

Oxadiazole-Functionalized Europium(III) β -Diketonate Complex for Efficient Red Electroluminescence

Fushun Liang, Quanguo Zhou, Yanxiang Cheng, Lixiang Wang,* Dongge Ma, Xiabin Jing, and Fosong Wang

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

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Organic light-emitting diodes (OLEDs) have been intensively studied throughout the world owing to their potential application in the next generation of full-color flat panel displays. Organic and polymeric electroluminescence (EL) across the whole visible region from blue to red has been demonstrated, and the efficiency, brightness, and device lifetime are rapidly approaching commercial target figures. However, it is difficult to achieve pure emission colors from small organic molecules or conjugated polymers because their emission spectra typically have a full-width at half-maximum wavelength of ca. 100 nm, which is not well-suited for actual display applications.

Luminescent lanthanide complexes are good candidates to solve this problem because lanthanide-based materials can generate extremely pure emission due to the $^5D_0 \rightarrow ^7F_2$ transition from central trivalent europium ion.^{1–6} However, the key problem met in the rare earth complexes is its very low EL efficiency when incorporated into LEDs due to the poor charge-carrier transporting ability.^{7–11} There have been some reports that focused on improving the EL efficiency by molecular design and physical methods such as blending or doping.^{3,12,13} For example, Wang et al. developed a terbium

complex with an oxadiazole-containing β -diketonate ligand with a light output of 100 cd/m² with an external quantum efficiency (EQE, photons/electrons) as high as 1.1% at 15 V.³ McGehee et al. described polymeric light-emitting diodes that emit pure red light with an EQE of 1.1% by making use of energy transfer from poly[2-(6'-cyano-6''-methylheptyloxy)-1,4-phenanthroline] (CN-PPP) to europium complex with β -diketonate and phenanthroline ligand.¹² Adachi et al. reported highly efficient EL devices based on a Eu complex doped into a wide energy-gap host (CBP, 4,4'-N,N-dicarbazolebiphenyl), showing an EQE of 1.4% at 0.4 mA/cm².¹³

In this communication we report an oxadiazole-functionalized europium complex (OXD-PyBM)Eu-(DBM)₃ (see Scheme 1), with the aim of realizing highly efficient red light emission. DBM (dibenzoylmethane) is chosen as the first ligand due to its relatively high PL efficiency in europium complexes. 2-(2-Pyridyl)benzimidazole (PyBM) is included as the second ligand since it is thought to enhance the electron transport of the material,¹⁴ in addition to saturating the coordination number of the europium ion and improving the volatility and stability of the europium complex.¹⁵ An oxadiazole moiety is introduced to the PyBM ligand through a flexible spacer for improving the electron-transporting properties and the solubility of the resulting complex. The functional moiety oxadiazole and the europium ion are expected to retain their own electron-transporting and emission properties, respectively. Therefore, the oxadiazole functionalized europium(III) is expected to exhibit the combined properties of europium-based complex and oxadiazole in its electroluminescent device, thus leading to highly efficient red electroluminescence.

The (OXD-PyBM)Eu(DBM)₃ complex was synthesized as shown in Scheme 1. 2-(2-pyridyl)benzimidazole and 2-(4-(4-bromobutyloxy)phenyl)-5-phenyl-1,3,4-oxadiazole were synthesized separately according to literature procedures.^{16,17} The second ligand OXD-PyBM was synthesized by a coupling reaction between 2-(2-pyridyl)benzimidazole and 2-(4-(4-bromobutyloxy)phenyl)-5-phenyl-1,3,4-oxadiazole in the presence of sodium hydroxide.¹⁸ The europium complex (OXD-PyBM)Eu-(DBM)₃ was synthesized by the conventional literature method.^{10,19,20}

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(18) A mixture of 2-(4-(4-bromobutyloxy)phenyl)-5-phenyl-1,3,4-oxadiazole (3.73 g, 10 mmol), 2-(2-pyridyl)benzimidazole (1.95 g, 10 mmol), sodium hydroxide (0.44 g, 11 mmol), and DMF (30 mL) was stirred and heated at 120 °C for 15 h under N₂. It was subsequently poured into ice water (100 mL). After extraction with dichloromethane (3 × 30 mL), the organic layer was washed with water and dried over anhydrous Na₂SO₄. The solvent was then evaporated. The resulting residue was purified by silica gel column chromatography (petroleum ether:ethyl acetate = 4:1 as eluent) to give 4.19 g of product (yield 86%), mp 190–192 °C. ¹H NMR (CDCl₃, 300 MHz): δ 1.94 (m, 2H), 2.20 (m, 2H), 4.10 (t, 2H), 5.04 (t, 2H), 7.01 (d, 2H), 7.43 (m, 3H), 7.56 (m, 4H), 7.95 (t, 1H), 8.01 (t, 1H), 8.07 (s, 1H), 8.11 (s, 1H), 8.15 (m, 2H), 8.67 (d, 2H).

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* Corresponding author. Tel: +86-431-5694787. Fax: +86-431-5685653. E-mail: lixiang@ciac.jl.cn.

