Estimation of energy levels of new Iridium cyclometalated complexes via cyclic voltammetry

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Cyclic voltammetry (CV) is one of the standard and useful methods for characterization of energy levels of organic compounds. In this article we present the CV investigation of newly synthesized Iridium cyclometalated complexes used for the first time as phosphorescent dopants in Organic Light Emitting Diodes (OLEDs). The energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of complexes dissolved in acetomitrile were estimated on the basis of theirs reduction half-wave potentials, taken from cyclic voltamograms and band gaps, obtained from UV (Ultraviolet–visible) absorption measurements. In this paper the obtained HOMO/LUMO values of complexes are discussed in connection with electroluminescent characteristics of OLEDs with hole transporting layer doped with the same complexes.

Keywords: HOMO, LUMO, cyclic voltametry, bang gap, organic compounds

INTRODUCTION

Phosphorescent organo-transition metal complexes are often applied as emitters in organic light emitting diodes (OLEDs) due to their high electroluminescence efficiencies. Among them, cyclometalated 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 [1, 2]. Knowledge of charge carrier energy levels in organic thin films is essential for the understanding and design of organic devices. For example, OLED usually consists of several layers of various stacked organic thin films [3] and differences between energies of separate layers act as potential energy barriers to the flow of charge and molecular excited states (or excitons). That's why the fine adjusting of HOMO and LUMO energy levels of different OLED's layers or between host and guest in doped devices is very important.

Two conventional methods to ascertain HOMO energies (E_{HOMO}) are cyclic voltammetry (CV) [4] and ultraviolet photoemission spectroscopy (UPS) [5]. Solution-based CV experiment is employed for determination of ionization potential (IP) and electron affinity (EA) of dissolved organic compound. IP and EA may be regarded as the HOMO and the LUMO levels of molecule, underwent electrochemical oxidation or reduction on the electrode (Fig. 1a) and can be estimated from the extrapolation onsets of its oxidation and reduction potentials. UPS refers to the measurement of kinetic energy spectra of photoelectrons emitted by molecules which have absorbed ultraviolet photons, in order to determine molecular energy levels in the valence region. UPS experiments determine the ionization energy (E_i) of a molecule on the surface of a thin film, where $E_i = -E_{HOMO}$ [6]. D'Andrade at all [7] have found, that the two spectroscopic techniques are quantitatively related by:

$$E_{HOMO} = -(1.4 \pm 0.1)\, qV_{CV} - (4.6 \pm 0.08)\, eV \quad (1)$$

for a wide range of organic materials, where E_{HOMO} is directly measured from the UPS spectrum and V_{CV} is molecular oxidation potentials, measured from CV and q is the charge of an electron. On account of high cost and complexity of UPS systems, CV is the preferable method used in many laboratories.

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The aim of this study was to estimate the HOMO and LUMO energy levels of four new synthesized Iridium cyclometalated complexes via cyclic voltammetry and discussed them in connection with electroluminescent characteristics of OLEDs, where these complexes were used as dopants.

EXPERIMENTAL

Instruments and measurements

^{1}H-NMR (600 MHz) spectra were referenced to internal tetramethylsilane (TMS) and recorded on a Bruker Avance II+ 600 at room temperature. The elemental analyses were made on Elementar Vario EL III. 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. The electroluminescent spectra (EL) and Commission Internationale de L'Eclairage (CIE) coordinates were obtained by Ocean Optics HR2000+ spectrometer. The luminescence (L) was measured in continuous DC mode and the light output was detected using a calibrated Hamamatsu silicon photodiode S2281-01.

