Synthesis, characterization and luminescent properties of a europium (III) complex


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Abstract

Rare earth chelates of Sm(III) (complex 1) and Eu(III) (complex 2) with β-diketone ligand (2-thienyl)trifluoroacetylacetone (HTTA) and triphenylphosphine oxide (TPPO) were prepared from their nitrate salts. Single crystal X-ray diffraction, FTIR and thermo-gravimetric analyses were used in the characterization. Both photoluminescence (PL) and electroluminescence (EL) properties of complex 2 were studied. In both crystalline powder and film states, the PL spectra exhibit emission peaks typical of europium (III) with the most intense at 615 nm. Single layer EL devices based on complex 2 fabricated by evaporation show only weak emissions, while double layer devices with a hole transporting layer of N,N-bis(3-methylphenyl)-N,N’-diphenyl-benzidine (TPD) exhibit enhanced intensity indicating better carrier injection balance.

Keywords: Electroluminescence; Europium (III); Samarium (III); Rare earth chelates

1. Introduction

Electroluminescence (EL) in organic thin-films has been extensively studied since the first reports by Tang and VanSlyke [1,2]. In these systems, energy released by recombination of injected holes and electrons excites molecules in an emitting layer and results in luminescence. Apart from fluorescent dyes and polymers, metal complexes form another most important category of EL materials. Metal ions used in OLED studies include B(III), Al(III), Ga(III), In(III), Mg(II), Be(II), Zn(II), Ru(II), Eu(III), Eu(II), Tb(III), Er(III), Dy (III) [3–14]. In comparison with other luminescence materials, one advantage of rare earth complexes is that they exhibit extremely sharp emission [5–11]. Since 4f orbitals are effectively shielded from the influence of the external forces by the overlying 5s2 and 5p6 orbitals, the various states arising from F configurations are split by external fields only to the extent of 100 cm⁻¹. Furthermore, the lanthanide ions can be excited via an intramolecular energy transfer from the triplet excited state of the ligands. This suggests that, apart from the singlet state, excitation energy of the ligand’s triplet state, which can be directly generated by carrier recombination, can also be utilized to excite the emitting center. So the second advantage using rare earth complexes as emitter layers is that up to 100% of internal quantum efficiencies for devices is theoretically possible. In this paper, we reported the synthesis, characterization and EL properties of an Eu(III) complex. Some characterization data of a Sm(III) complex will also be briefly discussed.

2. Experimental

2.1. Preparation

Two rare earth chelate complexes were prepared: Complex 1: Sm(NO₃)₃·6H₂O (44.4 mg, 0.1 mmol) was dissolved in 20 ml methanol and then the solution...
was added slowly into the mixed solution of (2-thienyl)trifluoro-acetylacetone (HTTA) (66.6 mg, 0.3 mmol) and triphenylphosphine oxide (TPPO) (55.6 mg, 0.2 mmol) in 20 ml methanol under stirring. After complete dissolution the clear solution was allowed to evaporate to obtain crystalline precipitate.

Complex 2 was prepared by the similar process as complex 1, except that Eu(NO₃)₅H₂O (42.8 mg, 0.133 mmol) was used instead of Sm(NO₃)₆H₂O.

2.2. Characterization

The molecular structure of complex 1 was obtained on Siemens P4 single-crystal X-ray diffractometer. Thermo-gravimetric analyses (TGA) were carried out under nitrogen gas. FTIR spectra were measured using KBr plate method. The photoluminescence (PL) and EL spectra were measured using a SPEX Fluorolog Fluorimeter and a RF-5301 PC Spectrofluorophotometer, respectively.

2.3. EL device fabrication

ITO-coated glass (60 Ω square⁻¹) was cut and patterned by concentrated hydrochloric acid wet etching, and then ultrasonically cleaned for 10 min in detergent, de-ionized water, acetone and methanol, respectively in sequence. For the fabrication of single layer devices, the organic chelate complex and the Al electrode were evaporated sequentially at pressures below 2×10⁻⁶ Torr inside a vacuum evaporator onto the ITO coated glass substrate. The double layer devices were fabricated in a similar procedure except that a TPD layer was first evaporated onto the ITO glass before the evaporation of the chelate complex. For PL spectra measurement, quartz was used as the substrate instead of the ITO coated glass.

All electrical testing and optical measurements were performed under ambient conditions with no protective coating applied to the devices.

