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Synthesis and Fluorescent Properties of New Binuclear Europium β-Diketone Chelates $Eu_mY_{1-m}(TTA)_3phen$ as Red Electroluminescent Materials

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Abstract: A new type of binuclear europium β-diketone chelates Eu_mY_{1-m} $(TTA)_3phen$ ($0 \leq m \leq 1$) and the influence of the proportion of Y^{3+} on fluorescence intensity of the Eu-complexes were studied. It was found the proportion of Y^{3+} could affect the fluorescence properties and the film formation seriously, only $m \geq 0.5$, Y^{3+} could increase the luminescent intensity and improve the film formation. As a result, three new binuclear europium β-diketone chelates consisted of Eu_mY_{1-m} $(TTA)_3phen$ (m=0.9, 0.7 and 0.5) were designed and synthesized. Their structures were elucidated by IR, UV, DSC and Elementary Analysis. Their PL properties were studied. The results showed that the three binuclear europium β-diketone chelates had better PL properties and film formation than $Eu(TTA)_3phen$. They could emit sharply red light, and fluorescent wavelength of them was all at 613nm (half bandwidth: 10nm). They can be used as red organic electroluminescent materials (OELMs) in organic electroluminescent devices (OELDS).

Keywords: Europium β-diketone chelate, synthesis, photoluminescence, fluorescence properties.

Organic thin film electroluminescent display (OTFELD) has gone into the stage of practical study, since Pioneer Co. reported the first commercial product of organic green EL display using small molecules [1]. As OTFELD has many advantages such as active emission, high brightness, low driving voltage, wide viewing angle, light weight, and potential low cost, it is attracting much attention as a candidate for new flat panel display. However, there are many subjects to realize the full color displays.

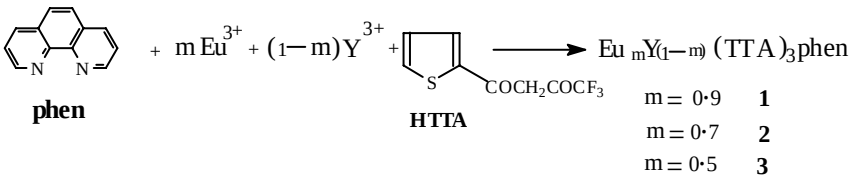
The organic red and blue EL displays are the basic essential to realize full color displays. In order to realize red and blue emission, apart from improving structure and fabricating technology of electroluminescent devices (ELDs), it is very important to design and synthesize organic red-emitting materials, and blue-emitting ones.

Europium β-diketone metal chelates had been investigated for many years [2]. They were regarded as the first selective materials which realized red organic EL display because they have many advantages, such as high quantum efficiency, good stability, pure color (half-bandwidth: 10 nm). But their poor carrier transporting properties and film formation affect their EL efficiency. Now the maximum luminance of their ELDs was only 460 cd/m^2 yet [3-6].

To solve the problems of their ELDs with low luminance and EL efficiency, we should improve carrier transporting property and film formation of Eu-complexes. One of the best methods is to design and synthesis novel Eu-diketone chelates with excellent EL properties.

By introducing Y^{3+} into the structure of Eu-complexes, we designed and synthesized a type of novel binuclear Eu-complexes of $Eu_mY_{1-m}(TTA)_3$phen ($0 \leq m \leq 1$) for the first time. The PL properties of three compounds were studied and the three compounds could emit red light. It was found that the PL properties of the novel binuclear Eu-complexes had been improved. As for their EL properties, we are currently developing.

Scheme of synthesis



phen **HTTA**

Results and Discussion

The luminescent property of Eu $(TTA)_3$phen was developed several years ago. It can emit pure red light and attract much attention all over the world. But for its poor carrier transporting property and film formation, its EL efficiency has been influenced seriously. In order to improve EL properties of Eu-complexes, we introduced isonuclear Y^{3+} in $Eu(TTA)_3$phen, and studied the fluorescent properties of the $Eu_mY_{1-m}(TTA)_3$phen ($0 \leq m \leq 1$). When $m \geq 0.5$ in $Eu_mY_{1-m}(TTA)_3$phen, the PL intensity had obviously increased, the film formation had improved. The PL intensity was listed in **Table I**.

