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Growth and Characterization of OLEDs with Europium Complex as Emission Layer

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In this work the growth and the characterization of red emitting triple-layer electroluminescent organic devices using vacuum deposited ($Eu(TTA)_3(TPPO)_2$) europium complex as emitting layer are described. The observed electroluminescence (EL) is characteristic of the Eu^{3+} emission. In this device the hole transport layer is obtained using a thin film of 1-(3-methylphenyl)-1,2,3,4 tetrahydroquinoline-6-carboxyaldehyde-1,1'-diphenylhydrazone (MTCD), while the tris(8-hydroxyquinoline aluminum) (Alq_3) is used as electron transport layer (ETL).

I Introduction

In the last years, electroluminescence (EL) from organic thin films has become a matter of great interest because of its potential to enable low-cost, full color, flat panel displays and other emissive devices [1]. By selecting the appropriate emitting layer, the light emission could be changed through almost the whole visible region. Since Tang and VanSlyke [2] reported the first architecture of the double-layered organic EL device, many researchers have developed high performance green organic EL using tris(8-hydroxyquinolinate) aluminum (Alq_3) [3,4,5]. Bright blue organic EL device have been reported using 5,5'-bis(dimesitylboryl)-2,2'-bithiophene (BMB-2T) as dopant in N-arylbenzimidazole (TPBI)[6]. Some orange and red organic EL devices using some complexes and/or organic dyes have been discussed [7,8]. Europium complex have been applied by several researches as emitting materials in red-emitting EL devices with sharp spectra [10-14].

There are two main advantages in fabricating EL devices using rare earth complexes: (i) theoretically the upper limit of inner quantum efficiency is near 100%, which is four times higher that of similar devices using other materials; and (ii) the sharp emission bands of rare earth ions is very suitable for full-color display. In particular, Eu^{3+} ions are known to be weakly fluorescent species due to their low quantum yields and poor molar absorption. The technique of ligand sensitized fluorescence has been found to be an efficient method for enhancing its fluorescence. In this method, an organic ligand with a higher molar absorption is complexed with the Eu^{3+}. On excitation in its absorption band, the ligand transfer a part of its excitation energy to the higher energy levels of Eu^{3+}, which then emits. Such an indirect way of excitation results in the fluorescence enhancement of Eu^{3+} compared to direct one. A number of organic ligands such as β-diketones, aromatic carboxylic acid or polymers have been used as sensitizing ligands for this purpose [11,15,16,17]. Generally, in EL devices using europium complexes the N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) is used as Hole Transport Layer (HTL), [10, 11, 13, 14]. PVK and NPB was also used in other devices [12].

This work is based on the use of the 1-(3-methylphenyl)-1,2,3,4, tetrahydroquinoline-6-carboxyaldehyde-1,1'-diphenylhydrazone (MTCD) as hole-transport layer in an organic LED where the emitting layer is constituted by the $Eu(TTA)_3(TPPO)_3$ complex. When this device is polarized with an appropriate voltage bias it is possible to observe a bright red light. The preparation, the characterization and the EL properties of this devices will be also discussed.

II Experimental

Figure 1 shows the chemical structures of the used materials while in Fig. 2 is reported the architecture of the EL diode.

In our device, the 1-(3-methylphenyl)-1,2,3,4 tetrahydroquinoline-6-carboxyaldehyde-1,1'-diphenylhydrazone (MTCD) is used as Hole Transport Layer (HTL), while the tris(8-hydroxyquinoline aluminum) (Alq_3) is used as Electron Transport Layer (ETL). Finally as emission layer a tris(α-

thenoyltrifluoroacetonate)bis(triphenylphosphine oxide) europium complex ($Eu(TTA)_3(TPPO)_2$) is used.

