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Bright red light-emitting organic electroluminescent devices based on a novel thiophene-containing europium complex as an emitting layer

Keizou Okada, Yan-Feng Wang,† Tian-Ming Chen,† Masaya Kitamura, Tadao Nakaya and Hideo Inoue*

Department of Bioapplied Chemistry, Faculty of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan. E-mail: keizo@bioa.eng.osaka-cu.ac.jp

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A novel europium complex, Eu(DTP)$_3$(dipphen) (DTP = 1,3-di(2-thienyl)propane-1,3-dione, dipphen = 4,7-diphenyl-1,10-phenanthroline), has been synthesized and applied to organic electroluminescent (EL) devices as an emitting and electron-transporting material. The EL device structure can be described as indium tin oxide (ITO)/hole-transporting layer (triphenyldiamine derivative (TPD))/emitting layer (Eu(DTP)$_3$(dipphen))/electron transport layer (Alq3)/AlLi (99 : 1). The emitting layers were formed by a codeposition technique. The deposited EL devices were observed to emit a bright red light originating from Eu(DTP)$_3$(dipphen) with a maximum luminance of 450 cd m^{-2} at 15 V and 200 mA cm^{-2}.

Introduction

Organic electroluminescent (EL) devices are of great interest because of their efficient emission in the visible region and their possible application to a new type of flat panel full color display.[1–6] These devices are of injection type and show a low driving voltage of <10 V. Since Tang and Van Slyke[1] reported the first double layered organic EL device, many researchers have developed high performance green organic EL devices with tris(8-hydroxyquinolinato)aluminium (Alq3).[2,3] Moreover, bright blue organic EL devices with distyryl derivatives have been reported by Hosokawa *et al.*[7] Some orange and red organic EL devices using metal complexes and/or organic dyes have also been reported.[3,8] However, a high performance bright red device has, as yet, not been fabricated.

Europium (Eu) compounds are known as excellent red phosphors which exhibit intense fluorescence at *ca.* 610 nm with a sharp spectral bandwidth. Conventionally available Eu(acetylacetone derivative)$_3$ complexes such as Eu(TTA)$_3$ (TTA = thienoyltrifluoroacetone), are also excellent red phosphors, but they cannot be deposited by vacuum vapor deposition, a popular and conventional technique for fabricating organic EL devices, owing to their lack of volatility. Kido *et al.* reported fabrication of EL devices with Eu(TTA)$_3$ as an emitting material,[9] in which Eu(TTA)$_3$ was introduced into a spin-coat film by mixing it with a hole transporting polymer. A red emission due to the Eu complex, with a maximum luminance of 0.3 cd m^{-2}, was reported.

The aim of this study is to design and synthesize a novel Eu complex which not only displays a good electron transportability but also gives a high luminescent efficiency. It is known that five-membered heterocyclic compounds, such as thiophene, often show a strong photoluminescence. Compared with the π-electron density of carbocyclic benzene (unity on each ring atom), the π-electron density on each ring atom of thiophene is greater than unity since there are six electrons distributed over five atoms, forming a π-electron excessive heterocyclic structure. From this point of view, it is of interest to synthesize novel Eu complexes with complete heterocyclic structures and to investigate their electroluminescent properties.

Here, we report on the fabrication of multilayer EL devices with emission from a Eu complex applied by vacuum-vapor deposition. A new Eu complex Eu(DTP)$_3$(dipphen) (DTP = 1,3-di(2-thienyl)propane-1,3-dione, dipphen = 4,7-diphenyl-1,10-phenanthroline) which was volatile, was synthesized and designed based on the concept of a synergistic effect. Synergism relates to introduction of a second ligand into a metal complex to saturate its coordination number. The polarity is decreased when a second ligand, dipphen, is introduced into Eu(DTP)$_3$. Low polarity Eu(TTA)$_3$(dipphen) can be sublimed *in vacuo* and forms a homogeneous film by vacuum deposition. Using Eu(DTP)$_3$(dipphen) as an emission layer, we succeeded in the fabrication of EL devices with sharp red emission and luminance of 168 cd m^{-2}. However, the performance of these devices was still not very high compared with conventional multilayer devices. Thus, in order to obtain high luminance, we attempted to improve the luminous efficiency by employing a codeposition technique with another material. From these points of view, a novel thiophene ring-containing europium complex was prepared for fabrication of multilayer bright red EL devices. The preparation, characterization and EL properties of this Eu complex are discussed.

