

# Photophysics of the Lanthanide Complexes with Conjugated Carboxylic Acids by Low Temperature Fluorescent Spectroscopy

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In the context, some lanthanide ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Sm}^{3+}$ ) complexes with conjugated carboxylic acids (pyridine-carboxylic acids derivatives) have been synthesized and characterized. The low temperature fluorescent spectra for these complexes have been measured at nitrogen atmosphere (77 K), indicating that the central  $\text{Ln}^{3+}$  ions locate in an equivalent coordination environment with low symmetry for most of these lanthanide complexes belonging to dimeric or polymeric structure. Therefore, the electronic dipole transition (supersensitive transition) ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$  for  $\text{Eu}^{3+}$ ,  $^5\text{D}_4 \rightarrow ^7\text{F}_6$  for  $\text{Tb}^{3+}$ ,  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$  for  $\text{Sm}^{3+}$ ) and magnetic dipole transition ( $^5\text{D}_0 \rightarrow ^7\text{F}_1$  for  $\text{Eu}^{3+}$ ,  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  for  $\text{Tb}^{3+}$ ,  $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$  for  $\text{Sm}^{3+}$ ) show the regular change in the corresponding split number of fluorescent spectra, which can be realized to predict the fine structure of lanthanide complexes.

**KEY WORDS:** Lanthanide complexes; pyridine-carboxylic acids ligands; photophysical property; low temperature fluorescent spectroscopy; coordination environment.

## INTRODUCTION

The photophysical properties of rare earth coordination compounds with organic ligands have been the subject of great interest because these functional complexes have great potential applications in such fields as the active center of luminescent materials and devices [1–3] or as structural and functional label for the chemical and biological macromolecule systems [4–6]. A lot of investigations were engaged in the luminescence, energy match and intramolecular energy transfer mechanism of rare earth complexes with  $\beta$ -diketones, aromatic carboxylic acids and heterocyclic ligands, which show good energy coupling and, afterwards good luminescent properties of rare earth ions [7–10]. We also have studied the energy match and intramolecular energy transfer process of binary and ternary lanthanide complexes with aromatic carboxylic acids and 1,10-phenanthroline in details [11–14].

Especially rare earth complexes of aromatic carboxylic acids have higher thermal or luminescent stabilities for practical applications than other lanthanide coordination systems because they readily form the dimer or polymeric structures [15–20].

Due to narrow f–f transitions of  $\text{Ln}^{3+}$ , a good sensitization on the  $\text{Ln}^{3+}$  luminescence can be achieved through the antenna effect. The lines of the emission spectra are generally sharp and dependent on the crystal field around the metal ions, resulting in the determination of the symmetry and geometry of corresponding coordination compounds. Some research was reported on the relationship between the molecular structure of lanthanide complexes with aromatic carboxylic acids and fine low temperature fluorescent spectra at liquid nitrogen temperature, which can be expected to elucidate the mutuality between spectral split number and coordination environment surrounding the central lanthanide ions. But the most research was mainly focused on the europium complexes systems, and little attention has been paid on other  $\text{Ln}^{3+}$  ( $\text{Sm}^{3+}$  or  $\text{Tb}^{3+}$ ) complexes of aromatic carboxylic acids [7–14,21]. For example, G. Vicentini *et al.* gave a detailed review on

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the luminescence and structure of europium complexes by their emission spectra and X-ray structural analyses [22].

In the context, some lanthanide ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Sm}^{3+}$ ) complexes with conjugated carboxylic acids (pyridine-carboxylic acids derivatives) were synthesized and the corresponding photophysical properties were studied in detail.