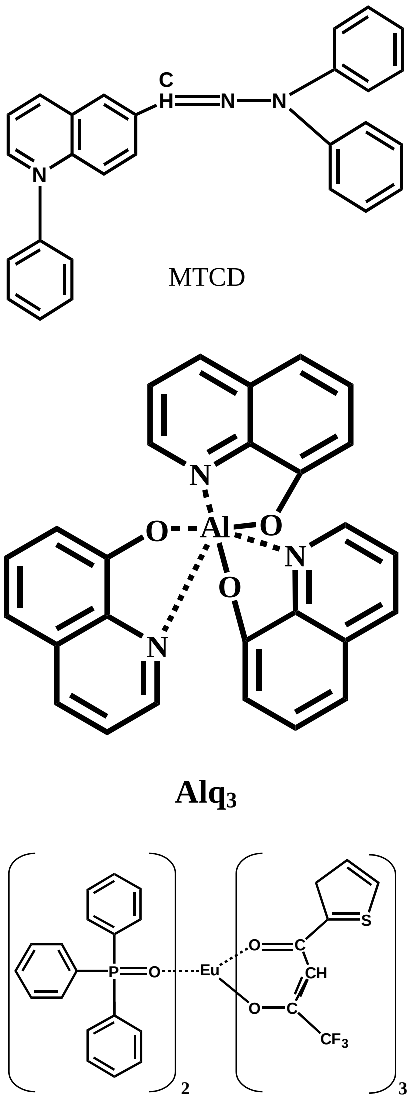

Figure 1. Molecular structure of the used materials.

The MTCD was kindly donated by Prof. Sung-Hoon Kim of the Department of Dyeing and Finishing, of the Kyunpook National University (South Korea) and was used as obtained. The Alq_3 was used as purchased from Aldrich. Finally, the $[Eu(TTA)_3(TPPO)_2]$ europium complex was prepared as follows: hydrated precursor $[Eu(TTA)_3(H_2O)_2]$ was dissolved in ethanol and TPPO, also dissolved in ethanol, was added to the solution in the molar ratio 1:2 (salt : ligand). Successively, the solution was allowed to mix until the formation of a pale-yellow precipitated. The solid so obtained was twice purified with acetone and then desiccated in vacuum.

The substrate for EL device fabrication is an indium-tin-oxide (ITO) coated glass with a sheet resistance of 8.1 Ω/□. The substrates were initially cleaned by ultrasonification first using a detergent solution, followed by toluene degreasing, and then cleaned newly by ultrasonification with pure isopropyl alcohol. After drying using an infrared lamp, the substrates were loaded into the vacuum chamber.

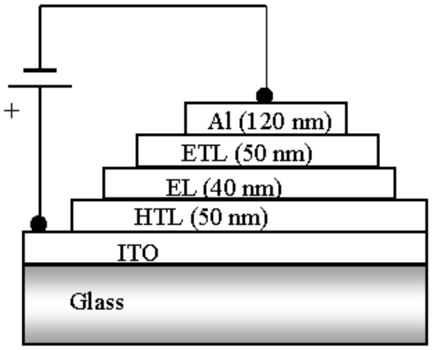

Figure 2. Eu doped OLED architecture. EL is the Eu doped layer.

The organic compounds were successively thermally evaporated onto ITO at room temperature from tungsten crucibles with rates in the range of 0.1-0.3 nm/s below a pressure of $5x10^{-5}$ Torr. To finalize the EL device an aluminum cathode was evaporated from a tungsten wire basket at higher rates (about 1.0 nm/s) in the same vacuum chamber. The layer thickness was *in situ* controlled through a quartz crystal monitor. The emission area was 50 mm^2 typically.

Photoluminescence (PL) and EL spectra were measured with a Photon Technology (PTI) Fluorescence spectrophotometer. The brightness was measured by using a calibrated radiometer/photometer by United Detector Technology, model 350. All measurements were carried out at room temperature under ambient atmosphere.

