Novel Europium and Osmium Complexes for Pure Red Light Emitting Diode Applications

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Summary: Pure and efficient red light-emitting diodes based on novel europium (Eu) and osmium (Os) complexes were demonstrated. The Eu complex, with dendron substituted diketone ligands, exhibits high photoluminescence efficiency of 45%. When a copolymer containing carbazole and 1,3,4-oxadiazole groups was used as the host, narrow electroluminescence at 617 nm was achieved, with a full width at half maximum of 4 nm and a maximum external quantum efficiency (η) of 0.80%. The Os complex shows pure red emission peaking at 650 nm. The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates (x, y) are (0.65, 0.33). Maximum η and brightness achieved were 0.82% and 590 cd/m^2, respectively.

Introduction

In the last decade, organic and polymer light emitting diodes (LEDs) have attracted a lot of attention and experienced rapid progress, due to their potential application in displays.[1-3] For full-color displays, efficient LEDs emitting three primary colors, *i.e.*, blue, green and red, are required. However, obtaining pure emission colors from conjugated polymers or small molecules is generally difficult because their emission spectra typically have a full width at half maximum (FWHM) of 50-200 nm.[4] Nevertheless, pure red emission can be achieved by using europium (Eu) complexes as the emitter because the emission coming from transition between *f* levels of the Eu^{3+} ion is sharp and narrow.[4-7] Pure red emission can also be made by using polymers or dyes whose emission starts in the red and extends into the infrared.[4] Osmium (Os) complex is such an emitter whose application in LED has not been explored yet. Here, we report efficient pure red electroluminescence (EL) from LEDs based on a Eu complex with dendron substituted ligands and an Os complex. The chemical structures of the Eu complex, tris{3 - [3'-5'-bis(phenylmethoxy) phenyl] -1-(9-phenanthyl-1) propane-1,3-dione} Europium (III) [Eu(PPD)$_3$], and the Os complex, [Osmium (II) bis(4-4'-diphenyl-2,2'-bipyridine)1,2-bis(diphenylarseno)ethane)]hepta-fluorobutyrate (OsAs), are shown

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in Fig. 1. Recently Fréchet et al studied lanthanide dendrimer complexes and found that the luminescence of the lanthanide ions were enhanced through the site isolation effect of the dendrons, which prevents their mutual interaction and decreases their rate of self-quenching.[8] It is expected that the dendrons on the PPD ligands will minimize the possibility of intermolecular interaction, leading to a decrease in self-quenching and an increase in photoluminescence (PL) efficiency of Eu(PPD)$_3$. LED devices were fabricated by doping Eu(PPD)$_3$ and OsAs into polymer hosts. The host materials used are poly(N-vinylcarbazole) (PVK), 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD), and a carbazole and 1,3,4-oxadiazole containing random copolymer CPVKPVO,[9] whose structure is also shown in Fig. 1.

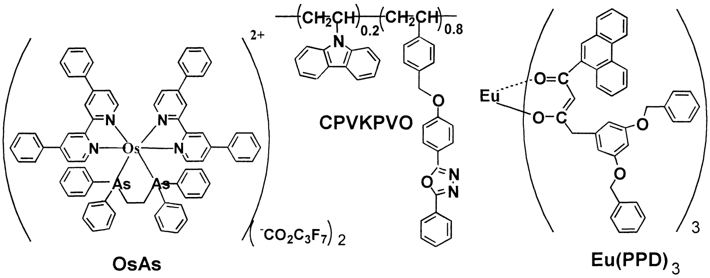

Figure 1. Chemical structures of OsAs, Eu(PPD)$_3$ and copolymer CPVKPVO.

