

Photo- and Electro-luminescence of the New Ternary Europium(III) Complex

Chen Xia DU^{1*}, Zhi Qiang WANG¹, Qi XIN², Yang Jie WU¹, Wen Lian LI^{2*}

¹Department of Chemistry, Zhengzhou University, Zhengzhou 450052

²Changchun institute of optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033

Abstract: A new luminescent europium complex [Eu(DBM)₃dpq] (DBM = 1, 3-diphenyl-1, 3-propanedionate and dpq=dipyrido[2,3-f][2',3'-h]quinoxaline) has been synthesized and shows intense red emission under UV excitation. With the device structure ITO/TPD/Eu(DBM)₃dpq:TPD (1:2)/Gd(DBM)₃bath/Mg:Ag, sharp-band red emissions with low turn-on voltage of 3V and high brightness of 304cd m⁻² were achieved.

Keyword: Europium complex, photoluminescence, electroluminescence.

In recent years, the interest in developing luminescent lanthanide complexes has been greatly stimulated by their potential use in electroluminescent displays¹. Europium complexes appear most attractive in view of the high photoluminescent efficiency and the high monochromatic red light that are widely exploited in full-color displays². It has been approved that the second ligand plays an important role in europium complexes, the synergistic complexation of the second ligand can not only lead to the construction of efficiently emitting europium(III) complexes but also improve the volatility and electron-transporting ability of the complexes³. Therefore, it is important to design europium complexes with new second ligands for practical application. Azatriphenylene-type ligands have been approved to be a very promising class of antennae for Eu(III) and Tb(III) luminescence in solution⁴. The feature of an exceptionally small energy gap between lowest single and triplet states implies that fast and essentially irreversible energy transfer to the lanthanide ions is possible, which is an important requirement to obtain efficient emitting europium complexes. In this paper, we prepared a new ternary europium complex Eu(DBM)₃dpq with dpq as second ligand, and investigated its photo- and electro-luminescent properties.

Experimental

The dpq ligand was prepared in a two-step process: 1,10-phenanthroline was firstly oxidized to a dione, which reacts with ethylenediamine to afford dpq⁵ (56% yield).

* E-mail: dcx@zzu.edu.cn

$\text{Eu}(\text{DBM})_3\text{dpq}$ was synthesized by mixing 1 mmol EuCl_3 , 3 mmol HDBM and 1 mmol dpq in ethanol solution, then neutralized with 3 mmol NaOH aqueous solution. The complex was further purified by reprecipitation from the mixed solvent of ethanol and acetone, and finally dried in vacuum at 80°C for 48 h (84% yield). mp: $168\sim 169^\circ\text{C}$. $\text{EuC}_{59}\text{H}_{41}\text{N}_4\text{O}_6$ Calcd.(%): C 67.24, H 3.89, N 5.32, Found(%): C 67.30, H 3.95, N 5.41.

EL devices were fabricated by sequential thermal desposition of the materials and the cathode onto an ITO substrate under the pressure of 10^{-7} Torr. The emission area is 10 mm^2 . The layer thickness was controlled in *vacuo* with a quartz crystal monitor. The EL and PL spectra were measured with a Hitachi 4000 fluorescence spectrophotometer and the brightness was measured by a 1980A spot photometer.

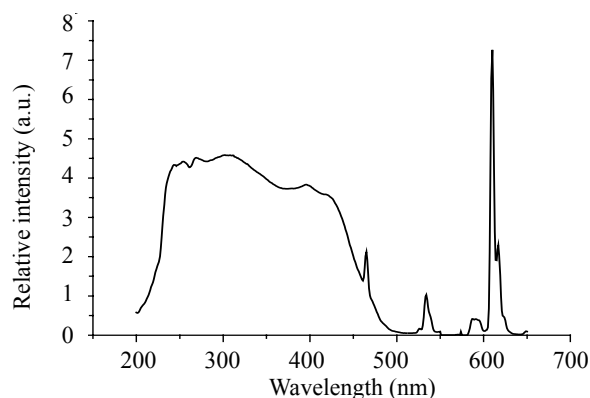
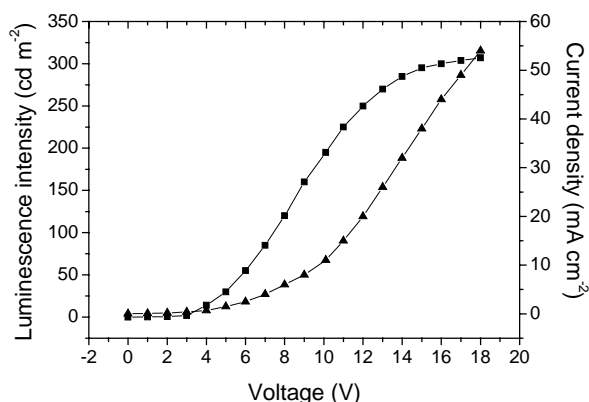
Results and Discussion

IR spectrum of the ternary complex shows the characteristic ring vibration of dpq at 1409 cm^{-1} . The strong band at 1596 cm^{-1} , 1550 cm^{-1} correspond to the $\nu_{\text{C=O}}$ stretching vibration of coordinated DBM ligands. The absence of absorption bands in the region of $3200\text{--}3500\text{ cm}^{-1}$ proves that there is no coordinated water in the complex. The thermogravimetric analytic(TGA) results indicate that the complex melts at 204°C , and decomposes immediately above 360°C , as indicated by a significant weight loss(83.5 %) in the range of $360\text{--}575^\circ\text{C}$.