Experimental

Materials

Sodium amide, acetone, tetrahydrofuran (THF), ethanol, propan-2-ol, hexane, dichloromethane, sodium hydroxide, anhydrous sodium sulfate, hydrochloric acid, deuteriochloroform and acetonitrile were purchased from Nacalai tesque Industry Co., Ltd., Japan. Acetone, THF and propan-2-ol were purified by standard distillation methods. Tris(8-hydroxyquinolinato)aluminium (Alq3), *N*,*N*′-diphenyl-*N*,*N*′-(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), 2-acetylthiophene, 2-thiophenecarboxylic acid ethyl ester and 4,7-diphenyl-1,10-phenanthroline were purchased from Tokyo Chemical Industry Co., Ltd., Japan. Europium(III) chloride hexahydrate was purchased from Kanto chemical Co., Ltd., Japan.

Indium tin oxide (ITO) coated glass substrates were purchased from Matsunami Glass Industry Co., Ltd., Japan. The ITO layer, having a sheet resistance of $10\,\Omega\,\square^{-1}$, was etched to form strips of 2 mm width which were used as anodes. High purity AlLi was deposited at right angles to the ITO,

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†Present address: Kohjin Co., Ltd., 1-1 Kohkoku, Yatsushiro City 866-8686, Japan.

forming linear cathodes of 2 mm width. Therefore, the active emitting area was controlled to be 2 × 2 mm^2.

Apparatus

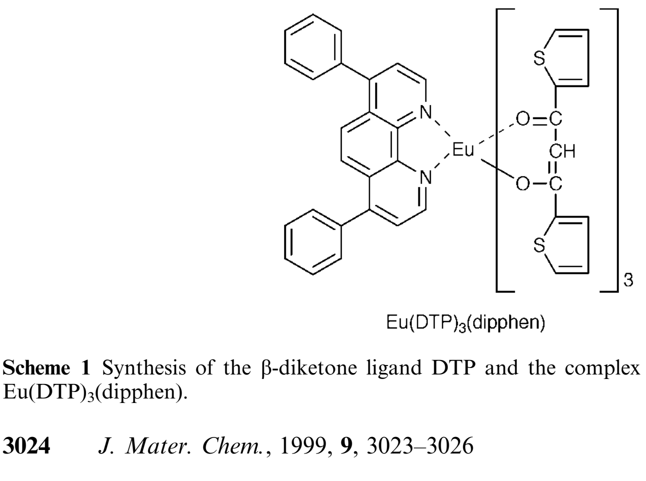
Proton (^{1}H, 400 MHz) NMR spectra were recorded at 25 °C on a JEOL α-400 instrument in $CDCl_3$ solution. Fourier transform IR studies were performed using a Shimazu FT-IR 8200A spectrometer. Melting points were determined on a Yanaco Model P apparatus. Photoluminescent properties were investigated with a Shimadzu RT-5000 spectrofluorophotometer. The thickness of vacuum-deposited films was measured with an Alpha Step profilometer. Luminance (cd m^{-2}) was measured by a TOPCON BM-7 Fast luminance colorimeter (TOPCON Co., Japan) at a measuring field of 0.2° (determined according to the object size, 2 × 2 mm^2).