## EXPERIMENTAL

### Synthesis of Lanthanide Complexes

Lanthanide oxides ( $\text{Eu}_2\text{O}_3$ ,  $\text{Tb}_4\text{O}_7$ ,  $\text{Sm}_2\text{O}_3$ ) were converted to their nitrates by treatment with concentrated nitric acid. The corresponding lanthanide complexes with aromatic acids (pyridine-3-carboxylic acid (HNIC), pyridine-3-carboxylic acid (HPIC), 2-chloropyridine-3-carboxylic acid (HCNIC), 5-bromo-pyridine-3-carboxylic acid (HBNIC)) were prepared by homogeneous precipitation. Conjugated carboxylic acids were dissolved into ethanol solutions whose pH value was adjusted to about 6.5. Then aqueous solution of lanthanide nitrates was added very slowly to the above solution, resulting in the white microcrystals, filtered off, washed with ethanol or water, dried and stored over silica gel. The compositions of the complex systems were confirmed by elemental analysis:  $\text{Ln}(\text{NIC})_3(\text{H}_2\text{O})_2$ , Ln = Eu, Tb, Sm. Anal. Calcd. for  $\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}_8\text{Eu}$ : C, 39.00; H, 2.91; N, 7.58; Found: C 39.21; H, 2.80; N, 7.74. For  $\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}_8\text{Tb}$ : C, 38.52; H, 2.87; N, 7.49; Found: C, 38.95; H, 2.61; N, 7.73. For  $\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}_8\text{Sm}$ : C, 39.11; H, 2.92; N, 7.60; Found: C, 38.76; H, 2.63; N, 7.82; C, 32.39; H, 2.42; N, 12.77.  $\text{Ln}(\text{PIC})_3(\text{H}_2\text{O})_2$ , Ln = Eu, Tb, Sm. Anal. Calcd. for  $\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}_8\text{Eu}$ : C, 39.00; H, 2.91; N, 7.58; Found: C, 38.66; H, 2.58; N, 7.55. For  $\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}_8\text{Tb}$ : C, 38.52; H, 2.87; N, 7.49; Found: C, 38.52; H, 2.87; N, 7.49. For  $\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}_8\text{Sm}$ : C, 39.11; H, 2.92; N, 7.60; Found: C, 38.79; H, 2.60; N, 7.42.  $\text{Ln}(\text{CNIC})_3(\text{H}_2\text{O})_2$ , Ln = Eu, Tb, Sm. Anal. Calcd. for  $\text{C}_{18}\text{H}_{13}\text{Cl}_3\text{N}_3\text{O}_9\text{Eu}$ : C, 32.88; H, 1.99; N, 6.39; Found: C 31.81; H, 1.76; N, 6.21. For  $\text{C}_{18}\text{H}_{13}\text{Cl}_3\text{N}_3\text{O}_9\text{Tb}$ : C, 32.53; H, 1.97; N, 6.32; Found: C, 33.00; H, 1.68; N, 6.58. For  $\text{C}_{18}\text{H}_{13}\text{Cl}_3\text{N}_3\text{O}_9\text{Sm}$ : C, 32.96; H, 2.00; N, 6.40; Found: C, 32.70; H, 1.77; N, 6.69.  $\text{Ln}(\text{BNIC})_3(\text{H}_2\text{O})_2$ , Ln = Eu, Tb, Sm. Anal. Calcd. for  $\text{C}_{18}\text{H}_{13}\text{Br}_3\text{N}_3\text{O}_9\text{Eu}$ : C, 27.33; H, 1.66; N, 5.31; Found: C 26.47; H, 1.92; N, 5.04. For  $\text{C}_{18}\text{H}_{13}\text{Br}_3\text{N}_3\text{O}_9\text{Tb}$ : C, 27.10; H, 1.64; N, 5.26; Found: C 26.43; H, 1.95; N, 4.97. For  $\text{C}_{18}\text{H}_{13}\text{Br}_3\text{N}_3\text{O}_9\text{Sm}$ : C, 27.39; H, 1.66; N, 5.32; Found: C 26.87; H, 1.92; N, 5.07.

### Physical Measurement

Elemental analyses (C, H, N) were carried out by the Elementar Carlo EL elemental analyzer. Infrared spectroscopy with KBr pellets was performed on a Nicolet Nexus 912 AO446 model spectrophotometer in the  $4000 \sim 400 \text{ cm}^{-1}$ . Ultraviolet absorption spectra of conjugated carboxylic acids and their lanthanide complexes were obtained with an Agilent 8453 spectrophotometer ( $10^{-4} \text{ molL}^{-1}$  ethanol solutions). The fluorescence (excitation and emission) spectra for the solid complex samples were determined with Perkin-Elmer LS-55 spectrophotometer with low temperature accessory at liquid nitrogen (77 K): excitation slit width = 10 nm, emission slit width = 2.5 nm; the solid samples were placed in a quartz tube with liquid nitrogen around.

