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Red Electroluminescence and Photoluminescence from Novel Binuclear Europium Complex with Squaric Acid Ligand

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Abstract: A novel binuclear europium β-diketone complex with squaric acid ligand was synthesized for the first time. Its structure was elucidated by IR, UV, and Elemental Analysis. Red light emitting diode (LED) was fabricated by using the novel europium complex as an emitting layer, tris(8-quinolinolate) aluminum (III) (Alq_3) as an electron-transporting layer, N, N'-diphenyl-N, N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) as a hole-transporting layer. A cell structure of indium-tin-oxide/TPD/Eu-complex/Alq_3/Mg: Ag was employed. Red electroluminescence was observed at room temperature with dc bias voltage of 2 V in this cell. Red emission peaks at about 613 nm with maximum luminance of over 106 cd/m^2. Compared with the EL luminance from those europium complexes reported before, one from the Eu-complex is best in the same cells.

Keywords: Europium chelate, squaric acid, electroluminescence (EL), photoluminescence (PL).

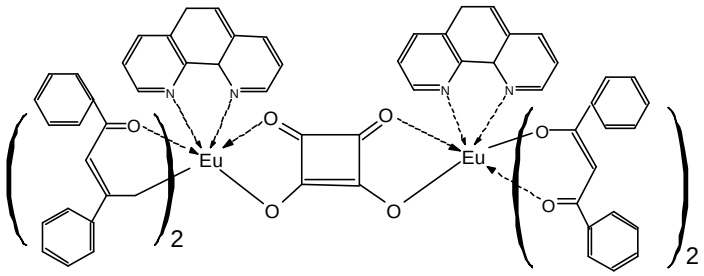
Organic electroluminescent devices (OELDs) have attracted much attention for several years because of their potential application in large area, multi-colored flat panel displays[1-5]. The green organic EL display using Alq_3 as emitter was commercialized in 1997[6]. However, red-emitting OELD with excellent properties has not been well developed.

In order to realize practical full-color OELDs, it is considered very important to develop red and blue emitting materials with excellent properties. There are a few red-emitting materials, but it is difficult to obtain pure red light because most organic EL spectra from them have broad bandwidth. Therefore, pure red emitting materials are been developing.

As europium complexes have high fluorescent quantum efficiency, sharp spectra and good stability, they have been used as red-emitting materials[7]. But the luminance of the devices using these Eu-complexes as emitters is relatively low. In this paper, we report a novel binuclear europium complex $Eu_2(DBM)_4(Sq)Phen_2$ with squaric acid and β-diketone ligands used as red emitter. It was designed and synthesized as red-emitting material in LED for the first time. The PL and EL properties were studied. It was found that its PL and EL properties had been much improved than that of those europium complexes reported before.

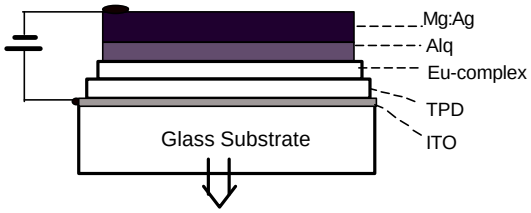
The schematic molecular structures of $Eu_2(DBM)_4(Sq)Phen_2$ and the cell structure used it as emitter were showed in **Figure 1** and **Figure 2** respectively.

Figure 1 The schematic molecular structures of $Eu_2(DBM)_4(Sq)Phen_2$



$Eu_2(DBM)_4(Sq)Phen_2$

Figure 2 LED cell structure used $Eu_2(DBM)_4(Sq)Phen_2$ as emitting layer



Results and Discussion

The PL spectrum of film (20 nm) of $Eu_2(DBM)_4(Sq)Phen_2$ and EL spectrum of the cell were illustrated in **Figure 3**. The film of $Eu_2(DBM)_4(Sq)Phen_2$ exhibited intense red fluorescence at 613 nm with a narrow half bandwidth of 10 nm, corresponding to the $^5D_0$-$^7F_2$ transition of europium ion. Bright red emission was observed from the LED when it operated under dc bias. The PL and EL spectra of $Eu_2(DBM)_4(Sq)Phen_2$ were almost identical, indicating that the emission of the cell was originated from the emitting layer.

The luminance-voltage characteristic of the cell was showed in **Figure 4**. The LED turned on at voltage of 4V and its emission intensity increased with increasing voltage and injected current. A maximum luminance of 106 cd/m^2 at voltage of 20 V from this cell was observed, which was much higher than one of the device with $Eu(DBM)_3Phen$ instead of $Eu_2(DBM)_4(Sq)Phen_2$. The enhancement of the luminance was obtained due to improvement of carrier-transporting properties of the novel Eu-complex. The ligand of squaric acid has excellent carrier-transporting properties as reported before[8], thus it is possible to improve carrier-transporting properties of europium complex of $Eu_2(DBM)_4(Sq)Phen_2$.