III Results and discussion

Red and uniform light emission was observed from the produced organic EL device, when a positive voltage was applied to the ITO electrode. The organic diode shown in Fig. 2 can operate both in continuos (*dc*) and/or pulsed mode. Its electrical behavior is similar to that of a rectifier diode, the forward bias corresponding to a positive voltage applied to the ITO electrode. Figure 3 shows the continuos dc current vs voltage ($I-V$) curve. During the experiments we noted that some of the produced EL devices showed a typical behavior of a electrical short circuit. However, after briefly running a current of several tens of mA through the device, the short circuit opens, and the device start to emit light. This behavior suggests the presence of microscopic conduction paths through the organic layers which are burned out on application of higher currents. The existence of these paths at the first stage of OLED operation can be due to the existence of not good uniformity at one or both of the organic/electrode interfaces, which may lead to non uniform electric fields across the device. This can results in the formation of high current "hot spots" or short circuits [18].

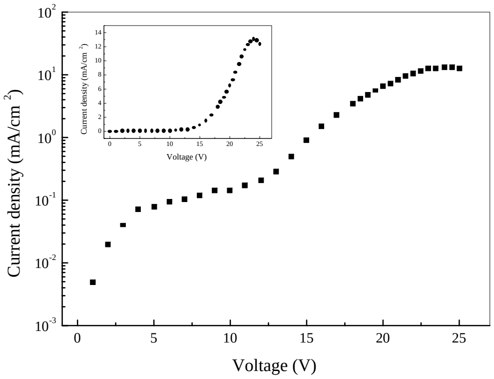

Figure 3. I-V curve of the device. The inset shows the same behavior in a linear scale.

Figure 4 shows the EL spectrum characteristic of the Eu^{3+} emission where the peaks at 540, 579, 590, 615, 650 nm correspond respectively to the $^5D_1 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7D_2$, $^5D_0 \rightarrow {}^7F_3$ transitions of the europium ion. In the spectrum it is possible to observe the main emission peak at 615 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion. So the device emits highly monochromatic red light.

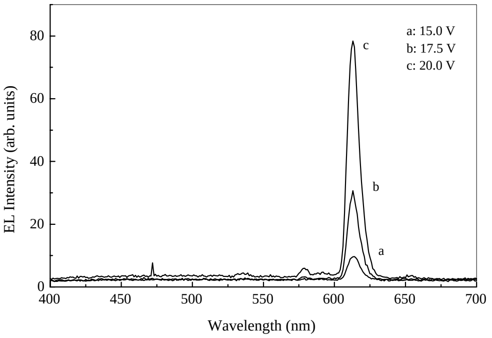

Figure 4. EL spectra for the Eu doped OLED for different values of bias voltage (a=15 V, b = 17,5 V, c = 20 V).

Generally, in lanthanide metal complexes, the central metal ion M^{3+} is excited through the excitation of the ligand [12]. Thus, the EL process of the device can be understood as following. Under EL operation, electrons are transported into the $[Eu(TTA)_3(TPPO)_2]$ complex layer from the Alq_3 film, while holes are transported into this layer through the MTCD compound. The excitation of the ligand is then realized by combination of the electrons and holes. Afterward, the excited energy in the ligand is transferred to the central ions through the ligand's triplet energy level [19] and finally the emission of the Eu^{3+} ions is observed.

Figure 5 shown a comparison between the EL spectrum of the ITO/MTCD/$[Eu(TTA)_3(TPPO)_2]$/Alq_3/Al OLED device and the PL spectrum taken from a $[Eu(TTA)_3(TPPO)_2]$ thermally deposited thin film excited with $\lambda = 350$ nm. The two spectra were measured at room temperature. As it is possible to see, the two spectra are quite similar, except that some transition in the EL spectrum doesn't appear so strong as in the PL one, as for example in the case of the $^5D_0 \rightarrow {}^7F_1$ transition. Moreover, the typical Alq_3 wide emission band, peaked at 520 nm, is absent in the PL spectrum. This result is different with respect to that found by H. Cao et al.[13] and it is still under investigation. A possible explanation can be due to the energy transfer from the triplet to the Eu^{3+} ion that is quite efficient and can quench the Alq_3 luminescence.