Synthesis of 1,3-di(2-thienyl)propane-1,3-dione (DTP)

1,3-Di(2-thienyl)propane-1,3-dione (DTP) was synthesized according to the Claizen condensation method as shown in Scheme 1.[10] 2-Thiophenecarboxylic acid ethyl ester and sodium amide were added to a solution of 2-acetylthiophene in THF. The mixture was stirred at 60 °C for 24 h. The solution was then evaporated to a small volume and acidified with hydrochloric acid solution. Then, the mixture was extracted with diethyl ether and purified by recrystallization from ethanol to give a pure product as yellow crystals (mp 96–98 °C). Yield 75%. Calc. for $C_{11}H_8O_2S_2$: C, 55.86; H, 3.39; O, 13.54; S, 27.08. Found: C, 55.78; H, 3.42; O, 13.77; S, 27.13%. IR (KBr): 3125, 1540, 1410, 790 and 720 cm^{-1}. ^{1}H FT-NMR (400 MHz, $CDCl_3$) δ 6.54 (s, 2H), 7.14–7.17 (q, 2H), 7.60–7.63 (q, 2H) and 7.77–7.78 (q, 2H).

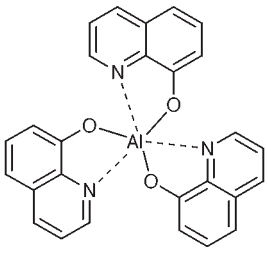
Synthesis of (4,7-diphenyl-1,10-phenanthroline)tris[1,3-di(2-thienyl)propane-1,3-dione]europium(III), Eu(DTP)$_3$(dipphen)

(4,7-Diphenyl-1,10-phenanthroline)tris[1,3-di(2-thienyl)propane-1,3-dione]europium(III), Eu(DTP)$_3$(dipphen), was synthesized by the conventional method as shown in Scheme 1.[11] An aqueous solution of $EuCl_3{\cdot}6H_2O$ was added dropwise at room temperature to a solution of DTP and 4,7-diphenyl-1,10-phenanthroline (dipphen) in ethanol, which had been stirred and neutralized with 1 M NaOH solution. Then, the mixture was stirred at 60 °C for 3 h. The crude product, which precipitated from the solution, was collected by filtration and purified by reprecipitation from hexane to afford the pure complex as a yellow solid. The neutral complex was readily sublimed *in vacuo*[11,12] (mp 151–152 °C). Yield 85%. Calc. for $Eu(C_{57}H_{37}N_2O_6S_3)$: C, 62.64; H, 3.39; N, 2.56; O, 8.79; S, 8.79. Found: C, 62.70; H, 3.42; N, 2.63; O, 8.80; S, 8.82%. IR (KBr): 3120, 1545, 1415, 792 and 725 cm^{-1}. ^{1}H FT-NMR (400 MHz, $CDCl_3$) δ 6.45 (s, 3H), 7.01–7.11 (q, 6H), 7.49–7.52 (q, 12H) 7.60–7.63 (q, 6H), 7.70–7.73 (q, 6H), 7.79–7.89 (s, 2H) and 9.24–9.25 (s, 2H).



Scheme 1 Synthesis of the β-diketone ligand DTP and the complex Eu(DTP)$_3$(dipphen).

The hole transport material was *N*,*N*′-diphenyl-*N*,*N*′-(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), the emitting material was Eu(DTP)$_3$(dipphen) and the electron transport material was tris(8-hydroxyquinolinato)aluminium (Alq3).



Alq3

Preparation of EL devices

Two types of EL devices structures were used: double-layer-type EL device: ITO/HTL(600 Å)/EML (600 Å)/cathode(Al : Li = 99 : 1) (2000 Å); triple-layer-type EL device: ITO/HTL(600 Å)/EML (Eu complex)(300–500 Å)/ETL(Alq3)(200–500 Å)/cathode(Al : Li = 99 : 1)(2000 Å). HTL: hole transport layer; EML: emitting layer; ETL: electron transport layer.

The organic layers and the top cathode of the AlLi alloy were successively vacuum deposited onto an indium tin oxide (ITO)-coated glass substrate at 3 × 10^{-6} Torr. The structure of the double-layer-type EL device is shown in Fig. 1.