Figure 3 PL spectrum of film(20nm) of $Eu_2(DBM)_4(Sq)Phen_2$ and EL spectrum of the cell.

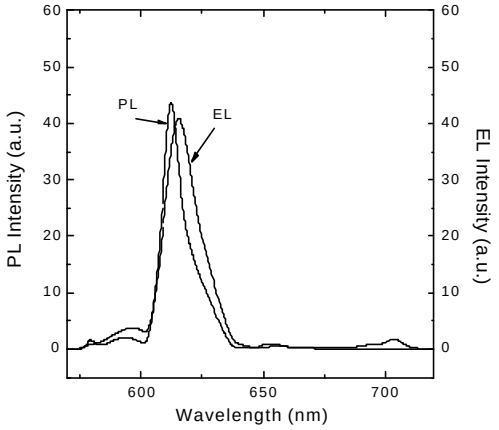
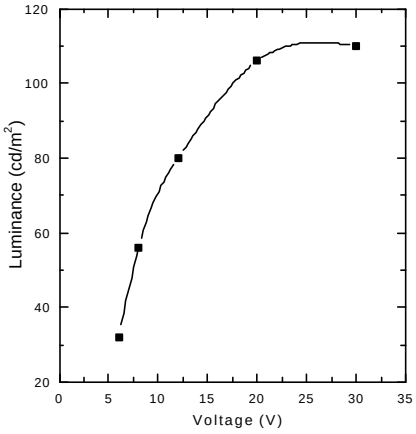


Figure 4 Luminance-voltage characteristic of the cell



The results of the excited fluorescence spectra showed that the maximum excited wavelength (Exmax) of 404 nm from film of $Eu_2(DBM)_4(Sq)Phen_2$ was longer than that of 300 nm from film of $Eu(DBM)_3Phen$. This implied that the PL excited energy of the former was lower than that of the latter. Since the PL and EL are similar at the excited state of europium ion in the final luminescent course, EL excited energy of $Eu_2(DBM)_4(Sq)Phen_2$ may be decreased in comparison with that of $Eu(DBM)_3Phen$ in the cell. So the cell used $Eu_2(DBM)_4(Sq)Phen_2$ as emitter had a decreased turn-on voltage.

In conclusion, red light emitting diode (LED) utilizing a novel europium complex with squaric acid ligand as emitter has been successfully realized for the first time. The results indicated that a new Eu-complex of $Eu_2(DBM)_4(Sq)Phen_2$ has excellent carrier-transporting and EL properties. The LED cell used it as emitter with a double-layer structure can emit strong red light with a luminance of 106cd/m^2. So the novel binuclear complex could be used as a promise red EL material in LED.

Experimental

Synthesis of compound $Eu_2(DBM)_4(Sq)Phen_2$: To a 100 mL flask containing a solution of squaric acid (Sq, 0.092 g, 0.8 mmol) dissolved in 20 mL of ethanol and a solution (0.8 mL) of sodium hydroxide (2 mmol/L) was added a solution of europium chloride (1.6 mmol) dissolved in 4 mL of water, which was obtained according to literature 3 procedure. The solution was stirred at 50~60°C for 10 min. A solution of dibenzoylmethane (HDBM, 0.719 g, 3.2 mmol) dissolved in 30 mL of ethanol was added to above solution. The reaction mixture was neutralized to *p*H = 6~7 with 2 mol/L sodium hydroxide and stirred for 1.0 hr at the same temperature. Then a solution of 1,10-phenanthroline monohydrate (0.319 g, 1.6 mmol) in 20 mL of ethanol was dropped to the above mixture. A yellow precipitate was formed. After being stirred for 3.0 hr

further, the reaction mixture was cooled to room temperature, filtered and washed with water and ethanol for several times. The yellow powder product was obtained after drying for 3 hr at 100°C with yield of over 84.2%, mp: 184~185°C, $Eu_2C_{88}H_{60}N_4O_{12}$ Calcd.: C 63.31, H% 3.62, N% 3.36. Found: C% 63.12, H% 3.73, N% 3.28.

The LED cell was fabricated by conventional vacuum vapor deposition in a vacuum of 5.0×10^{-4} Pa. The thickness of hole-transporting layer (HTL), emitting layer (EML), electron-transporting layer (ETL) and cathode were 40 nm, 20 nm, 20 nm and 200 nm respectively. The deposition rate was about 0.2 nm/s. The EL spectrum was recorded on a spectrophotometer (JOBONYVON-SPEX). The EL luminance was determined on a luminance meter (TOPCON, BM-8). The photoluminescence (PL) spectrum was done on a fluorescence spectrophotometer (HITACHI-850). All the measurements were carried out at room temperature in air. The area of the light-emitting diode was 2×2 mm square.

Acknowledgments

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