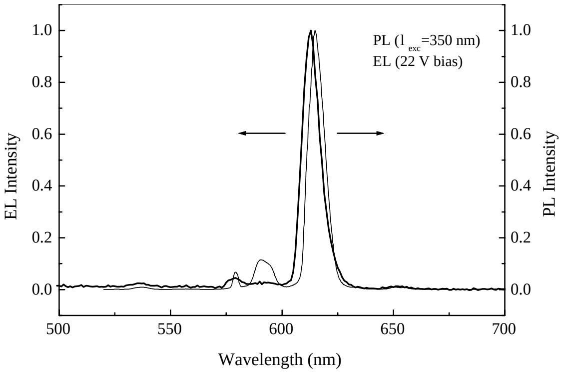

Figure 5. PL and EL spectra for a $[Eu(TTA)_3(TPPO)_2]$ thermally deposited thin film and the Eu doped OLED respectively. The PL spectrum was taken exciting with λ = 350 nm. In the case of the EL spectrum, the bias voltage used was 22 V.

In this figure it is also possible to observe a small shift of the EL band with respect to the PL one. The displacement is of the order of 2 nm and it is real, not depending from instrumental factors. However, the FWHM of both of the spectra is almost the same and its value is about of 0.03 eV. Also this effect, which can be due to the different nature of the mechanisms involved for the PL and the EL emissions, is under investigation.

Figure 6 shows the luminance vs voltage curve of our OLED device. The light emission start to be detected around 12 V, with a luminance of 0.01 cd/m^2 . The luminance grows linearly with the applied voltage. The maximum luminance obtained with this device was about 2.2 cd/m^2 applying 23 V bias voltage. This value is in good agreement with that obtained by H. Cao et al. [13] which reports a 10 cd/m^2 value with 18 V bias voltage in a different device which uses the TPD compound as HTL layer. Increasing the voltage more than 23 V results in a decreasing of the EL emission due to known degradation effects [20,21].

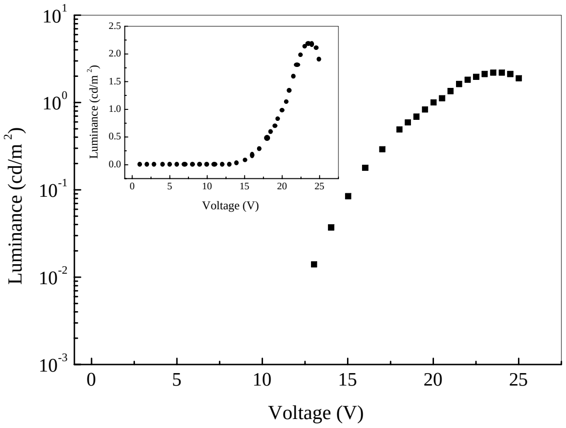

Figure 6. The luminance vs bias voltage curve for the Eu doped OLED.

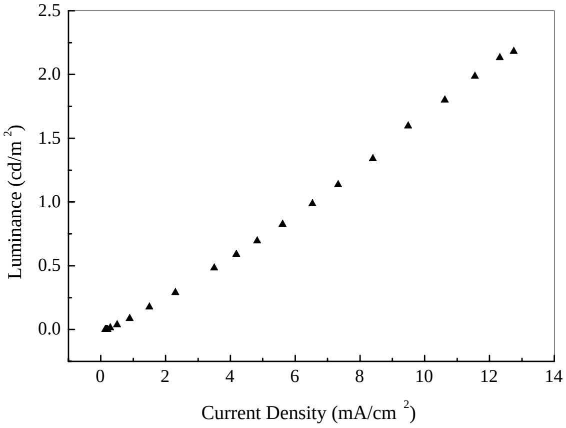

Figure 7. The luminance vs current density curve for the Eu doped OLED. It is possible to see the good linearity from 0.1 to 13 mA/cm^2.