Results and discussion

Characteristics of the double-layer-type EL device

Homogeneous thin films, as confirmed by SEM observations, were readily formed by vapor deposition. A bright red electroluminescence was observed from the EL device when a continuous forward bias was applied with ITO as the positive electrode. Fig. 2 shows the electroluminescence (EL) spectrum and the photoluminescence (PL) spectrum of Eu(DTP)$_3$(dipphen) in THF solution. It can be seen that the Eu complex containing thiophene groups exhibited a sharp intense PL peak at 611 nm, while the double-layered EL device shows a sharp red emission peak at 614 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} ion.[13]

The sharp luminescence spectrum of this complex shows a half spectral bandwidth of only *ca.* 7 nm. This suggests that the luminescence is essentially monochromatic and that filters are not necessary and is best suited for display applications if a high enough luminance level can be achieved. Moreover, the identical spectra in the EL device and in solution suggest that

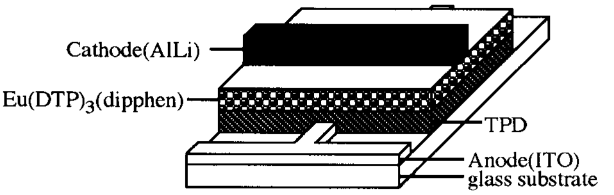


Fig. 1 Structure of the double-layer-type EL device.

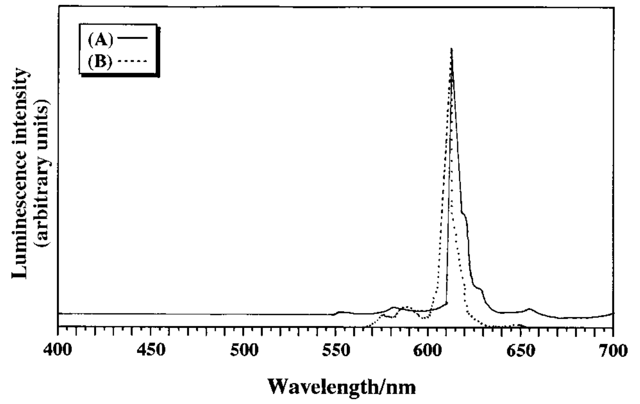


Fig. 2 (A) Electroluminescence spectrum of an ITO/TPD(600 Å)/Eu(DTP)$_3$(dipphen)(600 Å)/AlLi(2000 Å) device and (B) photoluminescence spectrum of Eu(DTP)$_3$(dipphen) in THF solution (λ_{ex} = 250 nm).

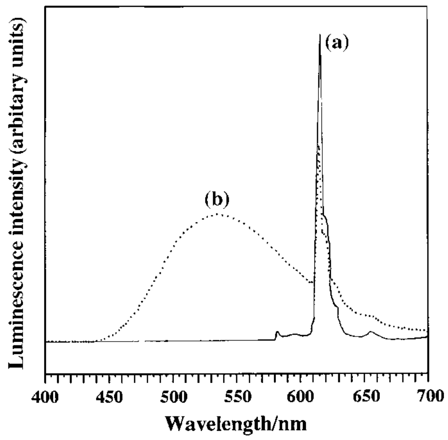


Fig. 4 Electroluminescence spectra of ITO/TPD/Eu(DTP)$_3$(dipphen)/Alq3/AlLi devices: (a) TPD(600 Å)/Eu(DTP)$_3$(dipphen)(500 Å)/Alq3(200 Å)/AlLi(2000 Å) and (b) TPD(600 Å)/Eu(DTP)$_3$(dipphen)(300 Å)/Alq3(500 Å)/AlLi(2000 Å).

there is no interaction between the TPD and Eu(DTP)$_3$(dipphen) layers, and indicate that hole–electron recombination occurs in the Eu(DTP)$_3$(dipphen) layer only.

The luminance–current-density–voltage characteristics of the double-layered EL device are shown in Fig. 3. It is seen that the luminance increases with increasing injection current as well as bias voltage. The turn-on voltage, which is defined as the voltage when the luminance is 1 cd m^{-2}, was measured and found to be <5 V. Red light with a maximum luminance of 168.0 cd m^{-2} was observed at 15 V and 200 mA cm^{-2}. The Commission Internationale de l'Eclarirage (CIE) coordinates of the emitted light are (0.68, 0.33) at 15 V, which is in the range of yellowish red light. Decreased luminance at voltages >16 V can be explained by the occurrence of dark spots generated mainly from the interface between Eu(DTP)$_3$(dipphen) and the AlLi cathode, as a result of humidity and the presence of oxygen.

