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Enhanced luminescence of novel rare earth complexes Eu(3,5-DNBA)$_3$Phen in nano-TiO$_2$

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ABSTRACT

Eu^{3+} (or Tb^{3+}) of 3,5-dinitrobenzoic acid and 1,10-phenanthroline ternary rare earth complexes were synthesized and characterized by thermal analysis, infrared spectroscopy, elemental analysis and fluorescence spectroscopy. In this study an organic–inorganic combined device indium tin oxide/poly(*N*-vinylcarbazole):RE(3,5-DNBA)$_3$Phen:TiO$_2$/Al was fabricated. The nano-TiO$_2$ has been used in the luminescence layer to change the electroluminescence property of RE(3,5-DNBA)$_3$ Phen (RE = Eu^{3+}or Tb^{3+}).

1. Introduction

Rare earth metal complexes have special characteristics, such as extremely narrow emission bands and high internal quantum efficiencies, which are suitable to be used as the emission materials [1–4]. Therefore, many rare earth complexes have been synthesized and used as organic electroluminescence devices [5–10]. Titanium dioxide (titania, TiO$_2$) with the rutile-type structure is transparent for light in the wide range of the visible spectrum. The absence of light absorption, along with its high refractive index ($n \sim 2.7$), makes rutile-type TiO$_2$ a fascinating material for photonic applications in the visible regions. In spite of this advantage, little attention has been paid to rare earth ternary complexes with Eu^{3+} (or Tb^{3+}), 3,5-dinitrobenzoic acid and 1,10-phenanthroline in nano-TiO$_2$.

The complexes of Eu(3,5-DNBA)$_3$Phen and Tb(3,5-DNBA)$_3$Phen were synthesized, and nano-TiO$_2$ was mixed with the rare earth complex and poly(*N*-vinylcar-bazole) to form the luminescence layer in the electroluminescence [11–16]. It was found that there was an efficient energy transfer process between the complex and nano-TiO$_2$, when the device was operating at low voltages. It shows that it is an effective method to improve the electroluminescence intensity of lanthanide complex by using electronic characteristics of inorganic semiconductor materials.

2. Experiments

2.1. Materials

The purity of europium (terbium) oxides was 99.99%. Other reagents were used in analytical grade.

2.2. Synthesis of materials RE(3,5-DNBA)$_3$Phen

1 mmol mixture of EuCl$_3$·6H$_2$O (or TbCl$_3$·6H$_2$O), and 3 mmol of 3,5-DNBA were dissolved in ethanol. The pH value of the mixture was adjusted to 6–7 by adding 3 mmol ammonia. Then 1,10-phenanthroline in ethanol solution was added to the reaction mixture, the molar ratio of 1,10-phenanthroline to RE^{3+} ion was 1:1. The precipitate was filtered, washed with water and ethanol, dried at room temperature, and then stored in a silica–gel drier. Nano-TiO$_2$ was prepared using the chemical vapor deposition (CVD) of TiCl$_4$ [17]. The compositions of the complexes were analyzed by IR and elements analysis according to the ordinary methods, and its chemical structure was shown in Fig. 1. Elemental analysis data of complexes were listed in Table 1.

2.3. Measurements

Elemental analyses were performed on a PerkinElmer 240 C analytical instrument. DTA–TG curves were obtained with a TGA–DTA 1700-PerkinElmer (in N$_2$). Infrared (IR) spectra were recorded in the range of 4000–400 cm^{-1} by a prostige-21IR spectrophotometer in KBr flake. The excitation and emission spectra measurements were

