Effect of the substituents on the photophysical, electrochemical and electroluminescence properties of OLED dopant Iridium bis(2-phenylbenzothiazolato-N,C2')(acetylacetonate)

P Ivanov, R Tomova* and P Petrova

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

E-mail: reni@iomt.bas.bg

Abstract. The effect of two substituents: chlorine and 1,3-diphenylpropane-1,3-dionate, placed on different position in the molecule of Iridium (III) bis(2-phenylbenzothiazolato-N,C2')-(acetylacetonate) (bt)2Ir(acac), on its electrochemical behaviour, photophysical and electroluminescence properties were investigated. Three complexes (bt)2Ir(acac), Iridium (III) bis[2-(4-chlorophenyl)benzothiazolato-N,C2']-acetylacetonate (Clbt)2Ir(acac), in which the Cl atom was introduced on the 4-position in the benzothiazole ring, and the new Iridium (III) bis[2-phenylbenzothiazolato-N,C2']-(1,3-diphenylpropane-1,3-dionate) (bt)2Ir(dbm), where ancillary acetylacetonate ligand was replaced by 1,3-diphenylpropionate-1,3-dionate, were synthesized and characterised by 1H-NMR and elemental analysis. The HOMO/LUMO energy levels of the complexes were determined by cyclic voltammetry (CV) and their properties were established by UV-Visible and fluorescence spectroscopy. The application of (Clbt)2Ir(acac), (bt)2Ir(bsm) and (bt)2Ir(acac) as dopants in hole transporting layer (HTL) of Organic light-emitting diodes(OLEDs). It was found that with respect to the reference (bt)2Ir(acac): both LUMO and HOMO of the substituted complexes were shifted to more positive values accordingly with 0.23 and 0.19 eV for (Clbt)2Ir(acac) and 0.14 and 0.12 eV for (bt)2Ir(dbm). OLEDs doped with 1 w% of the complexes irradiated the warm white light with Commission internationale de l'éclairage (CIE) coordinates: 0.24;0.38 for (Clbt)2Ir(acac), 0.30;0.44 for (bt)2Ir(acac) and 0.28;0.46 for (bt)2Ir(dbm). Devices doped with 10 w% of all complexes irradiated in the yellow orange region of the spectrum.

1. Introduction

Heavy metal complexes are of exceptional interest due to their applications in OLEDs. Efficient intersystem crossing caused by heavy metal ions in these complexes removes the spin-forbidden nature of the radiative relaxation of the triplet excited state, thus, both the electrogenerated singlet and triplet excited states contribute to light emission and can realize a theoretical internal quantum efficiency of nearly 100% [1, 2]. Among them, cyclopalladated iridium(III) complexes are the most promising because of their quasi-octahedral geometry permitted introducing of specific ligands in a controlled manner, good stability, high photoluminescence (PL) quantum yields 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 WOLEDs. The design and synthesis of new organic ligands for Ir complexes is highly desirable in order to improve the
efficiency and the color purity [3]. The photophysical properties of Ir phosphors can be tuned by varying the ligands [4], its substituent groups [2, 5, 6] and/or ancillary ligands [7, 8]. Such complexes are normally used as emitting guests in blends with host materials, where hole-transporting hosts include carbazole derivatives such as CBP (4, 4′-N,N′-dicarbazole)biphenyl and PVK [poly(9-vinylcarbazole)] [1, 9-11] or polyfluorenes [12, 13]. Researchers from Dupont de Nemours et al. have synthesized and characterized a series of iridium (III) complexes with fluorinated 2-arylpyridines and showed that the emissive colors of the materials can be finely tuned by systematic control of the nature and position of the substituents of the ligands [14]. 2-Phenylbenzo[d]thiazole (bt) is a general ligand framework to construct Ir(III) complexes such as yellow (bt)_2Ir(acac), which is particularly promising to develop two-color white OLEDs with simple architectures [16, 17]. Up to now, many (bt)_2Ir(acac) derivatives by structure modifications on bt ligand with adjustable color, high luminescent efficiency and electroluminescent performances have been synthesized and investigated [4, 17-18].

These research activities inspired us to initiate a study to investigate the role played from two different substituents chlorine and 1-Phenyl-eicosane-1,3-dione placed on two different position in (bt)_2Ir(acac): in benzothiazole ligand and instead of ancillary acetylacetonate ligand.