Characteristics of the triple-layer-type EL device

To obtain higher luminance, Eu(DTP)$_3$(dipphen) and a electron transport material (Alq3) were deposited to form an emitting layer in triple-layer-type EL devices. Generally, in lanthanide metal complexes, the central metal ion is excited through the excitation of the ligand. For Eu(DTP)$_3$(dipphen), the excited energy at the π conjugation of the ligand is transferred to the central ion through the triplet energy level of the ligand.[14] Therefore, under EL operation, Alq3 is first excited by the recombination of the carriers, then the excited energy is transferred to the ligand, and finally to the central Eu ion.

The spectral features vary with the thickness of the emitter layer. EL devices with a 500 Å thick emitter layer exhibits only emission from the Eu complex [Fig. 4(a)]; however, upon decreasing the thickness of the emitter layer, a broad peak appears at 535 nm from the electron transport layer arising from Alq3 [Fig. 4(b)]. This can be attributed to exciton migration in the emitter layer, followed by energy transfer from Eu(DTP)$_3$(dipphen) to Alq3 at their interface. Thus, a thickness of *ca.* 500 Å is necessary for the emitter layer to show luminescence only from the Eu complex.

A luminance (L)–voltage (V) curve for the ITO/TPD(600 Å)/Eu(DTP)$_3$(dipphen)(500 Å)/Alq3(200 Å)/AlLi device is shown in Fig. 5. In this EL device, the red luminescence originates only from the Eu complex. It is seen that the luminance increases with increasing injection current as well as bias voltage. The turn-on voltage, defined as above, was measured and found to be <5 V. Red light with a maximum luminance of 450 cd m^{-2} was observed at 15 V. Compared with the luminance of previously reported Eu-based devices[9] (*ca.* 0.3 cd m^{-2}), the luminance level is substantially improved due to the electron injecting layer. Because Alq3 can carry a higher current density than Eu(DTP)$_3$(dipphen) with a thinner emitter layer, a higher current density can be obtained, resulting in higher luminance. The CIE coordinates of the emitted light are (0.67, 0.32) at 15 V, in the range of yellowish red light.

The decreased luminance at voltages >16 V can be explained by the occurrence of dark sports generated mainly from the interface between Alq3 and the AlLi cathode, owing

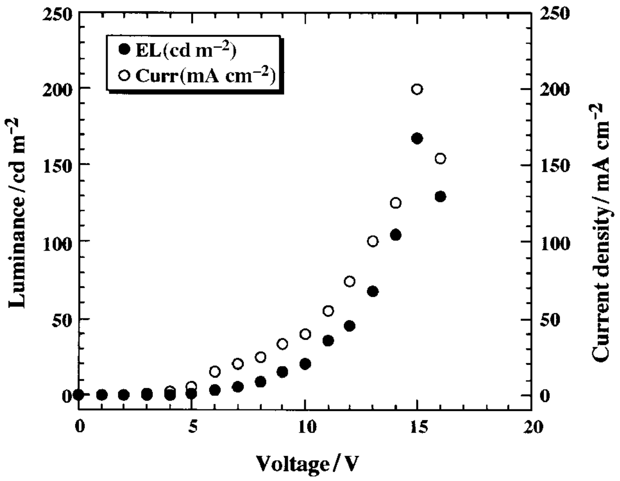


Fig. 3 Luminance–voltage and current-density–voltage characteristics of the double-layer-type EL device.

