

## Novel electroluminescent devices containing $\text{Eu}^{3+}$ -(2-acyl-1,3-indandionate) complexes with TPPO ligand

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### ABSTRACT

Fabrication and electroluminescent properties of devices containing europium complexes of general formula  $[\text{Eu}(\text{ACIND})_3(\text{TPPO})_2]$ , where ACIND, 2-acyl-1,3-indandionate ligands; and TPPO, triphenylphosphine oxide, as emitter layers are discussed. The double-layer devices based on these complexes present the following configurations: device **1**: ITO/TPD/ $[\text{Eu}(\text{AIND})_3(\text{TPPO})_2]/\text{Al}$ ; device **2**: ITO/TPD/ $[\text{Eu}(\text{ISOV-IND})_3(\text{TPPO})_2]/\text{Al}$  and device **3**: ITO/TPD/ $[\text{Eu}(\text{BIND})_3(\text{TPPO})_2]/\text{Al}$ , where AIND, 2-acetyl-1,3-indandionate; ISOVIND, 2-isovaleryl-1,3-indandionate; and BIND, 2-benzoyl-1,3-indandionate, respectively. These devices exhibited photo and electroluminescent emissions. An important characteristic presented by devices is that their electroluminescent (EL) spectra, in the region of  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  ( $j = 0, 1, 2, 3$  and  $4$ ) transitions of  $\text{Eu}^{3+}$  ion, show profiles that are different from photoluminescent (PL) ones. In addition to narrow bands arising from intraconfigurational- $4f^6$  transitions, devices **1** and **2** also exhibited a broad band with maximum at around 500 nm which is assigned to electrophosphorescence from the indandionate ligands. On the other hand, EL spectra of device **3** present only narrow bands from  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  transitions.  $[\text{Eu}(\text{ACIND})_3(\text{TPPO})_2]$  complexes are promising candidates to prepare efficient organic light-emitting devices (OLEDs) when compared with those containing  $\text{Eu}^{3+}$ -complexes of aliphatic  $\beta$ -diketonate anions.

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### 1. Introduction

Nowadays there is a great interest in the study of organic light-emitting devices (OLEDs) containing small molecules (SMOLEDs) and polymers (PLEDs) as emitting layers due to their wide emission region and low voltage for flat-panel displays application [1–4]. However, OLEDs using trivalent rare earth complexes as emitting layers may present additional advantages as a consequence of singular spectroscopic properties of  $\text{RE}^{3+}$  ions. These coordination compounds generally exhibit emission spectra dominated by narrow bands arising from intraconfigurational- $4f^N$  transitions centered on  $\text{RE}^{3+}$  ion, consequently, they are promising as almost monochromatic light-emitting center for full color in OLED [5]. As an example, if  $\text{Eu}^{3+}$  ion is not in a symmetry center and the ligand-to-metal (LTM) intramolecular energy transfer is efficient, its complexes display only characteristic narrow bands assigned to  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  ( $j = 0, 1, 2, 3$  and  $4$ ) transitions which are dominated by hypersensitive  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  around 612 nm. Due to this behavior, the red color exhibited by  $\text{Eu}^{3+}$ -compounds has CIE (Comission

Internationale l'Eclairage) chromaticity diagram color coordinates near to vertex (in the red region).

Another advantage in the usage of  $\text{RE}^{3+}$ -complexes in OLEDs is that their internal quantum efficiency is not limited, theoretically it can rise up to 100%, because both singlet and triplet excitons are involved in the emission process, and an efficient LTM intramolecular singlet–triplet–rare earth ion energy transfer is generally operative [5]. For this reason, the value of electroluminescence efficiency in devices based on rare earth complexes may be four times higher than those for similar organic devices using other materials when emission bands usually occur due to  $\pi \rightarrow \pi^*$  transitions with a full-width at half-maximum wavelength of around 100 nm.