In the UV spectrum of the complex, the most intense band is at 270 nm, corresponding to $\pi - \pi^*$ absorption of dpq ligand. The excitation spectrum of $\text{Eu}(\text{DBM})_3\text{dpq}$ is dominated by three poorly resolved broad absorption bands at 270 nm, 320 nm and 430 nm(**Figure 1**), the sharp peaks at 467, 536 nm originate from Eu^{3+} ion (${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$) absorption transitions. Comparison of the excitation and absorption spectra of the complex indicated that the dpq ligand exhibits strong antenna efficiency. The emission spectrum(**Figure 1**) measured following excitation of the organic ligands at 400 nm shows typical red emission of Eu^{3+} ion.

It is generally considered that only europium complexes with excellent PL properties can be considered as candidates of electroluminescent materials. For comparison, the relative PL intensities of $\text{Eu}(\text{DBM})_3\text{dppz}$ were also determined. When excited with the maximum absorption of the complexes at about 400 nm, the emission intensity of $\text{Eu}(\text{DBM})_3\text{dpq}$ is about twelve times stronger than that of $\text{Eu}(\text{DBM})_3\text{dppz}$ ⁶ and three times stronger than that of $\text{Eu}(\text{TTA})_3\text{dppz}$ ³. The excellent PL efficiency of $\text{Eu}(\text{DBM})_3\text{dpq}$ may be attributed to both the efficient ligand-to-metal energy transfer and inefficient nonradiation deactivations of the metal-centered excited state.

An earlier study^{7,8} confirmed that some destructive effects causing device degradation could be somewhat avoided by introduction of a mixed layer. Inspired by this result, devices with mixed layer of $\text{Eu}(\text{DBM})_3\text{dpq}$ and TPD were also described in this study. By mixing TPD and $\text{Eu}(\text{DBM})_3\text{dpq}$, a bipolar transport and emitting layer was formed and as a result, carrier recombination can be positioned inside the organic layer without a high local electric field. By properly selecting the mixing ratio of $\text{Eu}(\text{DBM})_3\text{dpq}$ to TPD, balancing electrons and holes injection and transport can be achieved, resulting in higher EL efficiency and better stability of the EL device. Further-

Figure 1 The excitation and emission spectra of $\text{Eu}(\text{DBM})_3\text{dpq}$ **Figure 2** The luminescence intensity-current density-voltage characteristics of Device 2

more, the emitting zone was significantly broadened in the structure compared to that in the devices with clear-cut interfaces, which could be another favorable factor for improving EL efficiency.

Three EL devices with structure of ITO/TPD(30 nm)/ $\text{Eu}(\text{DBM})_3\text{dpq}$:TPD(50 nm)/ $\text{Gd}(\text{DBM})_3\text{bath}$ (30 nm)/Mg:Ag were fabricated. The TPD-to- $\text{Eu}(\text{DBM})_3\text{dpq}$ weight ratios were 1:1 (Device 1), 2:1 (Device 2) and 3:1 (Device 3) respectively. Among these three devices, device 2 shows the highest EL efficiency throughout the measured current density range, which implies that balanced electrons and holes injection could be achieved in it. Considering the different carrier transport properties of TPD and $\text{Eu}(\text{DBM})_3\text{dpq}$, it is of great interest to compare this result with that of our early work⁷. With the same structure device, the optimum ratio of TPD-to- $\text{Eu}(\text{DBM})_3\text{bath}$ in the mixed layer was 1:2, while that of TPD-to- $\text{Eu}(\text{DBM})_3\text{dpq}$ in this study was 2:1, which suggested that complex $\text{Eu}(\text{DBM})_3\text{dpq}$ is a more efficient electron transporting material in comparison with $\text{Eu}(\text{DBM})_3\text{bath}$.

Device 2 shows a sharp red emission at 613 nm due to $^5D_0 \rightarrow ^7F_2$ transition of the Eu^{3+} ion, and no exciplex emission was observed. **Figure 2** shows the luminescence intensity-current density-voltage characteristics of the device. From **Figure 2** we can see that the turn-on voltage is 3V, the luminance intensity increases with increasing injection current and bias voltage, the maximum emission intensity of 304 cd m^{-2} is observed at 18V and 56 mA cm^{-2} . Considering the excellent PL property of $\text{Eu}(\text{DBM})_3\text{dpq}$, both the configurational and compositional structure of the present device need to be further optimized, the investigation is in progress.

Acknowledgments

This work is supported by the Natural Science Foundation of Henan, China (No. 0312000700).

References

1. J. Kido, Y. Okamoto, *Chem. Rev.*, **2002**, 102(6), 2357.
2. L. Huang, K. Z. Huang, C. H. Huang, F. Y. Li, *J. Mater. Chem.*, **2001**, 11, 790.
3. P. P. Sun, J. P. Duan, H. T. Shih, *Appl. Phys. Lett.*, **2002**, 81(5), 792.
4. B. H. Bakker, M. Goes, N. Hoebe, *Coord. Chem. Rev.*, **2000**, 208, 5.
5. J. Q. Tao, W. Z. Shi, X. Zhuang, *Chin. J. Inorg. Chem.*, **2002**, 18(3), 255.
6. B. Liang, M. X. Zhu, W. G. Zhu, *Chin. Chem. Lett.*, **2003**, 14(1), 43.
7. C. J. Liang, D. Zhao, Z. R. Hong, D. X. Zhao, *Appl. Phys. Lett.*, **2000**, 76(1), 69.
8. Z. R. Hong, C. J. Liang, R. G. Li, W. L. Li, *Adv. Mater.*, **2001**, 13(16), 1241.

Received 15 April, 2004