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4, 4, 4-三氟-1-(4′-邻三联苯基)-1, 3-丁二酮邻菲咯啉铕(Ⅲ)配合物的合成及发光

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摘要:合成了一个新配合物 EuL_3phen,[HL=4, 4, 4-三氟-1-(4′-邻三联苯基)-1, 3-丁二酮,phen =邻菲咯啉]。该化合物在半导体 InGaN 芯片发出的近紫外光激发下能够发出铕(Ⅲ)离子特征红光,发光量子效率为 9%。将配合物 EuL_3phen 和半导体 395 nm 发射 InGaN 芯片组合,成功地制备了红色发光二极管。在配合物和硅胶质量比为 1:25 时,器件色坐标为 x=0.6123, y=0.3128,光效为 0.68 $lm\cdot W^{-1}$。

关键词:铕配合物;化学合成;发光;发光二极管
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Synthesis and Luminescence of Eu(Ⅲ) Complex Based on 4, 4, 4-Trifluoro-1-(4′-*o*-terphenyl)-1, 3-butanedione and 1, 10-Phenanthroline

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Abstract: A new europium(Ⅲ) complex, EuL_3phen, [HL=4, 4, 4-trifluoro-1-(4′-*o*-terphenyl)-1, 3-butanedione, phen= 1, 10-phenanthroline] was synthesized. The complex shows red emission of Eu^{3+} ions under near ultraviolet(NUV) InGaN chip emission light with a quantum yield of 9%. Red luminescent LEDs were fabricated by assembly of EuL_3phen and 395 nm-emitting InGaN chips. When the mass ratio of the complex to the silicone is 1:25, the chromaticity coordinates is x=0.6113, y=0.3125, and the efficiency of the fabricated LED with the europium complex achieves 0.68 $lm\cdot W^{-1}$.

Key words: europium complex; chemical synthesis; luminescence; LEDs

There has been an increasing demand for white light based lighting emitting diodes(LEDs) as potential replacement for the incandescent bulbs and fluorescent lamps [1,2]. In the past years, white LEDs were obtained mainly by combining an 465 nm blue-emitting InGaN chip with a broad-band yellow-emitting phosphor, e.g., Ce^{3+}-doped yttrium aluminum garnet($YAG:Ce^{3+}$)[3].

However, such white LED shows low color-rendering index, low color reproducibility and low luminous efficiency because of the lack of red light component[4]. It is difficult to find stable red-emitting phosphors excited by blue light.

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Recently, with the development of LED chip technology, the emission bands of LED chips have been shifted from blue light (~465 nm) to near ultraviolet (NUV) range(370~400 nm), and the NUV light can offer higher energy to pump the phosphor. Thus, another new trend is to fabricate white LEDs with an NUV chip plus blue-, green- and red-emitting tricolor phosphors and this kind of white LEDs can show improved color-rendering index and a wide range of color temperatures. The commonly used red-emitting phosphor for NUV InGaN-based white LEDs is $Y_2O_2S:Eu^{3+}$. It is pity that this red phosphor exhibits lower efficiency and shorter working life-time under NUV irradiation compared with that of the blue (e.g. $BaMgAl_{10}O_{17}:Eu^{2+}$) and the green (e.g. $ZnS:Cu^{+}$, Al^{3+}) phosphors. Therefore, it is urgent to search for new red phosphors that can be efficiently excited by around ~400 nm-light. Organic phosphors usually possess strong absorptions in NUV region, which are produced by π-π^* transitions, and the emission colors can be easily adjusted by molecular design and structural modifications [5]. Europium (Ⅲ) β-diketonate complexes have long been known to give bright red emission under NUV irradiation because of the efficient energy transfer from the β-diketonate ligand to the central europium(Ⅲ) ions and widely used as organic electroluminenscence materials [6]. In our previous work, some europium(Ⅲ) -diketonate complexes were used as red phosphors to fabricate red LEDs with NUV-emitting InGaN chips[7~9].

