

Bright and monochromatic red light-emitting electroluminescence devices based on a new multifunctional europium ternary complex

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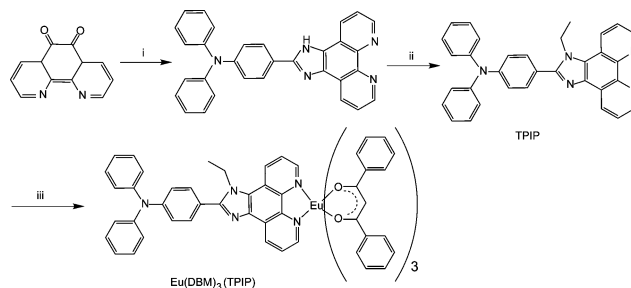
Received (in Cambridge, UK) 18th December 2002, Accepted 4th February 2003

First published as an Advance Article on the web 17th February 2003

A novel europium(III) complex, tris(dibenzoylmethanato)(2,4'-triphenylamino)imidazo[4,5-f][1,10-phenanthroline]europium(III), Eu(DBM)₃(TPIP), is synthesized. The light-emitting center, hole-transporting triphenylamine and electron-transporting phenanthroline fragments are integrated into one molecule. A single-layer device of ITO/Eu(DBM)₃(TPIP)(60 nm)/Mg_{0.9}Ag_{0.1}/Ag exhibits Eu^{III}-based pure red emission with a maximum brightness of 19 cd m⁻² at 13.5 V and 280 mA cm⁻², and an onset driving voltage of 8 V. A four-layer device of ITO/TPD (20 nm)/Eu(DBM)₃(TPIP) (40 nm)/BCP (20 nm)/AIQ(40 nm)/Mg_{0.9}Ag_{0.1}/Ag gives a maximum Eu^{III}-based pure red emitting luminance of 1305 cd m⁻² at 16 V and 255 mA cm⁻² with an onset driving voltage of 6 V; the maximum external quantum yield and luminous yield are estimated to be 0.85% and 1.44 lm W⁻¹, respectively, at 7.5 V and 0.25 mA cm⁻².

Transition metal and lanthanide complex-based electroluminescence (EL) devices are currently being keenly pursued. However, the EL device parameters reported for lanthanide (e.g. Eu^{III} and Tb^{III}) complexes, have not been as encouraging as expected, compared to those for certain transition metal complexes,^{1,2} although Eu^{III} or Tb^{III} complexes show sharp photoluminescence (PL) peaks with theoretical PL quantum yields up to unity.³ For single-layer EL devices based on pure Eu^{III} complexes, few of them could attain brightness greater than 10 cd m⁻².^{4,6} Hong and co-workers reported a highly efficient EL device made of a mixed Eu(DBM)₃(bath) and TPD layer with an external quantum efficiency of 4.6%, but the efficiency was attainable at current density of only 0.01 mA cm⁻².⁴ The multilayer devices using TPD as hole-transporting layer, AIQ as electron-transporting layer and BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) as hole-blocking layer,² could obtain greatly improved brightness, but few of them showed brightness greater than 1000 cd m⁻².⁵ By incorporating light-emitting center, hole-transporting triphenylamine and electron-transporting phenanthroline fragments into one molecule, we synthesized a new bidentate ligand and its Eu^{III} ternary complex. By using this newly synthesized Eu^{III} complex as dopant-free emitters, bright and high-efficient electroluminescence were obtained.

The new ligand TPIP and its Eu^{III} complex were synthesized by following the synthetic route shown in Scheme 1.† Both a single-layer device of ITO/Eu(DBM)₃(TPIP)(60 nm)/Mg_{0.9}Ag_{0.1}/Ag and a four-layer device of ITO/TPD(20 nm)/Eu(DBM)₃(TPIP)(40 nm)/BCP(20 nm)/AIQ(40 nm)/Mg_{0.9}Ag_{0.1}/Ag were made by successive thermal evaporation of organic materials and metal electrode materials in high vacuum (<8 × 10⁻⁴ Pa) onto pre-cleaned ITO substrate. The instrumentations for EL measurements were the same as before.⁷ EL spectra for the single- and four-layer devices, and PL spectra for Eu^{III} complex powder are compared in Fig. 1. The powder exhibited four PL peaks at 579, 594, 612 and 653 nm, corresponding to ⁵D₀ → ⁷F_j (j = 0–3) transitions, respectively. The single-layer EL device showed a shoulder centered at 538