The OLED light output as a function of the input current was also measured and it is shown in Fig. 7. The emission from the diode is linear in the range from 0.1 to 13 mA/cm^2.

The 13 mA/cm^2 value corresponding to a bias voltage of 23 V. Up this voltage, the current decreases and it is possible to observe small sparks in the device, while the luminance decrease too. In this case the device begin to work as a capacitor, the charge transport is less efficient in the organic layers, and the intense electric field ($\sim 10^8$ V/m) causes a dielectric breakdown starting to damage the organic molecules which compose the device.

By dividing the luminance for the current density, we can define another important item that is the EL emission efficiency having the dimensions of cd/A. As can be seen in Fig. 8, in our OLED the efficiency grows with the applied voltage. In particular, in the region between 13 and 17 V, the efficiency grows monotonously. Starting from this point, a further increase of the voltage does not correspond to an increase in the efficiency. This meaning that there is a loss of current, i.e. not all the current is converted in light. In the present device the efficiency reaches its maximum value (de 1.7x10^{-2} cd/A) for 23 V of bias voltage. This relatively low value of the efficiency when compared with others OLEDs can be probably ascribed to the typical Europium complex behavior when used as light emitter in a organic LED. Indeed, even though this particular complex has a high quantum efficiency of fluorescence when excited with photons, its EL efficiency fall at low values when it is used as emitting layer in OLEDs, due probably to the losses in the ligand-Eu^{3+} energy transfer process.

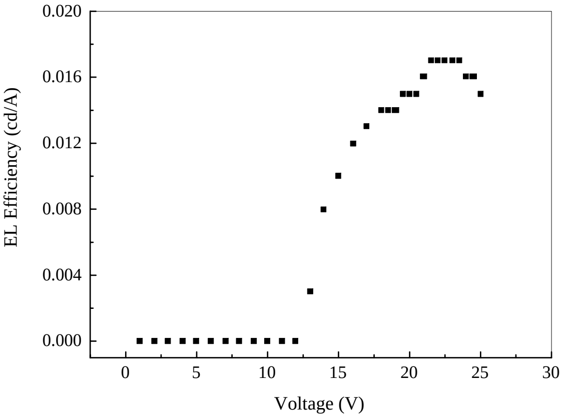

Figure 8. EL efficiency vs bias voltage curve for the Eu doped OLED. After 20 V begin the dieletric breakdown effect, lowering the efficiency and the luminance of the device.

Generally, the morphological properties of the organic layers are critical in the fabrication of optoelectronic thin-film devices. In particular, for the OLEDs it is necessary that all the layers that constitute the device must have low roughness values and high homogeneity. Moreover, the low value of the Tg (glass transition temperature) for the HTL layer it is an important factor in the degradation process. Indeed, by observing the MTCD thin films thermally evaporated onto glass substrates some hours after the deposition process, it is possible to detect some kind of crystallization in form of "*leaf*" (see Fig. 9). This crystallization, already observed in other systems [22], decreases the emission efficiency of the device, making difficult the circulation of the charge carriers through the layers.

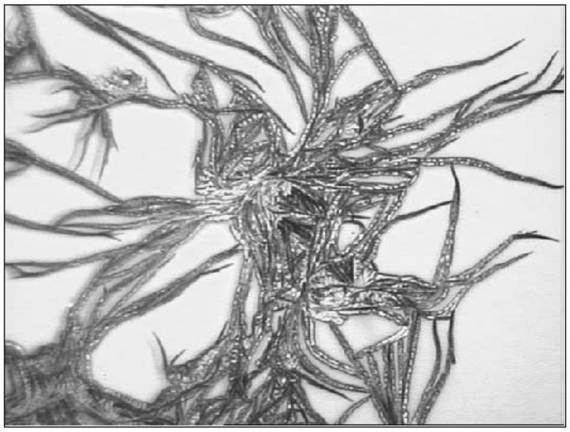

Figure 9. Crystallization effect in a thin film of MTCD some hours after the deposition observed at the optical microscope (x 500).

