Study on the Fabrication and Characterization of Red-Light-Emitting Organic Electroluminescent Devices Using Europium Complexes

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Abstract

Organic electroluminescent devices (OELDs) have received a great deal of attention due to their potential application as full-color displays. Europium complexes are known as excellent red light-emitting materials for OELDs since they show intense photoluminescence at around 612 nm with a narrow spectral bandwidth. In this study, a novel europium complex, $Eu(TTA)_3(TPPO)$ was synthesized and its photoluminescent and electroluminescent characteristics were investigated with a device structure of ITO/TPD/$Eu(TTA)_3(TPPO)$/ Alq_3/Al, where sharp emission at the wavelength of 615 nm has been observed. Details on the electrical properties of these structures was also discussed.

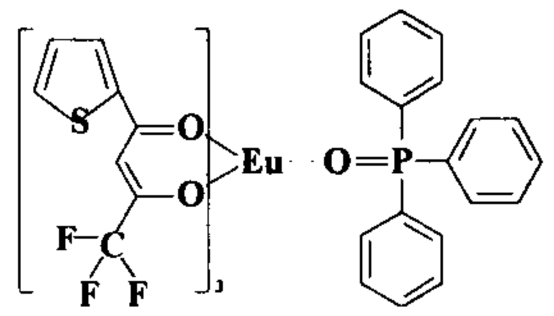
Introduction

Organic electroluminescent devices (OELDs) are of great interest because of their efficient emission in the visible region and their possible application to a new type of flat-panel full-color display. These devices are injection type and show a low driving voltage of less than 10V [1,2]. Rare earth metal complexes have a potential to be used as an emissive materials in OELDs because their photoluminescence exhibits sharp spectral band. For example, europium (Eu) complex is one of the promising candidate for sharp red emissive materials in OELDs [3,5]. Since Eu complexes emit red light at 615nm from Eu^{3+} ion via an intramolecular energy transfer from the triplet of the organic ligand to the 4f energy state of the Eu^{3+} ion, the theoretical internal quantum efficiency is principally not limited. From this point of view, it is possible to improve the quantum efficiency of the red light OELDs by using novel Eu complexes [6].

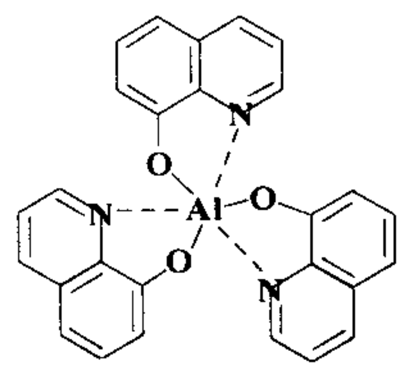
In this study, we synthesized a novel Eu complex, $Eu(TTA)_3(TPPO)$[tris-(4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dionate)-triphenyl phosphine oxide europium(III)], which was used as a red emissive material in OELDs. Electrical and EL characteristics of this Eu complex was investigated with a device structure of ITO/TPD/ $Eu(TTA)_3(TPPO)$/Alq_3/Al.

Experimental

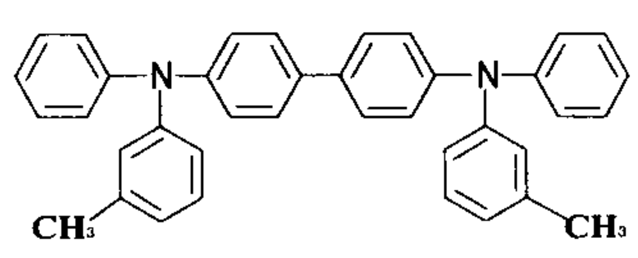
Figure 1 and 2 show the molecular structures of the materials and the schematic diagram of the OELDs used in this study, respectively. The OELDs were prepared as follows: The Eu complex was used as the emitting layer (EML) between a hole-transporting layer (HTL), TPD and a electron-transporting layer (ETL), Alq_3. The structure of the triple-layer OELD was a glass substrate/ITO anode/HTL (TPD = N, N'-bis-(3-methyl-phenyl)-N,N'-bis-(phenyl)-benzidine) (30 nm)/EML (Eu complex) (5 nm)/ ETL (Alq_3 = tris-(8-hydroxyquinoline) aluminum) (30 nm)/ cathode Al (150 nm). The organic layers and Al cathode were successively vacuum deposited onto indium-tin oxide (ITO)-coated glass substrate(Samsung Corning Co. Ltd.) at 5×10^{-6} Torr. The organic materials were loaded into separate Knudsen sells (K-cells), heated up to their sublimation temperatures, and subsequently deposited onto the substrate. The layer thickness of the deposited material was monitored *in situ* using an oscillating quartz thickness monitor. The deposition rates were maintained at 6-7 nm/min for the HTL and ETL materials and 0.4-0.7 nm/min for ETL material, respectively. The device area was $25mm^2$.