There is also a great interest in the study of  $\text{RE}^{3+}$  ions for application such as selective luminescent probes of biological structure [6] and fluoroimmunoassay agents [7]. However, particular attention has been dedicated to the studies of complexes containing  $\beta$ -diketonates as ligands. This kind of ligands has been successfully employed as *antenna*, absorbing ultraviolet radiation, overcoming intrinsic drawback of low absorption coefficients of rare earth ions and transferring their energy efficiently to these metal ions [8,9].

In order to improve the device performance, obtaining OLEDs with high electroluminescence efficiency and high brightness,

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several combination of  $\text{Eu}^{3+}$ -complexes, hole- and electron-transporting materials have been used to fabricate multilayer devices. Besides, it was recently demonstrated that EL performance of OLEDs based on rare earth complexes can be effectively improved by chemical modification of  $\beta$ -diketone ligands [10,11].

Unlike aliphatic  $\beta$ -diketonates, few studies in literature report spectroscopic properties of 2-acyl-1,3-indandione based rare earth complexes [12–14]. In recent work [15] it was demonstrated that they exhibit high luminescence intensity as the aliphatic ones, presenting an efficient intramolecular LTM energy transfer. It was also showed that volatility and stability of 2-acyl-1,3-indandione rare earth complexes are improved by coordination of triphenylphosphine oxide ligand to  $\text{Eu}^{3+}$  ion. Besides these interesting spectroscopic properties, up to now, no electroluminescent investigation has been reported on these kinds of complexes.

In this work, the fabrication and the characterization of double-layer OLEDs using new europium complexes with 2-acyl-1,3-indandionates (2-acetyl-, 2-isovaleryl- and 2-benzoyl-1,3-indandionate) ligands as the emitting layer are reported. Electroluminescent properties of the fabricated devices are discussed based on their EL spectra from 400 to 720 nm and energy diagram of molecular orbitals for TPD and  $\text{Eu}^{3+}$ -complexes. From these data it was possible to evaluate the ability of  $\text{Eu}$ -(2-acyl-1,3-indandionates) to act also as electron injection layers. In order to increase the emission intensity of europium ion in diketonate complexes, triphenylphosphine oxide (TPPO) ligand was coordinated to metal ion replacing water molecules in the first coordinated sphere. The difference between PL and EL spectra indicates that the carrier trapping is the main electroluminescence process. Indeed, in this case,  $\text{Eu}$  complex acts as a trap carriers (for electrons and holes) enabling the direct recombination on the  $\text{Eu}$  complex [16].

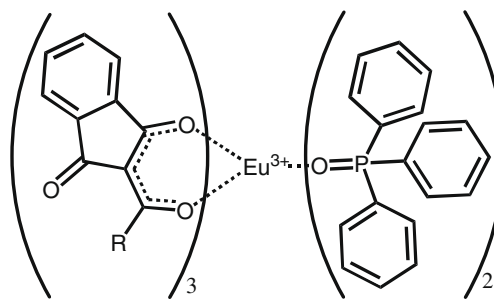
## 2. Experimental

Hydrated europium complexes were prepared by adding aqueous solution of  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  to indandione ligand according to method recently described in reference [6]. The yellow precipitated with powder form, was filtered, washed with water in order to remove traces of excess ligand and dried in vacuum desiccators. To obtain  $\text{Eu}(\text{ACIND})_3(\text{TPPO})_2$  complexes acetone solutions of TPPO and hydrated precursor  $\text{Eu}(\text{ACIND})_3(\text{H}_2\text{O})_2$  complexes were mixed, under stirring in a molar ratio complex:TPPO equal to 1:2.5. After evaporation of part of solvent a yellow precipitate was formed, which was filtered and dried. The synthesis and characterization details of complexes have been recently published in reference [15].

EL devices with  $\text{Eu}^{3+}$ -complexes as emitting layer were deposited by thermal evaporation onto indium–tin–oxide (ITO) coated glass substrate with a resistance of  $8.1 \Omega/\square$  supplied by Asahi Glass Co.