Table I The PL intensity of $Eu_mY_{1-m}(TTA)_3$phen ($0 \leq m \leq 1$) in Solid State

Complexes	i	ii	iii	iv	v	vi	vii	viii	ix	x	xi
m	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
PL Intensity	++	+++	+++	+++	++	++	+	+	-	-	-

+++ very strong ++ strong + middle – weak or no

The three binuclear Eu-complexes (m=0.9, 0.7 and 0.5) were designed, synthesized, and were measured by IR, UV, DSC and Elementary Analysis. The results indicated that one of the three compounds was not a simple mixture of $Eu(TTA)_3$phen and $Y(TTA)_3$phen, but was an isonuclear metal chelate with Eu^{3+} and Y^{3+}. As Eu^{3+} and Y^{3+} have almost the same radius, they were easy to form a component solid solution compound.

As Y^{3+} has stable electronic structure ($4s^2 4p^6$), there was not energy transfer between Y^{3+} and ligand HTTA, $Y(TTA)_3$phen can not emit light. When Y^{3+} and Eu^{3+} formed binuclear metal chelates, Y^{3+} could make Eu^{3+} to emit strongly light for it made energy transfer easy. Meanwhile, it could improve the film formation of Eu_mY_{1-m} $(TTA)_3$ phen ($m \geq 0.5$).

The PL properties were listed in **Table II**. The PL data of **1, 2** and **3** compounds could emit sharply red light. The reason lies in the triplet energy of ligand HTTA can more efficiently transfer to excited state of Eu^{3+} due to "Antenna Effect" between Eu^{3+} and HTTA. It was found that their PL properties and film formation were obviously superior to that of Eu $(TTA)_3$phen, the fluorescent intensity of them had enhanced 40 percent of Eu $(TTA)_3$phen.

Table II PL property of compound **1, 2** and **3** (λ_1: 10^{-4}M in chloroform solution; λ_2: Solid state)

Complexes	1		2		3	
	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2
λ_{EXmax} (nm)	347	295	344	307	342	307
λ_{EMmax} (nm)	613	613	613	613	613	613

We can draw conclusion from our study that the three new binuclear europium metal chelates can be used as red OELMs, because PL has similar luminescent mechanism to EL.

Experimental

Synthesis of compound **1, 2 and 3**: Europium oxide (**m**/2 mmol, m=0.9, 0.7 and 0.5) and yttrium oxide (0.5– **m**/2 mmol) were dissolved in concentrated hydrochloric acid (36%), removed surplus HCl by vaporizing, and diluted with 10 ml of water. The solution of thienyltrifluoroacetone (3.0 mmol) in 30 ml of ethanol was dropped into the solution of europium chloride with stirring, neutralized to *p*H=6-7 with 2N sodium hydroxide. The mixture was heated to 50-60 ^{0}C for 1.0 hr. The solution of 1,10-phenanthroline monohydrate (1.0 mmol) in 10 ml of ethanol was added. A granular precipitate formed within several seconds. After being stirred for 1.0 hr, the reaction mixture was cooled to room temperature, filtered and washed with water and ethanol for several times. The pale powder product was obtained after drying under vacuum at 120 ^{0}C, with yield of over 80%.

Compound **1:** yellow powder, Mp:250^{0}C, $Eu_{0.9}Y_{0.1}C_{36}H_{20}F_9N_2O_6S_3$ C%:43.70, H%:2.04, N%:2.83, Eu%:13.82, Y%: 0.90. Found: C%:43.58, H%:2.01, N%:2.79, Eu%:13.60, Y%:0.85.

Compound **2:** yellow powder, Mp:245^{0}C, $Eu_{0.7}Y_{0.3}C_{36}H_{20}F_9N_2O_6S_3$ C%:44.27, H%:2.06, N%:2.87, Eu%:10.89, Y%:2.73. Found: C%:44.06, H%:2.05, N%:2.82, Eu%:10.75, Y%:2.70.

Compound **3:** yellow powder, Mp:247^{0}C, $Eu_{0.5}Y_{0.5}C_{36}H_{20}F_9N_2O_6S_3$ C%:44.85,

H%:2.09, N%:2.91, Eu%:7.88, Y%: 4.61. Found: C%:44.67, H%:2.05, N%:2.88, Eu%:7.62, Y%:4.56.

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