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Synthesis and Photoluminescence of New Europium Complex $Eu(DBM)_3(DPPZ)$ with Dipyridophenazine Ligand

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Abstract: Dipyrido [3, 2-a:2′,3′-c] phenazine moiety has been introduced as neutral ligand in europium complex. Therefore, a new europium complex with saturated emission, strong fluorescent intensity and good solubility was designed and synthesized for the first time. Its photoluminescence and UV properties were examined. The experimental results showed that this new Eu-complex could be used as red electroluminescent materials.

Keywords: Europium complexes, dipyridophenazine, synthesis, photoluminescence (PL) property.

Organic/polymer electroluminescent devices (OLEDs/PLEDs) have attracted much attention because of their potential application in large area, multi-colored flat panel displays[1-2]. A variety of electroluminescent materials (ELMs), including organic small molecular materials, metal complex and polymers have been synthesized for these years. The high emission efficiency of OLEDs/PLEDs has also been achieved [3-4]. But there are some serious issues to be solved such as broad bandwidth and emission annihilation in OLEDs/PLEDs. To design and synthesize new ELMs with sharp spectra and higher emission efficiency, and obtain highly monochromatic light are in need.

It is well known that rare earth complexes not only have high fluorescent quantum efficiency, but also exhibit photoluminescence with sharp spectral band (FWHM<10nm). Pure red and green light emitting diodes (LEDs) based on rare earth complexes have already been developed[5-6]. But the high efficiency of these LEDs has not been achieved. Recently, Li *et al*. reported that LEDs based on $Eu(DBM)_3$bath with luminance of 820cd/m^2 was achieved[7]. Z. Hong showed that the external quantum efficiency of LEDs based on a new europium complex was 4.6%[8]. It is obvious that the structure of rare earth complexes besides structure of devices has a strong influence on photoluminescent (PL) and electroluminescent (EL) properties.

Verhoeven reported currently that di- and tetra-azatriphenylene derivatives constitute a very promising new class of antennae to sensitize most lanthanides luminescence in dry acetonitrile[9]. The influence of azatriphenylene derivatives on PL properties of ionic Eu-complexes (EuL_2Cl_3) in solution was only investigated, in which L represents

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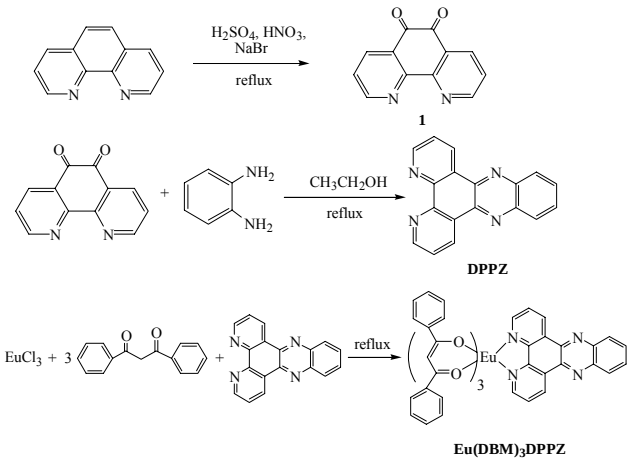
azatriphenylene derivatives ligands. Some ionic europium complexes with di- and tetra -azatriphenylene in solution showed excellent PL properties. But the neutral rather than ionic Eu-complexes with azatriphenylene derivatives and antennae effect of azatriphenyl -ene derivatives in the Eu-complex have not been reported. As azatriphenylene derivatives have strong antennae effect in ionic Eu-complexes solution, it is considered that they may improve luminescent properties of neutral Eu-complexes solid. Only europium complexes with excellent PL properties and film-formation can be first considered as candidates of electroluminescent materials. Therefore, we report the synthesis of a novel europium complex $Eu(DBM)_3(DPPZ)$, in which 1, 3-diphenyl- 1, 3-propanedione (DBM) and dipyrido[3, 2-a:2′, 3′-c]phenazine (DPPZ) were used as monoanionic and neutral ligands, respectively. The PL and UV properties of $Eu(DBM)_3(DPPZ)$ were studied. It was found that this new europium complex also exhibited excellent fluorescent intensity and good solvency. The schematic synthesis of $Eu(DBM)_3(DPPZ)$ was shown in **Scheme 1.**

Scheme 1 The schematic synthesis of Eu $(DBM)_3(DPPZ)$



Experimental

1,10-phenanthroline-5, 6-dione **1** was synthesized according to literature[10].

Synthesis of DPPZ: A solution of **1** (0.515 g, 2.45 mmol) with 15 mL of ethanol was added into *o*-phenylenediamine (0.530 g, 4.91 mmol) with 10 mL of ethanol and trace *p*-toluene sulfuric acid. The mixture was gentlely boiled and stirred for 3 hr, then removed some ethanol and cooled to room temperature. A brown precipitate was obtained and recrystallized from aqueous ethanol to give brown-orange needle with yield of 74%[11], mp. 248~249°C (lit[11]: mp. 250°C). GC-MS: M^+, 282.