## RESULTS AND DISCUSSION

All the IR spectra of these lanthanide complexes show the similar features. Compared the IR spectra of free conjugated carboxylic acids to those of their dysprosium complexes, the characteristic absorption bands of C=O and C—O bands belonging to the free carboxylic acids ligands disappear, while the characteristic absorption peaks of carboxylic group  $\text{COO}^-$  appear, suggesting that the oxygen atoms of carbonyl group of conjugated carboxylic acids are coordinated to  $\text{Ln}^{3+}$ . Besides, it can be observed that the absorption frequency of Ln—O bond lies at around  $400 \text{ cm}^{-1}$  in the low frequency of IR spectra for some complexes. It needs to refer that some apparent bands are noted at about 3450 and  $1613 \text{ cm}^{-1}$  in IR spectra of  $\text{Dy}(\text{TBBA})_3 \cdot 2\text{H}_2\text{O}$ , which are attributed to the stretching vibration band and in-plane bending band of  $\text{H}_2\text{O}$  molecules. The absorption bands corresponding to the in-plane swing vibration of coordinated  $\text{H}_2\text{O}$  molecules have also been observed in the range of  $605\text{--}585 \text{ cm}^{-1}$ , suggesting both coordinated water molecules and lattice water molecules exist in these lanthanide complexes [23].

Fig. 1 shows the ultraviolet absorption spectra of selected terbium complexes with pyridine-carboxylates derivatives in the range of 190–400 nm. One absorption band from 255 to 300 nm can be observed and the maximum absorption peak at around 270 nm can be attributed to the characteristic absorption of pyridine-cycle group. Compared with the absorption spectra of corresponding free ligands (HNIC, HPIC, HCNIC and HBNIC) at about 265–267 nm, the absorption bands for the corresponding complexes show some red shifts, which suggest that the coordination of  $\text{Tb}^{3+}$  to ligands is easily to form more extensive conjugated localized systems so as to cause the

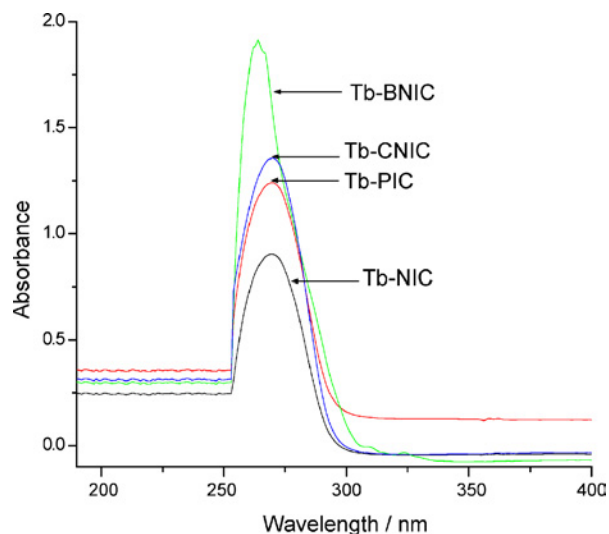


Fig. 1. Ultraviolet absorption spectra of selected spectra of lanthanide complexes of conjugated carboxylic acids.

energy decrease and red-shift of absorption band. Other lanthanide complexes show the similar features.

The fluorescent excitation spectra for these lanthanide complexes at 77 K were measured. Fig. 2 gives the excitation spectra for  $\text{Eu}(\text{NIC})_3(\text{H}_2\text{O})_2$  complex under the red emission of 613 nm. In narrow-wavelength region (Fig. 2A), seven apparent absorption peaks appear at 221.5, 239, 243.5, 253, 257, 271.5, and 280 nm, respectively. In long-wavelength region (Fig. 2B), another four strong excitation peaks situate at 340, 363, 377 and 296 nm, separately. Fig. 3 shows the excitation spectra for  $\text{Tb}(\text{NIC})_3(\text{H}_2\text{O})_2$  complex under the red emission of 545 nm. In narrow-wavelength region (Fig. 2A), seven apparent excitation peaks situate at 207, 223.5, 233.5, 241, 247.5, 254.5, and 263 nm, separately. In long-wavelength region (Fig. 2B), a broad band ranged in 300–435 nm with maximum excitation peak of about 332 nm. Selected excitation under these wavelengths, the emission spectra show the similar luminescent position except for different luminescent intensities. This indicates that the four excitation bands are all the effective energy sensitizer for the luminescence of Ln ions. Other excitation spectra

Fig. 4 and 5 present the corresponding low temperature fluorescent emission spectra of europium complexes at 77 K. From Fig. 4, two emission spectra of  $\text{Eu}(\text{NIC})_3(\text{H}_2\text{O})_2$  monitored under narrow wavelength (235 nm) and long wavelength (396 nm) wear the similar emission of  $\text{Eu}^{3+}$ , which can be ascribed to the characteristic  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  transitions ( $J = 0, 1, 2, 3, 4$ ) of  $\text{Eu}^{3+}$  ion, where the term symbols refer to be atomic spectral term of  $\text{Eu}^{3+}$  ions, among five is the spin multi which

