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Bright red electroluminescent devices using novel second-ligand-contained europium complexes as emitting layers

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With two novel second ligands, 2-(2-pyridyl)benzimidazole (HPBM) and 1-ethyl-2-(2-pyridyl)benzimidazole (EPBM), two europium complexes, $Eu(DBM)_3HPBM$ and $Eu(DBM)_3EPBM$ (DBM = dibenzoylmethanato), were prepared and used as emitting materials in organic electroluminescent (EL) devices. The devices with the structures ITO/TPD/$Eu(DBM)_3HPBM$ (or $Eu(DBM)_3EPBM$)/Al and ITO/TPD/$Eu(DBM)_3EPBM$/AlQ/Al emit red light originating from the europium complexes. The EL luminance of $Eu(DBM)_3EPBM$ is much higher than that of $Eu(DBM)_3HPBM$. A maximum luminance of 180 cd m^{-2} in the triple layered device of $Eu(DBM)_3EPBM$ was achieved at 18 V.

Introduction

Organic electroluminescent diodes (OELD) have been intensively studied throughout the world owing to their potential application in the next generation of full-color flat panel displays. For commercial application, three primary colors of blue, green and red are basically required. Europium complexes are the most suitable luminescent materials for red EL devices because they can emit highly monochromatic red light at around 614 nm, while other red organic emitting materials give broad emission spectra with bandwidths of around 100 nm which result in dull colors. Hence, europium complexes have been studied for nearly ten years.[1–5] However, compared with green and blue devices, a bright red device has not yet been fabricated with sufficiently high performance in spite of their excellent photoluminescence (PL) properties.

One of the ways to improve the europium complexes' EL performance is to introduce a second ligand, such as 1,10-phenanthroline (Phen), into the complex. The role of the second ligand is not only to saturate the coordination number of the europium ion but also to improve the volatility and stability of the europium complex.[6] Li *et al.* reported that carrier-transport characteristics and light-emitting properties can be improved by using bathophenanthroline (Bath) as the second ligand, which has two more phenyl groups than Phen.[7] We found previously that different second ligands can give rise to not only PL but also EL of rare earth complexes.[8] Hence, it is obvious that the second ligand plays an important role in europium complex-based OELD. However until now, only Phen and Bath have been reported to be used in this way. It is necessary to find other suitable second ligands to study the relationship between the chemical structure and EL properties.

In this paper, DBM was chosen as the first ligand due to its high PL and EL efficiency in europium complexes. We designed and synthesized two novel second ligands, 2-(2-pyridyl)benzimidazole (HPBM) and 1-ethyl-2-(2-pyridyl)benzimidazole (EPBM), because these two ligands can coordinate with the europium ion *via* two nitrogen atoms, just like Phen. However, the C–C bond next to the nitrogen atoms of these two ligands can rotate freely compared with the rigid structure of Phen. In addition, the hydrogen atom bonding with the nitrogen atom on the benzimidazole ring can be substituted by alkyl chains or other electron-donating groups. We expect that alkyl chains could improve the film formation, as occurs in Langmuir–Blodgett films. For these reasons, two volatile europium complexes were prepared for the fabrication of double-layer-type and triple-layer-type EL devices. The preparation, characterization and EL properties of these europium complexes are discussed.

Experimental

HPBM was synthesized according to the procedures in reference 9. The melting point agreed with the previously reported data.

EPBM was prepared according to the following procedure: NaH, which was washed with anhydrous hexane, was added into anhydrous *N*,*N*-dimethylformamide (DMF, 15 mL) and dried HPBM (4.3 g) under N_2. The mixture was stirred for 0.5 h at room temperature. After adding with C_2H_5Br (2.4 g), the mixture refluxed for 10 hours. The resulting solid was filtered off. Then water was added dropwise to the filtered solution until it became turbid. The crude product was solidified at room temperature and recrystallized from a mixed DMF–water solvent. The residue was passed through a column with alumina ($CH_2Cl_2 : CH_3OH = 9 : 1$) to remove impurities. The solvent was evaporated off on a rotary evaporator and the residue dried under vacuum for 4 hours to give a pure product as yellow crystals (mp 58 °C). Calc. for $C_{14}H_{13}N_3$: C, 75.10; H, 10.10; N, 9.38. Found: C, 75.34; H, 10.07; N, 9.40%. ^1H NMR (300 MHz, $CDCl_3$) δ 1.52 (t, 3H), 4.90 (q, 2H), 7.38 (m, 3H), 7.51 (d, 1H), 7.91 (m, 2H), 8.51 (d, 1H), 8.72 (d, 1H).