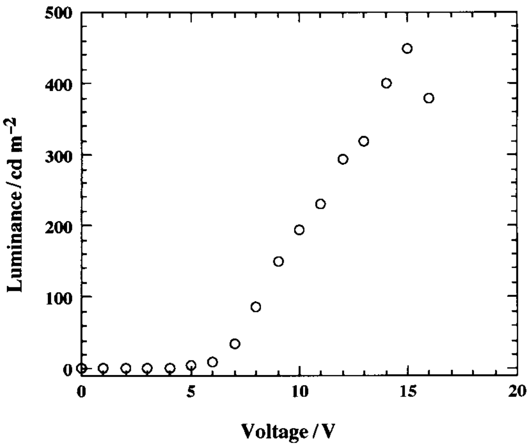


Fig. 5 Luminance–voltage characteristics of an ITO/TPD(600 Å)/Eu(DTP)$_3$(dipphen)(500 Å)/Alq3(200 Å)/AlLi(2000 Å) triple-layer-type EL device.

to the presence of humidity and oxygen. A device with a thinner emitter layer, such as TPD(600 Å)/Eu complex(300 Å)/Alq3(500 Å)/AlLi, yields a higher luminance at the same drive voltages (maximum luminance of >3850 cd m^{-2}). Unfortunately, however, the expected red color was not observed because of co-emission originating from both Alq3 (*ca.* 535 nm) and the Eu complex (*ca.* 614 nm) as shown in Fig. 4(b). The CIE coordinates of the emitted light are (0.54, 0.45) at 16 V, in the range of yellowish orange light.

The luminance (L)–current (I) curve of the above device is plotted in Fig. 6. In the low current density region, the efficiency (luminance/current density) increases as the current density increases. In this region, the majority of the carriers may be holes because the hole mobility in the TPD layer is higher than the electron mobility in the Alq3 layer.[15] Since the electric field across the Alq3 and Eu complex layer is increased due to the confinement of holes in the TPD layer, electron injection, and consequently, recombination efficiency increases as the current density increases. After reaching its maximum value, the efficiency then decreases with high current densities. This can be partly attributed to quenching of the excited state of the Eu complex by charge carriers since the concentration of these increases with increased current density. Since the luminescence lifetime of lanthanide complex is generally long (a few hundred µs),[16] due to highly prohibited f–f transitions, the probability of quenching by charge carriers should be much higher than that for organic luminescent dyes which have shorter fluorescence lifetimes.

It is thus concluded that a fluorescent sublimable complex such as Eu(DTP)$_3$(dipphen) can be used as an emitting material. It appears that the necessary condition for a complex emitting material for use in organic EL devices is the formation of an inner complex salt (no charge and a saturated coordination number) as found for Eu(DTP)$_3$(dipphen). Alq3[1] is an excellent emitting material with a luminance of >1000 cd m^{-2} since Alq3 forms an inner complex salt. Eu(TTA)$_3$ has been reported as a non-volatile complex[6] since this complex contains a coordinatively unsaturated Eu ion.

Conclusions

A novel volatile Eu complex was synthesized and used to prepare a multilayer EL device. A very sharp bright red EL spectral band centered at 614 nm and with a maximum luminance of 450 cd m^{-2} was observed from a triple-layer-type EL device. The present study may be important for the development of red and multicolored EL display applications. The necessary condition for a complex emitting material for use in an organic EL device appears to be the formation of an inner complex salt. We are currently designing and preparing other metal ion complexes to obtain different luminescent colors such as yellow and blue.

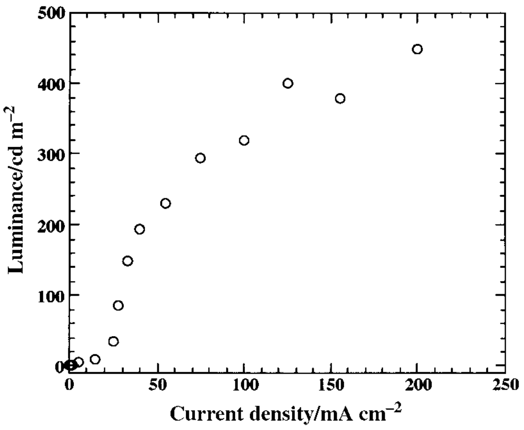


Fig. 6 Luminance–current density characteristic of an ITO/TPD(600 Å)/Eu(DTP)$_3$(dipphen)(500 Å)/Alq3(200 Å)/AlLi(2000 Å) triple-layer-type EL device.

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