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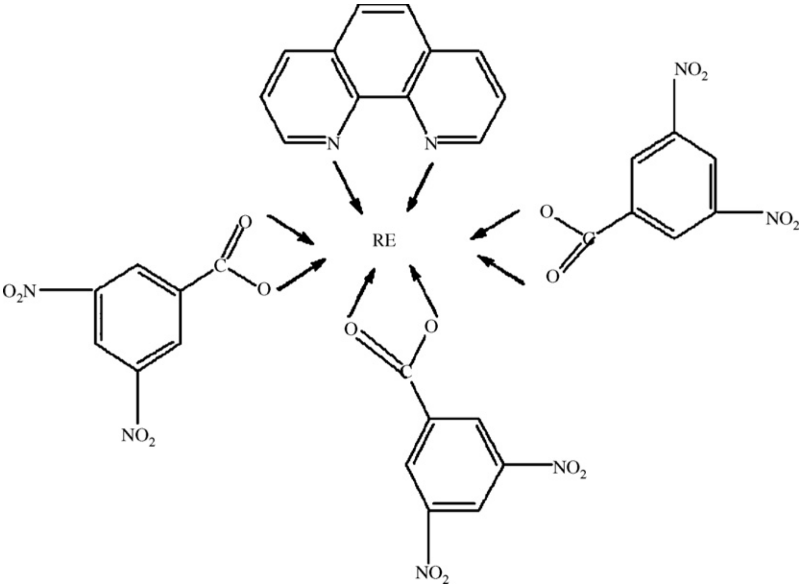

Fig. 1. Chemical structure of ternary complexes of RE(3,5-DNBA)$_3$Phen.

Table 1
Elemental analysis.

Complex	RE%	Analytically found (calculated)%		
		C	H	N
Eu(3,5-DNBTA)$_3$Phen	15.72 (15.74)	41.03 (41.01)	1.78 (1.76)	11.62 (11.60)
Tb(3,5-DNBTA)$_3$Phen	16.37 (16.35)	40.70 (40.72)	1.76 (1.75)	11.51 (11.52)

performed on a Shimadzu 5301 spectrofluorophotometer equipped with a 150 W xenon lamp as the excitation source. Spectra were recorded using monochromator slit widths of 1.5 nm on both excitation and emission sides. The PL and EL spectra were measured on a fluorolog-3 Spectrophotometer of the American SPEX Company. The luminance was measured by PR-650 spectra-scan spectrometer.

3. Results and discussion

3.1. DTA–TG analysis

DTA–TG plots of Eu(3,5-DNBA)$_3$Phen are shown in Fig. 2. DTA–TG plots of complex Tb(3,5-DNBA)$_3$Phen showed similar curve patterns. For DTA plots of Eu(3,5-DNBA)$_3$Phen, exothermic peak at 245 and 410 °C, the gross weight loss is 75%. RE(3,5-DNBA)$_3$Phen decompose in two steps, ranging from 450 to 700 °C, TG curves prove that the complexes are stable.

3.2. IR spectra analysis of the complexes

FTIR absorption spectra of complexes are shown in Fig. 3. It is noted that similar results are obtained from Eu(3,5-DNBA)$_3$Phen and Tb(3,5-DNBA)$_3$Phen complexes. The band in the spectra of complexes at about 525 cm^{-1} (which cannot be observed in the ligands) reveals the presence of O → RE. The band at wave number 1560 cm^{-1} is due to stretching vibration of –N=C, while at 721 cm^{-1} is corresponding to $r_{\text{C–H}}$ vibration of 1,10-phenanthroline. In addition, typical asymmetric vibration of $V_{\text{C=O}}$ group bands is detected at about 1608 and 1531 cm^{-1}.

3.3. Photoluminescence properties

All excitation spectra were recorded by monitoring the luminescence at 614 nm for Eu^{3+} and 545 nm for Tb^{3+} in Fig. 4. For ligand (3,5-DNBA) and RE(3,5-DNBA)$_3$Phen, the excitation spectrum consists of a broad band ranging from 260 to 400 nm, and their λ_{ex} are 312 and 315 nm, respectively in Fig. 4(a). Fig. 4(b) shows the emission spectra of ligand and RE(3,5-DNBA)$_3$Phen, which were obtained by exciting these complexes with ultraviolet. It can be observed that the spectra are the typical ligand centered transitions in 414 nm. The experiment results prove that the RE^{3+} absorbs the