Firstly, the substrates were cleaned by ultrasonification using detergent solution, followed by toluene degreasing. Then, they were cleaned again by ultrasonification with pure isopropyl alcohol. After that, hole transporter (TPD) and europium complexes, in Tungsten crucibles, were sequentially deposited with a rate of about  $0.1\text{--}0.3 \text{ nm s}^{-1}$  under high vacuum and with a base pressure around  $9 \times 10^{-6}$  Torr that increased to  $\sim 5 \times 10^{-5}$  Torr, during the evaporation process. Finally, 150-nm-thick aluminum cathode was evaporated from a tungsten wire basket at approximately  $0.5 \text{ nm s}^{-1}$  rate in the same chamber and all the process was performed without breaking vacuum. So bi-layer devices based on  $\text{Eu}^{3+}$ -complexes present the following configurations:

Device 1: ITO/TPD(50 nm)/[ $\text{Eu}(\text{AIND})_3(\text{TPPO})_2$ ](160 nm)/Al(200 nm);



**Fig. 1.** Structural formula of the  $\text{Eu}^{3+}$ -complexes used as emitting layers:  $\text{Eu}(\text{AIND})_3(\text{TPPO})_2$  for  $R=\text{CH}_3$ ,  $\text{Eu}(\text{ISOVIND})_3(\text{TPPO})_2$  for  $R=\text{CH}_2\text{CH}(\text{CH}_3)_2$  and  $\text{Eu}(\text{BIND})_3(\text{TPPO})_2$  for  $R=\text{C}_6\text{H}_5$ .

Device 2: ITO/TPD(50 nm)/[ $\text{Eu}(\text{ISOVIND})_3(\text{TPPO})_2$ ](160 nm)/Al(200 nm);

Device 3: ITO/TPD(50 nm)/[ $\text{Eu}(\text{BIND})_3(\text{TPPO})_2$ ](160 nm)/Al(200 nm).

where, AIND, 2-acetyl-1,3-indandionate; ISOVIND, 2-isovaleryl-1,3-indandionate; and BIND, 2-benzoyl-1,3-indandionate, respectively. The structural formula of  $\text{Eu}^{3+}$ -complexes used in emitting layers and OLED configurations are shown in Fig. 1.

The thickness of the deposited layer and the evaporation rate of individual materials were monitored in situ with quartz crystal monitors and confirmed by a successive profilometer measurement. The fabricated EL devices presenting an active area of about  $25 \text{ mm}^2$  were operated in forward bias voltage, with ITO as positive electrode and Al as negative.