4, 4, 4-Trifluoro-1-(4′ -*o*-terphenyl)-1, 3-butanedione (HL) bears an *o*-terphenyl unit with a suitable -conjugated system and β-diketonate group. Thus, the ligand HL could absorb the near emission light from InGaN chips and transfer the absorbed energy to europium ion. Here we report the synthesis of europium complex based on 4, 4, 4-trifluoro-1-(4′ -o-terphenyl)-1, 3-butanedione and application of the complex as red phosphor in InGaN lighting diodes.

1 Experimental

1.1 Reagents and Physical measurements

o-Terphenyl (98%), ethyl trifluoroacetate (99%), potassium *tert*-butoxide(99%) were purchased from Alfa Aesar. Eu_2O_3 (99.99%) was purchased from Zhujiang Refinery. Epoxy resin was purchased from ShengHong Opto-electron Huizhou Company. InGaN chip was purchased from Shenzhen Yuanchuang Electron Science and Technology Company. The solvents (CH_2Cl_2 and toluene) were analytical reagents and were dried before use. $EuCl_3 \cdot 6H_2O$ was obtained from the reaction of Eu_2O_3 and HCl(36%). 4-acetyl-*o*-terphenyl was synthesized from *o*-terphenyl through Friedel-crafs according to the reported literature[10].

Elemental analyses were performed on an Elementar vario EL elemental analyzer. The content of Eu element was determined according to the reported method [11]. Infrared spectra (400 ~4 000 cm^{-1}) were recorded with samples as KBr pellets using a Nicolet NEXUS 670 FTIR spectrophotometer. ^1H NMR spectra were measured using a Mercury-Plus 300MHz nuclear magnetic resonance spectrometer with $CDCl_3$ as solvent and TMS as internal reference. FAB-MS spectra were measured on a DSQ EI-mass spectrometer. UV/Vis spectra were recorded on UV-3150 UV-Vis-NIR Spectrophotometer. Excitation and emission spectra and fluorescence lifetime were measured with an Edinburgh FLSP920 Combined Fluorescence Lifetime and Steady State Spectrometer. Thermogravimetric analyses (TG) was performed on a TG209F3 Tarsus Thermogravimetry from 30 ~600 ℃ in the N_2 atmosphere. Luminescence quantum yield was measured according to the method reported by Pilipescu using $Eu(TTA)_3(phen)$ (Φ=0.365 in DMF, TTA =2-thenoyltrifluoroacetonate) as a standard [12]. The emission spectrum of the fabricated LEDs was measured with an Everyfine PMS-50 Plus UV-Vis-near IR Spectrophotocolorimeter at room temperature.

1.2 Synthesis of the ligand

Potassium *tert*-butoxide (0.68 g, 0.012 mol), 4-acetyl-*o*-terphenyl(2.72 g, 0.010 mol) and ethyl trifluoroacetate(1.21g, 0.010 mol) were mixed in 50 mL of dry toluene. The mixture was stirred in a sealed flask for 3 h at room temperature. Then, the mixture was treated with 50 mL of 15% HCl. The organic phase was separated and washed with water (20 mL×3). The crude product was obtained after removing of the solvent toluene under reduced pressure. The light solid was purified by column chromatography(petroleum ether-CH_2Cl_2) (yield:

1.6 g, 40.4%). The elemental analysis data for $C_{22}H_{15}F_3O_2$ were: [found (cald.)/%] C, 72.10 (71.74), H, 4.07 (4.10), IR (KBr, cm^{-1}): 3416, 3047, 1611, 1481, 1281, 1189, 850, 750, ^{1}HNMR ($CDCl_3$, δ, ppm): 7.72 (4H, m), 7.53 (3H, m),7.36 (2H, m), 7.15 (2H, m), 7.02 (2H, t) 6.42 (1H, s) EI-Ms, 369.