(a) $Eu(TTA)_3TPPO$



(b) Alq_3



(c) TPD

Figure 1. The molecular structures of materials used in this study.

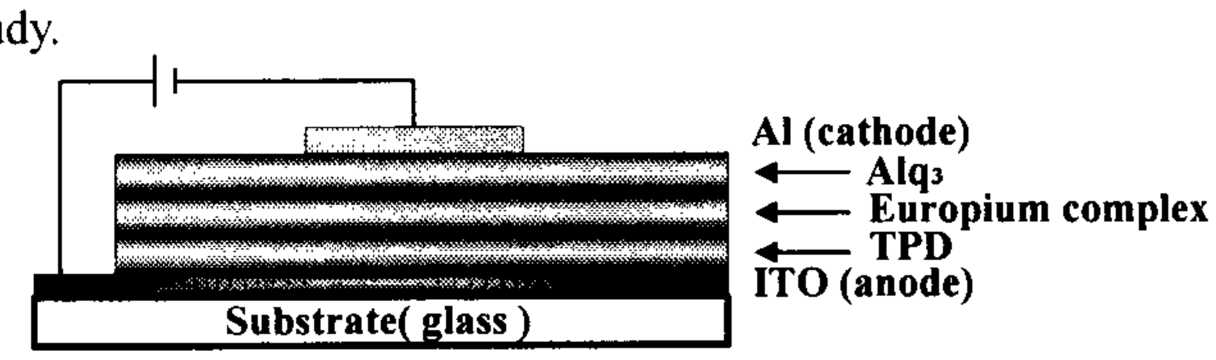


Figure 2. The schematic diagram of the OELDs prepared in this study.

Results and Discussion

Figure 3 shows the EL spectrum of OELD with a device structure of glass substrate/ITO/HTL/$Eu(TTA)_3(TPPO)$/ETL/Al and the PL spectrum of $Eu(TTA)_3(TPPO)$ film itself. As expected, the PL emission peak of $Eu(TTA)_3(TPPO)$ has been observed at the wavelength of 615 nm. It can be seen that the sharp photoluminescence peak in the spectrum of this complex shows a half spectral bandwidth of about 5-7 nm. This means that the luminescent color purity is excellent and the color filter may not be necessary. Therefore, Eu complex can be best suited for the actual flat panel display application as a red emitting material if its high power efficiency can be achieved. It was shown in this figure that the EL spectrum of OELD containing $Eu(TTA)_3(TPPO)$ emits its electroluminescence in red region with maximum emission at about 615 nm and the EL spectrum of the OELD containing $Eu(TTA)_3(TPPO)$ is the same as the PL spectrum of $Eu(TTA)_3(TPPO)$.

