Bright red light-emitting electroluminescence devices based on a functionalized europium complex

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The complex tris(dibenzoylmethanato)(1-ethyl-2-(4′-carbazole-9-yl)phenyl imidazo[4,5-*f*]1,10- phenanthroline) europium (III), Eu(DBM)$_3$(CPIP), was newly synthesized. Devices using this complex as emitter showed greatly enhanced performance benefiting from the improved hole-transporting properties of the complex and good stability. A double-layer device with the configuration of ITO/TPD(50 nm)/Eu(DBM)$_3$(CPIP)(60 nm)/Mg$_{0.9}$Ag$_{0.1}$(200 nm)/Ag(80 nm) exhibited Eu^{3+} based pure red emission with a brightness of 537 cd m^{-2} at 13 V and the power efficiency of 0.089 lm W^{-1} at 6 V, 33 cd m^{-2}. A triple-layer device with the configuration of ITO/TPD(40 nm)/Eu(DBM)$_3$(CPIP)(30 nm)/Eu(DBM)$_3$ Bath(50 nm)/Mg$_{0.9}$Ag$_{0.1}$ (200 nm)/Ag (80 nm) also emitted pure red light with a highest brightness of 1050 cd m^{-2} at 16 V and the highest power efficiency of 0.50 lm W^{-1} at 8 V, 8 cd m^{-2}. The highest brightness 1460 cd m^{-2} at 14 V was obtained from a four-layer device with the configuration of ITO/TPD(40 nm)/Eu(DBM)$_3$(CPIP)(40 nm)/BCP(20 nm)/AlQ(10 nm)/Mg$_{0.9}$Ag$_{0.1}$(200 nm)/Ag(80 nm) and the highest power efficiency of 0.54 lm W^{-1} at 7 V, 56 cd m^{-2}.

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[1–9] because they can emit highly monochromatic red light at around 612 nm, furthermore, it can offer 100% emission quantum efficiency theoretically since this kind of transition is not restricted by the spin inhibition rule,[10] then both singlet and triple excitations are involved in the emission process. However, compared with green and blue devices, a bright red device has not yet been fabricated with satisfying performance in spite of their excellent photoluminescence (PL) properties. One of the ways to improve the europium complexes' EL performance is to introduce a proper second ligand, such as 1,10-phenanthroline (Phen) into the complex. However the device using a europium complex, tris(dibenzoylmethanato)(1,10-phenanthroline)europium(III) (Eu(DBM)$_3$(Phen)) as emitter only gave a highest brightness of 50 cd m^{-2} at 15 V, although its configuration was optimized.[6] This fact may originate from the poor ability of the carrier-transporting properties of the lanthanide complexes. Unbalanced injection and transport of the charge carriers would cause the recombination at locations other than the emitting layer.[11] Doping the europium complexes in hole-transporting materials such as *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)-1,1′-diphenyl-4,4′-diamine (NPB) or 4,4′-*N*,*N*′-dicarbazolebiphenyl (CBP), is a generally used method to get better device performance. When Eu(DBM)$_3$(Phen) was doped with 20% NPB,[6] the device performance was increased to 200 cd m^{-2} from 50 cd m^{-2}. Another example is Eu(DBM)$_3$Bath, the highest luminance was increased from 400 cd m^{-2} to 820 cd m^{-2} when the pure complex was doped with TPD in the same configuration device,[12,2] where Bath stands for 4,7-dibenzoyl-1,10-phenanthroline. However, the doping technique usually leads to phase separation when the device is undergoing operation. Another way to improve the poor carrier transporting property of the lanthanide complex is to introduce the charge-transporting group into the corresponding lanthanide complex. Z. P. Zheng *et al.*[11] reported an efficient OLED using an oxadiazole-functionalized terbium complex as emitter. In their work, the function group oxadiazole, a widely employed electron-transporting material, was incorporated into a β-diketone platform.

