New cyclometalated iridium(III) complex as a phosphorescent dopant in organic light emitting devices

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Abstract. A new cyclometalated iridium (III) bis[2-(4-chlorophenyl)benzothiazolato-N,C2']-acetylacetonate, (Cl-bt)2Ir(acac), was synthesized and identified by 1H NMR and elemental analysis. The application was studied of the new compound as a dopant in the hole transporting layer (HTL) of the following organic light emitting diode (OLED) structure: HTL/EL/ETL, where HTL was 4,4'-bis(9H-carbazol-9-yl)biphenyl (CBP) or N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD), incorporated in a poly(N-vinylcarbazole) (PVK) matrix; EL was an electroluminescent layer of bis(8-hydroxy-2-methylquinoline)-(4-phenylphenoxyl) aluminum (BAIq); and ETL was an electron-transporting layer of bis[2-(2-benzothiazolyl) phenolato]zinc(II) (Zn(btz)2). We established that the electroluminescence spectra of the OLEDs at different dopant concentrations were basically the sum of the greenish-blue emission of BAIq and the yellowish-green emission of the Ir complex. It was also found that increasing the dopant concentration resulted in an increase in the relative electroluminescent intensity of the Ir complex emission, while that of BAIq decreased, thus a fine tuning of the OLED color was observed.

1. 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 OLEDs [1, 2]. Extensive investigations of this materials have been focused on heavy metal complexes of Os(II), Pt(II) and Ir(III) [3, 4]. A 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]. In the past decade, we have witnessed an explosive growth in the interest in and application of luminescent cyclometallated iridium(III) complexes. The choice of iridium is of special interest, because: it has a quasi-octahedral geometry permitting the introduction of specific ligands in a controlled manner; iridium possesses stable and accessible oxidation and reduction states; the photophysical and electrochemical properties of iridium complexes can be tuned in a predictable way; cyclometallated iridium complexes are known for their highest triplet quantum yields (QY). The development of new iridium complexes is an area of

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activity of many research groups. For instance, Thompson et al. synthesized a neutral emissive cyclometalated Ir(III) complexes [6] suitable as a phosphorescent dopant in OLEDs. The group of Grushin et al. reported a series of Ir(III) complexes with fluorinated 2-arylpypyridines ligands [7], and Cheng et al., with substituted 2-phenylbenzothiazoles ligands [8]. Both of them showed that the complexes exhibit excellent processing and electroluminescent properties and emissive colors which can be fine-tuned via controlling the nature and position of the substituents on the aromatic rings and ligands. In this paper we present the synthesis and photophysical properties of a new benzothiazole-based iridium complex (Cl-bt)2Ir(acac) and discuss its application in phosphorescent OLEDs (PhOLEDs) as a triplet emitter that is solution processable in a poly(N-vinylcarbazole) (PVK) polymeric host.

2. Experimental

2.1. Instruments and measurements

$^{1}H$-NMR (600 MHz) spectra were recorded on a Bruker Avance II+ 600 device at room temperature. The spectra were referenced to the internal standard, tetramethylsilane (TMS). The elemental analyses were conducted on an Elementar Vario EL III apparatus. The UV and fluorescence 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 the CIE (Commission Internationale de l'Éclairage) coordinates were obtained by an Ocean Optics HR2000+ spectrometer. The current-voltage ($I-V$) curves were measured by a power supply programmable with Labview. The luminescence ($L$) was determined in a DC (direct current) mode and the light output was detected using a calibrated Hamamatsu silicon photodiode S2281-01. The electroluminescent efficiency ($\eta_L$) was calculated by equation (1) and used for quantifying the properties of the OLEDs.

$$\eta_L = \frac{L}{I}, \text{ cd/A},$$

where $L$ is the luminescence (in cd/m²) and $I$ is the current density (in A/m²).

2.2. Synthesis of the iridium complex

Ligand 1 (figure 1) was obtained according to the procedure reported in [9]. The other initial reagents and solvents were purchased from Merck and used without any purification.