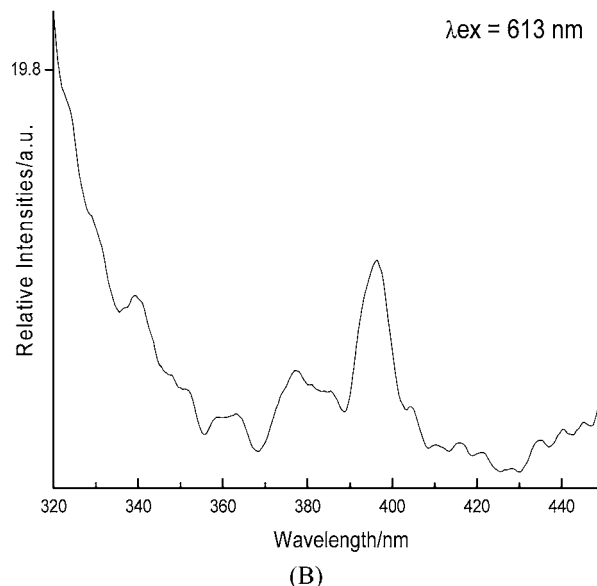
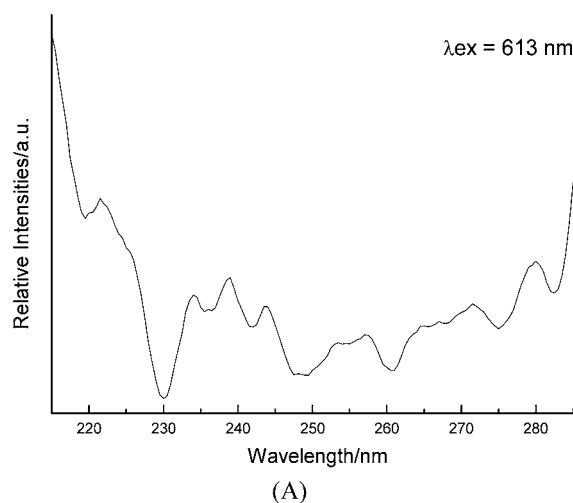
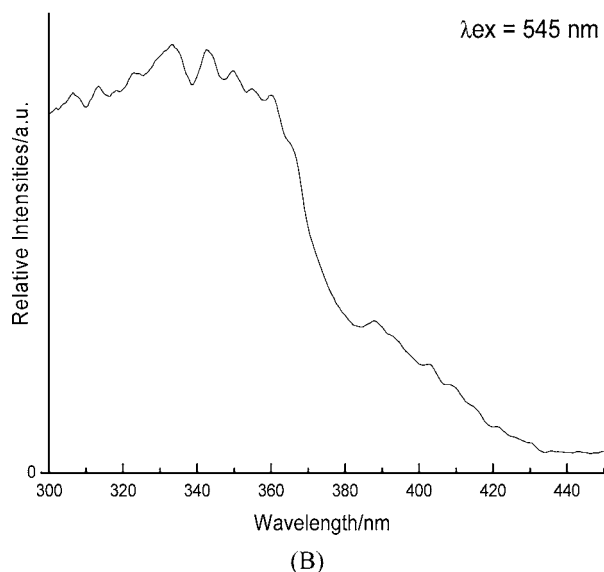
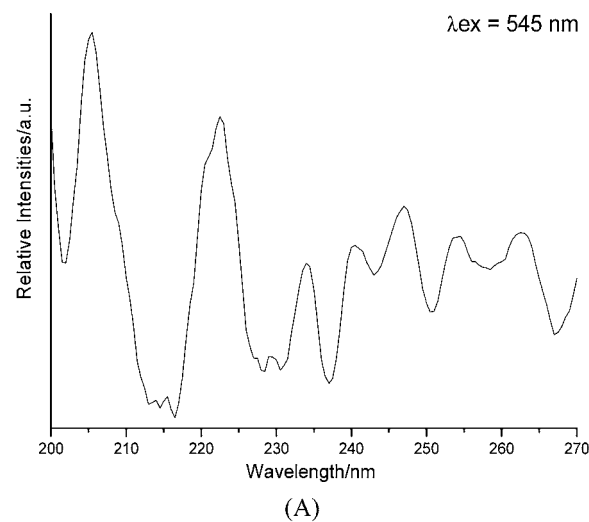