Experimental

UV-Vis spectra were measured using a PE Lambda-9 UV/VIS/NIR spectrophotometer. PL spectra were recorded with an Oriel InstaSpec IV CCD camera. PL efficiency was measured using the CCD camera and a nitrogen purged Newport integrating sphere from Eu(PPD)$_3$ thin film, with monochromated excitation at 348 nm from a mercury lamp.[10] LED devices were fabricated on ITO substrates that were cleaned before use. A layer of 35~40 nm thick hole-transport material (HTL), a perfluorocyclobutane polymer containing tetraphenyldiamine, was first fabricated.[11] Then a layer of 5.0 *w*% Eu(PPD)$_3$, 3.0 *w*% OsP or OsAs doped PVK, PVK:PBD (blend of PVK and PBD, 71/29 *w*/*w*) or CPVKPVO was spin coated from the corresponding 1,2-dichloroethane solution (10~12 mg/mL) at 2000 rpm. A layer of 30-nm-thick calcium (Ca) was vacuum deposited at 1×10^{-6} torr through a mask, and another layer of 120-nm-thick silver (Ag) deposited as a protecting layer. All testing was carried out in air at room temperature. Current-voltage characteristics were measured on a HP 4155B semiconductor parameter analyzer. EL spectra were measured with either the CCD camera or a Photo Research PR650 colorimeter. The EL emission power was measured using a Newport 2835-C multi-function optical meter in combination with a calibrated photodiode. Brightness was calculated from the emission power and EL spectra of the devices, assuming Lambertian distribution of the EL emission,[12] and conformed by the PR650 colorimeter. Thickness was measured on a Sloan Dektak 3030 profilometer.

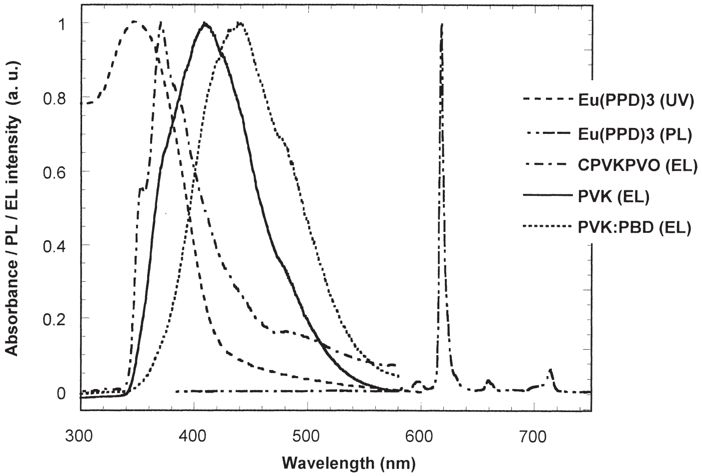

Figure 2. UV absorption and PL spectra of Eu(PPD)$_3$ thin film on a quartz substrate and EL spectra of ITO/CPVKPVO/Ca, ITO/PVK/Ca, and ITO/PVK:PBD/Ca devices.

Results and discussion

UV absorption and PL spectra of Eu(PPD)$_3$ film are shown in Fig. 2. The absorption peak is at 348 nm. The PL of Eu(PPD)$_3$ shows only the characteristic sharp emission bands from Eu^{3+}. The emission of the PPD ligands is completely quenched, implying efficient energy transfer from the PPD ligands to Eu^{3+} ion. The emission is dominated by a very narrow peak at 617 nm with a FWHM of only 4 nm. It is essentially monochromatic. The PL efficiency measured from Eu(PPD)$_3$ thin film on a quartz substrate is as high as 45%. As expected, the dendron enhances the emission efficiency of Eu(PPD)$_3$ by isolating the central Eu^{3+} ions from each other through the dendron-induced increase in the distance between neighboring Eu^{3+} ions.