$Eu(DBM)_3HPBM$ and $Eu(DBM)_3EPBM$ were synthesized by the conventional method.[10] 3 mmol HDBM and 1 mmol HPBM (or EPBM) were dissolved in hot ethanol under stirring. After cooling, 3 mmol of a 2 mol mL^{-1} NaOH aqueous solution was added to the resulting solution under stirring before dropwise addition of 1 mmol $Eu(NO_3)_3$ aqueous solution. Then, the mixture was stirred at 60 °C for 0.5 h. The crude product was collected by filtration and washed with ethanol. The complexes were purified by reprecipitation from

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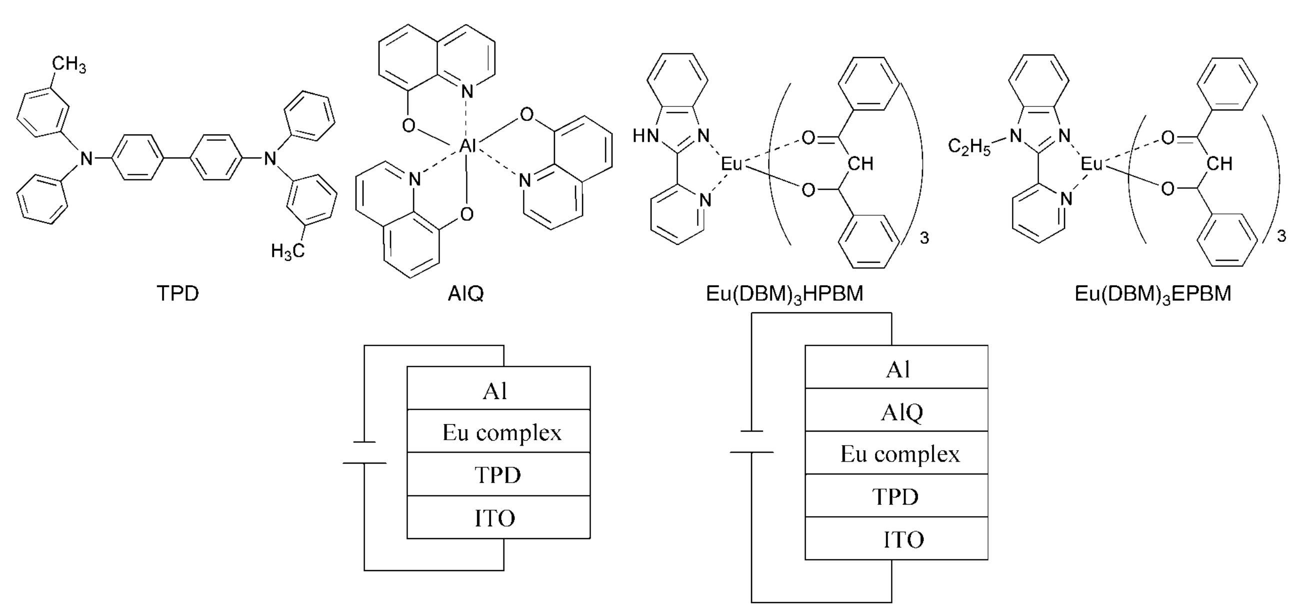

Fig. 1 The chemical structures of the materials and the structures of the EL devices.

ethanol and vacuum drying. Calc. for Eu(DBM)$_3$HPBM ($C_{57}H_{42}O_6N_3Eu$): C, 67.32; H, 4.13; N, 4.13. Found: C, 66.48; H, 4.09; N, 4.56%. Calc. for Eu(DBM)$_3$EPBM(H_2O) ($C_{59}H_{48}O_7N_3Eu$): C, 66.80; H, 4.45; N, 3.83. Found: C, 66.69; H, 4.52; N, 3.95%.

Fig. 1 shows the chemical structures of the materials and the configurations of the EL devices. The double-layer-type devices were fabricated as ITO/*N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) (40 nm)/Eu complex (40 nm)/Al (100 nm) while the triple-layer-type EL device was fabricated as ITO/TPD (40 nm)/Eu(DBM)$_3$EPBM/tris(8-quinolinolato)aluminium (AlQ)/Al (100 nm) with different thicknesses of Eu(DBM)$_3$EPBM and AlQ. The total thickness of the Eu complex and AlQ layer was 80 nm.

