New yellow-emitting phosphorescent cyclometalated iridium(III) complex

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Abstract. We have synthesized a new yellow iridium complex Iridium(III) bis[2-phenylbenzothiazolato-N,C2’-(1-phenylicosane-1,3-dionate) (bt)2Ir(bsm)], based on the benzothiazole derivative. The synthesized molecule was identified by 1H NMR and elemental analysis. The UV-Visible absorption and photoluminescence (PL) spectra of (bt)Ir2(bsm) in CH2Cl2 solution were found at 273 nm and 559 nm, respectively. The complex was used as a dopant into a hole-transporting layer (HTL) in a multilayered organic light emitting device (OLED) structure: ITO/doped-HTL/EL/ETL/M. ITO was a transparent anode of In2O3:SnO2, M- a metallic Al cathode, HTL- 4,4’-bis(9H-carbazol-9-yl)biphenyl (CBP) 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-hydroxyquinolinato)aluminum (Alq3). The electroluminescent (EL) spectra of OLEDs were basically the sum of the emissions of BAlq at 496 nm and the emission of (bt)2Ir(bsm) at 559 nm. With increasing (bt)2Ir(bsm) concentration, the relative electroluminescent intensity of greenish-blue emission (at 496 nm) decreased, while the yellow (at 559 nm) – increased and CIE coordinates of the device shifted from (0.21, 0.33) at 0 wt % to (0.40, 0.48) at 8 wt % of the dopant. It was found that OLED with 0.5 wt % (bt)2Ir(bsm) had the best performance and stable color chromaticity at various voltages.

1. Introduction
Phosphorescent heavy metal complexes play a very important role in organic light-emitting diodes (OLEDs), because they can fully utilize both singlet and triplet excitons though the strong spin-orbital coupling caused by the heavy metal ions in complexes. Since Forrest and Thompson’s group reported the first example of electrophosphorescence at room temperature [1], phosphorescent OLED materials and devices have been intensively studied due to their high external quantum efficiencies (EQEs) [2,3]. It has been widely accepted that the strong spin-orbit coupling induced by a heavy metal ion, such as Ir, Pt and Os promotes an efficient intersystem crossing (ISC) between the singlet and the triplet excited state manifold. Therefore, both singlet and triplet excitons can be harnessed and the strong electroluminescence with an internal efficiency theoretically approaching to 100% can be achieved. Of these phosphorescent materials, iridium complexes have been regarded as the most appropriate emitters because of their relative short lifetime and high quantum efficiency. The electronic transitions responsible for the phosphorescence in these complexes has been assigned to the
mixture of metal-to-ligand charge transfer ($^1$MLCT, $^3$MLCT) and ligand-centred (LC) $^3$($\pi-\pi^*$) lowest excited states [4, 5, 6, 7]. The holes and electrons in OLED are injected into opposite surfaces of a planar multilayer organic thin film. The holes and electrons migrate through the film, to a material interface, where they recombine to form radiative excited states or excitons. This electrically generated exciton can be either a singlet or a triplet. Both theoretical predictions and experimental measurements give a singlet/triplet ratio for these excitons of 1 to 3 [8]. The fluorescent materials typically used for OLEDs fabrication do not give detectable triplet emission (i.e. phosphorescence), nor is there evidence for significant intersystem crossing between the triplet and singlet manifolds at room temperature. The singlet/triplet ratio thus implies a limitation of 25% for the internal quantum efficiency for OLEDs based on the fluorescence. Baldo [1] and Thompson [9] have shown by doping OLEDs with heavy metal phosphors, that the singlet-triplet limitation can be eliminated. The excited states generated by electron-hole recombination are trapped at the phosphor, where strong spin-orbit coupling leads to singlet-triplet state mixing and, hence, efficient phosphorescent emission at room temperature. Both singlet and triplet excited states can be trapped at the phosphor. OLEDs with these heavy metal complexes are the most efficient OLEDs prepared to date, with internal quantum efficiencies exceeding 75% (photons/electrons) (>15% external efficiency) [10]. Furthermore, OLEDs have been prepared with (C$^N$)$_2$Ir(LX) phosphor dopants, giving efficient green, yellow or red emission. The external quantum efficiencies for these devices vary from 5% to nearly 20%.