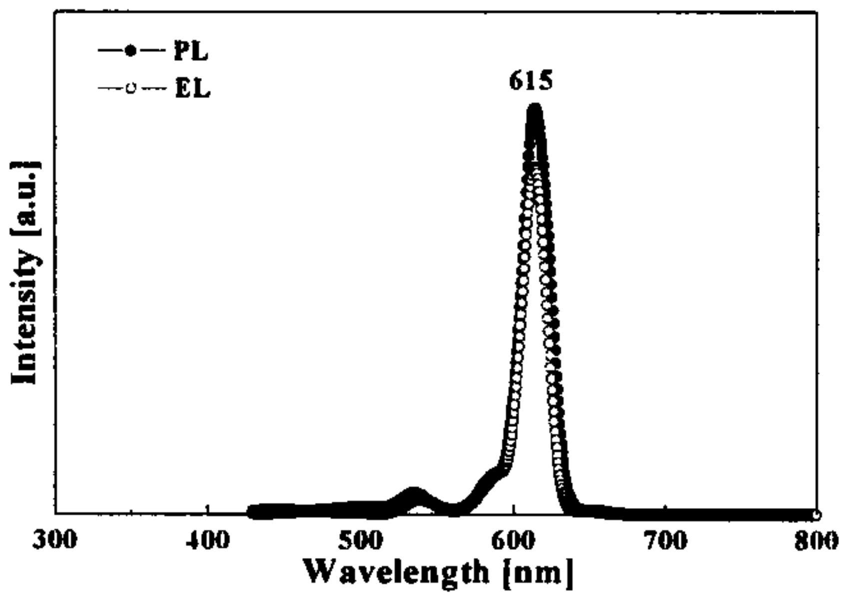


Figure 3. EL spectrum of an $ITO/TPD/Eu(TTA)_3(TPPO)/Alq_3/Al$ (open circle) and PL spectrum of $Eu(TTA)_3(TPPO)$ (solid circle).

The electrons injected from the Al cathode move to the lowest unoccupied molecular orbitals (LUMO) states of the Alq_3 and are transferred to the LUMO state of the ligand of $Eu(TTA)_3(TPPO)$. The injected holes from the ITO anode are transmitted to the highest occupied molecular orbital (HOMO) states of the ligand of $Eu(TTA)_3(TPPO)$ via LUMO state of TPD. Excitons are formed at the ligand sites of $Eu(TTA)_3(TPPO)$ and are transferred to the Eu^{3+} sites. The energy relaxation from ^5D to ^7F states in Eu^{3+} sites results in sharp emission at 615 nm. The identical two spectra in the figure 3 suggest that indicate that the hole-electron recombination occurs only in the $Eu(TTA)_3(TPPO)$ layer.

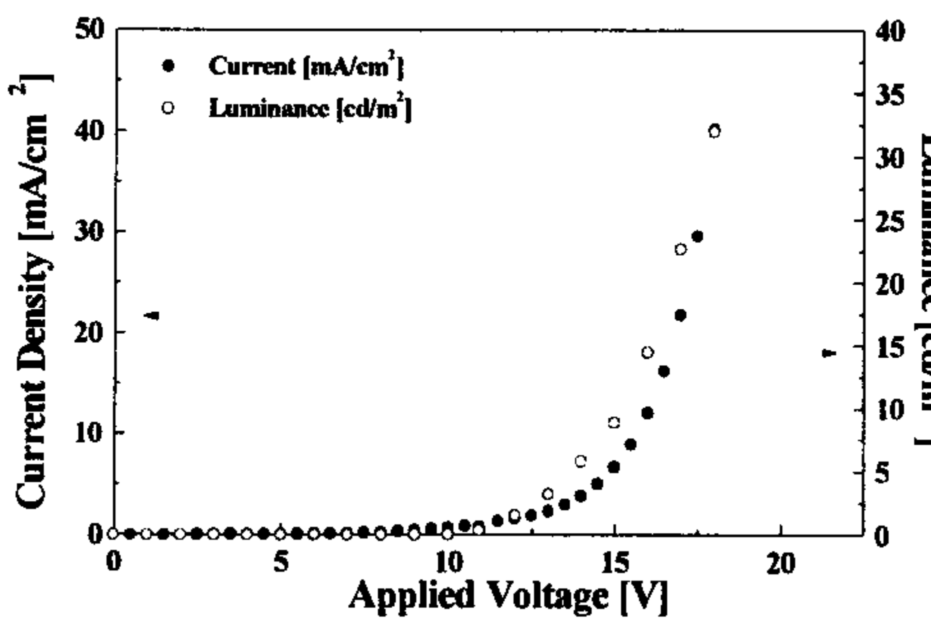


Figure 4. Current density-luminance-voltage characteristics of the OELD with a $ITO/TPD/Eu(TTA)_3(TPPO)/Alq_3/Al$ structure.

