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Electron-transport properties of rare earth chelates in organic electroluminescent devices

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Abstract

Electron-transporting properties of a series of trivalent rare earth ion (RE^{3+}) complexes in multilayer organic electroluminescent (OEL) devices have been studied. The emitting layer (EML) in the devices consists of trivalent europium (Eu^{3+}) complexes dispersed into PVK [poly(*N*-vinylcarbazole)] film. © 1997 Elsevier Science S.A.

Keywords: Organic electroluminescent devices; Rare earth chelates

1. Introduction

High radiance of multilayer organic electroluminescent (OEL) devices can be achieved at a low operating voltage because a carrier-transporting layer is introduced into the devices. Currently used electron-transporting materials, e.g., Alq_3 and PBD, however, have their own shortcomings. The former has an apparent electroluminescence (EL) which disturbs the EL emission spectrum of the emitting layer (EML). Other sorts of organic electron-transport layer (ETL) materials, e.g., the latter, have really poor stability. For these reasons, new ETL materials with good stability and no EL emission need to be developed.

Kido et al. have already reported red and green emissions from Eu^{3+} and trivalent terbium (Tb^{3+}) in their OEL devices, suggesting that rare earth (RE) complexes do not have good carrier-transport properties [1,2]. In this study the ETL properties of a series of RE chelates, RE(acetylacetonato)$_3$(monophenanthroline) [RE(AcA)$_3$phen] (RE = Y, La, Gd and Er) are first found. Since the RE chelates have excellent stability and no EL emission properties, they do not disturb the spectral properties of the EML, although the ETL and EML properties of OEL in Tb^{3+} complex have been observed already [3].

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2. Experimental details

RE(AcA)$_3$phen, Eu complexes and PVK were prepared by ourselves according to conventional methods.

Figs. 1 and 2 show the cell configurations and molecular structures of the materials used in this study, respectively. By changing the ratio of PVK:Eu complex, the concentration of PVK and Eu complex and the thickness of the ETL, we found that an optimal experimental condition is as follow: PVK (100 mg) and Eu(dibenzoylmethanato)$_3$(monophenanthroline) [Eu(DBM)$_3$phen] or Eu(dibenzoylmethanato)$_3$(bathophenanthroline) [Eu(DBM)$_3$bath] (50 mg) were dissolved in 10 ml $CHCl_3$ and then the solutions were spin-coated onto a glass substrate with ITO (20 Ω/□) anode to form a thin film which has hole-transport layer (HTL) and EML functions, respectively. RE(AcA)$_3$phen and an Al cath-

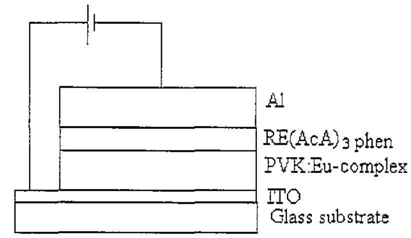

Fig. 1. The cell configuration used in this study. The cell structure is ITO/PVK:Eu(DBM)$_3$phen [or Eu(DBM)$_3$bath]/RE(AcA)$_3$phen (RE = Y, La, Gd and Er)/Al.

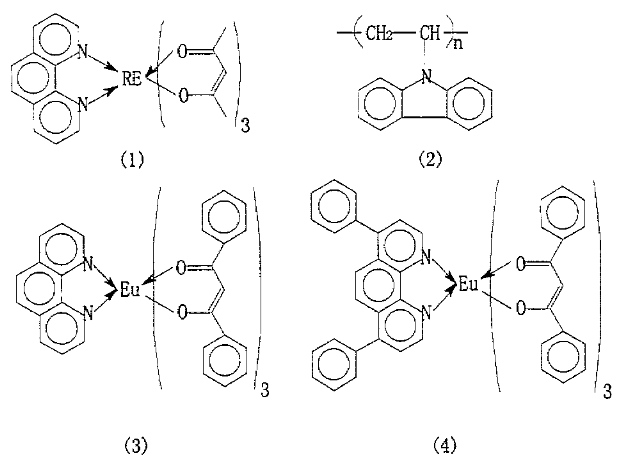

Fig. 2. The molecular structures of the materials used in the study: (1) $RE(AcA)_3phen$ (RE = Y, La, Gd and Er); (2) PVK; (3) $Eu(DBM)_3phen$; (4) $Eu(DBM)_3bath$.

ode were vacuum deposited onto the PVK:Eu complex layer successively. The thickness of the dispersed PVK layer was about 100 nm. Then a 30 nm thick $RE(AcA)_3phen$ (RE = Y, La, Gd and Er) layer was vacuum deposited at 2×10^{-5} torr onto the polymer layer. A 150 nm thick aluminium layer was deposited on the organic layer as the top electrode at 5×10^{-5} torr. The deposition rates were maintained at 0.2–0.4 nm s^{-1} for the ETL materials, and 1–2 nm s^{-1} for aluminium, respectively. The emitting area of the cells with the structure shown in Fig. 1 was 3 mm × 8 mm, and luminance was measured with a 198A1 Luminance Meter at room temperature. The EL spectra of the devices are determined with a Hitachi F-4000 spectrophotometer.