In this paper we have synthesized a new benzothiazole-based iridium complex, Ir(III)bis[2-phenylbenzothiazolato-N,C$^2$]-1-phenylcosamic-1,3-dionate), (bt)Ir(bsm), as a solution processable triplet emitter for organic electrophosphorescent devices. Poly(N-vinylcarbazole) (PVK) was used as the polymeric host for the synthesized iridium complex and the optical and electroluminescence properties of the composite and OLEDs were studied.

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 TMS. The elemental analyses were made on Elementar Vario EL III. The UV and fluorescence spectra of the complex in solution were recorded on a Thermo Spectronic Unicam 500 spectrophotometer and a Varian Cary Eclipse fluorescence spectrophotometer, respectively. The electroluminescent spectra (EL) were obtained with an Ocean Optics HR2000+ spectrometer. The current-voltage (I-V) curves were measured by programmable with Labview power supply. The luminescence (L) was measured in continuous DC mode and the light output was detected using a calibrated Hamamatsu silicon photodiode S2281-01. The electroluminescent and external quantum efficiency ($\eta_L$, $\eta_{EQE}$) were calculated by equations (1) and (2) and used for quantifying the properties of the OLEDs.

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

$$\eta_{EQE} = (I\phi / I).100 , \%$$

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

2.2. Synthesis of iridium complex

2.2.1. Synthesis of bis{di(2-phenylbenzothiazole)-$\mu$-chloroiridium(III)}. Cyclometalated Ir(III) $\mu$-chlorobridged dimer of formula (bt)$_2$Ir($\mu$Cl)Ir(bt)$_2$ were synthesized by the method reported by Nonoyama [11]. 2-Phenylbenzothiazole (for synthesis see [12]) (2.2 equiv), iridium trichlorid hydrate (1 equiv),
2-ethoxyethanol : water = 3 : 1 were heated and stirred at 110 °C for 20 h under argon. After cooling to room temperature, the crude solution was filtrated to give an orange-yellow precipitate. Then the precipitate was washed with ethanol and hexane for several times. After dried of room temperature, a cyclometalated (bt)$_2$Ir(µ-Cl)$_2$Ir(bt)$_2$ dimer was obtained.

2.2.2. Synthesis of iridium(III)bis[2-phenylbenzothiazolato-N,C$_2$']-(1-phenylicosane-1,3-dionate).
Dimer with 2.5 equiv of 1-phenylicosane-1,3-dione and 5 equiv Na$_2$CO$_3$ were heated and stirred at 110 °C in the presence of 2-ethoxyethanol under argon for 20 h (scheme 1). After cooling to room temperature, the crude product was filtrated to give an orange-yellow precipitate. Then the precipitate was washed with water, ethanol and hexane for several times. Finally, the crude product was purified using liquid chromatography (silica, dichloromethane) and dried. Yield: 80%. $^1$H NMR (600 MHz, CDCl$_3$), δ[ppm]: 1.06-1.09 (m, 3H), 1.19 (bs, 32H), 5.70 (s, 1H), 6.39-6.41 (m, 1H), 6.45 (d, 1H, J=7.2Hz), 6.57-6.60 (m, 2H), 6.79-6.83 (m, 2H), 7.09-7.12 (m, 1H), 7.17 (s, 1H), 7.26-7.33 (m, 5H), 7.58-7.63 (m, 4H), 7.77-7.79 (m, 2H), 7.96 (d, 1H, J=8.4Hz), 8.01-8.03 (m, 1H); C$_{52}$H$_{57}$N$_2$O$_2$S$_2$Ir.
Elemental analysis: Calc. C 62.56%, H 5.75%, N 2.81%. Found: C 62.52%, H 5.76%, N 2.80%.