In this paper, DBM was chosen as the first ligand due to its high PL and EL efficiency in europium complexes, and a novel second ligand 1-ethyl-2-(4′-carbazole-9-yl)phenylimidazo[4,5-*f*]1,10-phenanthroline (abbreviated as CPIP) was designed and synthesized, since this ligand contained carbazole, which is a well known hole-transporting group. The photoluminescence (PL) and electroluminescence (EL) of this new carbazole functionalized europium complex Eu(DBM)$_3$(CPIP) was investigated.

Experimental

Synthesis

Synthesis routes of the ligand (CPIP) and the complex [Eu(DBM)$_3$(CPIP)] are presented in Scheme 1.

4-(Carbazolo-9-yl)benzonitrile(A) was synthesized according to the following procedure: carbazole (1.67 g, 0.01 mol) and 4-fluorobenzonitrile (1.21 g, 0.01 mol) in 20 ml of DMSO was allowed to react with K$_2$CO$_3$ (4.14 g). The mixture was stirred for 12 h at 140 °C. The resulting solid was filtered off. An addition of a large amount of water gave a gray precipitate, which was chromatographed on a silica gel column with

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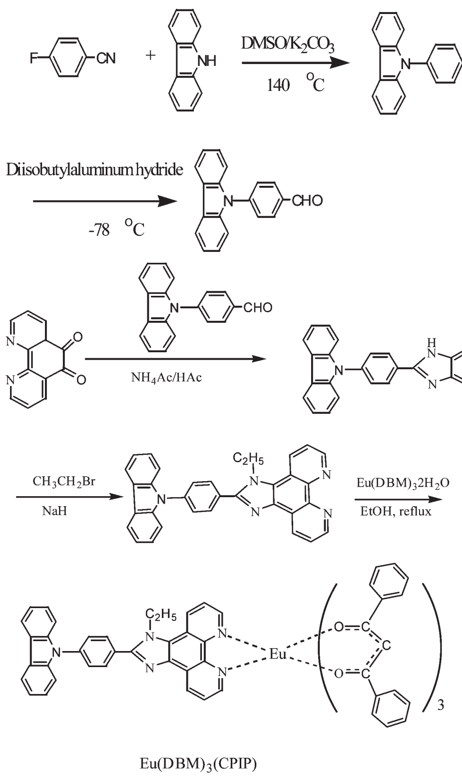

Scheme 1 Synthetic routes for CPIP and europium complex $Eu(DBM)_3CPIP$.

CH_2Cl_2–hexane (2 : 3, v/v) as eluent to get white crystals (60% yield). ^1H-NMR (400 MHz, $CDCl_3$), δ: 8.13–8.15 (d,2H); 7.88–7.91 (d,2H); 7.72–7.75 (d,2H); 7.43–7.46 (m,4H); 7.31–7.35 (m,2H).

2-(4′-Carbazole-9-yl)phenylimidazo[4,5-*f*]1,10-phenanthroline(B) was synthesized as follows: diisobutylaluminium hydride (2 ml, 1 M solution in toluene) was added dropwise to 4-(carbazolo-9-yl)benzonitrile(A) (0.536 g, 2 mmol) in 20 ml of THF under N_2, after stirring for 0.5 h at −78° C (acetone and dry ice), the mixture continued to react for 1 h at room temperature. Then 1,10-phenanthroline-5,6-dione (0.32 g, 1.5 mmol) in HAc (2 ml) and NH_4Ac (2.2 g) in 10 ml ethanol were added in turn according to a modified imidazole ring preparation method established by Steck.[13] The resulting solution was further refluxed for 4 h. The crude product was purified by recrystallization from a mixture of CH_2Cl_2 and hexane to get straw yellow crystals in a yield of 40%.