3. Results and discussion

For the devices with a $RE(AcA)_3phen$ (RE = Y, La, Gd and Er) layer and those without such a layer, threshold voltages are 11 and 17 V, respectively. Thus it was found that the threshold voltage of the devices using RE chelates (about 11 V) was much lower than that of the devices without the chelates (17 V). Luminescence of 48 cd m^{-2} was observed from the devices using RE chelates for an applied voltage of 17 V. It was interesting that for the devices with an RE chelate layer the luminance increased with increasing voltage up to 24 V, and that for the devices without a chelate layer only very faint EL emissions from the Eu^{3+} and blue breakdown sparkles were observed when the d.c. voltage was up to or above 17 V. By inserting a $RE(AcA)_3phen$ thin film between the Al electrode and emitting layer, the OEL emission intensities of the devices were considerably increased in comparison with those of the devices without an RE complexes layer. So we can say that, as we expected, the RE chelates have good ETL properties.

It is well known that the RE^{3+} (RE = Y, La and Gd) ions have inert electron structures and do not have light-emission properties and that Er^{3+} chelate also does not have luminescent properties. Because the chemical properties of these ions are extremely similar to that of Tb^{3+}, the chelates of these RE^{3+} cations with the same organic ligands, like $Tb(AcA)_3phen$, might exhibit ETL ability too. So we tried to use Y, La, Gd or Er chelates to substitute for $Tb(AcA)_3$-phen as ETL materials. These RE chelates should possess stability because the ternary chelates have the structure of inner complex salts. They are more enduring to heat, electricity and oxidation than current ETL materials, e.g., PBD. Moreover these materials can be made into thin films by vacuum deposition or molecularly dispersed in the polymer skeleton by spin-coating. Fig. 3(a) and (b) shows the spectra

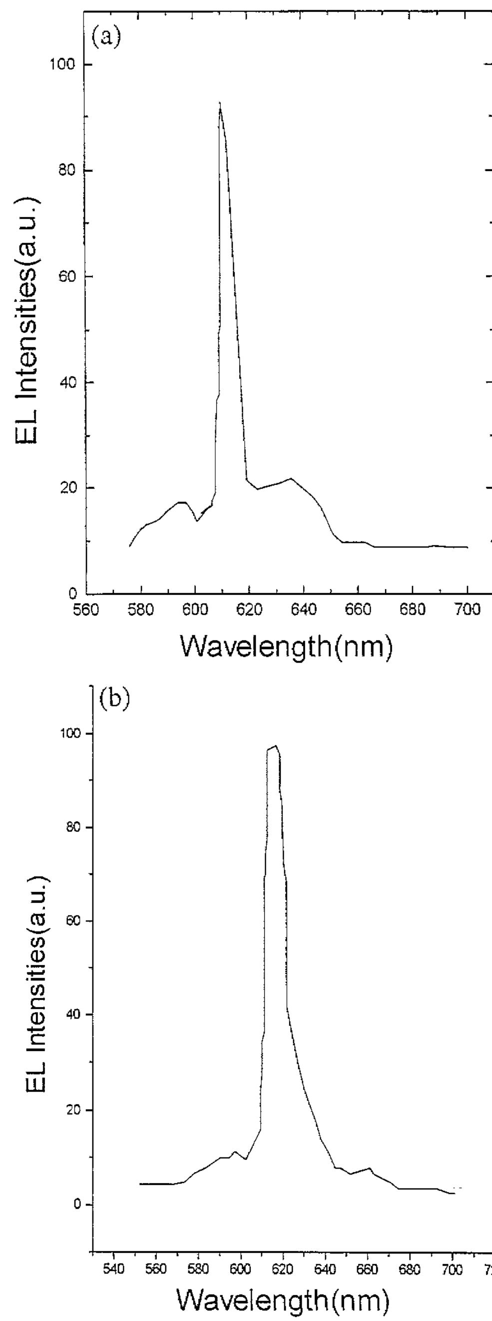

Fig. 3. The spectra of the devices: (a) emitting layer is PVK:$Eu(DBM)_3$-phen; (b) Emitting layer is PVK:$Eu(DBM)_3bath$.

of the devices using Eu(DBM)$_3$phen or Eu(DBM)$_3$bath as emitting layer, respectively.

4. Conclusions

In conclusion, the RE chelates were used as ETL materials. The ETL can increase the EL luminance of devices consisting of ITO/PVK:Eu complexes/RE chelates. The purpose of choosing a PVK polymer-dispersed Eu complex is to obtain OEL devices with high durability. Our results indicated that the RE chelates really lowered the driving voltage and increased the stability of OEL devices.

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