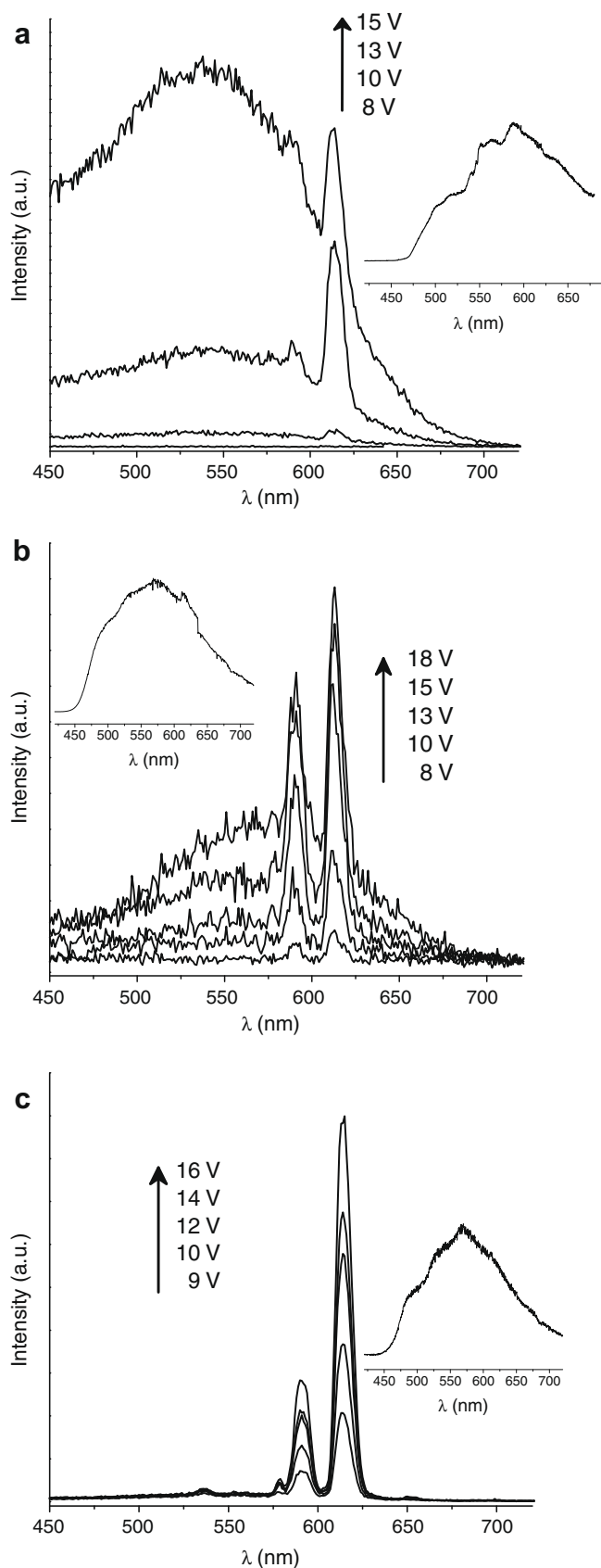
Absorption spectra of complexes in acetonitrile solution were recorded on a (UV–Vis) Spectrophotometer Shimadzu U3000. Photoluminescent spectra of [ $\text{Eu}(\text{ACIND})_3(\text{TPPO})_2$ ] complexes in solid state were recorded at room temperature at an angle of  $22.5^\circ$  (front face) in a spectrofluorimeter (SPEX-Fluorolog 2) with double grating 0.22 m monochromator (SPEX 1680), and a 450 W Xenon lamp as excitation source while PL and EL spectra of devices 1, 2 and 3 were measured with a Photon Technology International (PTI) fluorescence spectrophotometer. The current–voltage ( $I$ – $V$ ) characteristics were measured simultaneously with EL spectra.

Cyclic voltammetry was performed in a single cell with three electrodes at a sweep rate of  $30 \text{ mV s}^{-1}$ . The counter electrode and reference electrode were Pt wire and Ag/AgCl, respectively. The electrolyte was a  $0.1 \text{ mol L}^{-1}$  solution of KCl in water. The spectra were carried out with a Microquimica model MQPG-01 potentiostat. Typical experiments were conducted with a film of europium complex deposited onto graphite electrode from an acetone solution at room temperature.

## 3. Results and discussion

In order to investigate the ability of europium complexes to act as electron-transporting layer (ETL), double-layer OLEDs were fabricated using them and TPD as hole transporting layer. This configuration allows also to avoid the influence of  $\text{Alq}_3$  or others ETLs in the devices electrical and emission performance.

EL spectra for devices with configurations 1, 2 and 3 recorded at different bias voltages, in the spectral range of 400–720 nm at 298 K, are shown in Fig. 2. The values of luminance efficiency and brightness for the devices 1, 2 and 3 are summarized in Table 1. The results show very low efficiency principally due to the device architecture not optimized for this purpose. The best result



**Fig. 2.** EL spectra recorded at room temperature (298 K) as a function of bias voltage of: (a) device **1**, (b) device **2** and (c) device **3**. The phosphorescence spectra of Gd-complexes using the same ligands are reported in the inset of the correspondent figure. All the spectra are recorded at room temperature.