2. Experimental

2.1. Synthesis of Iridium complex

The cyclometalated Ir(iii) complexes used in this study (figure 1) have been synthesized according a method reported by Nonoyama [19]. The details of the synthesis, the ^1H-NMR spectra and elemental analysis of the complexes are described elsewhere [20, 21].

![Chemical structure of used Ir(III) complexes](image)

Figure 1. Chemical structure of used Ir(III) complexes and energy diagram of investigated OLED.

2.2. OLED fabrication

We investigated (Clbt)_2Ir(acac), (bt)_2Ir(acac) and (bt)_2Ir(dbm) as dopants into a HTL in multilayered OLED structure: ITO/doped-HTL/EL/ETL/M. 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 (BAIq) and ETL - electron-transporting layer of Bis[2-(2-benothiazolyl)phenolato]zinc(II) (Zn(bt)_2). This structure was chosen in order of obtaining a white light by mixing of red emission from the dopants and blue emission from the EL of BAIq. Devices with area 1cm^2 were prepared on commercial polyethylene terephalate (PET) substrates coated with ITO (40Ω/sq). The layer (30nm) of PVK:CBP_{10%}(relatively to PVK) + Ir(III) complex composite films were prepared by spin-coating from 0.75% solution in dichloroethane at 2000 rpm. All organic layers: BAIq (40nm), Zn(bt)_2 (35nm) and the Al cathode (100nm) were deposited in succession by thermal evaporation in vacuum better than 10^{-4} Pa at rates 2-5 Å/s, without breaking vacuum. The layers
thicknesses were controlled with quartz crystal microbalance sensor, positioned near the PET/ITO substrate.

2.3. Instruments and measurements
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 CIE 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 ($\eta_L$) were calculated by equations (1) and used for quantifying the properties of the OLEDs.

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

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

The CV measurements were done on air in 0.001M solution of Ir complexes in acetonitrile in presence 0.1M LiClO$_4$ as supporting electrolyte, on air, in standard three-electrode electrochemical cell with platinum plates as working and counter electrodes and Ag/AgCl - as reference electrode, using potentiostat Gamry PC 3.

3. Result and discussion
3.1 Cyclic voltammetric measurements
CV was employed to investigate the electrochemical behaviour of the Ir complexes and estimation of their ionization potentials ($I_p$) and electron affinities ($E_a$) in accordance with the theory proposed by Pommerehne et al. [22].

$$I_p = E_{1/2^{\text{ox}}} + 4.8$$  (2)

$$E_a = E_{1/2^{\text{red}}} + 4.8$$  (3)

$$E_g = I_p - E_a$$  (4)

where: $E_{1/2^{\text{ox}}}$ and $E_{1/2^{\text{red}}}$ are electrochemical potentials over ferrocenium/ferroene (Fc$^+/\text{Fc}$) reference (vs. Ag/AgCl), and 4.8 eV is the value of Fc with respect to zero vacuum level. $I_p$ and $E_a$ may be regarded as the HOMO and the LUMO and the electrochemical gap between them as the band gap ($E_g$) of the complex. $E_g$ may be evaluated from the long-wavelength absorption edge pursuant to the theory reported by Burrows et al. [23] using the equation (5):

$$E_g = \frac{h}{c} = \frac{1241}{\lambda},$$  (5)

where: $h$ is Planck’s constant; $c$ is the speed of light and $\lambda$ is the wavelength in nm.

During the cathodic CV scan (anodic scan was compromised by the presence of oxygen), shown in figure 2, all complexes exhibited two reversible reduction waves with very close potentials (0.98 - 1.22 V vs Ag/AgCl). The first of them was taken for estimation of $E_a$ and LUMO level of the complexes. The data of absorption-edges and electrochemical potentials $E_{1/2^{\text{red}}}$, determined from figures 3 and 2, and $E_g$, $E_a$ and $I_p$, calculated according to Eqs. (5), (3) and (4), are summarized in table 1. Both substitutions: of H with electron withdrawing Cl in benzothiazole ligand and of two CH$_3$ groups with two electron withdrawing phenyl groups in ancillary acetilacetonate ligand, shifted the reduction potentials of (Clbt)$_2$Ir(acac) and (bt)$_2$Ir(dbm) to more negative values, in comparison with...
the base (bt)Ir(acac), with 0.24 V and 0.15 V respectively. As, the values of absorption-edges were not significantly different from each other, the optical bandgaps were almost the same and as a result, both the LUMO and the HOMO of the complexes were shifted to more positive values with 0.23 and 0.19 eV for (Clbt)₂Ir(acac) and 0.14 and 0.12 eV for (bt)₂Ir(dbm).