3. Results and discussion

Single crystals of complex 1 can be obtained by natural evaporation of the solvent from its iso-propanol solution, but attempts to obtain single crystals of complex 2 failed due apparently to rapid weathering after removal from the mother liquor. The molecular structure of complex 1 obtained by single crystal X-ray diffraction is shown in Fig. 1. The detailed structural results will appear in another report. It has a composition of Sm(TTA)₅(TPPO)₅NO₃. In the structure Sm(III) is coordinated by eight oxygen atoms from the ligands and a nitrate ion in the molecule is identified instead of another TTA. This is thought to be caused by the high acidity of the solution, the coordination ability and smaller size of nitrate, although the reactant HTTA was added according to the molar ratio of 3:1 to the quantity of Sm(NO₃)₃·6H₂O. The generation of protons in the
reaction is the reason of high acidity of the solution and is formulated as follows.

$$\text{Sm}^{3+} + 2\text{HTTA} + 2\text{TPPO} + \text{NO}_3^- \rightarrow \text{Sm(HTTA)}_2(\text{TPPO})_2\text{NO}_3 + 2\text{H}^+$$

The TGA results of the complexes were shown in Fig. 2. It can be seen that the TGA curve of complex 1 is smooth, whereas that of complex 2 shows a weight loss of approximately 1.5% at 146 °C. Both complexes decompose to the similar products, approximately 20% of the original weight, corresponding approximately to a composition of SmONO or EuONO, respectively for complexes 1 and 2. From these results, the composition of complex 2 is deduced to be Eu(HTTA)$_2$(TPPO)$_2$NO$_3$H$_2$O, with a water content of 1.5% coinciding exactly to the weight loss at 146 °C in the TGA curve. So in complex 2, there exists a water molecule, which can either coordinate to the central metal or just occupy an empty space. Considering the usual coordination number of nine for Eu(III), the former case should be true, i.e. it is a coordination water donating another coordinating oxygen atom to satisfy the greater coordination number of Eu(III). The schematic structure of this compound is shown in Fig. 2 as an inset.

Almost identical FTIR spectra of the two complexes were obtained as shown in Fig. 3. Because of the high degree of similarity of their chemical bonding properties, the two rare earth metals have almost the same effects on the IR spectra. This experimental fact gives additional evidence for the similarity in composition of the two complexes.

Although PL emission at 645 nm can be observed from complex 1, it is not so intense as complex 2 as an emitting center. Thus, we focus on complex 2 in the PL and EL study.

A nitrate containing europium chelate, Eu(NO$_3$)$_3$phen was previously reported to emit strong red light when doped in a PVK (polyvinylcarbazole) film prepared by spin coating from chloroform solution [7]. In the system, PVK acted as energy receiver and transfer the energy to the metal chelate. Bright red emissions were also observed in device prepared based on Eu(NO$_3$)$_3$phen as light emitter doped in PVK using a triple layer structure. Using TTA to replace the inorganic nitrate ligand will reduce the ionic inter-molecular interaction and make materials more sublimable so that vacuum evaporation method can be used. TTA is one of the most typical fluorinated β-diketones which has higher sensitizing efficiencies than non-fluorinated ones and is used most often as a chelate ligand [11].

PL measurements were carried out on both the powder and thin film samples of complex 2, with the latter obtained by vacuum evaporation onto quartz substrate. The results are shown in Fig. 4. The two emission spectra exhibit no significant difference in peak positions with a pattern similar to that from aqueous solution. For the most intense emission at 615 nm, a full width at half maximum of 12 nm can be observed from the film sample, a little broader than that from the powder sample. This emission is assigned to a $^5$D$_0$–$^7$F$_2$ transition. There are also other less intense emissions at 591, 534 and 701 nm, which can be ascribed, respectively, to
$^{5}D_0-^{7}F_1$, $^{5}D_1-^{7}F_0$ and $^{5}D_0-^{7}F_4$, as reported previously [8]. The most significant difference occurs in the excitation spectra. In the spectrum of the powder sample, two excitation peaks appear, one at 374 nm and another at 393 nm. Nevertheless, only one peak appears at 374 nm in the spectrum of the film. The peak at 393 nm from the powder sample coincides well with that from aqueous solution of Eu(III) salt [15], while the most intense peak at 374 nm is originated from the ligands indicating exciting energy can be effectively transferred to the emitting metal center. The disappearance of the peak at 393 nm from the excitation spectrum of the powder sample indicates the loss of water from the material during the thermal evaporation process. Water molecule has quenching effect on the excited state by vibronic deactivation. However, no such effect exists in film state because of the easy loss of water during the evaporation process. Uniform films can be obtained by the thermal evaporation method, but it was observed that some black residual remains were left without sublimation at the end of vacuum evaporation process indicating further composition change after the loss of water. UV–Vis absorption spectrum of the film sample shown in Fig. 4 shows a maximum at 346 nm and the peak overlaps with the excitation spectrum. Similar PL and absorption spectra were reported for vacuum evaporated film of mixed complex (Eu$_{0.1}$Gd$_{0.9}$)(TTA)$_3$(TPPO)$_2$ [9] and complex Eu(DBM)$_3$(TPPO), where DBM is another β-diketone ligand dibenzoylmethide [8]. Excitation spectra were obtained in these two cases with the absorption onset at approximately 400 nm as here reported.