Cyclic voltammetry (CV) measurements

CV is potentiodynamic electrochemical measurement. It is accomplished with a three electrode arrangement (with three-electrode electrochemical cell) whereby the potential relative to some reference electrode is scanned at a working electrode while the resulting current flowing through a counter (or auxiliary) electrode is monitored in a quiescent solution. A typical cyclic voltammogram where $i_{1/2}^{ox}$ and $i_{1/2}^{red}$ show the peaks of cathodic and anodic current respectively for a reversible reaction along with corresponding oxidation and redaction reactions are shown in Fig. 1. CV were done in acetonitryle solutions containing 0.001 M Ir(III)-complex and 0.1 M $LiClO_4$ as supporting electrolyte, at scan rate of 100 mV/s via Potentiostat Gamry PC 3 voltammetric analyzer. Platinum plates were used as working and counter electrodes and Ag/AgCl - as reference electrode. For ease of comparison, all electrode potentials were converted using the ferrocene/ferrocenium redox couple as a reference point (E_{FeC} = 0 mV) [8]. An empirical relationship between $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ and *Ip* and *Ea* were proposed by Pommerehne et al. [9].
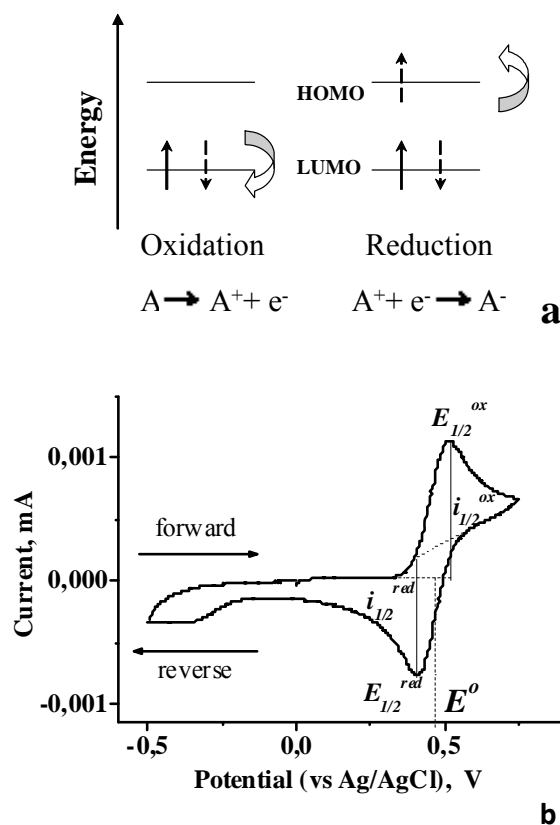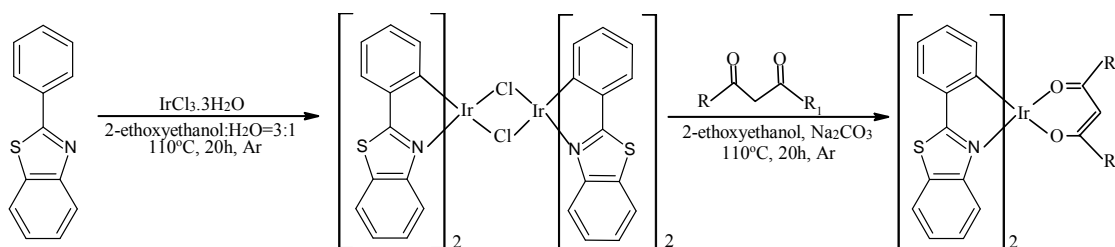

Fig. 1. a) The oxidation and reduction of an organic molecule involve electron transfers; b) **-** A typical cyclic voltammogram.

Synthesis and characterization of iridium diketonato complexes

Four new cyclometalated iridium diketonato complexes based on benztiasole ligands were synthesized according to Scheme 1.

Iridium(III)bis[2-phenylbenzothiazolato-N,$C^{2'}$]-(1,3-diphenylpropane-1,3-dionate), (bt)₂Ir(dbm) Yield: 70%. ^{1}H NMR (600 MHz, CDCl₃), δ[ppm]: 6.49 (s, 1H), 6.55 (d, 2H, J=7.2Hz), 6.71 (td, 2H, J₁=1.2Hz, J₂=7.2Hz), 6.93 (td, 2H, J₁=1.2Hz, J₂=7.8Hz), 7.18-7.21(m, 2H), 7.30-7.36 (m, 6H), 7.40-7.42 (m, 2H), 7.74-7.77 (m, 6H), 7.86 (dd, 2H, J₁=8.4Hz, J₂=0.6Hz), 8.09 (d, 2H, J=8.4Hz); $C_{41}H_{27}N_2S_2O_2Ir$. Elemental analysis: Calc. C 58.90%, H 3.26%, N 3.35%. Found: C 58.85%, H 3.30%, N 3.30%.