1.3 Synthesis of complexes

EuL_3(phen) (phen=1, 10-phenanthroline): A solution of 0.073 g(0.02 mmol) $EuCl_3 \cdot 6H_2O$ in 2 mL ethanol was added dropwise to a solution of 0.221 g(0.06 mmol) ligand HL(HL=4, 4, 4-trifluoro-1-(4′-*o*-terphenyl)-1, 3-butanedione) and phen (0.040 g, 0.02 mmol) in 20 mL ethanol, resulting in a pale yellow solution. A solution of 1 mol·L^{-1} NaOH was added dropwise to this solution to pH=9, light yellow precipitate formed rapidly. The mixture was stirred at 60 ℃ for 1 h, then cooled to the room temperature and was added to 20 mL water, filtered, and the precipitate washed with ethanol, H_2O and dried under vacuum to give the desired product (yield: 0.18 g, 62.7%). The elemental analysis data for $C_{78}H_{50}EuF_9N_2O_6$ were: [found(cald.)/%] C, 65.21(65.32), H, 3.77(3.51), N, 1.91(1.95), Eu, 10.38(10.60). IR(KBr, cm^{-1}): 3086, 1605, 1520, 1292, 1186, 852, 753.

$GdL_3(H_2O)_2$: The gadolinium(Ⅲ) complex was synthesized with a similar method to the europium complex except for $GdCl_3 \cdot 6H_2O$ instead of $EuCl_3 \cdot 6H_2O$ and absence of phen. The elemental analysis data for $C_{66}H_{46}GdF_9O_8$ were:[found(cald.)/%] C, 60.91(61.06), H, 3.85(3.80).

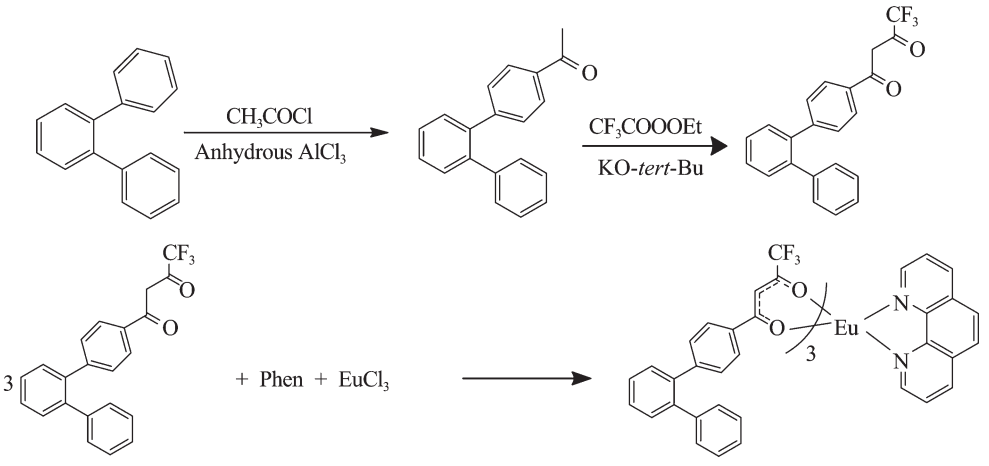
1.4 Fabrication of red lighting emitting device

Red light-emitting diodes were fabricated by combination of a ~395 nm-emitting InGaN chip with complex as a phosphor. The phosphor was blended with silicone in order to be precoated onto the LED chip. The thickness of the admixture precoated onto the chip was the same due to the fixed size of the reflector cup. The admixture was cured in an oven at 150 ℃ for 1 hour. In order to prevent the phosphor from dispersing into the epoxy resins, another silicone layer was coated onto the phosphor and was cured for another 1 h. The whole LED lamp was encapsulated with transparent epoxy resin.