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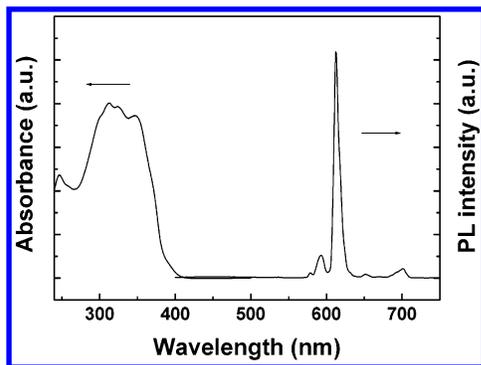
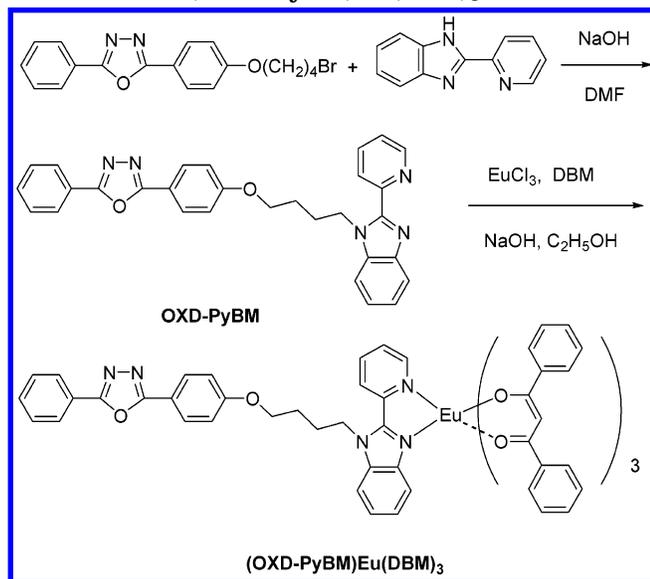


Figure 1. Absorption and emission spectra of (OXD-PyBM)Eu(DBM)₃ in CHCl₃ solution ($\lambda_{\text{ex}} = 365$ nm).

Scheme 1. Synthetic Route toward (OXD-PyBM)Eu(DBM)₃



The UV-vis spectrum was recorded in chloroform solution on a Varian Cray 50 spectrometer. A typical concentration of 1.5×10^{-5} mol/L was used for the measurements. The photoluminescent spectrum was obtained from the same solution using a Perkin-Elmer LS50B luminescence spectrometer. Figure 1 shows the absorption and photoluminescence spectra of (OXD-PyBM)Eu(DBM)₃ in CHCl₃ solution. The bands at 311 and 325 nm are attributed to the absorption of oxadiazole segment. The absorption peak located at 349 nm is associated with the β -diketonate ligand.¹² The sharp spectral bands of PL are the characteristic emissions of the Eu³⁺ ion. The main emission peak at 612 nm corresponds to the $^5D_0 \rightarrow ^7F_2$ transition of Eu³⁺ ion.

To investigate the electroluminescent properties of compound (OXD-PyBM)Eu(DBM)₃, a double-layer device with the structure of ITO/TPD(40 nm)/ (OXD-

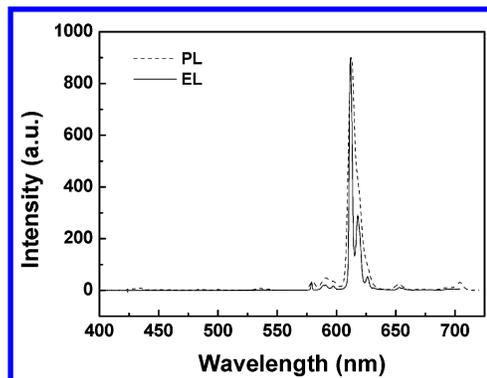


Figure 2. EL spectra of the double-layer device with the configuration of ITO/TPD/(OXD-PyBM)Eu(DBM)₃/LiF/Al and the PL spectrum of (OXD-PyBM)Eu(DBM)₃ film ($\lambda_{\text{ex}} = 365$ nm).

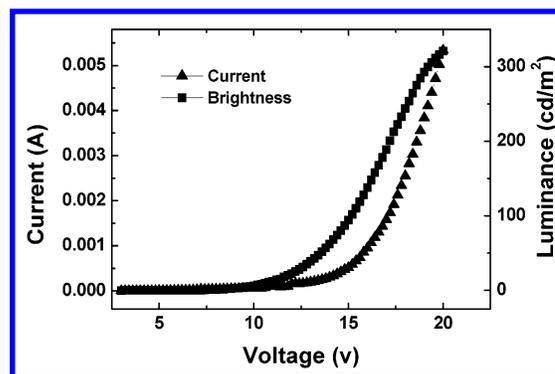


Figure 3. Luminance-current-voltage characteristics of the double-layer device.