Iridium(III)bis[2-phenylbenzothiazolato-N,$C^{2'}$]-[4,4,4-trifluoro-1-(thiophen-2-yl) butane-1,3-dionate], (bt)₂Ir(tta) Yield: 70%. ^{1}H NMR (600

R	R$_1$	complex
C$_6$H$_5$-	C$_6$H$_5$-	**(bt)$_2$Ir(dbm)**
CF$_3$-	C$_4$H$_3$S-	**(bt)$_2$Ir(tta)**
p-F-C$_6$H$_4$-	p-CH$_3$O-C$_6$H$_4$-	**(bt)$_2$Ir(fmtdbm)**
C$_6$H$_5$-	C$_{17}$H$_{35}$-	**(bt)$_2$Ir(bsm)**
CH$_3$	CH$_3$	**(bt)$_2$Ir(acac)**

Scheme 1. Synthesis of Ir complexes.

MHz, CDCl$_3$), δ[ppm]: 5.98 (s, 1H), 6.36 (t, 2H, J=8.4Hz), 6.58-6.62 (m, 2H), 6.80-6.86 (m, 2H), 6.91-6.92 (m, 1H), 7.12-7.15 (m, 1H), 7.29-7.48 (m, 5H), 7.60-7.62 (m, 2H), 7.78-7.84 (m, 3H), 8.00-8.03 (m, 1H); C$_{34}$H$_{20}$N$_2$O$_2$S$_3$F$_3$Ir. Elemental analysis: Calc. C 48.97%, H 2.42%, N 3.36%. Found: C 48.90%, H 2.38%, N 3.31%.

Iridium(III)bis[2-phenylbenzothiazolato-N,C$^{2'}$]-[1-(4-fluorophenyl)-3-(4-methoxyphe-nyl)propane-1,3-dionate], (bt)$_2$Ir(fmtdbm) Yield: 75%. ^{1}H NMR (600 MHz, CDCl$_3$), δ[ppm]: 3.72 (s, 3H), 6.29 (s, 1H), 6.44 (dd, 2H, J$_1$=2.4Hz, J$_2$=7.2Hz), 6.59-6.62 (m, 2H), 6.71-6.72 (m, 2H), 6.82-6.88 (m, 4H), 7.07-7.10 (m, 2H), 7.23-7.26 (m, 2H), 7.64-7.67 (m, 6H), 7.76 (dd, 2H, J$_1$=3.0Hz, J$_2$=7.2Hz) 7.97 (dd, 2H, J$_1$=5.4Hz, J$_2$=8.4Hz); C$_{42}$H$_{28}$N$_2$S$_2$O$_3$FIr. Elemental analysis: Calc. C 57.06%, H 3.19%, N 3.17%.

Iridium(III)bis[2-phenylbenzothiazolato-N,C$^{2'}$]-(1-phenylicosane-1,3-dionate), (bt)$_2$Ir(bsm) 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%.

OLED fabrication

Devices with area of 1cm^2 were prepared on commercial polyethylene terephtalate (PET) substrate, precoated with anode of ITO (90% In$_2$O$_3$, 10% SnO$_2$) (40Ω/sq). The (30nm) composite films of PVK:CBP(or TPD)$_{10 \text{ wt}\%}$:(Ir complex)$_{X \text{ w}\%}$

(relatively to PVK) were formed by spin-coating from 0.75% solution in CH$_2$Cl$_2$ at 2000 rpm. The films of Bis(8-hydroxy-2-methylquinoline)-(4-phenylpheno-xy) aluminum (BAlq) (40nm), as electroluminescent layer (EL), Bis[2-(2-benzothiazoly) phenolato]zinc(II) (Zn(btz)$_2$) (35nm) ETL as electron-transporting layer and Al cathode (120nm), were thermal evaporated in vacuum better than 10^{-4} Pa at rates of 2-5 Å/s, controlled with a quartz crystal microbalance.

RESULTS AND DISCUSSION

Cyclic voltammetric measurements

Cyclic voltammetry (CV) was employed to investigate the electrochemical behavior of the Ir complexes and was applied for the estimation of the ionization potential (Ip) and electron affinity (Ea). Ip and Ea of the complexes were estimated from the extrapolated onsets of their oxidation and reduction potentials, respectively. The empirical relationships were proposed by Pommerehne et al. [9].

$$Ip = E_{1/2}^{ox} + 4.8 \tag{3}$$

$$Ea = E_{1/2}^{red} + 4.8 \tag{4}$$

$$Eg = Ip - Ea, \tag{5}$$

where $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ are electrochemical potentials over ferrocenium/ferrocene (Fc$^+$/Fc) reference (vs. Ag/AgCl), and 4.8 eV is the value of Fc with respect to zero vacuum level. Ip and Ea may be regarded as the HOMO and the LUMO and the electrochemical gap between them as the band gap (Eg) of the complex. On the other hand according to the theory reported by Burrows et al.