1-Ethyl-2-(4′-carbazole-9-yl)phenylimidazo[4,5-*f*]1,10-phenanthroline(CPIP) was synthesized according to the following procedure: 2-(4′-carbazole-9-yl)phenylimidazo[4,5-*f*]1,10-phenanthroline(B) was allowed to react with bromoethane under the presence of sodium hydride to obtain 1-ethyl-2-(4′-carbazole-9-yl)phenylimidazo[4,5-*f*]1,10-phenanthroline (CPIP). The crude product was chromatographed on a silica gel column with CH_2Cl_2–methanol (15 : 1, v/v) as eluent to get yellow crystals (60% yield). ^1H-NMR (400 MHz, $CDCl_3$), δ: 9.21–9.22 (d,2H),8.17–8.19 (d,2H), 8.01–8.03 (d,2H), 7.83–7.85 (d,2H), 7.75 (d,2H), 7.54–7.56 (q,2H), 7.47–7.49 (q,2H), 7.34–7.36 (q,2H), 7.26 (d,2H), 4.79–4.84 (f,2H), 1.63–1.75 (t,3H).

$Eu(DBM)_3(CPIP)$ was synthesized by the conventional method.[14] 3 mmol DBM and 1 mmol CPIP were dissolved in hot ethanol under stirring. After cooling, 3 mmol of a 2 mol L^{-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 complex was purified by reprecipitation from ethanol and vacuum drying. Calc. for $Eu(DBM)_3(CPIP)(2H_2O)$: ($C_{78}H_{56}N_5O_6Eu{\cdot}2H_2O$): C, 69.55; H, 4.45; N, 5.20%. Found: C,69.56; H, 4.11; N, 5.00%.

Preparation of EL devices

The devices using this new complex as emitter were fabricated by sequentially depositing organic layers in one run under high vacuum ($< 8 \times 10^{-4}$Pa) thermal evaporation onto a precleaned indium–tin oxide glass substrate with a sheet resistance of 15 Ohms $sq.^{-1}$ which was kindly supplied by China Southern Glass Holding Co., Ltd. as a gift. A shadow mask with 5 mm diameter openings was used to define the cathode of a 200 nm thick layer of $Mg_{0.9}Ag_{0.1}$ alloy, with a 80 nm thick Ag cap. The thickness of the deposited layer and the evaporation speed of the individual materials were monitored in vacuum with quartz crystal monitors. The deposition rates were maintained to be 0.1–0.3 nm s^{-1} for organic materials, 1.0–1.3 nm s^{-1} for $Mg_{0.9}$: $Ag_{0.1}$ alloy. All electric testing and optical measurements were performed under ambient conditions. The fluorescence (PL) and electroluminescence (EL) spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer. The current–voltage (*I–V*) and luminance–voltage (*L–V*) characteristics were measured with a computer controlled Keithley 2400 Sourcemeter unit with a calibrated silicon diode. The chemical structures of the materials and the structures of the EL devices was shown in Fig. 1.

Results and discussion

PL properties

The photoluminescence spectra of $Eu(DBM)_3(CPIP)$ are shown in Fig. 2 (solid line). It is clear, the complex mainly emits the characteristic line-like spectrum from Eu^{3+} ion at 612 nm, which can be assigned to $^5D_0 \rightarrow {}^7F_2{\cdot}4f$ electronic transition. What should be noticed is that no emission from CPIP can be detected, indicating that the energy absorbed by CPIP was transferred to the complex completely.

Double layered EL device

A double-layer device **1** with the configuration of ITO/TPD (50 nm)/$Eu(DBM)_3(CPIP)$(60 nm)/$Mg_{0.9}Ag_{0.1}$ (200 nm)/Ag(80 nm) was fabricated and its electroluminescence (EL) spectrum with characteristic europium emission peaks is shown in Fig. 2 (dashed line), no emission from the carbazole moiety is detected just as the PL of the complex. Benefitting from the good hole-transporting property and the efficient energy transfer due to the introduction of a carbazole group in the complex, device **1** presents a highest brightness of 537 cd m^{-2} at 13 V, and a turn-on voltage of 4 V. This is one of the best performances of a double layer device based on pure europium complexes as emitter.