Single layer devices of complex 2 were fabricated by vacuum evaporation. The EL spectrum is shown in Fig. 5. At lower bias voltage, only one emission peak at 612 nm can be observed, but with the increase of the bias voltage other emissions appear at 534 and 460 nm. The emissions at 612 and 534 nm can obviously be ascribed to complex 2, whereas the emission at 460 nm can not be assigned to any of the f–f transitions. This new emission appears neither in the EL spectra at low voltage nor in the PL spectrum of the film sample evaporated.
in the same run of evaporation as the device fabrication. So its occurrence is not originated from any species in the as-evaporated film, but related to some kind of undetermined species formed in the high electric field at higher bias voltage. In the single layer device the complex layer is evaporated directly onto the ITO surface. Hence, it is possible that some kind of electrochemical interaction happens between the complex and the ITO anode surface at higher bias voltage and the new interfacial species act as exciton traps to result in this additional emission peak which even becomes the most intense in the spectrum under high voltages.

Attempts were made to improve the emission efficiency by introduction of a hole transporting layer. Shown in Fig. 6a are the EL spectra of a typical double layer device using TPD as the hole transporting material at different bias voltages. No emission from TPD can be observed from the double layer device, which should be approximately 410 nm. The most intense emission is at 612 nm. With increasing bias voltage, emissions at other wavelengths, such as 587 and 534 nm become relatively stronger. The pattern of the EL spectra is in general most similar to that of the PL spectrum of complex 2. The turn on voltage of the double layer devices is approximately 10 V (Fig. 6b), higher than that of the single layer device (≈8 V) caused by the increased thickness of the device.

The EL spectra of single layer device show low signal-noise ratio, while double layer device shows high signal to noise ratio and gives well defined EL spectra. So the emission performance is improved with the introduction of the TPD layer indicating that the hole transporting layer gives better carrier injection balance and results in relatively higher quantum efficiency of the device. Another significant difference is that no emission can be observed at wavelengths less than 500 nm in EL spectra of double layer device. This is perhaps due to the fact that the emitting layer and the ITO layer are separated by the hole transporting layer and hence the interfacial interaction between them that occurs in single layer devices under high bias voltage is completely suppressed in the double layer devices.

Rare earth chelates with the same β-diketone ligands and structures should have similar energy levels. Hence, we can make use of reported energy levels of similar compounds to discuss charge injection in the complex 2 based devices. Among TTA containing complexes, Eu(TTA)phen was reported with respective lowest unoccupied molecular orbit (LUMO) and highest occupied molecular orbit (HOMO) values of −3.1 and −6.3 eV [16]. Considering that the work function of ITO is in the range of 4.6–4.8 eV, we get an energy barrier of more than 1.5 eV in the single layer device at the interface between ITO and the complex 2. The LUMO and HOMO values for TPD was reported as −2.2 and −5.4 eV, respectively. So in the double layer devices we get injection barriers of less than 0.8 eV at the ITO/TPD interface and 0.9 eV at the TPD/complex 2 interface. The introduction of hole transport layer lowers the hole injection barrier and enhances the hole transporting efficiency. This is the reason of the enhanced emission performance in the double later devices compared with that in the single layer ones. The work function of Al cathode is approximately −4.2 eV. Hence, an electron injection barrier of approximately 1.1 eV is resulted. Therefore, the device structure is far...
from optimized. Further study is being carried out to make further improvement.

4. Conclusions

Rare earth chelates of Sm(III) and Eu(III) were prepared from the reaction of their nitrate salts with HTTA and TPPO. The compositions of the complexes in the crystalline state are Sm(TTA)$_2$(TPPO)$_2$NO$_3$ and Eu(TTA)$_2$(TPPO)$_2$NO$_3$H$_2$O, respectively. The europium (III) complex shows identical emission pattern from both the crystalline powder and evaporated film, but their excitation spectra behave differently due to the existence of water molecules in the former. Because of poor carrier transporting balance single layer devices exhibit only very weak EL emission. Enhancement of EL efficiency was observed with the addition of hole transporting layer (TPD). The fact that decomposition occurs during evaporation indicates that although complex 2 contains only one nitrate and the ionic bonding is much less than that in the case of Eu(NO$_3$)$_3$phen, vacuum evaporation is not a suitable method to fabricate its thin films.

References