[10] Eg may be evaluated from the long-wavelength absorption edge using the equation (6)

$$Eg = h.f = h.c / \lambda = 1241 / \lambda, \tag{6}$$

where: *h* is Planck's constant; *c* is the speed of light and λ is the wavelength in nm.

Absorption spectra and reduction CV scans of new Ir complexes and (bt)$_2$Ir(acac) as reference are shown in Figs. 2 and 3. The oxidation CV scans are not presented, because the measurements were not provided in inert atmosphere.
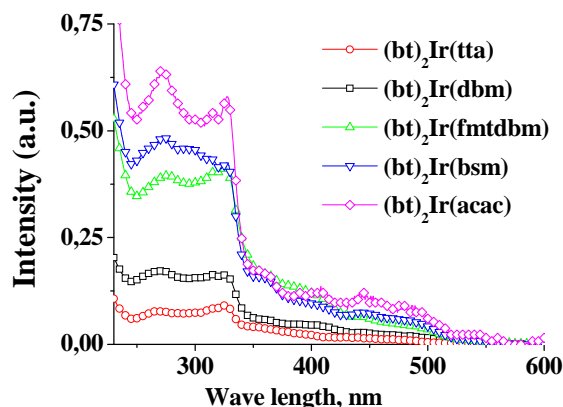

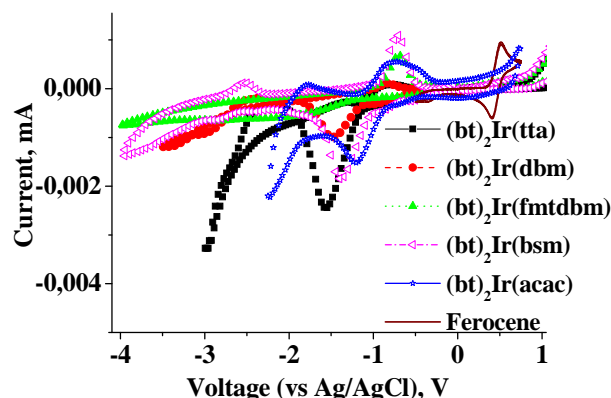**Fig. 2.** Absorption spectra of Ir complexes, dissolved in $C_2H_2Cl_2$.

Fig. 3. Reduction CV waves of 0.001 M of Ir complexes and Ferrocene in acetonitryle and 0.1 M LiClO$_4$, at scan rate 100 mV/min.

The all complexes exhibited two reversible reduction waves with very close potentials. The first of them was taken for estimation of *Ea* and LUMO level of the complexes. The data of absorption-edges and electrochemical potentials $E_{1/2}^{red}$ (determined from Figs. 2 and 3) and *Eg, Ea* and *Ip,* calculated according to Eqs. (6), (4) and (3), are summarized in Table 1.

The value of $E_{1/2}^{red}$ (0.98 V vs Ag/AgCl) obtained for (bt)$_2$Ir(acac) are nearly the same (0.96 V vs Ag/AgCl) to this, presented by Xu at all.[11], that confirms the reliability of all our CV results.

Table 1. Electrochemical reduction potentials, optical energy gaps, HOMO and LUMO energy levels of iridium complexes

complex	$E_{1/2}^{red}$ vs Ag/AgCl [V]	$E_{1/2}^{red}$ vs Fc/Fc$^+$ [V]	Absorption edge [nm]	Eg [eV]	Ip (- HOMO) [eV]	Ea (- LUMO) [eV]
(bt)$_2$Ir(tta)	1.17	1.64	550	2.25	5.41	3.16
(bt)$_2$Ir(dbm)	1.13	1.60	580	2.14	5.34	3.20
(bt)$_2$Ir(fmtdbm)	1.11	1.58	590	2.10	5.33	3.22
(bt)$_2$Ir(bsm)	1.02	1.50	590	2.10	5.40	3.30
(bt)$_2$Ir(acac)	0.98	1.46	585	2.12	5.46	3.34

Electroluminescence

The El of OLED structure PVK:CBP: (bt)$_2$Ir(dbm)$_{xw\%}$/BAlq/Zn(btz)$_2$ at different doping concentration are shown in Fig.4. It is seen that increasing of the dopants concentration caused increasing of the intensity of irradiated from the dopant light (peaked at 554 nm) and shifted the CIE coordinates of OLEDs from greenish blue (0.22, 0.37) at 0 wt % to orange (0.34, 0.44) at 10 wt %.