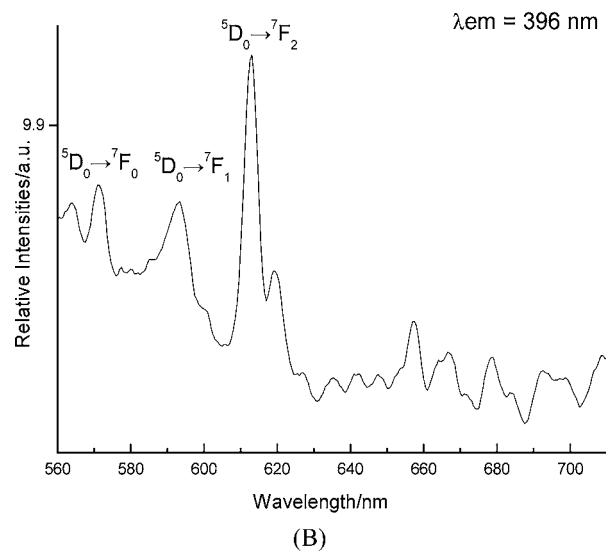
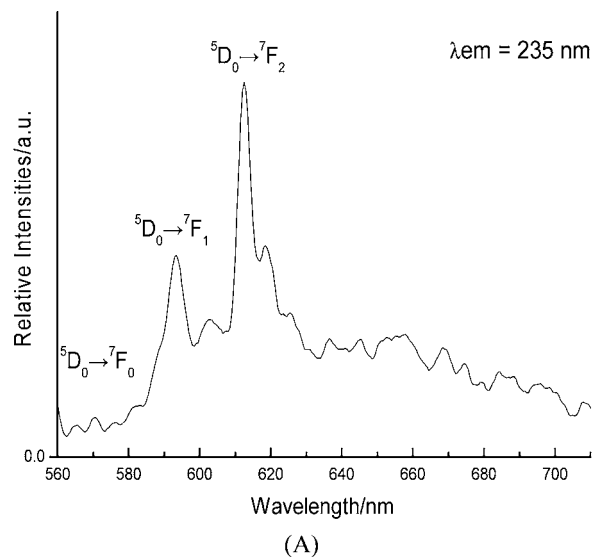
Fig. 2. Selected low temperature fluorescent excitation spectra of  $\text{Eu}(\text{CNIC})_3(\text{H}_2\text{O})_2$ .

equal to be  $2S + 1$  ( $S = \text{spin quantum number}$ ),  $D$  represents the orbital quantum number, and  $J$  is the  $J$  (inner quantum number,  $J = L \pm S$ ). Besides this, the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  transition of  $\text{Eu}^{3+}$  exhibits only one peak at 583 nm without split, which suggest there exist one coordination environment for  $\text{Eu}^{3+}$  ion in this compound. As we known,  $\text{Ln}(\text{NIC})_3(\text{H}_2\text{O})_2$  belongs to be a dimeric structure with formulae  $[\text{Ln}(\text{NIC})_3(\text{H}_2\text{O})_2]_2$  ( $\text{Ln} = \text{light lanthanide La-Gd}$ ) [24], and the two europium ions are completely equivalent with same coordination environment. So the feature observed from the low temperature fluorescent spectra takes agreement with the corresponding molecular



**Fig. 3.** Selected low temperature fluorescent excitation spectra of  $\text{Eu}(\text{CNIC})_3(\text{H}_2\text{O})_2$ .

structure. The strongest emission is the red supersensitive  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition, indicating no inverse center for  $\text{Eu}^{3+}$  within the complex. The split number for  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  ( $J = 0, 1, 2, 3, 4$ ) transitions are 1, 2, 3, 5, and 7, respectively, and especially the split number of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  is 3, close to  $J + 1/2$  ( $2 + 1/2$ ), which verify the central europium ion locates at site in low symmetry without inversion center. Figure 5A and B show the low temperature fluorescent spectra for  $\text{Eu}(\text{CNIC})_3(\text{H}_2\text{O})_2$  and  $\text{Eu}(\text{BNIC})_3(\text{H}_2\text{O})_2$  complexes. Both of them show the similar feature to that for  $\text{Eu}(\text{NIC})_3(\text{H}_2\text{O})_2$ , exhibiting the similar emission of  $\text{Eu}^{3+}$ , corresponded to the characteristic  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  transitions ( $J = 0, 1, 2, 3, 4$ ) of