![Scheme 1](image1.png)

2.3. OLED fabrication
We investigated (bt)$_2$Ir(bsm) as a dopant into a hole-transporting layer (HTL) in multilayered organic light emitting device (OLED) structure: ITO/doped-HTL (30 nm)/EL (40 nm)/ETL (35 nm)/M (90 nm). ITO was a transparent anode of In$_2$O$_3$:SnO$_2$, M - a metallic Al cathode, HTL - 4,4'-Bis(9H-carbazol-9-yl)biphenyl (CBP) incorporated in poly(N-vinylcarbazole) (PVK) matrix, EL - electroluminescent layer of Bis(8-hydroxy-2-methylquinoline)-(4-phenylphenoxy) aluminum (BAlq) and ETL - electron-transporting layer of Tris (8-hydroxyquinolinat0) Aluminum (Alq$_3$) or Bis[2-(2-benzothiazoly)phenolato]zinc(II) (Zn(btz)$_2$).

Devices with area 1cm$^2$ were prepared on commercial polyethylene terephthalate (PET) substrates coated with ITO (40Ω/sq). The layer (30nm) of PVK:CBP$_{10}$Ir(bsm)$_{10}$ composite films were prepared by spin-coating from 0.75% solution in dichloroethane at 2000 rpm. BAlq, Alq$_3$ (or Zn(btz)$_2$) and metal cathode were deposited by thermal evaporation in vacuum better than 10$^{-4}$ Pa at rates 2-5 Å/s.

3. Result and discussion
3.1. UV-VIS absorption and photoluminescence
The plot in figure 1 presents the UV-VIS absorption spectrum of (bt)$_2$Ir(bsm) and photoluminescence spectra (PL) of: (bt)$_2$Ir(bsm), PVK and CBP in dichloromethane. The absorption spectrum of the complex (curve 1) is a typical for that kind of complexes. It is not well resolved and shows complicate structure because of overlapping of various bands. It can be considered as composed of two parts. The region below 360 nm contains bands for electronic transitions, which lead to excitations in the bt-ligand. Most probably, the band around 330 nm is due to transition to lowest singlet ligand centred ($^1$LC) 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 1S 0 → 3MLCT detectable in absorption spectrum (around 480 nm). The band for 1MLCT transition is centred at 440 nm.

The complex showed emission in yellow region (table 1) with peak at 559 nm and shoulder around 590 nm (curve 2) while PVK (curve 3) and CBP (curve 4) – in blue region with peaks at 367 and 385 nm respectively. It can be expected that the efficient Förster and Dexter energy transfer from PVK and CBP to (bt)2Ir(bsm) would be possible since 1MLCT and 3MLCT absorption spectra of the dopant has broader spectral overlap with fluorescence spectra of PVK and CBP.

| Complex      | Absorption λ [nm], (lgε) | Emission λ max [nm] | QY |
|--------------|--------------------------|---------------------|----|
| (bt)2Ir(bsm) | 273(4.68), 298(4.66), 314(4.64), 327(4.63), 359(4.19), 400(3.98), 444(3.88), 485(3.75) | 559 | 0.20 |

The PL spectra of spin coated pure and doped with (bt)2Ir(bsm) PVK:CBP films and thermal evaporated BAIIq, Alq3 and Zn(btz)2 films are shown in figure 2. It is seen that the blue emission at ~395 nm, attributed to PVK:CBP film, reduces significantly with increasing of dopant concentration from 0 to 5 wt %, indicating that energy transfer from PVK and CBP to (bt)2Ir(bsm) not only take place, but also increases with doping concentration and was completely brought to an end at 1.25 wt %. BAIIq and Alq3 were peaked at 496 nm (curve 4) and 525 nm (curve 5) respectively and Zn(btz)2 demonstrated a peak at 490 nm and shoulder at 529 nm (curve 6).