Quadruple layered EL device

To optimize the performance of the device by introducing TPD as hole-transporting material, BCP as hole blocking layer and AlQ as electron-transporting layer, device **2** with the configuration of ITO/TPD (40 nm)/$Eu(DBM)_3(CPIP)$ (40 nm)/BCP(20 nm)/AlQ(10 nm)/$Mg_{0.9}Ag_{0.1}$(200 nm)/Ag(80 nm) was fabricated. The luminance–current density–voltage characteristics of device **2** is shown in Fig. 4, the turn-on voltage was 4 V, and data shows that the luminescence increases with increasing injection current as well as bias voltage, since the complex has very good hole transporting property. Comparing device **1** and **2**, one can find that device **1** has higher current densities when the two devices reach the same level of luminescence, this is because of the insufficient electron injection and consequently

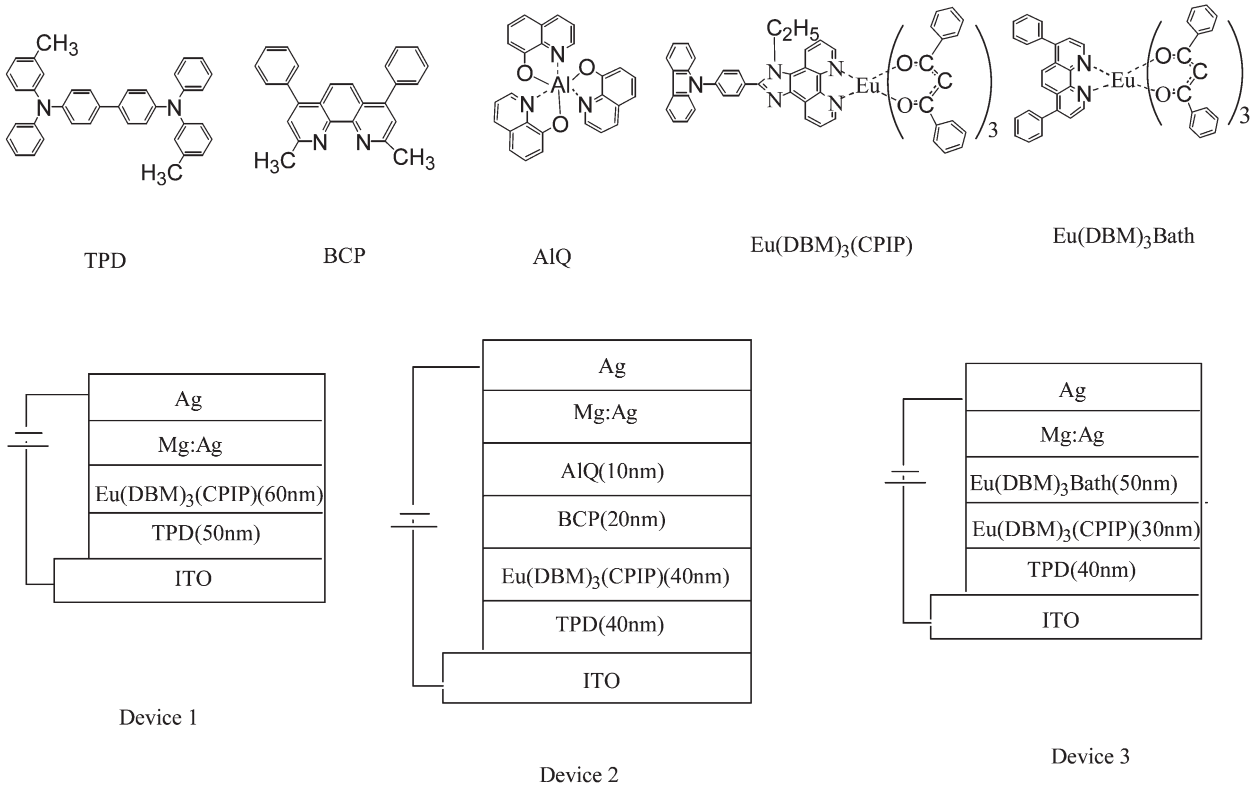

Fig. 1 The chemical structures of the materials and the structures of the EL devices.