Synthesis of $Eu(DBM)_3(DPPZ)$: A solution of DBM(0.256 g, 1.18 mmol) and DPPZ(0.109 g, 0.386 mmol) dissolved in 30 mL of ethanol was neutralized with solution of sodium hydroxide (2 mmol/L, 0.06 mL). Then a solution of europium chloride (0.386 mmol) dissolved in 4 mL of water was added dropwise into the flask with stirring.

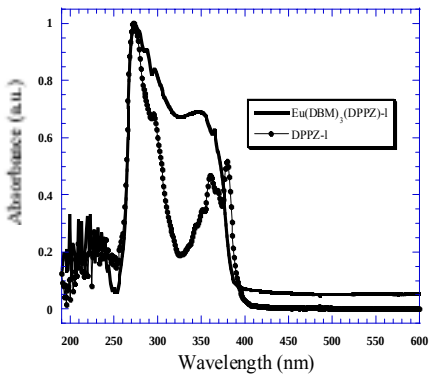
The mixed solution was stirred at 65~70°C for 3.0 hr. The formed yellow precipitate was filtered and washed with water and ethanol for several times. The product was obtained after recrystallization from chloroform and petroleum in yield over 58.0%, mp.165~166°C, $EuC_{63}H_{43}N_4O_6$ Calcd (%): C: 68.54, H: 3.93, N: 5.07. Found (%): C: 68.27, H: 3.85, N: 5.02.

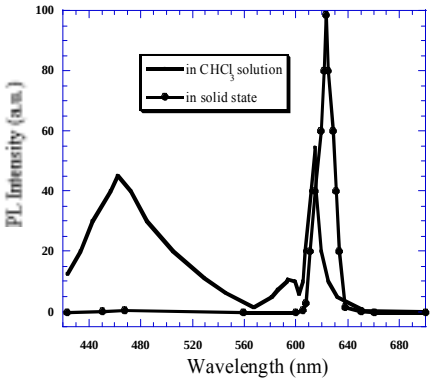
GC-MS data were obtained using Trace GC-MS-2000 Series System (Finnigan). Elemental analysis was performed on Harrios Elemental Analysis Instrument. The UV-Visible absorption spectra of films from europium complex or ligand were recorded with a HP-8453 UV Visible System. The photoluminescence (PL) spectrum was recorded on a fluorescence spectrophotometer (HITACHI-850).

Results and Discussion

The UV-visible spectra of chloroform solution of europium complex $Eu(DBM)_3(DPPZ)$ and ligand DPPZ were showed in **Figure 1**. We know that an extremely weak absorption of europium ion in near UV-vis region constitutes a major obstacle in luminescent application[12]. But an intense UV absorption from DPPZ and its europium complex was observed in **Figure 1**. The UV absorption peaks in chloroform were located at 274 nm, 361 nm, 380 nm from DPPZ, and 274 nm, 350 nm from $Eu(DBM)_3(DPPZ)$, respectively. This implied that UV-vis absorption property of europium complex could be improved by introduction of neutral ligand with intense UV absorption. There is the same UV absorption peak at 274 nm for DPPZ and its europium complex, indicating that europium ion was coordinated with ligand DPPZ.

Figure 1 UV-vis spectra from $Eu(DBM)_3(DPPZ)$ **Figure 2** PL spectrum from $Eu(DBM)_3(DPPZ)$





The photoluminescence (PL) properties of $Eu(DBM)_3(DPPZ)$ in solid state and in chloroform solution were studied. The maximum excited wavelength (λ_{Exmax}) of 310 nm from film and 401 nm from chloroform solution of 2.0×10^{-4} mol L^{-1} for $Eu(DBM)_3(DPPZ)$ were recorded. The PL spectra of $Eu(DBM)_3(DPPZ)$ were shown in **Figure 2**. It is very interesting that PL spectrum in chloroform solution is different from that in solid state of $Eu(DBM)_3(DPPZ)$. There are three fluorescent peaks at 614

nm, 593 nm, 462 nm in chloroform solution of $Eu(DBM)_3(DPPZ)$, but only a fluorescent peak at 623 nm for the film of $Eu(DBM)_3(DPPZ)$. It was not clear why there were different PL spectra in two states of this Eu-complex, but this result indicated that efficient energy tranfer could take place from DPPZ ligand to europium ion in Eu-complex solid.

The triplet energy of many azatriphenylene derivatives is sufficiently high to allow fast and essentially irreversible energy transfer to most lanthanides reported before[13]. $Eu(DBM)_3(DPPZ)$ exhibited intensive red fluorescence at 622 nm with a narrow half bandwidth of 10 nm rather than 462 nm from DPPZ ligand, it implied that DPPZ ligand could also have strong sensitized effect to europium ion in this Eu-complex. Although PL intensity of $Eu(DBM)_3(DPPZ)$ was a bit weaker than that of $Eu(DBM)_3(bath)$, it is very important to further study the influence of this type of ligand with electron-transporting property on PL and EL properties of Eu-complexes. Because DPPZ derivatives have excellent electron-transporting property reported before[14]. The systematic research about the influence of this type of ligands on PL and EL property of Eu-complexes is currently in developing.

In conclusion, a novel Eu-complex with an azatriphenylene derivative ligand was synthesized and its red fluorescence peaked at 622 nm was achieved for the first time. The excellent antennae effect between neutral ligand DPPZ and europium ion may be useful to improve not only the PL property, but also the electroluminescent property.

Acknowledgments

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