The devices were fabricated by sequential thermal deposition of the organics and the aluminium cathode onto an indium tin oxide (ITO) substrate below a pressure of 1×10^{-3} Pa in one run. The ITO glass, supplied by China Southern Glass Holding Co., Ltd., is about 150 nm thick with a sheet resistance of $15\,\Omega\,\square^{-1}$. The cleaning procedure included sonication in detergent solution, pure water, acetone, toluene and ethanol. The organic materials were evaporated from molybdenum crucibles with deposition rates in the range of 0.1–0.3 nm s^{-1}. The Al cathode was evaporated from a tungsten wire basket at higher deposition rates (1.2 nm s^{-1}). The mask could be changed automatically by patterning contacts and the emitting area was about 20 mm^2. PL and EL were measured with a Hitachi F-4500 fluorescence spectrophotometer. The brightness was measured with a ST-86LA spot photometer and a close-up lens providing a focal spot of 5 mm. The layer thickness was controlled *in vacuo* with an IL-1000 quartz crystal monitor and was also corrected by a Dektak[11] surface profile measuring system. All measurements were carried out at room temperature under ambient atmosphere.

Results and discussion

Double layered EL device

The PL spectra of the two europium complexes in films on quartz substrates and the EL spectra of ITO/TPD (40 nm)/Eu(DBM)$_3$HPBM (or Eu(DBM)$_3$EPBM) (40 nm)/Al (100 nm) double-layered devices are shown in Fig. 2 and 3, respectively. It can be seen that the EL and PL spectra are very similar, indicating hole–electron recombination in the europium complex layers only. They both exhibit five sharp emission peaks at 580, 590, 612, 651 and 696 nm corresponding to the $^5D_0 \rightarrow ^7F_j$ ($j = 0$–4) transitions of trivalent europium ion, respectively. However, the EL peak at 536 nm (in Fig. 3) cannot be ascribed to the europium complexes. It is thought to

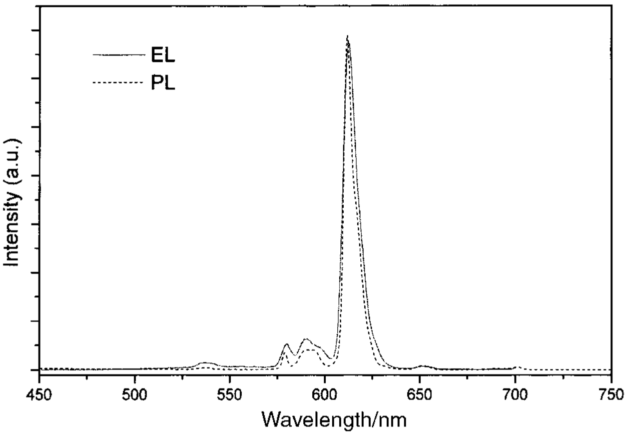

Fig. 2 The PL spectrum (dashed line) of Eu(DBM)$_3$HPBM in a film on a quartz substrate ($\lambda_{ex} = 360$ nm) and the EL spectrum (solid line) of the ITO/TPD (40 nm)/Eu(DBM)$_3$HPBM (40 nm)/Al (100 nm) device.

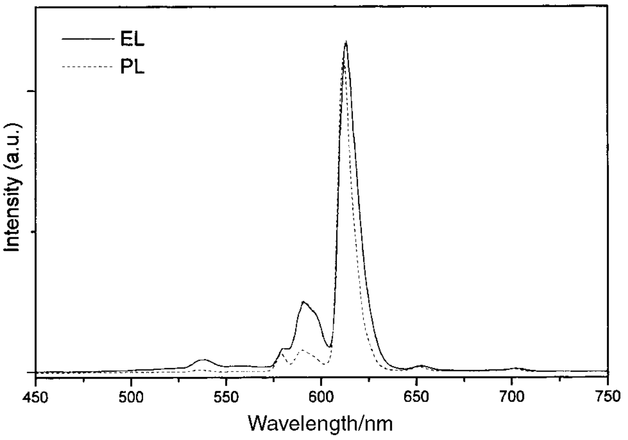

Fig. 3 The PL spectrum (dashed line) of Eu(DBM)$_3$EPBM in a film on a quartz substrate ($\lambda_{ex} = 360$ nm) and the EL spectrum (solid line) of the ITO/TPD (40 nm)/Eu(DBM)$_3$EPBM (40 nm)/Al (100 nm) device.

be the result of exciplex formation at the interface of the europium complex and TPD layers.[5]

For Eu(DBM)$_3$HPBM, red light emission with a maximum luminance of 1.14 cd m^{-2} was observed at 23 V and 36 mA cm^{-2}. For the Eu(DBM)$_3$EPBM, brightness of 29 cd m^{-2} was achieved at 11 V and 210 mA cm^{-2}. It is apparent that the EL luminance of Eu(DBM)$_3$EPBM is much higher than that of Eu(DBM)$_3$HPBM. In contrast, the relative PL efficiency of Eu(DBM)$_3$EPBM in chloroform solution is lower than that of Eu(DBM)$_3$HPBM. This unusual fact still remains to be addressed.