holes annihilated by electrons at the cathode. By introducing BCP as a hole blocking layer and AlQ as a electron-transporting layer, charge injection was balanced in the emitting layer and the EL efficiencies were greatly enhanced. Fig. 3 shows that when applied voltage was not higher than 12 V, device **2** gave only characteristic emissions originating from the central europium ion (Fig. 3a), and the brightness and power efficiency of the device was 375 cd m^{-2} and 0.19 lm W^{-1} respectively. When the bias voltage is larger than 12 V, the emission from AlQ peaked at 520 nm is detectable and increases slightly as the voltage increased (Fig. 3b,c). This phenomenon is also observed in the doped devices in literature.[4,5] Since the hole injection barrier between the emitting layer (HOMO energy level 6.4 eV[1]) and the hole blocking layer BCP (HOMO energy level 6.7 eV[15]) is 0.3 eV, at higher voltage, holes would inject into the AlQ layer and recombine with electrons injected from the cathode and therefore gave the emission peak at 520 nm from AlQ. The highest brightness obtained from this device can be higher than 1460 cd m^{-2}, however, the color becomes orange because of the increased emission from AlQ. It should be noted that no matter how the voltages were increased, no emission from TPD appeared, indicating that an electron is still the minor carrier in the emitting layer although AlQ was introduced, and this may be caused by the lower electron mobility in the AlQ layer.[16]

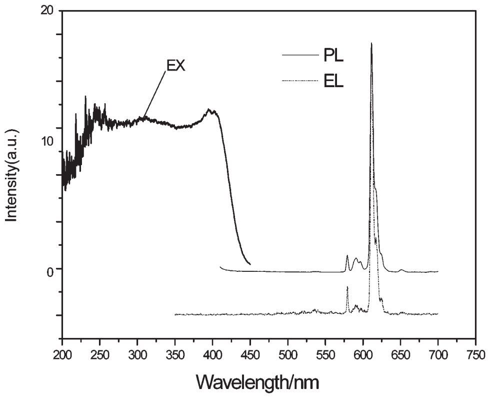

Fig. 2 The PL spectra of Eu(DBM)$_3$CPIP (solid line) in solid states. Excitation spectra were measured by monitoring emission wavelengths of 612 nm, and emission spectra were measured at an excitation wavelength of 398 nm. The EL spectra (dashed line) of device **1**, ITO/TPD (50 nm)/Eu(DBM)$_3$(CPIP) (60 nm)/Mg$_{0.9}$Ag$_{0.1}$(200 nm)/Ag(80 nm).

Triple layered EL device

In order to get higher pure red emission, by choosing better electron transporting material Eu(DBM)$_3$Bath, device **3** with the configuration of ITO/TPD(40 nm)/Eu(DBM)$_3$(CPIP) (30 nm)/Eu(DBM)$_3$ Bath(50 nm)/Mg$_{0.9}$Ag$_{0.1}$(200 nm)/Ag(80 nm) was fabricated. The turn-on voltage was 6 V and the highest power efficiency was 0.50 lm W^{-1} at 7 V. The luminance–current density–voltage characteristics of device **3** is shown in Fig. 5. Compared to device **2**, as shown in Fig. 3d, when the voltage was greater than 14 V, device **3** also exhibited Eu^{3+} based pure red emission with a highest brightness of 1050 cd m^{-2} at 16 V.

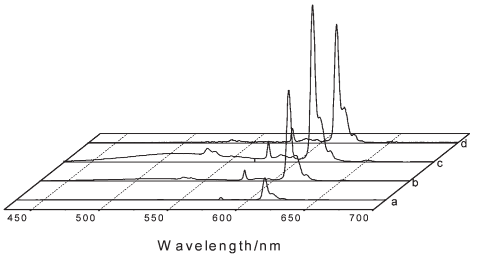

Fig. 3 EL spectra of device **2** (a,b.c) at applied voltage 10, 12 and 14 V respectively and device **3** (d) at applied voltage 14 V.