**Table 1**

Efficiency and brightness values of the fabricated devices.

Device	Efficiency at 15 V (Cd/A)	Brightness at 15 V (Cd/m <sup>2</sup> )
<b>1</b>	0.026	1.7
<b>2</b>	0.005	0.3
<b>3</b>	0.1	220

was obtained for device **3** that also exhibits the best EL emission, as discussed below. As it can be seen, EL spectra for devices containing [Eu(AIND)<sub>3</sub>(TPPO)<sub>2</sub>] (Fig. 2a) and [Eu(ISOVIND)<sub>3</sub>(TPPO)<sub>2</sub>] (Fig. 2b) complexes are characterized by an intense broad band in the 460–650 nm range that overlaps the narrow lines coming from Eu<sup>3+</sup> ion. This band appears in the same spectral region as the phosphorescence band for similar Gd<sup>3+</sup>-complexes using the same ligands (in the inset of Fig. 2). Consequently, it can be assigned to the electrophosphorescence (EP) from indandionate AIND and ISOVIND ligands coordinated to metal ion. The appearance of EP in Eu<sup>3+</sup> β-diketones complexes based OLEDs was already observed in previous works [17,18] and can be due to the spin-orbit coupling and consequent MTL energy interaction.

The narrow lines peaked at 580, 600, 612, 650 and 700 nm are attributed to the intraconfigurational-4f<sup>6</sup> <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>J</sub> transitions, where J = 0, 1, 2, 3 and 4, respectively, centered on Eu<sup>3+</sup> ion. It is important to observe that both EP and <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>J</sub> transitions in EL spectra for devices containing Eu<sup>3+</sup>-complexes as emitting layers increase in intensity when the DC bias voltage is increased from 6 to 23 V.

In contrast with the EL spectra for [Eu(AIND)<sub>3</sub>(TPPO)<sub>2</sub>] and [Eu(ISOVIND)<sub>3</sub>(TPPO)<sub>2</sub>] complexes those for [Eu(BIND)<sub>3</sub>(TPPO)<sub>2</sub>] (Fig. 2c) exhibit mainly narrow bands due to <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>J</sub> transitions, which are dominated by hypersensitive <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition around 612 nm. These results are good evidence of an efficient energy transfer process from BIND ligand to the central Eu<sup>3+</sup> ion, when compared with the complexes with AIND and ISOVIND as ligands.

In order to verify that the Eu<sup>3+</sup>-complexes were not degraded during deposition process, PL spectra of devices were also recorded (Fig. 3) exciting the S<sub>0</sub> → S<sub>1</sub> transition of the indandionate ligand (at 350 nm). In this case, the spectra show only the bands assigned to intraconfigurational <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>J</sub> transitions, which gives evidence that the “antenna” effect, is operative: (i) absorption of indandionate ligands; (ii) energy transfer from excited states of ligands to excited levels of Eu<sup>3+</sup> ion and (iii) efficient emission from <sup>5</sup>D<sub>0</sub> emitting level. The broad band with a tail around 550 nm can be assigned to emission from the TDP organic compound that is used as hole injection layer [10]. In Fig. 3c the contribution of this band is less visible due to the best energy transfer from the ligand to the central metal ion. For rare earth complexes, it is generally recognized [5] that the ligands play a main role in the energy transfer to the central ion. However, in the electroluminescence (EL) process the energy of the exciton which is used to promote this energy transfer can, when this transfer is not very efficient, also be used in other radiative processes as, for example, the emission from the TPD compound. This is what can be seen in Fig. 3a and b. However, the BIND ligand, containing aromatic benzoyl group, presents a better electron-transporting ability (showed by a lower EL bias voltage and higher EL intensity) and this reflects in a more efficient energy transfer lowering the TPD emission with respect to the Eu emission (Fig. 3c).