**Fig. 4.** Low temperature fluorescent spectra of  $\text{Eu}(\text{NIC})_3(\text{H}_2\text{O})_2$ .

$\text{Eu}^{3+}$  ion. Besides this, the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  transition of  $\text{Eu}^{3+}$  presents only one peak at 581 nm (for Fig. 4A) and 582 nm (for Fig. 4B) with no split, suggesting only one coordination environment for  $\text{Eu}^{3+}$  in the structures of these two complexes. Both  $\text{Ln}(\text{CNIC})_3(\text{H}_2\text{O})_2$  and  $\text{Ln}(\text{BNIC})_3(\text{H}_2\text{O})_2$  form similar dimeric structure with formulae  $[\text{Ln}(\text{CNIC})_3(\text{H}_2\text{O})_2]_2$  and  $[\text{Ln}(\text{BNIC})_3(\text{H}_2\text{O})_2]_2$  ( $\text{Ln} = \text{light lanthanide La-Gd}$ ) [25], and the two central europium ions both locate in a equipollent coordination environment, which is in harmony with the predict from low temperature fluorescent emission spectra. The strongest emission is still the red supersensitive  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition, indicating no inverse center at  $\text{Eu}^{3+}$  sites

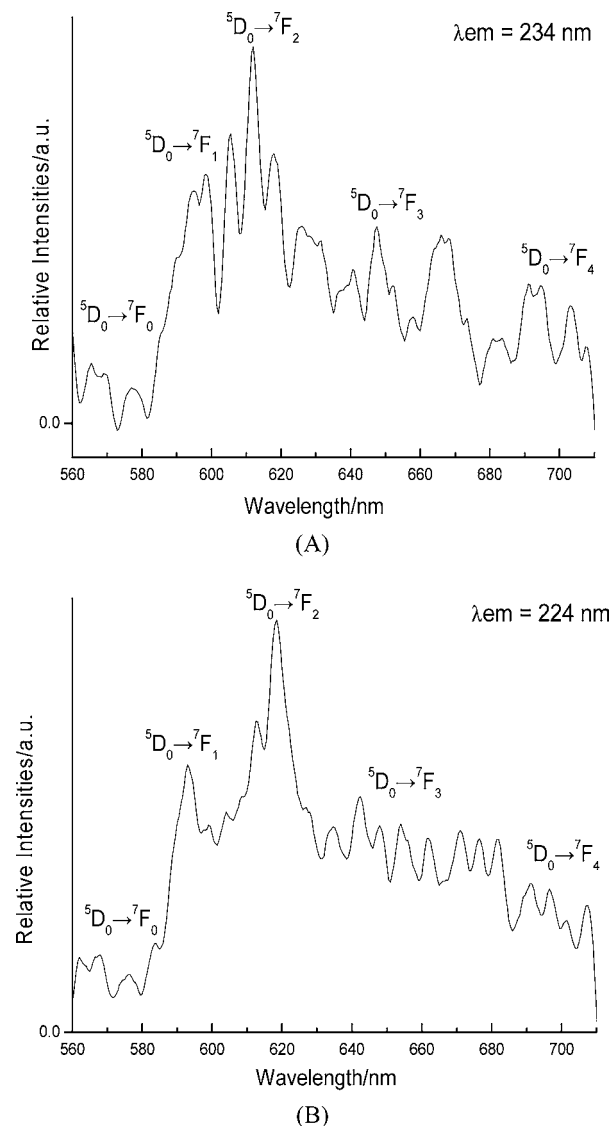


Fig. 5. Low temperature fluorescent spectra of  $\text{Eu}(\text{CNIC})_3(\text{H}_2\text{O})_2$  and  $\text{Eu}(\text{BNIC})_3(\text{H}_2\text{O})_2$ .

inner the two complexes. The split number for  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  ( $J = 0, 1, 2, 3, 4$ ) are 1, 2, 3, 5, 6 (Fig. 5A) and 1, 2, 3, 5, 7 (Fig. 5B), particularly the split number of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  is 3, close to  $J + 1/2$  ( $2 + 1/2$ ), indicating the central europium ions with low symmetry.