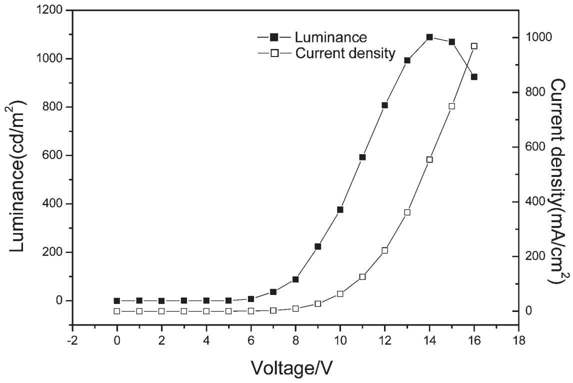

Fig. 4 Current density–luminance–voltage curves for the device **2**: ITO/TPD (40 nm)/Eu(DBM)$_3$(CPIP) (40 nm)/BCP(20 nm)/AlQ (10 nm)/Mg$_{0.9}$Ag$_{0.1}$(200 nm)/Ag(80 nm).

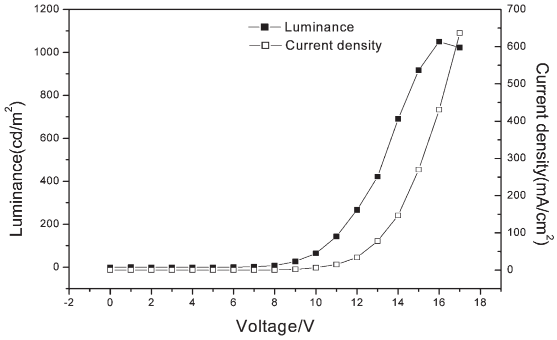

Fig. 5 Current density–luminance–voltage curves for the device **3**: ITO/TPD (40 nm)/Eu(DBM)$_3$(CPIP) (30 nm)/Eu(DBM)$_3$Bath(50 nm)/Mg$_{0.9}$Ag$_{0.1}$(200 nm)/Ag(80 nm).

Device stability during operating is very important for application. Devices using this complex as emitter show very good stability. Device **3** was left in ambient conditions without any protection after the measurement of current–voltage (*I*–*V*) and luminance–voltage (*L*–*V*) curves. 24 hours later, the *I*–*V* curves measured under the same conditions (shown in Fig. 6 (1)) showed the same characteristic as the initial measurement and this measurement was repeated 30 times without any apparent change. Study on the lifetime of the device is in progress.

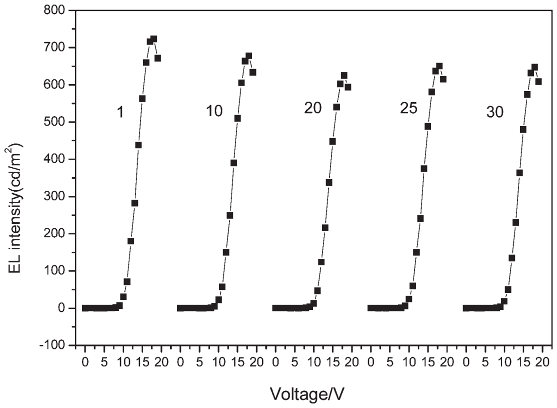

Fig. 6 Luminance–voltage curves of device **2** measured consecutively after it was left under ambient conditions for 24 h. 1, 10, 20 25 and 30 represent the number of the run measured.

Conclusions

In summary, we report the synthesis and EL application of a europium complex functionalized with a hole-transporting group. Devices using this complex as emitter show good performance, stability and operating repeatability. OLED property analysis shows that the device current is apparently electron limited; introducing hole blocking and electron-transporting layer balanced the carrier injection and enhanced the device performance. Although the devices were not optimized, the device brightness in double layer or multilayer devices is so far the highest compared with other corresponding ones using pure europium complex as emitter.[12] Our results suggest that incorporating hole-carrier functional group into complex is a viable strategy for modifying the hole-transporting characteristic of lanthanide complexes.

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