2 Results and discussion

2.1 Synthesis and thermal stability of the complex

The ligand was synthesized from Friedel-Crafs and Claisen condensation reaction. The complex was obtained from reaction between the ligand HL and $EuCl_3 \cdot 6H_2O$ in the presence of a base(Fig.1). Elemental analysis for ligand and complex are in good agreement with the calculated values. In IR spectra, there is a typical vibration of C=O at 1 611 cm^{-1} for the ligand, but in the complex this peak splits into two peaks at 1 605 cm^{-1} and 1 520 cm^{-1}, indicating that C=O coordinates to Eu(Ⅲ) ions. Thermogravimetric analysis(TG) shows that the thermal stability of the complex is 170 ℃, which meets the requirement for normal working temperature of LEDs[5].



CF_3COOEt=ethyl trifluoroacetate, KO-*tert*-Bu=potassium *tert*-butoxide

Fig.1 Synthetic routes for HL and EuL_3(phen)

2.2 UV-Vis absorption and fluorescence spectra

The UV-Vis absorption spectra for 1×10^{-5} mol·L^{-1} ligand and the complex in DMF (Fig.2) exhibit a broad band within 250~380 nm, attributed to singlet-singlet $\pi\rightarrow\pi^*$ enol absorption, characteristic of the enol form of β-diketones. The shapes of the absorption spectra of complex are similar to the free ligand, suggesting that the β-diketonate ligands contribute to the absorption of the complex and the coordination of europium(Ⅲ) ions do not have a significant influence on the $\pi\rightarrow\pi^*$ state energy. The high molar absorption coefficient (10^5 L·mol^{-1}·cm^{-1}) reveals that the β-diketonate ligand has a strong ability to absorb light.

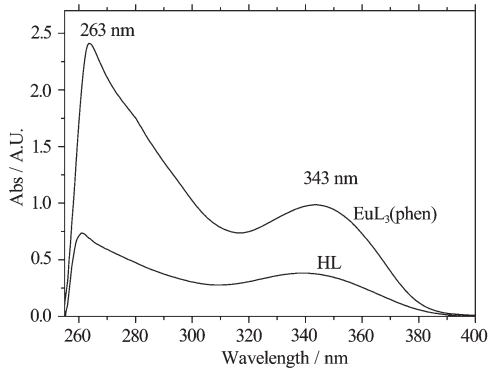


Fig.2　Absorption spectra of the ligand HL and complex EuL_3(phen) in DMF(1×10^{-5} mol·L^{-1})

The excitation and emission spectra of the powder samples of the complex are shown in Fig.3. Monitored at 613 nm, there is a wide strong excitation band from 240 nm to 420 nm, the intensity is still strong enough at 395 nm, matching to the emission wavelength of an InGaN NUV chip, and thus the complex could be efficiently excited by the chip. The complex shows strong orange-red emission under 395 nm NUV-light excitation.

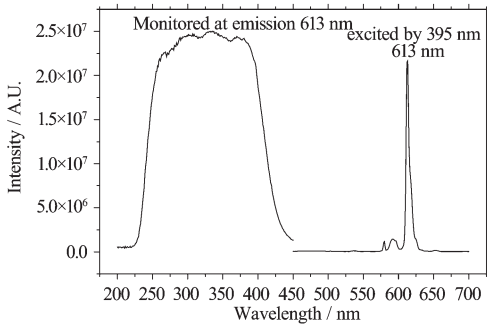


Fig.3　Excitation(λ_{em}=613 nm) and emission spectra (λ_{ex}=395 nm) for the powder sample of the complex EuL_3(phen)

The lowest triplet state energy of the ligand(L^-) is determined to be 17 857 cm^{-1} estimated from the shortest wavelength transition in the phosphorescence spectra of $GdL_3(H_2O)_2$ at 20 K. The lowest triplet state energy(17 857 cm^{-1}) of the ligand(L^-) is higher than the lowest excited state of Eu^{3+}, $^5D_0$(17 267 cm^{-1}), confirming the suitability of the ligand as a sensitizer to Eu^3-emission. The luminescence quantum yield of the complex in DMF is shown to be 9% at room temperature. The results indicate that the complex is red luminescence and can act as red light color-conversion material.