Double-layer LEDs based on Eu(PPD)$_3$ were fabricated by doping 5.0 *w*% Eu(PPD)$_3$ into PVK, PVK:PBD and CPVKPVO. EL spectra from these devices are essentially the same as the PL of Eu(PPD)$_3$. The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates (x, y) for the emission are (0.65, 0.34). The performance of ITO/HTL/PVK:Eu(PPD)$_3$/Ca (Device I), ITO/HTL/PVK:PBD:Eu(PPD)$_3$/Ca (Device II), and ITO/HTL/CPVKPVO:Eu(PPD)$_3$/Ca (Device III) are summarized in Table I. In these devices, the EL process includes the following steps: 1) Singlet (S_1) state excitation is first generated on the host material by carrier injection and recombination, with efficiency $\eta_{exciton}$. 2) The excitation is then transferred to the PPD ligands, with efficiency η_{ET1}. 3) PPD S_1 state undergoes intersystem crossing and changes into T_1 state. 4)The excitation transfers from PPD T_1 states to the excited state of Eu^{3+}, with efficiency η_{ET2}. 5) Eu^{3+} relaxes through $^5D_X \rightarrow {}^7F_X$ transitions and emits light, with efficiency η_{PL}. The external quantum efficiency $\eta \propto \eta_{exciton} \times \eta_{ET1} \times \eta_{ET2} \times \eta_{PL}$. For the three devices, η_{ET2} and η_{PL} are the same because of the same dopant Eu(PPD)$_3$. So the efficiency for different device will be determined by the product of $\eta_{exciton}$ and η_{ET1}. Because PVK is a hole transporting material, electrons and holes are quite unbalanced in Device I. Electrons and holes are more balanced in Device II and III due to the introduction of the electron transporting 1,3,4-oxadiazole groups. Hence $\eta_{exciton}$ in the three devices is in the following order: $\eta_{exciton}$(Device II) $\cong$ $\eta_{exciton}$(Device III) > $\eta_{exciton}$(Device I). Since the energy transfers from the host to Eu(PPD)$_3$ through dipole-dipole interaction (Förster energy transfer), η_{ET1} will depend on the overlap between the emission spectrum of the host and the absorption spectrum of Eu(PPD)$_3$. We note here that EL instead of PL emission should be used because in some case the EL emission of the host may shift from its PL. The EL spectra of ITO/PVK/Ca, ITO/PVK:PBD/Ca and

Table I. Performance of Eu(PPD)$_3$ and OsAs based LEDs.

Device configuration [a)]	V_1 (V)[b)]	B_{max} (cd/m^2)[c)]	QE $_{max}$[d)]	PE_{max} (cd/A)[e)]
HTL/PVK:Eu(PPD)$_3$	12.4	152	0.048%	0.038
HTL/PVK:PBD:Eu(PPD)$_3$	8.8	245	0.21%	0.26
HTL/CPVKPVO:Eu(PPD)$_3$	11.4	62	0.80%	1.0
PVK:PBD:OsAs	9.0	140	0.23%	0.11
HTL/PVK:PBD:OsAs	9.3	310	0.64%	0.31
HTL/PVK:PBD:OsAs/Alq$_3$	7.0	590	0.82%	0.40

[a)] HTL: 35~40 nm; Eu(PPD)$_3$ or OsAs doped layer: 40~45 nm (doping ratio: 5.0% *wt.* for Eu(PPD)$_3$ and 3.0% *wt.* for OsAs); Alq$_3$: 25 nm. [b)] V_1: voltage needed for brightness of 1 cd/m^2. [c)] B_{max}: maximum brightness. [d)] QE_{max}: maximum external quantum efficiency. [e)] PE_{max}: maximum photometric efficiency.

ITO/CPVKPVO/Ca are shown in Fig. 2. As can be seen, the overlap between the EL of CPVKPVO and the absorption of Eu(PPD)$_3$ is the best, while that between PVK:PBD and Eu(PPD)$_3$ is the worst. So η_{ET1} is in the following order: η_{ET1}(Device III) > η_{ET1}(Device I) > η_{ET1}(Device II). The external quantum efficiencies of Device I, II and III are 0.048%, 0.21% and 0.80%, respectively. Compared Device II with Device I, the increase in η_{exciton} outplays the decrease of η_{ET1}, resulting in a higher efficiency. The efficiency of Device III is the highest because both η_{exciton} and η_{ET1} are the highest among the three devices. However, the brightness of the devices doesn't follow the same order because brightness of LED devices depends on both the current density and the efficiency. The brightness of Device III is the lowest because of the poor carrier mobility of CPVKPVO.[9] The brightness of Device II is higher than that of Device I, mainly because of the improved efficiency. The operating voltages are all relatively high because of the poor charge injection/transport ability of the host materials.