As it can be seen, an interesting characteristic of EL spectra for devices **1**, **2** and **3** is that the relative intensities of intraconfigurational <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>J</sub> transitions are different from those shown in their respective PL spectra. This difference between PL and EL spectra indicates that, also for these complexes, the carrier trapping continues to be the main process acting in the electroluminescence.

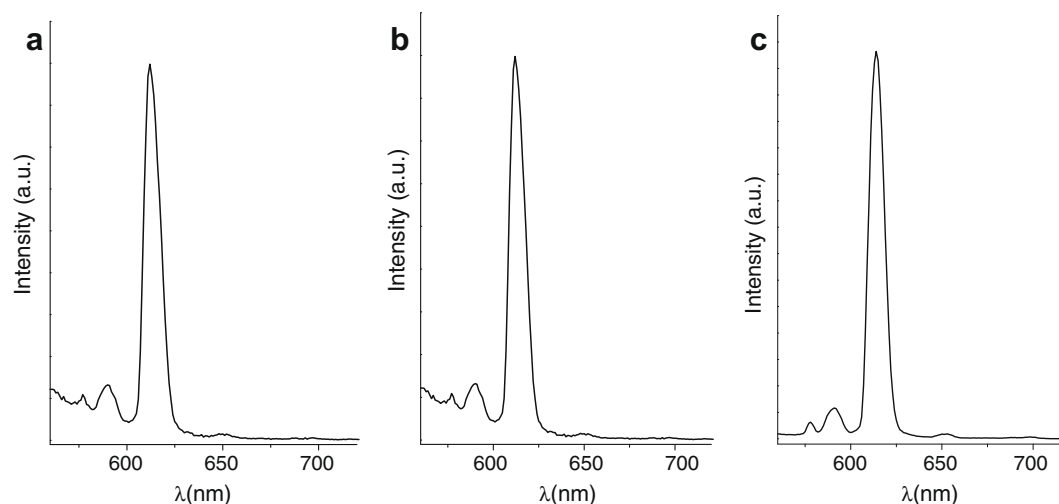


Fig. 3. PL spectra of OLEDs recorded at room temperature (298 K) with excitation at 350 nm for: (a) device 1, (b) device 2 and (c) device 3.

So, the injected electrons and holes are first trapped by  $\text{Eu}^{3+}$ -complex and successively form excitons [11]. To understand the differences in the spectra it is also important to note that while photoexcitation directly produce singlet excitons, the electrical excitation process in OLEDs brings together electrons and holes from opposite electrodes and, statistically can generate singlet and triplet states.

Moreover, as can be observed from the spectra, the bands assigned to the  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  (around 579 nm) and  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  (around 592 nm) transitions are situated near to the maximum of the electrophosphorescence (EP) broad band (around 560 nm), while the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  (around 612 nm) transition is displayed in the low-energy tail of the same EP band. Consequently, the  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transitions gain more intensity due to the contribution coming from the EP band with respect to the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  band. Although the EL spectrum of  $\text{Eu}(\text{BIND})_3(\text{TPPO})_2$  complex shows an EP band with smaller intensity as compared as europium centered emission bands, it can also contribute for the observed behavior. On the other hand, phosphorescence bands are completely absent in the photoluminescent spectra.

Finally, it is important to remember that differences on relative intensities of the Eu transitions in PL spectra of these compounds can be also observed when they are pumped with different excitation wavelengths [19] or with different power intensities [20,21]. The dependence of the PL emission (and the relative peak intensities) with the source power or energy is associated with the rate equations which depend from the absorption rate. In this way, the EL excitation process can be thought as a combination between different excitations and powers aging on the system and therefore inducing differences with respect to the PL spectra where the power and the excitation wavelength are well defined.