The luminescence decay curve of Eu^{3+} related to the $^5D_0\rightarrow{}^7F_2$ emission in the complex powder sample is presented in Fig.4. The lifetime measurement for the excited state of the Eu(Ⅲ) ion was recorded under the excitation at 395 nm at room temperature. The luminescence lifetime of the $^5D_0$ emitting level for complex is 432 μs. The decay curve can be fitted with a single exponential model, consistent with one symmetric site for the Eu(Ⅲ) ion.

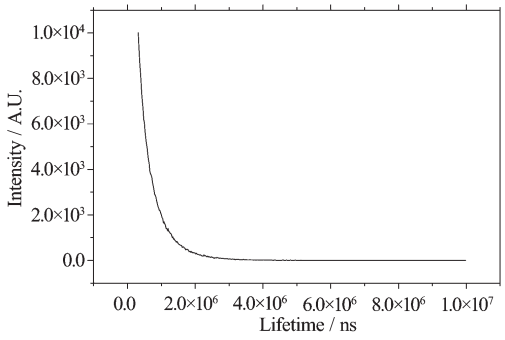


Fig.4　Decay curve of Eu^{3+} $^5D_0$ excited state of the complex EuL_3(phen)

2.3 Fabrication of red lighting emitting diodes

Red light-emitting diodes was fabricated by combination of a 395 nm-emitting InGaN chip with the complex as phosphor while an original LEDs without phosphor was also made for comparison. Fig.5 shows the emission spectra of the InGaN-complex LEDs and the original InGaN LEDs without phosphor under 20 mA forward bias. The sharp and intense peak at 614 nm for the complex-LEDs is due to the Eu^{3+} emission from the complex in the LEDs. Comparison of the excitation

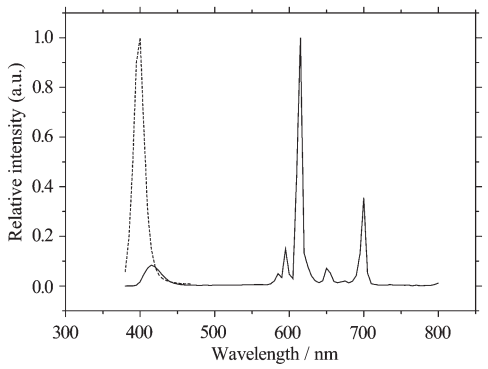


Fig.5 Emission spectra of the original InGaN chip without phosphor(dashed line), the LED with complex $EuL_3(phen)$ (solid line) under 20 mA forward bias

spectra of the Eu^{3+} complex and the emission band of the original InGaN chip confirms that the complex can be efficiently excited by the ~395 nm-light emitted from the InGaN chip. The remained emission intensity from the InGaN chip in the emission spectra of the complex-LEDs is related to the mass ratio of the phosphor to the silicone. At a higher ratio of the red phosphor to the silicone, more emitting light from the InGaN chip is absorbed and more red light is emitted. When the mass ratio of the red phosphor to the silicone is 1:25, the CIE chromaticity coordinates of the complex-LEDs are calculated to be x=0.6113, y=0.3125 based on their emission spectra. The efficiency of the original LEDs without phosphor is only 0.31 $lm \cdot W^{-1}$. However, the efficiency of the fabricated LEDs with the europium complex achieves 0.68 $lm \cdot W^{-1}$. The complex has no absorption in blue and green emission band, and the remained ~395 nm emission from the InGaN chip in the complex-LEDs can be used to excite blue and green phosphors to generate white light. Therefore, this europium complex may potentially act as a red component in fabrication of white LEDs if appropriate blue and green phosphors with a suitable mass ratio are chosen.

3 Conclusions

A new europium complex based on 4, 4, 4-trifluoro-1-(4-*o*-terphenyl)-1, 3-butanedione was synthesized. The complex emits red light under near UV irradiation. Bright red light-emitting diode was fabricated by coating the complex onto 395 nm-emitting InGaN chips, suggesting that this europium complex can potentially act as a red component in fabrication of white LEDs.

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