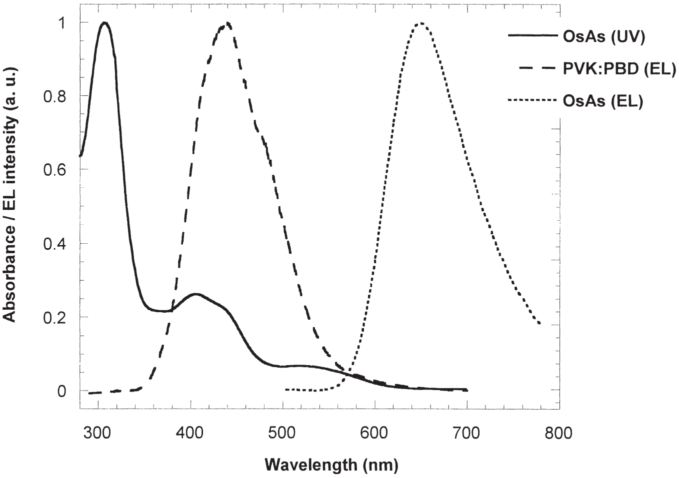

Figure 3. UV absorption of OsAs thin film on a quartz substrate and EL spectra of ITO/PVK:PBD/Ca and ITO/HTL/PVK:PBD:OsAs(3 *w*%)/Ca devices.

LEDs based on OsAs were fabricated by doping OsAs (3 *w*%) into PVK:PBD. The absorption spectrum of OsAs is shown in Fig. 3 together with the EL spectrum of PVK:PBD. As can be seen, the EL emission of PVK:PBD and the absorption of OsAs overlap strongly with each other. Therefore, the energy transfer from PVK:PBD host to OsAs is very efficient. Doping at 3 *w*% is sufficient to quench the emission of the

PVK:PBD host. The EL emission of OsAs peaks at 650 nm. The emission comes from the triplet states of the metal-to-ligand-charge-transfer excited state. Compared with the EL spectrum of the Eu complex, it is much broader, with a FWHM of 100 nm. However, since the emission starts in the red and extends into infrared, the CIE chromaticity coordinates (x, y) are (0.65, 0.33), very close to those of $Eu(PPD)_3$, indicating that the emission of OsAs is also pure red. The performance of the single, double and three-layer devices are summarized in Table I. Even with a single layer structure ITO/PVK:PBD:OsAs/Ca, an external quantum efficiency of 0.23% and brightness of 140 cd/m^2 were achieved. When a layer of HTL was introduced, the efficiency and brightness were more than doubled. With a three layer ITO/HTL/PVK:PBD:OsAs/Alq_3/Ca configuration, high efficiency and brightness of 0.82% and 590 cd/m^2 were obtained, clearly demonstrating that OsAs is a potential candidate for red emitting LED applications.

Conclusions

Novel Europium (Eu) and Osmium (Os) complexes that are promising for red light-emitting diode application are demonstrated. The Eu complex, with dendron substituted diketone ligands, exhibits high PL efficiency of 45%. Narrow EL emission at 617 nm with a FWHM of 4 nm was realized by doping the Eu complex into polymer hosts. $\eta_{\max}$ and $B_{\max}$ for the Eu complex devices were 0.80% and 245 cd/m^2, respectively. The Os complex shows pure red emission that starts in the red and peaks at 650 nm. The CIE chromaticity coordinates (x, y) are (0.65, 0.33). $\eta_{\max}$ and $B_{\max}$ achieved were 0.82% and 590 cd/m^2, respectively.

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