![Figure 2. Reduction CV waves of 0.001 M Ir complexes and Ferrocene in acetonitrile and 0.1 M LiClO₄, at scan rate 100 mV/min.](image)

Evidently the both substituents brought only a small difference to the HOMO and LUMO levels and the electronic behaviour of these iridium complexes

### Table 1. Electrochemical data.

| Complex         | -E\textsubscript{1/2}\textsuperscript{red} vs. Ag/AgCl(V) | -E\textsubscript{1/2}\textsuperscript{red} vs. Fc/Fc'(V) | Absorption edge (nm) | Eg (eV) | Ip(-HOMO) (eV) | Ea(-LUMO) (eV) |
|-----------------|----------------------------------------------------------|----------------------------------------------------------|----------------------|---------|----------------|----------------|
| (Clbt)₂Ir(acac)| 1.22                                                      | 1.69                                                     | 570                  | 2.16    | 5.27           | 3.11           |
| (bt)₂Ir(acac)   | 0.98                                                      | 1.46                                                     | 585                  | 2.12    | 5.46           | 3.34           |
| (bt)₂Ir(dbm)    | 1.13                                                      | 1.60                                                     | 580                  | 2.14    | 5.34           | 3.20           |

3.2 UV-VIS absorption and photoluminescence

The UV-VIS absorption (curves 1-3) and PL spectra (curves 4-6) of three Ir(III) complexes in CH₂Cl₂ are shown in figure 3 and all data are summarized in table 2. The absorption spectra could be divided into two regions. 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 centered (¹LC) excited state. This is consistent with publications about similar complexes published before [4]. 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 these complexes lead to mixing of the singlet and triplet states making the band for resonant transition ¹S₀→³MLCT detectable in absorption spectrum (around 480 nm). The bands for ¹MLCT transition are centered at 440 nm. Under excitation at 330 nm light, (Clbt)₂Ir(acac), (bt)₂Ir(acac) and (bt)₂Ir(dbm) exhibited strong yellow or orange phosphorescence with maximum emission peaks at 552, 558, 558 nm and shoulders at 590, 593, 600 nm, respectively, which could be attributed to predominantly ³MLCT state. It is seen that the PL spectrum of (Clbt)₂Ir(acac) was blue-shifted with 6
nm with respect to the PI spectrum of the (bt)₂Ir(acac), that is typical for derivates containing electron withdrawing substituent in benzothiazole ring [24]. The PI spectrum of (bt)₂Ir(dbm) was almost the same with this of (bt)₂Ir(acac), except that the shoulder at 600 nm was red shifted with 7 nm and more pronounced. The PVK and CBP (curves 7 and 8) emitted a blue light with peaks at 367 and 385 nm respectively.

The MLCT absorption bands of three Ir(III) complexes ranged from 360 nm to 480 nm, exhibiting good spectral overlap with the PL emission bands of PVK and CBP, which is a good prerequisite for the efficient Förster or Dexter energy transfer from the host (PVK:CBP) to the iridium complex guests would be expected.

Table 2. Photophysical data of (Clbt)₂Ir(acac), (bt)₂Ir(acac) and (bt)₂Ir(dbm) in Ar-saturated CH₂Cl₂.

| Complex          | Absorbtion, λ[nm] (lgε)* | Emission λmax/shoulder[nm] |
|------------------|--------------------------|---------------------------|
| (Clbt)₂Ir(acac)  | 272(3.89), 320(3.92), 331(3.94), 400(3.23), 442(3.18) | 552/590                 |
| (bt)₂Ir(acac)    | 272(3.93), 315(3.86), 327(3.88), 07(3.21), 442(3.19), 489(3.03) | 558/593                 |
| (bt)₂Ir(dbm)     | 269(4.23), 315(4.21), 327(4.21), 362(3.75), 407(3.64), 445(3.45), 492(3.25) | 558/600                 |