Fig. 4 shows the voltage versus current curves for devices 1, 2 and 3. These plots have characteristics of a typical diode behavior. However, it is observed that the value in which the current begins to increase depends on the complex used as emitting layer. They are around 15, 20 and 10 V for devices 1, 2 and 3, respectively, reaching maxima at approximately 21 V, when begins the degradation of the devices. It is important to note that among the devices studied in this work, the device 3 containing the  $\text{Eu}(\text{BIND})_3(\text{TPPO})_2$  complex as emitting layer displays the EL at lowest voltage bias ( $\sim 9$  V). This behavior is probably due to the highest electron transporter ability of BIND ligand that contains an aromatic benzoyl group as constituent, in contrast to the AIND and ISOVIND ligands that present acetyl and isovaleryl groups, respectively.

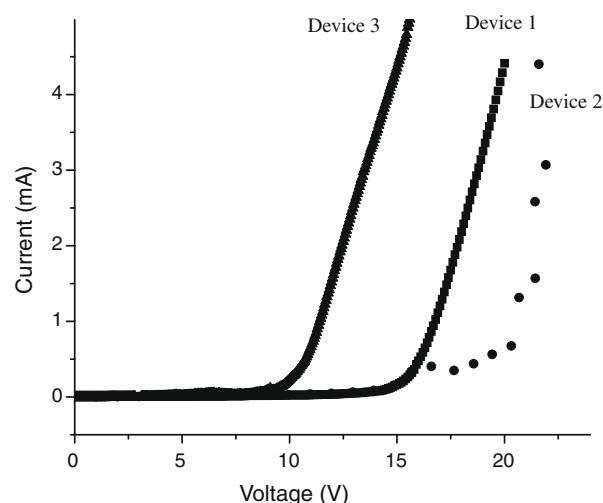


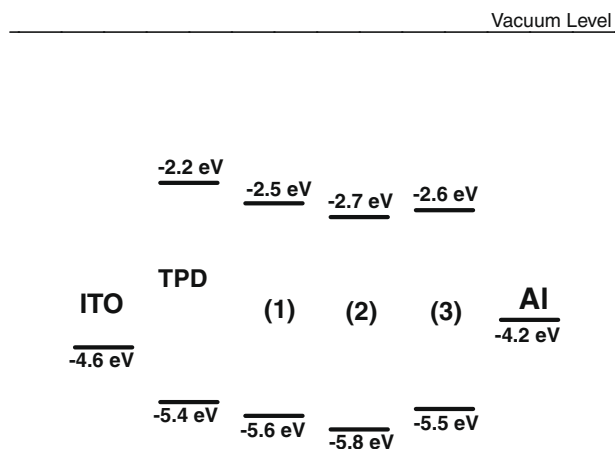
Fig. 4. Current-voltage ( $I$ - $V$ ) curves of OLEDs for devices 1, 2 and 3.

In order to describe EL mechanism of the devices, the energy level diagrams of (HOMO) and (LUMO) molecular orbitals for  $\text{Eu}^{3+}$ -complexes and TPD were estimated according to the procedure described by Micaroni and co-workers [22], which use cyclic voltammetry and absorption spectroscopy data. The energy levels of frontier molecular orbitals were correlated with other useful quantities like aluminum and indium-tin transparent conducting oxide electrode work functions (Fig. 5).