Scheme 1 Synthetic route to TPIP and Eu(DBM)₃(TPIP). Reagents and conditions: i, 4-triphenylaminobenzaldehyde, HAc–NH₄Ac, 4 h, 80%; ii, dmf, NaH, C₂H₅Br, reflux 24 h, 53%; iii, CHCl₃, Eu(DBM)₃·2H₂O, reflux 1 h.

nm assigned to ⁵D₁ → ⁷F₁ transition,⁸ in addition to three peaks for ⁵D₀ → ⁷F_j (j = 0–2) transitions at 579, 590 and 612 nm respectively. For the four-layer device, three peaks due to ⁵D₁ → ⁷F₁ transition at 538 nm, ⁵D₀ → ⁷F₀ transition at 580 nm and ⁵D₀ → ⁷F₂ transition at 612 nm were strong enough to be recognizable, while ⁵D₀ → ⁷F₁ transition at ~580 nm almost vanished compared to the single-layer device. It is worth mentioning that the EL spectra for both of the EL devices were of the feature with Eu^{III}-centered electric dipolar transition (⁵D₀ → ⁷F₂) being the strongest, similarly to that observed for the powder, indicating that the recombination of excitons and holes occurred in the Eu^{III} complex layer. As seen from Fig. 2, the maximum luminance of 19 cd m⁻² which was achieved at 13.5 V and 280 mA cm⁻² for the single-layer device, compares favourably to similar devices so far reported.⁶ The turn-on voltage, which is defined as the voltage required to achieve the luminance of 1 cd m⁻² for this device, was found to be ~8 V which is comparable in magnitude to many organic EL devices, and is obviously superior to EL devices made in our group with simple bidentate N-heterocyclic ligand-containing Eu^{III} ternary

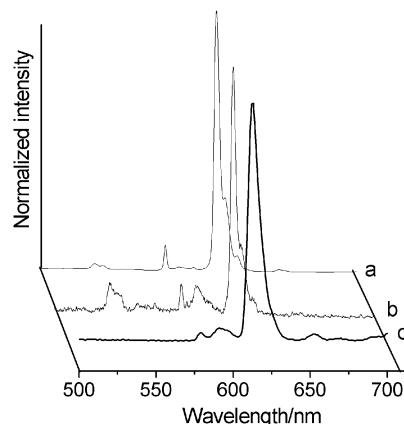


Fig. 1 Normalized EL spectra for the four-layer device at bias voltage of 16 V (a) and the single-layer device at 12 V (b), and PL spectrum for the Eu^{III} complex powder (c).

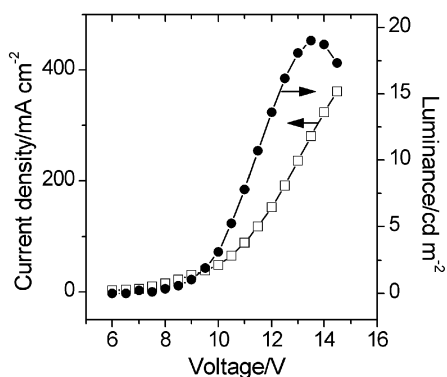


Fig. 2 Current density–luminance–voltage curves for the single-layer EL device.

complexes (the single-layer device usually showed brightness lower than 1 cd m^{-2}).⁷ These demonstrated that the incorporation of triphenylamine moiety played a key role. The successfulness of the material design was once more evidenced by the four-layer device. Fig. 3 shows current density and luminance vs bias voltage curves. The performance for this device is quite impressive. A maximum luminance for the Eu^{III} emission was found to be as high as 1305 cd m^{-2} at 16 V and 255 mA cm^{-2} with an onset driving voltage of as low as 6 V . For the same device, the maximum external quantum yield (η_{ext}) of 0.85% and luminous efficiency of 1.44 lm W^{-1} were achieved at a bias voltage of 7.5 V and a current density (J) of 0.25 mA cm^{-2} . These device parameters are encouraging, compared to the representative EL devices made of Eu^{III} complexes so far reported (see Table 1).³ It is noteworthy that a four-layer device made of a similar Eu^{III} complex without the triphenylamine fragment gave a maximum luminance of only 190 cd m^{-2} . Accordingly, the introduction of the hole-transporting triphenylamine fragment into the Eu^{III} complex is responsible for the outstanding device performance observed.