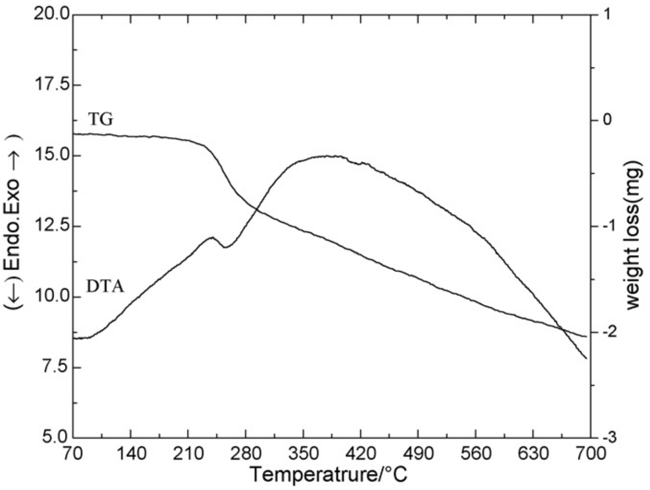

Fig. 2. DTA–TG plots of Eu(3,5-DNBA)$_3$Phen.

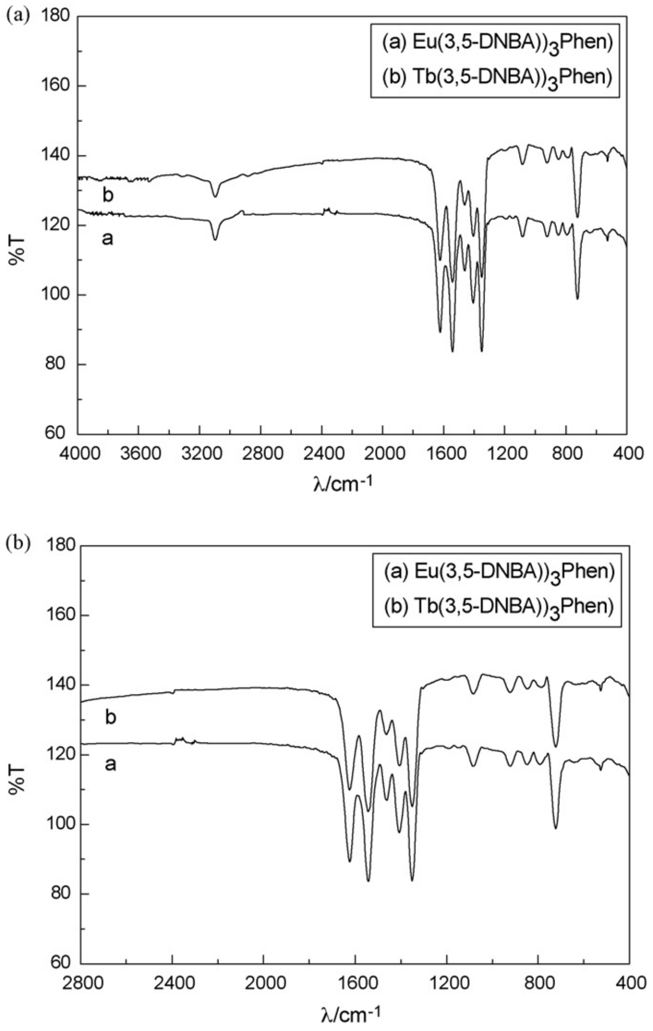

Fig. 3. (a) Infrared spectra of RE(3,5-DNBA)$_3$Phen in the range 4000–400 cm^{-1}. (b) Infrared spectra of RE(3,5-DNBA)$_3$Phen in the range 2800–400 cm^{-1}.

energy and transferred it to the ligands, and then the ligands emit typically blue luminescence.

3.4. Electroluminescence properties

Two electroluminescence devices with different structures were fabricated, which were denoted as A and B, respectively. Their structure can be abbreviated as ITO/PVK:RE(3,5-DNBA)$_3$Phen:TiO$_2$/Al for A and ITO/PVK:RE(3,5-DNBA)$_3$Phen/Al for B. In device A, nanometer material of TiO$_2$ was used as a function layer for the transportation and acceleration of electron.