![Figure 1. Synthesis of the iridium acetylacetonate complex (Cl-bt)2Ir(acac).](image)

2.2.1. Synthesis of μ-chloro-bridged iridium dimmer (2). The cyclometalated Ir(iii) μ-chloro-bridged dimmer (Cl-bt)2Ir(μ-Cl)Ir(Cl-bt)2 was synthesized following a method reported by Nonoyama [10]. 2-(4-Chlorophenyl)benzothiazole (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. Then, the reaction mixture was cooled to room temperature and filtrated to obtain an orange-yellow precipitate. The precipitate was then washed with ethanol and hexane several times and dried at room temperature.
2.2.2. **Synthesis of iridium acetylacetonate complex (3), (Cl-bt)\textsubscript{2}Ir(acac).** Dimmer (2), 2,4-pentanediione (2.5 equiv) and Na\textsubscript{2}CO\textsubscript{3} (5 equiv) were stirred for 20 h at 110 °C in 2-ethoxyethanol under argon. After cooling to room temperature, the product obtained was filtrated yielding 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[2-(4-chlorophenyl)benzothiazolato-N,C\textsubscript{2}']-acetylacetonate, (Cl-bt)\textsubscript{2}Ir(acac): Yield: 80%. ¹H NMR (600 MHz, CDCl\textsubscript{3}) δ [ppm]: 1.79 (s, 6H), 5.16 (s, 1H), 6.33 (d, J=1.8 Hz, 2H), 6.92 (dd, J\textsubscript{1}=1.8 Hz, J\textsubscript{2}=8.4 Hz, 2H), 7.46-7.51 (m, 4H), 7.61 (d, J=7.8 Hz, 2H), 7.94-7.95 (m, 2H), 8.04-8.06 (m, 2H); C\textsubscript{31}H\textsubscript{21}Cl\textsubscript{2}N\textsubscript{2}S\textsubscript{2}O\textsubscript{2}Ir. Elemental analysis: Calc. C 47.69%, H 2.71%, N 3.59%. Found: C 47.52%, H 2.68%, N 3.49%.

2.3. **OLED fabrication**

Devices with an area of 1 cm\textsuperscript{2} were prepared on commercial polyethylene terephthalate (PET) substrates pre-coated with ITO (40 Ω/sq). The 30-nm composite films of PVK:CBP(or TPD) X wt% (relative to PVK) were formed by spin-coating from a 0.75% solution in CH\textsubscript{2}Cl\textsubscript{2} at 2000 rpm. The films of BAlq (40 nm), Zn(btz)\textsubscript{2} (35 nm) and the Al cathode (120 nm) were thermally evaporated in vacuum better than 10\textsuperscript{-4} Pa at rates of 2×10\textsuperscript{-5} Å/s, as controlled by a quartz crystal microbalance.

3. **Results and discussion**

3.1. **UV-VIS absorption and photoluminescence**

Figure 2 presents normalized UV-VIS absorption spectra of the complexes (bt)\textsubscript{2}Ir(acac) and (Cl-bt)\textsubscript{2}Ir(acac) and photoluminescence spectra (Pl) of: (bt)\textsubscript{2}Ir(acac), (Cl-bt)\textsubscript{2}Ir(acac), PVK and CBP dissolved in CH\textsubscript{2}Cl\textsubscript{2}. The absorption spectra of both complexes (curves 1 and 2) had almost identical shapes with peaks at 327 and 332 nm (table 1), typical for this type of complexes.