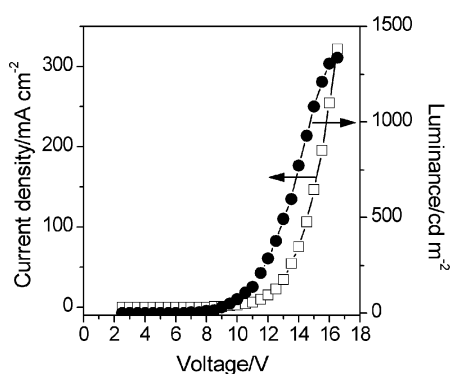


Fig. 3 Current density–luminance–voltage curves for the four-layer EL device.

Table 1 Summary of representative Eu^{III} -based EL devices in literature

| Emitter layer | $\eta_{\text{ext}}/100\%$; $J/\text{mA cm}^{-2}$ | $L/\text{cd m}^{-2}$; voltage/V | Reference |
|----------------------------------------------------------------------|------------------------------------------------------|-------------------------------------|-----------|
| $\text{Eu}(\text{DBM})_3(\text{TPIP})$ | 0.85; 1.44 | 1305; 16.0 | This work |
| $\text{Eu}(\text{ECHM})_3(\text{phen})$ | 0.3; 15 | 50; — | 6 |
| $\text{Eu}(\text{TTA})_3(\text{DPPz})/\text{CBP}$ (4.5%) | 2.1; 1.23 | 1670; 13.6 | 5 |
| $\text{Eu}(\text{DBM})_3(\text{bath})/\text{TPD}$ (3/1) | 1.0; 0.6 | 820; 18.0 | 9 |
| $\text{Eu}(\text{DBM})_3(\text{bath})/\text{TPD}$ (2/1) | 4.6; 0.01 | —; — | 4 |
| $\text{Eu}(\text{TTA})_3(\text{phen})/\text{CBP}$ (1%) | 1.4; 0.4 | 505; 12.0 | 10 |
| $\text{Eu}(\text{DCNP})(\text{DBM})_2(\text{phen})/\text{PBD}$ (10%) | 3.5; 0.17 | 924; — | 11 |

In conclusion, a newly synthesized Eu^{III} complex combining light-emitting center, hole- and electron-transporting groups into one molecule, was demonstrated to be a promising red-light emitting material in EL devices. Further efforts on the directional assemblies of functional groups and elucidation of the operational mechanism of the devices are in progress.

This project was supported by the State Key Program of Fundamental Research (G1998061308), National Natural Science Foundation of China (20071004), and Scientific Research Foundation for the Returned Overseas Chinese Scholars (State Education Ministry, to K.-Z. W.).

Notes and references

† ^1H NMR spectroscopic and elemental analyses: TPIP: δ_{H} (500 MHz, DMSO-d_6): 9.19 (t, 2H), 9.06 (d, 1H), 8.61 (d, 1H), 7.72 (m, 2H), 7.62 (d, 2H), 7.33 (m, 4H), 7.22 (m, 8H), 7.13 (t, 2H), 4.71 (m, 2H), 1.65 (t, 3H). Anal. Calc. for $\text{C}_{33}\text{H}_{25}\text{N}_5\text{O}\cdot 0.5\text{H}_2\text{O}$: C, 79.17; H, 5.24; N, 13.9. Found: C, 79.44; H, 5.15; N, 13.6%.

$\text{Eu}(\text{DBM})_3(\text{TPIP})$: Anal. Calc. for $\text{C}_{74}\text{H}_{56}\text{EuN}_5\text{O}_6\cdot \text{H}_2\text{O}$: C, 69.36; H, 4.56; N, 5.47. Found: C, 69.45; H, 4.81; N, 5.10%.

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