In this experiment, no electroluminescence for device B with the pure organic structure. Fig. 5 shows a typical EL spectrum of Eu(3,5-DNBA)$_3$Phen in device A, the characteristic emissions of europium ions are obtained at a driving voltage of 11 V. The emission peak at 594 nm is corresponding to the energy level transitions of $^5D_0$–$^7F_1$ of europium ion (Eu^{3+}), the $^5D_0$–$^7F_1$ has strong orange luminescence emission. Compared to device B, the luminescence property of Eu^{3+} complex changed obviously in device A. Under the same conditions, no emission band was observed for the complex Tb(3,5-DNBA)$_3$Phen. Semiconductor TiO$_2$ thin film acts as electron function layer and hole blocking layer according to its electronic characteristics and energy level [18–20]. Therefore, the EL property of Eu(3,5-DNBA)$_3$Phen has been greatly changed.

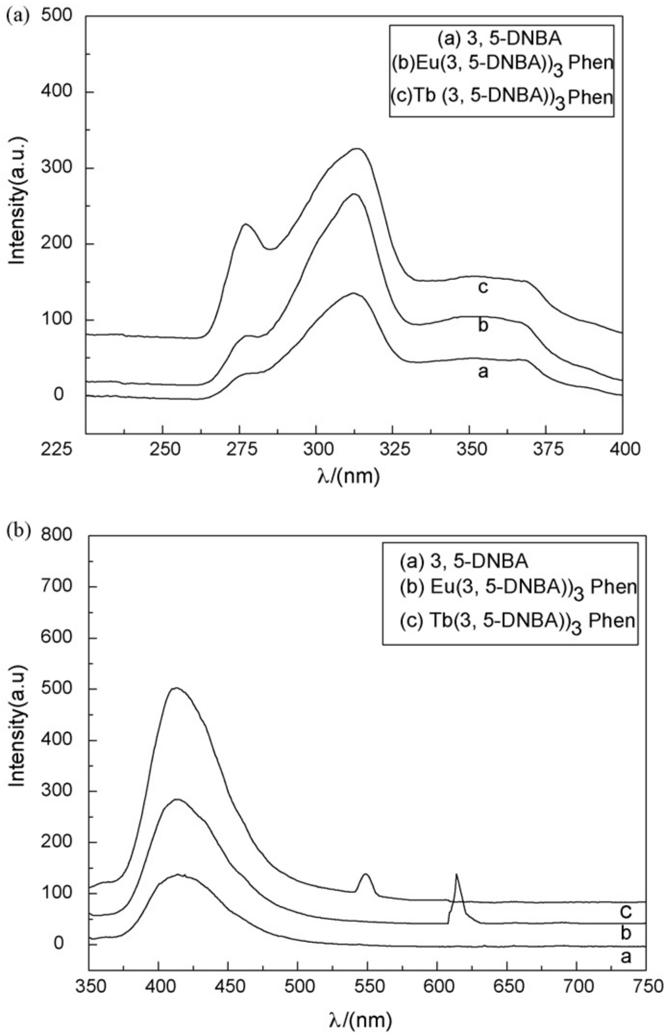

Fig. 4. (a) Typical excitation spectra of ligands and complex RE(3,5-DNBA)$_3$Phen. (b) Typical emission spectra of ligands and complex RE(3,5-DNBA)$_3$Phen.

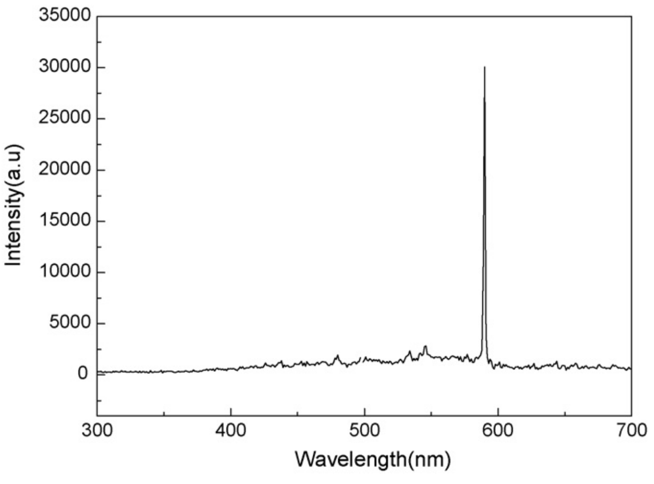

Fig. 5. EL spectrum of Eu(3,5-DNBA)$_3$Phen at a driving voltage of 11 V.