The spectra can be considered as composed of two parts. The region below 360 nm contains bands of electron transitions, which leads to excitations in the bt-ligand. Most probably, the band around 330 nm is due to a transition to the lowest singlet ligand centered (¹LC) excited state. This statement is in accordance with papers discussing similar complexes published before. The shoulders above 360 nm are assigned to singlet and triplet metal-to-ligand charge transfer bands (¹MLCT, ³MLCT), respectively. The effective spin-orbit coupling (SOC) in this complex leads to mixing of the singlet and triplet states, thus making the band of the resonant transition ¹S\textsuperscript{0}→³MLCT detectable in the absorption spectrum (~480 nm). The band of the ¹MLCT transition is centered at 440 nm. Both complexes showed emission in the yellowish-green region (table 1) with peaks at 557 nm for (bt)\textsubscript{2}Ir(acac) and 543 nm for (Cl-bt)\textsubscript{2}Ir(acac) and shoulders, respectively, at 594 and 576 nm (curves 4 and 3). It is seen that the PI spectrum of (Cl-bt)\textsubscript{2}Ir(acac) was blue-shifted with 15 nm with respect to the PI spectrum of the unsubstituted (bt)\textsubscript{2}Ir(acac); this is typical for derivates containing electron withdrawing substituent [11, 12]. The PVK (curve 5), CBP (curve 6) and TPD (curve 7) emitted a blue
light with peaks at 367, 385 and 414 nm respectively. This is why it could be expected that energy transfer from PVK and CBP (or TPD) to both complexes would be possible, since the 1MLCT and 3MLCT absorption spectra of the dopants had a broad spectral overlap with the fluorescence spectra of PVK and CBP (TPD). The PL spectra of thermally evaporated neat Zn(btz)2 and BAq films shown in figure 2 (curves 7 and 8) were very close to each other, with comparatively broad peaks centered at ≈ 490 nm.

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

| Complex | Absorption λ [nm], (lg ε)* | Emission λmax [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 |
| (Cl-bt)2Ir(acac) | 272(3.89), 320(3.92), 331(3.94), 400(3.23), 442(3.18) | 543 | 0.40 |

* ε is the molar absorption coefficient (molar absorptivity)

3.2. Electroluminescence

The electroluminescence spectra (El) of devices with two types of HTL with different concentrations of the dopant, taken at 16 V DC, are shown in figures 3 and 4. For comparison, the El spectra of devices with an undoped HTL and an EL of BAq, Zn(btz)2 and BAq/Zn(btz)2 are presented as well. It is seen that the device with the EL of BAq emitted at λmax 496 nm, while that with Zn(btz)2, at 524 nm (figures 3 and 4). The shape of the El of the OLED with successively evaporated layers of BAq/Zn(btz)2 was just the same as that of the OLED with an EL of BAq. In our opinion, it is due to the fact that in both cases the recombination zone is near the HTL/BAq interface. As the HOMO Zn(btz)2 level (5.05 eV) is lower than the HOMO BAq (5.90 eV) level, Zn(btz)2 does not stop the holes, which flow unimpeded from the Zn(btz)2 layer. This is why, in the BAq/Zn(btz)2 structure, Zn(btz)2 acts as an ETL only. The El spectra of the doped devices did not include any Zn(btz)2, PVK and CBP (or TPD) emission and were basically the sum of the (Cl-bt)2Ir(acac) and BAq emissions. Increasing the (Cl-bt)2Ir(acac) concentration caused a decrease in the relative intensity of the greenish-blue emission (496 nm) and an increase of the yellow emission (559 nm) of the devices. As the overlapping between the absorption spectra of the dopant and the PL spectra of TPD (curve 7) was broader than that between the dopant and CBP (curve 6), a more intensive energy transfer to the dopant was observed in the devices with an HTL of PVK:TPD. Thus, at one and the same concentration, the ratio of the red-peak intensity (Iλred) to the blue peak intensity (Iλblue) was bigger for devices with TPD and the CIE coordinates of these devices were red-shifted compared to those with CBP (table 2).

Figure 3. El spectra of devices with HTL of PVK:BCP doped with (Cl-bt)2Ir(acac) at 16 V DC.