Triple layered EL device

In order to obtain higher luminance, AlQ was added as an electron transport layer and Eu(DBM)$_3$EPBM was used as an emitting layer in the triple-layer-type EL devices. When the total thickness of the europium complex and AlQ layers was kept constant at 80 nm, we found the spectral features varied with the thickness ratio of the two layers.

Fig. 4 shows the EL spectra with different thickness ratios of Eu(DBM)$_3$EPBM and AlQ. It can be seen that the spectral features are sensitive to the thicknesses of the emitting and electron-transporting layers. The EL device with 40 nm thick Eu(DBM)$_3$EPBM and 40 nm thick AlQ exhibits only the emission from Eu(DBM)$_3$EPBM, which is characteristic of the Eu^{3+} transition of $^5D_0 \rightarrow {}^7F_j$($j = 0$–4). However, upon reducing the thickness of the emitter layer, a broad band with a maximum at 510 nm appears and increases, owing to the emission from the electron transporting layer AlQ. To the naked eye, the color of the emission changes from red to yellow-orange. This can be attributed to the synergistic emission from both the europium complex and AlQ layers. In the ITO/TPD (40 nm)/Eu(DBM)$_3$EPBM (40 nm)/AlQ (40 nm)/Al (100 nm) device a pure, bright red colour was obtained with a maximum luminance of 180 cd m^{-2} at 18 V.

Compared with the luminance of the ITO/TPD (40 nm)/ Eu(DBM)$_3$EPBM (40 nm)/Al double layered device, the luminance level of the triple layered device is substantially improved because AlQ is a good electron-transporting material and Eu(DBM)$_3$EPBM, like most europium complexes, shows poor carrier transport properties.[6,7]

Compared with the luminance of the previously reported complex Eu(DBM)$_3$Phen,[7] the luminance level of Eu(DBM)$_3$EPBM is also improved due to the different chemical structures of Phen and EPBM. Among the three europium complexes, the EL luminance of the europium complex with EPBM as the second ligand is the highest.

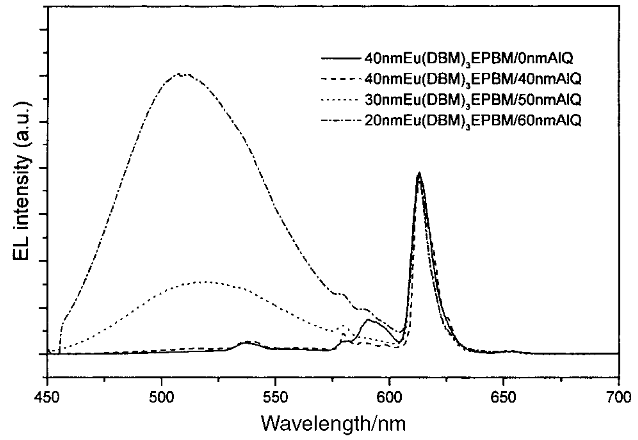

Fig. 4 The normalized EL spectra of the double- (solid line) and triple-layer-type devices with different Eu(DBM)$_3$EPBM and AlQ thickness ratios. The total Eu(DBM)$_3$EPBM and AlQ thickness is fixed at 80 nm.

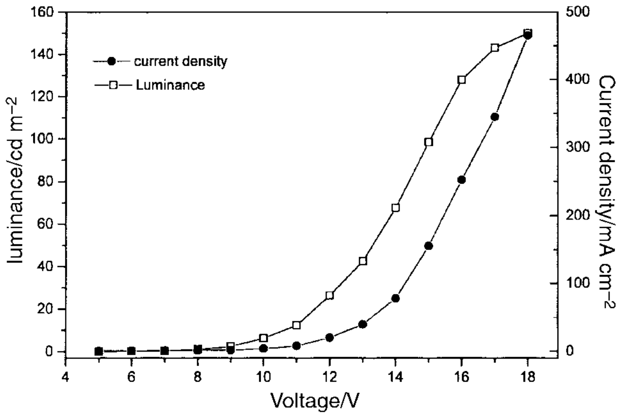

Fig. 5 The luminance–current density–voltage characteristics of an ITO/TPD (40 nm)/Eu(DBM)$_3$EPBM (40 nm)/AlQ (40 nm)/Al (100 nm) triple-layer-type device.