Figure 6 is the representative low temperature fluorescent emission spectra of  $\text{Tb}(\text{CNIC})_3(\text{H}_2\text{O})_2$  and  $\text{Tb}(\text{BNIC})_3(\text{H}_2\text{O})_3$ . The characteristic transition of terbium ion is not as sensitive as europium ion to the nearby environment. Besides, terbium complexes show the more strong emission than other lanthanide complexes for the more suitable energy match and more effective energy transfer between pyridine carboxylic acids derivatives and

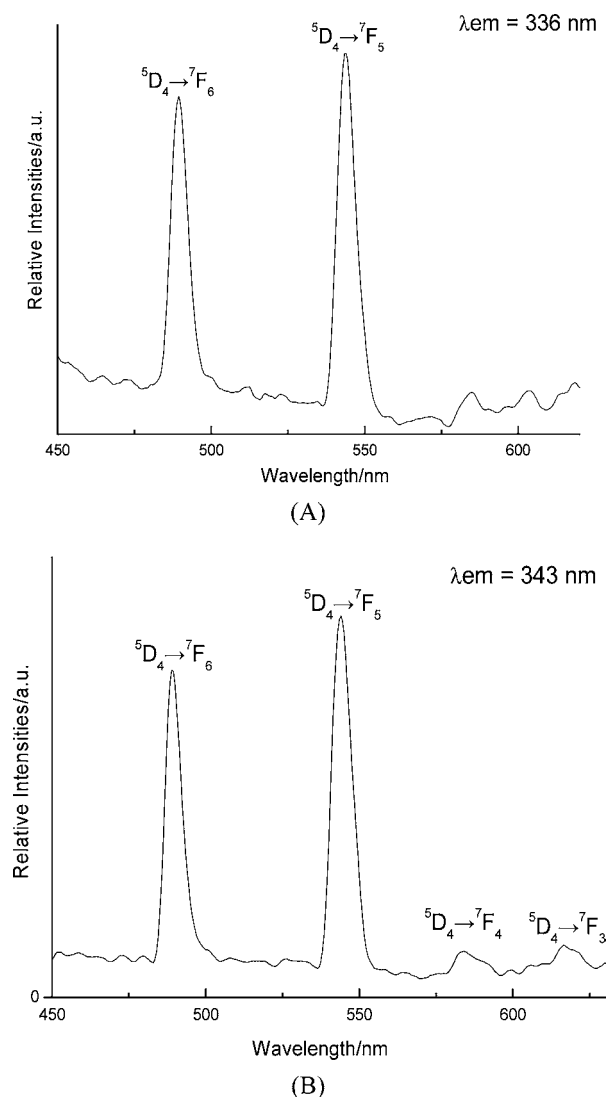


Fig. 6. Low temperature fluorescent spectra of  $\text{Tb}(\text{CNIC})_3(\text{H}_2\text{O})_2$  and  $\text{Tb}(\text{BNIC})_3(\text{H}_2\text{O})_2$ .

$\text{Tb}^{3+}$  ion than  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  [26–30]. Four main emission peaks can be attributed to the characteristic emissions originated from the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$  ( $J = 6, 5, 4, 3$ ) transition of  $\text{Tb}^{3+}$  ion (atomic spectral term of  $\text{Tb}^{3+}$ ). The emission to the magnetic dipole transition ( ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$ ) shows not split, which indicates that the central terbium ions are in the same one coordination environment. Different from light lanthanide complexes with HCNIC and HBNIC, the terbium and other heavy lanthanide ions complexes of HCNIC and HBNIC belong to one-dimensional chain like coordination polymeric structure with formulae of  $[\text{Tb}(\text{CNIC})_3(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}]_n$  and  $[\text{Tb}(\text{CNIC})_3(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O}]_n$  [23,25]. In this 1-D molecular structure, the central Tb ions are the entirely equipollent

with the same coordination geometry, resulting in the above fluorescent emission spectra. Furthermore, the emission intensities for electronic dipole  $^5D_4 \rightarrow ^7F_6$  transition are stronger than that for magnetic dipole  $^5D_4 \rightarrow ^7F_5$  one, i.e., the green luminescence of  $Tb^{3+}$  is the strongest. This can be interpreted that the former is less influenced by the ligand field [31].