Figure 4. El spectra of devices with HTL of PVK:TPD doped with (Cl-bt)2Ir(acac) at 16 V DC.
Table 2. CIE coordinates and ratio of intensity of the red ($I_{\lambda \text{red}}$) to the blue peak ($I_{\lambda \text{blue}}$) for devices (PVK:CBP+(Cl-bt)$_2$Ir(acac))/BAIq/Zn(btz)$_2$ and (PVK:TPD+(Cl-bt)$_2$Ir(acac))/BAIq/Zn(btz)$_2$.

| Dopant in layer, w% | CIE(x,y) | $I_{\lambda \text{red}}/I_{\lambda \text{blue}}$ | CIE | $I_{\lambda \text{red}}/I_{\lambda \text{blue}}$ |
|---------------------|----------|---------------------------------|-----|---------------------------------|
| 10%                 | (0.3590,0.4203) | 1.09 | (0.3689,0.4545) | 1.50 |
| 8%                  | (0.3516,0.4013) | 0.97 | (0.3545,0.4492) | 1.30 |
| 6%                  | (0.2936,0.4103) | 0.83 | (0.3220,0.4349) | 1.02 |
| 4%                  | (0.2613,0.3888) | 0.73 | (0.3279,0.4557) | 0.90 |
| 2%                  | (0.2552,0.3999) | 0.67 | (0.2632,0.4029) | 0.69 |
| 1%                  | (0.2394,0.3824) | 0.62 | (0.2736,0.4348) | 0.60 |
| 0                   | (0.2025,0.4348) | 0.51 | (0.2178,0.3711) | 0.54 |

The influence of the dopant concentration on the electroluminescent performance of OLEDs with HTL of PVK:TPD and of PVK:CBP is illustrated in figure 5. We established that, at one and the same voltage, the devices containing CBP demonstrated a higher $L$ in comparison to those with TPD. Increasing the dopant concentration from 0 to 4 w% initially decreased $L$ and $\eta_L$ of devices with CBP (respectively, from 664 to 480 cd/m$^2$ and from 2.32 to 2.05 cd/A); and in devices with TPD, from 440 to 410 cd/m$^2$ and from 2.19 to 2.08 cd/A. The further increase of the dopant concentration to 10 w% caused an increase of $L$ and $\eta_L$ to 685 cd/m$^2$ and 2.8 cd/A in devices with BCP, and to 575 cd/m$^2$ and 2.46 cd/A in devices with TPD. In addition, the EL spectra and CIE of the devices with TPD, taken at one and same concentration, were very stable for a wide range of applied voltages (figure 6).

Figure 5. Luminescence (at 16 V DC) and $\eta_L$ (at 200 cd/m$^2$) of devices with HTLs of PVK:TPD and PVK:CBP doped with different concentration of (Cl-bt)$_2$Ir(acac).

Figure 6. EL spectra at different voltages and CIE coordinates of devices doped with 6 w% (Cl-bt)$_2$Ir(acac) in HTL of PVK:TPD.

The electroluminescence in PhOLEDs originates either from the energy transfer from the host to the guest molecules, as described previously, or from charge trapping by the guest molecules, where the dopant acts as a trap site which can capture a charge carrier. As was shown by Diouf et al. [13], four main factors – exciton confinement, charge trapping, dopant concentration and molecular structure, directly affect the performance of PhOLEDs. These factors are dependent on each other and predominate individually depending on the situation. The weakly increase of the OLEDs efficiency as the dopant concentration is increased and the absence of any PVK, CBP (or TPD) emission in the EL spectra of doped devices (figures 3 and 4), even at low concentrations of the dopant, are consistent
with the charge trapping in the Ir complex, rather than the energy transfer, being the dominant mechanism in the OLEDs investigated.

4. Conclusions
A new iridium complex, (Cl-bt)2Ir(acac), emitting in the greenish-yellow range was synthesized and characterized as a dopant in the hole transporting layer of an OLED. It was established that a fine tuning of the emitted color from blue-greenish to orange can be achieved depending on the dopant concentration.

Including (bt)2Ir(acac) in electroluminescent devices increased the luminescence, tuned the color of emitted light in the yellow region, and raised more than twice the electroluminescent and external quantum efficiencies of the devices.

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