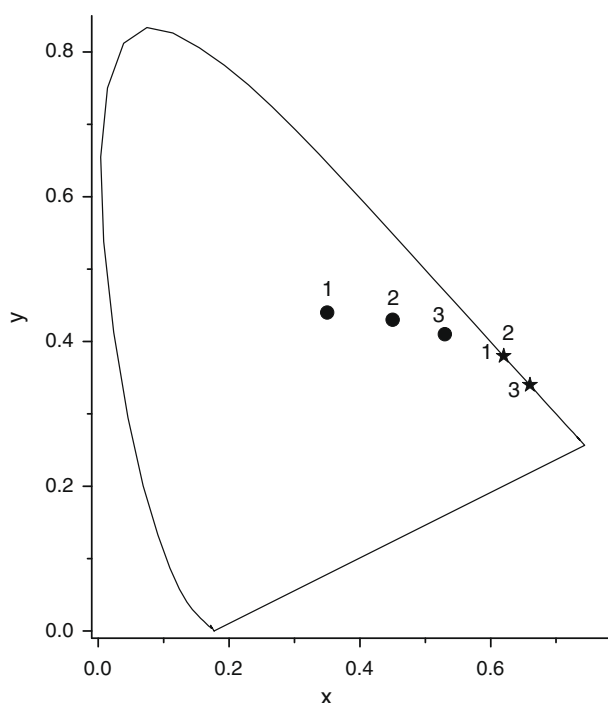
Two important features may be observed in Fig. 5. The first one is that the HOMO levels for  $\text{Eu}^{3+}$ -indandionate complexes are around 5.6 eV, showing that there is only a small energy barrier ( $\sim 0.2$  eV) when compared with HOMO level for TPD and 1.2 eV below the Fermi level. The second one is that there is a large electron injection barrier around 2.4 eV between Fermi level for Al electrode and LUMO level of indandionate complexes. Consequently, holes are more efficiently injected than electrons.

Fig. 5 also shows that the changes in substituent group in indandionates (acetyl, isovaleryl and benzoyl) do not alter significantly the energy of HOMO and LUMO, consequently no effective improvements in hole and electron injections are expected from device (1) to (3). However, the more efficient energy transfer together with the highest EL intensity of the  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  transitions





**Fig. 5.** Energy level diagram for devices **1**, **2** and **3** as calculated from electrochemistry and optical measurements.



**Fig. 6.** CIE chromaticity diagram calculated from PL (stars) and EL (circles) spectra for device **1** (at 15 V), device **2** (at 18 V) and device **3** (at 16 V).

for device (**3**) is probably due to a better electron-transporting ability of BIND ligand that contains an aromatic benzoyl group.

As it can be seen, the EL emission of OLEDs containing  $\text{Eu}^{3+}$ -indandionate complexes as emitting layer can be increased by the addition of a thin electron injection layer of a compound with the energy of LUMO between Fermi level for aluminum and LUMO level of europium indandionate complexes. This special condition could be obtained using, for example,  $\text{Alq}_3$  compound as electron injection layer (energy of LUMO around 3.0 eV) decreasing the electron injection barrier from the Al electrode to the indandionate layers.

The values of the  $(x, y)$  color coordinates show that when devices are photoexcited they present color coordinates that are in

the red region on the CIE chromaticity diagram (Fig. 6). On the other hand, when they are electrically excited, devices **1** and **2** display yellowish-orange close to white region of chromaticity diagram, while the coordinate color for device **3** is in the orange region (Fig. 6). For devices **1** and **2**, this result is due to the higher intensity of the EP band from AIND and ISOVIND ligands (that cover the green and yellow spectral regions) when compared with that from intraconfigurational  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition (in the red region). Moreover, although no EP emission is detected from device **3**, its EL spectra exhibit the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  line (at 591 nm) with higher emission intensity than in the PL case and, consequently, the color of the luminescence emission is shifted from red (PL) to orange (EL) region as can be seen in the CIE diagram (Fig. 6).

#### 4. Conclusions

It has been demonstrated that 2-acyl-1,3-indandione ligands may serve as useful *antenna* for energy-transfer luminescence for the  $\text{Eu}^{3+}$ -complexes. The EL results also suggest that an employment of the electron injection layer such as  $\text{Alq}_3$ , which present LUMO energy level between Fermi level for aluminum and LUMO level of europium indandionate complexes can improve electroluminescence emission and decreases the device turn-on voltage. Differences between PL and EL spectral data confirm that different species are involved in photo and electrical excitation processes, suggesting that the carrier trapping is the main route acting in the EL phenomenon. The devices with  $\text{Eu}^{3+}$ -(ACIND) complexes containing TPPO as second ligand have potential applications as molecular light converters materials to fabricate new OLEDs.

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