4. Conclusion

Eu^{3+} and Tb^{3+} of 3,5-dinitrobenzoic acid and 1,10-phenanthroline ternary complexes had been synthesized and characterized. The experiment results showed that the RE^{3+} absorbs the energy and the energy was transferred to ligands, then the ligands emit typical blue luminescence.

A novel electroluminescence device with organic–inorganic structure was fabricated based on layered optimization scheme. Nano-TiO_2 was utilized as electron function layer in the organic–inorganic combined structure, so the excitation of lanthanide can be carried out in a new route, which means electrons directly impact excitation the lanthanide ions through resonant energy transfer. It was found that the combined structural device may be an effective way to improve the electro-luminescence intensity of rare earth complex. Thus, it can be expected that nano-TiO_2 material play an important role in improving electroluminescence intensity of lanthanide complex.

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References

[1] J. Kide, H. Hayase, K. Hongawa, Appl. Phys. Lett. 65 (1994) 2124–2128.
[2] Q. Wang, B. Yan, X. Zhang, J. Photochem. Photobiol. A: Chem. 174 (2005) 119–124.
[3] H. Miki, I. Ayumi, K. Shinobu, J. Photochem. Photobiol. A: Chem. 178 (2006) 220–224.
[4] H. Song, J. Wang, J. Lumin. 118 (2006) 220–226.
[5] M. Norio, N. Rei, M. Jun, A. Tomita, J. Lumin. 107 (2004) 256–260.
[6] G. Zhong, Y. Wang, C. Wang, B. Pu, J. Lumin. 99 (2002) 213–222.
[7] T. Kiyomi, G. Norihiko, K. Masao, J. Photochem. Photobiol. A: Chem. 169 (2005) 109–114.
[8] K.K. Mahato, S.B. Rai, A. Rai, Spectrochim. Acta Part A 60 (2004) 979–985.
[9] Y. Liu, C. Ye, G. Qian, J. Qiu, M. Wang, J. Lumin. 118 (2006) 158–164.
[10] H. Shen, Z. Xu, D. Tao, J. Rare Earth 21 (2003) 519–523.
[11] H. Cao, X. Cao, C. Huang, Appl. Surf. Sci. 161 (2000) 443–447.
[12] Y. Wang, F. Teng, Z. Xu, Y. Hou, Appl. Surf. Sci. 236 (2004) 251–255.
[13] Y. Fu, J. Zhang, Z. Huang, X. Wang, Y. Lv, W. Cao, J. Photochem. Photobiol. A: Chem. 197 (2008) 329–334.
[14] S. Elias, L. Panagiotis, Chem. Phys. Lett. 417 (2006) 406–411.
[15] Y. Sun, H. Jiu, D. Zhang, J. Gao, Chem. Phys. Lett. 410 (2005) 204–209.
[16] J. Kido, Y. Okamoto, Chem. Rev. 102 (2002) 2357–2368.
[17] S. Pilkenton, S.-J. Hwang, D. Raftery, J. Phys. Chem. B 103 (1999) 11152–11156.
[18] Y. Lv, J. Zhang, W. Cao, F. Zhang, Z. Xu, J. Photochem. Photobiol. A: Chem. 188 (2007) 155–160.
[19] Y. Lv, J. Zhang, W. Cao, L. Song, Z. Xu, Mater. Lett. 62 (6/7) (2008) 1107–1109.
[20] Y. Lv, J. Zhang, W. Cao, Y. Fu, J. Alloys Compd. 462 (2008)153–156.