I–V curve

The luminance–current density–voltage characteristics of a triple-layer-type EL device of ITO/TPD (40 nm)/ Eu(DBM)$_3$EPBM (40 nm)/AlQ (40 nm)/Al (100 nm) is shown in Fig. 5. It shows that the luminescence increases with increasing injection current as well as bias voltage. The maximum EL efficiency of 0.05 lm W^{-1} in the triple-layer-type device was obtained at 10 V. However, the efficiency at the maximum luminance was only 0.0056 lm W^{-1} (Fig. 6).

It is thus concluded that two fluorescent sublimable complexes, Eu(DBM)$_3$HPBM and Eu(DBM)$_3$EPBM, can be used as emitting materials, especially Eu(DBM)$_3$EPBM.

Conclusions

Two europium complexes with two different novel second ligands were synthesized and used to prepare double-layer and triple-layer EL devices. A very sharp bright red EL spectral band originating from Eu(DBM)$_3$EPBM was obtained with a maximum luminance of 180 cd m^{-2} from a triple-layer-type EL device. By comparing the EL luminance and the chemical structures of three europium complexes with different second ligands (Phen, EPBM, HPBM), some helpful information was obtained for the development of red and multicolor EL display applications. In order to obtain higher luminance, other methods, such as using LiF/Al or Mg : Ag cathodes or employing a codeposition technique with other materials, are in progress.

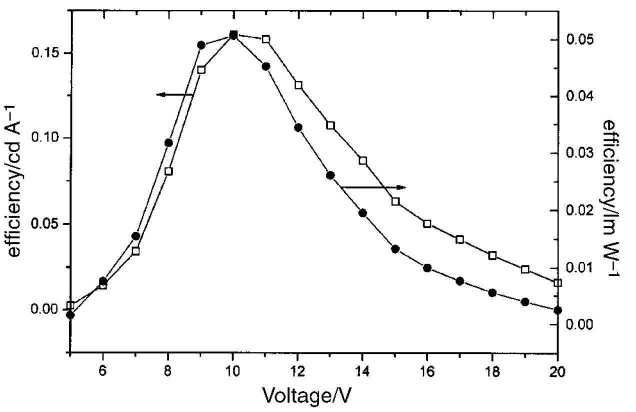

Fig. 6 The EL efficiency in lm W^{-1} and cd A^{-1} characteristics of the ITO/TPD (40 nm)/Eu(DBM)$_3$EPBM (40 nm)/AlQ (40 nm)/Al (100 nm) triple-layered device.

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References

1 J. Kido, K. Nagai, Y. Okamoto and T. Skothein, *Chem. Lett.*, 1991, 1267.

2 J. Kido, H. Hayase, K. Hongawa, K. Nagai and K. Okuyama, *Appl. Phys. Lett.*, 1994, **65**, 3124.

3 K. Okada, Y. F. Wang, T. M. Chen, M. Kitamura, T. Nakaya and H. Inoue, *J. Mater. Chem.*, 1999, **9**, 3023.

4 C. Adachi, M. A. Baldo and S. R. Forrest, *J. Appl. Phys.*, 2000, **87**, 8049.

5 C. J. Liang, D. Zhao, Z. R. Hong, D. X. Zhao, X. Y. Liu, W. L. Li, J. B. Peng, J. Q. Yu, C. S. Lee and S. T. Lee, *Appl. Phys. Lett.*, 2000, **76**, 67.

6 T. Sano, M. Fujita, T. Fujii, Y. Hamada, K. Shibata and K. Kuroki, *Jpn. J. Appl. Phys.*, 1995, **34(4A)**, 1883.

7 L. Liu, W. L. Li, Z. R. Hong, J. B. Peng, X. Y. Liu, C. J. Liang, Z. B. Liu, J. Q. Yu and D. X. Zhao, *Synth. Met.*, 1997, **91**, 267.

8 X. C. Gao, H. Cao, C. H. Huang, S. Umitani, G. Q. Chen and P. Jiang, *Synth. Met.*, 1999, **99**, 127.

9 A. W. Addison and P. J. Burke, *J. Heterocycl. Chem.*, 1981, **18**, 803.

10 L. R. Melby, N. J. Rose, E. Abramson and J. C. Caris, *J. Am. Chem. Soc.*, 1964, **86**, 5117.

11 J. Kido, K. Nagai and Y. Okamoto, *J. Alloys Compd.*, 1993, **192**, 30.