acts as a trap site which can capture a charged carrier. As was shown by Diouf et al [13],
four main elements - exciton confinement, charge trapping, dopant concentration and molecular structure directly affect the performance of PhOLEDs. These factors are dependent each other and individually predominant depending on the situation. In our case weakly increasing of OLED’s efficiency with increasing of dopant concentration are consistent with the charge trapping of the Ir complex, rather than the energy transfer, as the dominant mechanism in investigated OLEDs.

4. Conclusion
The new iridium complex (Me₂N-bt)₂Ir(acac) irradiating in yellow region has been synthesized and characterised as a dopant in hole transporting layer of OLED. It was established that the fine tuning of the emitted light of OLED in yellow orange region can be obtained depending on the dopant concentration. It was found that the lightly-doped (around 1.5 wt%) samples exhibit better luminescence efficiency than the highly-doped samples at all applied voltages and exhibit peak luminescence efficiency at relatively low applied voltage in comparison with the undoped device.

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