IV Conclusion

Triple-layer electroluminescent organic devices using 1-(3-methylphenyl)-1,2,3,4 tetrahydroquinoline-6-carboxyaldehyde-1,1'-diphenylhydrazone (MTCD) as the hole transport layer, $Eu(TTA)_3(TPPO)_2$ europium complex as the emission layer and the Alq_3 as the electrons transport layer were grown and characterized. Photoluminescence (PL) and electroluminescence (EL) spectra were recorded at room temperature and compared. In both the spectra it is possible to identify the typical Eu^{3+} sharp emission line. Work is currently in progress to produce others organolanthanide-based electroluminescent devices.

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References

[1] J. R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman, and A. Stocking, Science **273**, 884 (1996).

[2] C.W. Tang and S.A. Van Slyke, Appl. Phys. Lett. **51**, 913 (1987).

[3] C.W. Tang, S.A. VanSlyke, and C.H. Chen, J. Appl. Phys. **65**, 3610 (1989).

[4] C. Adachi, K. Nagai, and N. Tamoto, Appl. Phys. Lett. **66**, 2679 (1995).

[5] G. Giro, M. Cocchi, P. Di Marco, E. Di Nicolo, V. Fattori, J. Kalinowski, and M. Ghedini, Synt. Metals **102**, 1008 (1999).

[6] B. Chen, X.H. Zhang, X.Q. Lin, H.L Kwong, N.B. Wong, C.S. Lee, W.A. Gambling, and S.T. Lee, Synt. Metals **118**, 193 (2001).

[7] C. Adachi, S. Tokito, T. Tsutsui, and S. Saito, Jpn. J. Appl. Phys. **27**, L269 (1998).

[8] J. Kido and J. Endo, Chem. Lett. **7**, 633 (1997).

[9] R.J. Curry and W.P. Gillin, Synt. Metals **111**, 35 (2000).

[10] K. Okada, Y. Wang, and T. Nakaya, Synt. Metals **97**, 113 (1998).

[11] Y. Miyamoto, M. Uekawa, H. Ikeda, and K. Kaifu, J. of Luminesc. **81**, 159 (1999).

[12] C.J. Liang, Z.R. Hong, X.Y. Liu, D.X. Zhao, D.Z. Zhao, W.L. Li, J.B. Peng, J.Q. Yu, C.S. Lee, and S.T. Lee, Thin Sol. Films **359**, 14 (2000).

[13] H. Cao, X. Gao, C. Huang, Appl. Surface Sc. **161**, 443 (2000).

[14] N. Takada, J. Peng, and N. Minami, Synt. Metals **121**, 1745 (2001).

[15] H.F. Brito, O.L. Malta, and J.F.S. Menezes, J. Alloys Comp. **336**, 303 (2000).

[16] O.L. Malta, H.F. Brito, J.F.S. Menezes, F.R. Gonçalves, S.A. Silva Jr, F.S. Farias, and A.M. de Andrade, J. Lumin. **75**, 255 (1997).

[17] C. Liang, W. Li, Z. Hong, X. Liu, J. Peng, L. Liu, Z. Lu, M. Xie, Z. Liu, J. Yu, and D. Zhao, Synt. Metals **91**, 151 (1997).

[18] P.E. Burrows, V. Bulovic, S.R. Forrest, L.S. Sapochak, D. M.McCarty, and M.E. Thompson, Appl. Phys. Lett. **65**, 2922 (1994).

[19] G.A. Crosby, R.E. Whan, and R.M. Alire, J. Chem. Phys. **34**, 743 (1961).

[20] H. Aziz and G. Xu, Synt. Metals **80**, 7 (1996).

[21] Lee-M. Do, M. Oyamada, A. Koike, Eun-M. Han, N. Yamamoto, and M. Fujihira, Thin Solid Films **273**, 209 (1996).

[22] Eun-Mi Han, Lee-Mi Do, N. Yamamoto, and M. Fujihira, Thin Solid Films **273**, 202 (1996).