3.2. Electroluminescence

The electroluminescence spectra (EL) of two types OLED with ETL of Alq3 and Zn(btz)2 at different concentrations of the dopant are presented in figures 3 and 4. In contrast to the discussed above PL spectra, in the EL spectra any PVK or CBP induced emission near ~400 nm was not observed, irrespective of the dopant concentration for two types of devices. The absence of major PVK related
emission features has implied a charge trapping rather than an exciton transfer mechanism. The EL spectra were basically the sum of the emissions of (bt)_{2}Ir(bsm) (at 559 nm) and BAlq (at 496 nm). With increasing of (bt)_{2}Ir(bsm) concentration, the relative intensity of the greenish-blue emission (496 nm) decreased, while the yellow (559 nm) - increased and Commission Internationale de L’Eclairage (CIE) coordinates of OLEDs shifted from blue (0.21,0.33) at 0 wt % to yellow (0.40,0.48) at 8 wt % of the dopant for device with ETL of Alq_{3} (table 2) and from greenish-blue (0.24,0.43) at 0 wt % to greenish-yellow(0.31,0.45) at 1 wt % of the dopant for device with ETL of Zn(btz)_{2}.

**Figure 3.** EL spectra of OLED with ETL of Alq_{3} at different doping concentrations at DC 16 V.

**Figure 4.** EL spectra of OLED with ETL of Zn(btz)_{2} at different doping concentrations at DC 16 V.

All devices became visible between 10 - 12 V depending on the doping concentration. The luminescence-voltage characteristics of OLEDs are shown in figures 5 and 6 and results for electroluminescent and external quantum efficiencies are summarized in tables 2 and 3.

**Figure 5.** Luminescence-voltage characteristics of device with ETL of BAlq.

**Figure 6.** Luminescence-voltage characteristics of device with ETL of Zn(btz)_{2}.

Both type of devices showed maximum external quantum and current efficiency at 0.5 wt % of the dopant. The efficiencies were 2-3 times higher in comparison with undoped devices. The values of these parameters for device with ETL of Alq_{3} (0.76 %, 1.46 cd/A) were nearly two times lower than
that of the device with ETL of Zn(btz)$_2$ (1.58 %, 3.02 cd/A). We suppose that better performance of the device with ETL of Zn(btz)$_2$ is due to its better electron-transport properties [13].

**Table 2.** OLED characteristics of device ITO/PVK:CBP+(bt)$_2$Ir(bsm)$_X$%/BAlq(40nm)/Alq(35nm)/Al.

| Doping concentrations | $\lambda_{\text{max}}$ (nm) | $L_{\text{max}}$ (cd/m$^2$) | Current efficiency(cd/A) | External QE (%) | CIE (x,y) |
|-----------------------|-----------------------------|-----------------------------|--------------------------|-----------------|---------|
| 0%                    | 501                         | 198                         | 0.73                     | 0.26            | (0.21,0.33) |
| 0.5%                  | 558                         | 434                         | 1.46                     | 0.76            | (0.31,0.45) |
| 1%                    | 558                         | 360                         | 0.56                     | 0.28            | (0.34,0.47) |
| 2%                    | 559                         | 455                         | 0.56                     | 0.29            | (0.36,0.48) |
| 4%                    | 561                         | 322                         | 0.93                     | 0.50            | (0.41,0.50) |
| 8%                    | 562                         | 313                         | 0.53                     | 0.27            | (0.40,0.48) |

**Table 3.** OLED characteristics of device ITO/PVK:CBP+(bt)$_2$Ir(bsm)$_X$%/BAlq(40nm)/Zn(btz)$_2$(35nm)/Al.

| Doping concentrations | $\lambda_{\text{max}}$ (nm) | $L_{\text{max}}$ (cd/m$^2$) | Current efficiency(cd/A) | External QE (%) | CIE (x,y) |
|-----------------------|-----------------------------|-----------------------------|--------------------------|-----------------|---------|
| 0%                    | 510                         | 201                         | 0.95                     | 0.49            | (0.24,0.43) |
| 0.5%                  | 555                         | 1448                        | 3.02                     | 1.58            | (0.28,0.45) |
| 1%                    | 556                         | 1064                        | 3.00                     | 1.20            | (0.31,0.45) |

### 4. Conclusion

New yellow iridium complex (bt)$_2$Ir(bsm) has been synthesized as a triplet emitter for organic electrophosphorescent devices. It was found that inserting of (bt)$_2$Ir(bsm) in hole-transporting layer of electroluminescent devices increased the luminescence, tuned the color of illuminated light in yellow region, and raised more than twice the electroluminescent and external quantum efficiencies of the devices.

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