We further measure the low temperature fluorescent emission spectra at 77 K of samarium complexes with conjugated carboxylic acids (Fig. 7), which exhibits four predominantly characteristic emission corresponded to the  $^4G_{5/2} \rightarrow ^6H_J$  ( $J = 5/2, 7/2, 9/2, 11/2$ ) transitions of  $Sm^{3+}$  ion (atomic spectral term of  $Sm^{3+}$ ). The electronic dipole transition  $^4G_{5/2} \rightarrow ^6H_{9/2}$  exhibits the highest rel-

ative emission intensity around 667 nm. The fluorescent emission spectrum show that the transitions split in a maximum number of ( $J + 1/2$  for transition  $^4G_{5/2} \rightarrow ^6H_{9/2}$ ), suggesting that  $Sm^{3+}$  ion occupies a site with lower symmetry [32,33], which takes agreement with  $Sm^{3+}$ 's polyhedron of a slightly distorted square antiprism.

## CONCLUSIONS

In summary, for low temperature fluorescent spectra of lanthanide complexes with pyridine-carboxylic acids derivatives, the  $^5D_0 \rightarrow ^7F_0$  transition for  $Eu^{3+}$ ,  $^5D_4 \rightarrow ^7F_6$  for  $Tb^{3+}$  and  $^4G_{5/2} \rightarrow ^6H_{5/2}$  for  $Sm^{3+}$  wear no split and indicates the central Ln (Eu, Tb, Sm) ions are situated in actually equivalent coordination environment in these dimeric or polymeric structures. The most strongest emission corresponds to the characteristic transitions for  $Ln^{3+}$  (i.e.,  $^5D_0 \rightarrow ^7F_2$  transition for  $Eu^{3+}$ ,  $^5D_4 \rightarrow ^7F_5$  transition for  $Tb^{3+}$  and  $^4G_{5/2} \rightarrow ^6H_{9/2}$  transition for  $Sm^{3+}$ ), and the split number for  $^5D_0 \rightarrow ^7F_J$  ( $Eu^{3+}$ ), the  $^5D_4 \rightarrow ^7F_J$  ( $Tb^{3+}$ ) and  $^4G_{5/2} \rightarrow ^6H_J$  ( $Sm^{3+}$ ) transitions are close to  $J + 1/2$  ( $2 + 1/2$ ), which verify that the central europium ions belong to low symmetry without inversion center.

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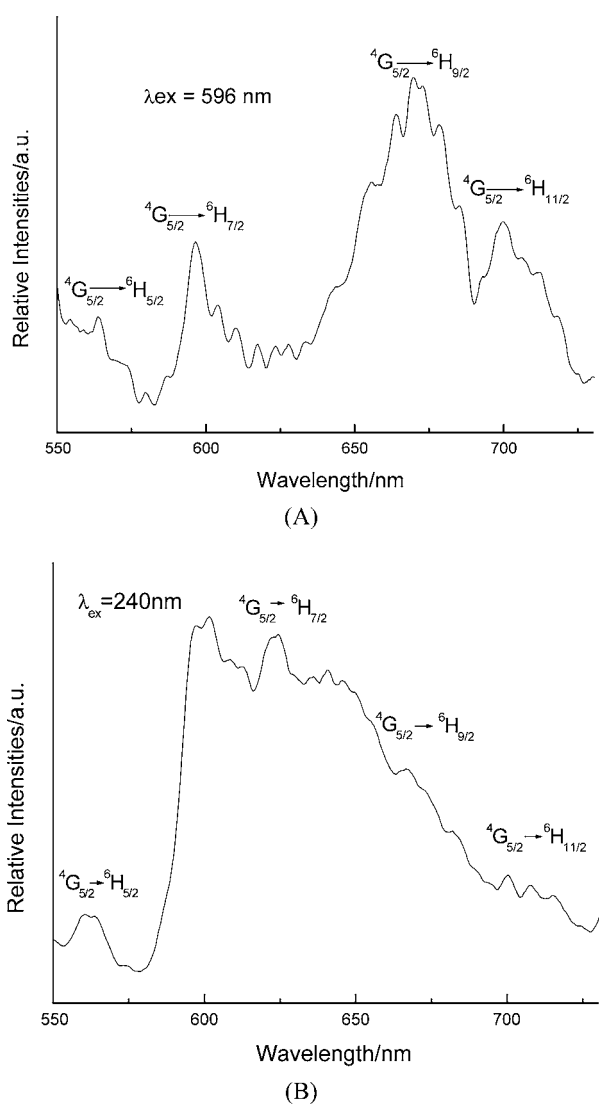


Fig. 7. Low temperature fluorescent spectra of  $Sm(NIC)_3(H_2O)_2$  and  $Sm(PIC)_3(H_2O)_2$ .

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