* ε is the molar absorption coefficient (molar absorptivity)

2.2. Electroluminescence

The electroluminescence (EL) spectra of devices doped with three investigated complexes, at two different concentrations and theirs CIE coordinates, taken at 16 V DC, are shown in figure 3. For comparison, the EL spectra of devices with undoped HTL and EL of BAlq, Zn(bt)₂ and BAlq/Zn(bt)₂ are presented as well. It is seen that the device with the EL of BAlq emitted at 496 nm, and that with Zn(bt)₂ at 524 nm. The shape of the EL spectra of OLED with successively evaporated layers of BAlq/Zn(bt)₂ was just the same as that of the OLED with EL of BAlq. In our opinion, it is due to the fact that in both cases the recombination zone is near the HTL/BAlq interface. As the HOMOZn(bt)₂ level (5.05 eV) is lower than the HOMOBAlq level (5.90 eV) (figure 1), Zn(bt)₂ did not stop the holes, which flow unimpeded from the Zn(bt)₂ layer. This is why, in the BAlq/Zn(bt)₂ structure, Zn(bt)₂ acted as an ETL only. The EL spectra of the doped devices did not include any Zn(bt)₂, PVK
and CBP emission. The addition of iridium complexes into HTML caused the red shifting of the EL spectra of devices, in comparison with undoped device. As can be seen from the CIE coordinates and colour diagram, shown in inset, at the low concentration (1 w%) of the dopants all three devices irradiated the warm white light (0.24;0.38 for (Clbt)2Ir(acac), 0.30;0.44 for (bt)2Ir(acac) and 0.28;0.46 for (bt)2Ir(dbm)), close to the absolute white (0.33, 0.33). At the higher concentration (10 w%) of the dopants all devices irradiated in the yellow orange region of the spectrum (0.35;0.43 for (Clbt)2Ir(acac), 0.42;0.45 for (bt)2Ir(acac) and 0.34;0.44 for (bt)2Ir(dbm)) and theirs EL spectra were basically the sum of predominantly emissions of the dopants (at: 551 nm for (Clbt)2Ir(acac), 560 nm for (bt)2Ir(acac) and 556 nm for (bt)2Ir(dbm)) and BA1q (at 496 nm).

The L-I-V characteristics and EL efficiencies of base OLED structure HTL/BAlq/Zn(bt)2 and doped with 1 and 10 w% of Ir complexes devices are shown in figures 5a, 5b and 5c. Inside in the figures are presented the voltages provided the luminance 500 cd/m² (V\textsuperscript{w% 500cd/m²}), and the current density 200 A/m² (V\textsuperscript{w% 200A/m²}), and EL efficiencies at the luminance 500 cd/m² (η\textsuperscript{w% 500cd/m²}).

**Figure 5.** Luminance-voltage (a), Current density-voltage (b) and Electroluminiscent efficiency – luminance (c) characteristics for undoped and doped with 1 and 10 w% of the complexes devices.

It is seen that the adding of all three dopants to the HTL of the base device reduced V\textsuperscript{w% 500cd/m²} and V\textsuperscript{w% 200A/m²} at both concentrations. The only exception was the device doped with 1 w% (bt)2Ir(acac), in which there was rise of V\textsuperscript{w% 500cd/m²} and V\textsuperscript{w% 200A/m²} in comparison with undoped device. At the same time the EL efficiencies for all doped devices, at the both concentrations, were lower than this of the
base structure. All devices doped with 10w% showed lower efficiencies than those of devices doped with 1w%, except device doped with (Clbt)$_2$Ir(acac), at which $\eta_{500\text{cd/m}^2}^{10\text{w}%=500\text{cd/m}^2} > \eta_{500\text{cd/m}^2}^{1\text{w}%=500\text{cd/m}^2}$.

Electroluminescence in phosphorescent OLED 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. The increasing of current densities and decreasing of OLED efficiency with increasing of the dopant concentration on the one hand and the absence of any PVK and BCP emission in El spectra of doped devices, even at low concentrations of the dopant, on the other hand, showed the charge trapping in the Ir complex, rather than the energy transfer, as the dominant mechanism in investigated OLEDs. Since the holes injected from the anode fall directly on the HOMO level of the dopant without any difficulties (figure 1), the trapping of electrons on the LUMO level is the process determining the intensity of electroluminescent emission of devices. Therefore the lower LUMO levels, respectively shallower electrons traps, of both substituted complex in comparison with this of reference (bt)$_2$Ir(acac), are the reason for higher electroluminescence of devices with (Clbt)$_2$Ir(acac) and (bt)$_2$Ir(dbm).