PyBM)Eu(DBM)₃ (50 nm)/LiF (1 nm)/Al (200 nm) was constructed.²¹ *N,N*-Bis(3-methylphenyl)-*N,N*-diphenylbenzidine (TPD) was used as the hole-transporting layer. Figure 2 shows the EL spectrum of the resulting device. It can be seen that the EL spectrum is identical to the photoluminescent (PL) spectrum, indicating that the EL emission at 612 nm originates from the Eu³⁺ ion in compound (OXD-PyBM)Eu(DBM)₃.

Figure 3 shows the typical current-luminance-voltage (I - L - V) characteristics. The EL efficiencies as a function of the current are presented in Figure 4. Pure red emission was observed at as low as 7.8 V. The brightness of the device increases with the current density and the EL spectrum was independent of the bias voltage. It is reported that exciplex emission is often observed between the hole-transporting layer and emitting layer in lanthanide-based OLEDs.^{3,9,22} However, in our experiment no exciplex emission was observed at bias voltages ranging from 8 to 21 V. The possible explanation may be the balanced charge carrier injection and transport, and thus effective recombination.

(20) A solution of dibenzoylmethane (0.672 g, 3 mmol) and OXD-PyBM (0.487 g, 1 mmol) was dissolved in a mixture of hot ethanol and chloroform under stirring. The solution turned yellow immediately after sodium hydroxide (3 mL, 1 M) was added. Then EuCl₃(H₂O)₆ (0.366 g, 1 mmol) was dissolved in 2 mL of ethanol and added dropwise to the stirred solution. The mixture was stirred at 60 °C for 1 h. The yellowish white product was collected by filtration and recrystallized from ethanol, resulting in 75% yield, mp 132–134 °C. Elemental analysis for C₇₅H₅₈EuN₅O₈. Calcd: C, 68.77; H, 4.43; N, 5.39. Found: C, 67.88; H, 4.50; N, 5.23. The synthesized complex was readily soluble in common organic solvents such as CHCl₃ and THF and can be thermally evaporated, which is in favor of the fabrication of OLEDs.

(21) The device was grown on an ITO glass substrate. The ITO glass was routinely cleaned by ultrasonic treatment in detergent solutions, followed by being rinsed with acetone, boiled in 2-propanol, and rinsed in methanol and then in deionized water. The glass was dried in a vacuum oven between each cleaning step earlier. The electroluminescent device was fabricated by high-vacuum (2×10^{-6} Torr) thermal evaporation techniques. The shadow mask with 3×3 mm² openings was used to define the cathodes. The EL spectra were recorded with JY-SPEX CCD-3000 V spectrometer. The current-luminance-voltage characteristics were measured using a Keithley source measurement unit with a calibrated silicon photodiode.

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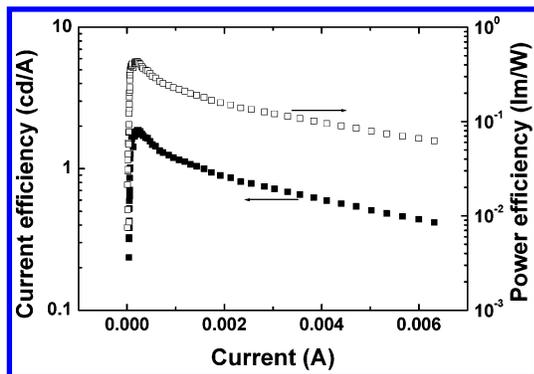


Figure 4. EL efficiencies as a function of current of the double-layer device.

The maximum brightness of the double-layer EL device is about 322 cd/m^2 at a driving voltage of 21 V. The current efficiency is estimated to be 1.9 cd/A at 57 cd/m^2 and 13.8 V, corresponding EQE as high as 1.7%.²³ To the best of our knowledge, this value is the highest among simple double-layer devices fabricated by vacuum deposition in OLEDs based on rare-earth complexes. The control device utilizing (*N*-alkyl-substituted PyBM)-Eu(DBM)₃ as an emitter exhibited poor performance with the current efficiency of 0.03 cd/A and power efficiency of 0.01 lm/W under the same condition, which is not comparable to the oxadiazole-functionalized europium device. These results suggest that the electron-transporting ability of the resulting complex is signifi-

cantly improved by the introduction of the oxadiazolyl group in the complex. The fact that inserting an additional electron-transporting layer of Alq₃ between the emitting layer and the cathode did not improve the device performance as compared to that of the double-layer device further demonstrates that the oxadiazole segment in (OXD-PyBM)Eu(DBM)₃ indeed plays an important role in achieving high efficiency.

In summary, we have designed and synthesized a europium(III) complex with an electron-transporting oxadiazolyl moiety which was attached through a spacer linkage. Pure red emission at 612 nm for the simple double-layer device was observed with the maximum brightness of 322 cd/m^2 , the luminous efficiency of 1.9 cd/A, and the quantum efficiency of 1.7%. The results demonstrate that incorporation of an oxadiazolyl group into the rare earth complex not only enhances the charge carrier transport, and thus improves the OLED performance, but also simplifies the device structure. It seems that the electroluminescent efficiency of rare-earth complexes can be significantly enhanced by improving their charge-carrier transport capabilities. Further investigation on modification of the first and the second ligand in a rare earth complex by introducing charge carrier groups are in progress.

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