In Fig. 5 are presented the El spectra (at 16 V DC) of OLEDs doped with different complexes at concentration 8 w%, where the intensity of the peaks of BAlq at 503 nm and (bt)$_2$Ir(dbm) at 554 nm were roughly the same and the CIE coordinates of devices (0.33;0.44) were the most close to white (0.33;0.33). All devices emitted in light orange region (CIE (x,y) from (0.33;0.44) to (0.38;0.48)) and only device doped with (bt)$_2$Ir(tta) emitted in green-yellow region (0.26;0.43). This blue shift was in accordance with the wider with nearly 0.10 eV energy gap Eg (2.25 eV) of (bt)$_2$Ir(tta) in comparison to that of the other complexes (Table 1).
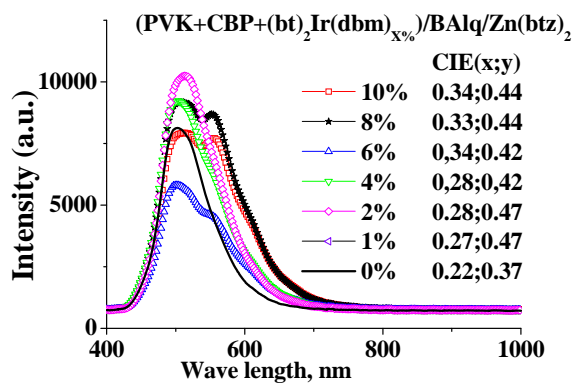
(PVK+CBP+(bt)₂Ir(dbm)ₓ₎%)/BAlq/Zn(btz)₂

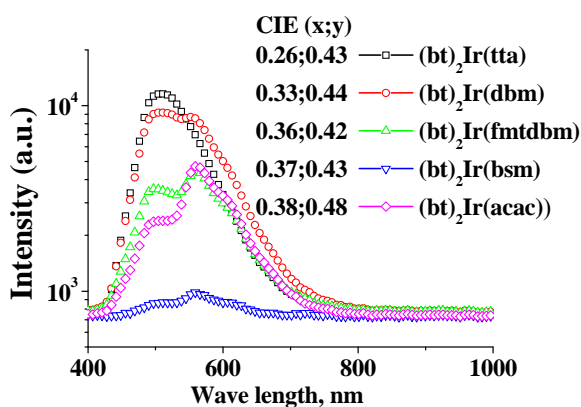**Fig. 4.** El spectra and CIE of devices doped with (bt)₂Ir(dbm) at different doping and DC 16 V.

Fig. 5. El spectra and CIE of devices doped with different complexes at 8 wt% doping concentration and DC 16 V.

CONCLUSION

In summary we have successfully designed, synthesized and characterized four new cyclometalated iridium diketonato complexes, based on benztiasole ligands. We estimated their HOMO, LUMO and band gap by means of combination of cyclic voltammetry and UV absorption measurements. The complexes were applied as dopants in OLEDs and it was established that depending on the dopant concentration they were very useful for fine tuning of emitted colour.

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ОПРЕДЕЛЯНЕ НА ЕНЕРГЕТИЧНИТЕ НИВА НА НОВОСИНТЕЗИРАНИ ИРИДИЕВИ ЦИКЛОМЕТАЛНИ КОМПЛЕКСИ ПОСРЕДСТВОМ ЦИКЛИЧНА ВОЛТ-АМПЕРОМЕТРИЯ

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(Резюме)

Цикличната волт амперометрия (CV) е един от стандартните и широко използвани методи за определяне на енергетичните нива на органичните съединения. В тази статия ние представяме едно CV изследване на новосинтезирани иридиеви циклометални комплекси, намиращи приложение като фосфоресцентни допанти в Органични Светоизлъчващи Диоди (OLEDs). Енергиите на най-високата заета (HOMO) и най-ниската незаета (LUMO) молекулни орбитали на разтворени в ацетонитрил комплекси бяха пресметнати въз основа на измерените волтаметрично редукционни потенциали и стойностите на ширините на забранените зони, определени от UV абсорбционните им спектри.