4. Conclusion
We investigated the effect of Cl and 1,3-diphenylpropane-1,3-dionate as substituents placed in (bt)$_2$Ir(acac). The present results show that the incorporation of an electron-withdrawing substituent either on the benzothiazole ring of the 2-phenylbenzothiazole ligand or in ancillary ligand, only has a subtle tuning effect on the energy bandgap so that the phosphorescence of substituted complexes is still located in the same orange range as that of the parent (bt)$_2$Ir(acac). Both substituents shifted the HOMO/LUMO levels of the complexes to more positive values and thereby enhance the electroluminescence of OLEDs.

References
[1] Bauer R, Finkenzeller W, Bogner U, Thompson M and Yersin H, 2008 Org. Electron. 9 641
[2] Wang R, Deng L, Zhang T and Li J 2012 Dalton Trans. 41 6833
[3] Seo J, Seung Lee C, Kim Y and KimY 2008 Thin Solid Films 517 1346
[4] Lamansky S, Djurovich P, Murphy D, Razzaq F, Lee H, Adachi C, Burrows P, Forrest S and Thompson M 2001 J. Am. Chem. Soc. 12 4304
[5] Zhang L, Li L, Shi L and Li W 2009 Opt. Mater. 31 905
[6] Choi J, Jung C, Kwon J, Cho H, Lee J, Lee J-Ik, Chu H and Hwang D 2009 Synth. Met. 159 1517
[7] Liu Z, Bian Z, Ming L, Ding F, Shen H, Nie D and Huang C 2008 Org. Electron. 9 171
[8] Hu J, Zhang J, Shih H, Jiang X, Sun P and Cheng C 2008 J. Organomet. Chem. 693 2798
[9] Tavasli M, Moore T, Zheng Y, Bryce M, Fox M, Griffiths G, Jankus V, Al-Attar H and Monkman A 2012 J. Mater. Chem. 22 6419
[10] Kawamura Y, Goushi K, Brooks J, Brown J, Sasabe H and Adachi C 2005 Appl. Phys. Lett. 86 071104
[11] Adachi C, Baldo M, Forrest S, Lamanski S, Thompson M and Kwong R 2001 Appl. Phys. Lett. 78 1622
[12] Ha S and Noh Y 2013 Jpn. J. Appl. Phys. 52 10MB11
[13] Chang J, An J and Im Ch 2005 J. of Korean Phys. Soc. 47 1028
[14] Grushin V, Herron N, Lecloux D, Marshall W, Petrov V and Wang Y 2001 Chem. Commun. (Cambridge) 1494
[15] Chen P, Xie W, Li J, Guan T, Duan Y, Zhao Y, Zhang L and Li B 2007 Appl. Phys. Lett. 91 023505
[16] Zhao B, Su Z, Li W, Chu B, Jin F, Yan X, Zhang F, Fan D, Zhang T, Gao Y and Wang J 2012 Appl. Phys. Lett. 101 053310
[17] Liu D, Ren H, Deng L and Zhang T 2013 ACS Appl. Mater. Inter. 5 493744
[18] Li M, Zeng H, Meng Y, Sun H, Liu S, Lu Z, Huang Y and Pu X, 2011 Dalton Trans. 40 7153
[19] Nonoyama M 1974 Bull. Chem. Soc. Jpn. 47 767
[20] Ivanov P, Tomova R, Petrova P, Stanimirov S and Petkov I 2012 J. Phys. Conf. Ser. 398 012052
[21] Ivanov P, Tomova R, Petrova P, Stanimirov S and Petkov I 2014 J. Phys. Conf. Ser. 514 012038
[22] Pommerehne J, Vestweber H, Guss W, Mahrt R, Bässler H, Porsch M and Daub J 1995 Adv. Mater. 7 551
[23] Burrows P, Chen Z, Bulovic V, McCarty D and Forrest S 1996 J. Appl. Phys. 79 7991
[24] Adachi C, Baldo M, Forrest S and Thompson M 2000 Appl. Phys. Lett. 78 1704