Figure 4 shows the dependence of the injection current and luminance on the applied voltage in the triple-layered OELD under the forward bias condition. The current density increased superlinearly with increasing applied voltage under the forward bias condition. The turn-on voltage of the triple-layer OELD was found to be 10V. It was found that the luminance increases with increasing injection current as well as applied voltage. The emission intensity reaches 32 cd/m^2 at the injection current density of 40 mA/cm^2. The EL power efficiency at this condition was calculated to be $2.37x10^{-2}$ lm/W at 16V and 12 mA/cm^2.

The band gap Eg, molecular ionization energy I and the electron affinity A of TPD, $Eu(TTA)_3(TPPO)$, and Alq_3 are (3.08, -5.37, and –2.29 eV), (2.92, -5.67, and –2.75 eV) and (2.64, -5.78, and –3.14 eV), respectively. These values are all measured by the cyclic voltammetric method. Figure 6. shows the schematic diagram of the energy band model of the triple-layer devices at the forward bias.

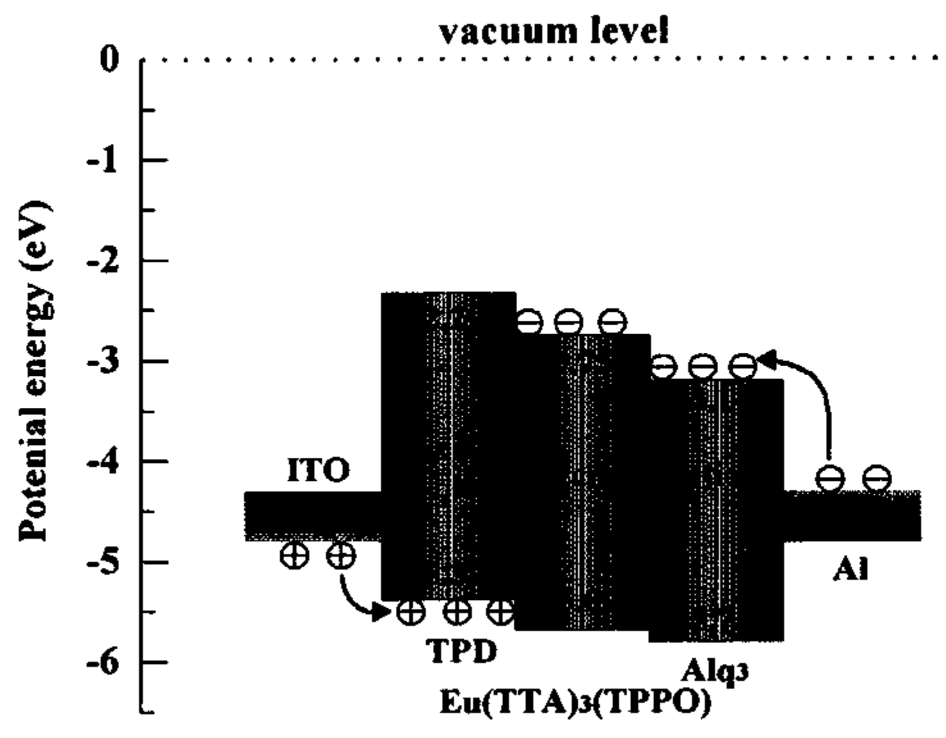


Figure 6. Schematic description of energy band diagram of the OELD with a $ITO/TPD/Eu(TTA)_3(TPPO)/Alq_3/Al$ structure.

Conclusions

A novel volatile Eu complex was synthesized and its EL characteristics were also investigated using a triple-layer OELD. A very sharp EL spectral band centering at the wavelength of 615 nm and bright red light with maximum luminance of 32 cd/m^2 were observed and very highly pure red emission has been obtained from the three-layered OELD, even though the EL power efficiency of the OELD containing $Eu(TTA)_3(TPPO)$ is not enough for the practical application. In order to improve the EL power efficiency, it may be good to use $Eu(TTA)_3(TPPO)$ as a dopant into appropriate electron transporting material and these work is being executed in our lab.

Acknowledgements

This work was fully supported by ETRI(Electronics and Telecommuncations Research Institute).

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