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Studies on the Controllable Luminescence Properties from Red to Green of Rare Earth Complexes

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Photoactive rare earth compounds, such as europium and terbium complexes with organic ligands, exhibit intense narrow band emission *via* an effective energy transfer from ligands to metal centers under near UV excitation (Antenna effect) [1–3]. Aromatic carboxylate and their derivatives have excellent conjugate chromogene to activate both Eu^{3+} and Tb^{3+} to give out their characteristic lights and their luminescent complexes have been widely investigated [4–6]. Unfortunately, all attentions were focused on their monochromatic luminescent properties. That is to say, the complexes of Eu^{3+} give out red light and those of Tb^{3+} give out green light. In the present work, a new tripodal ligand 1,1,1-tris{[(2′-benzylaminoformyl)phenoxyl]methyl}ethane (L) have been synthesized which can activate both Eu^{3+} and Tb^{3+} to give out their characteristic lights. Furthermore, according to the principle of paints, the luminescence of these complexes can be adjustable from red to green by controlling the ratio of two metal ions when preparing these complexes. So the rare earth complexes with yellow or orange luminescence property have been firstly realized.

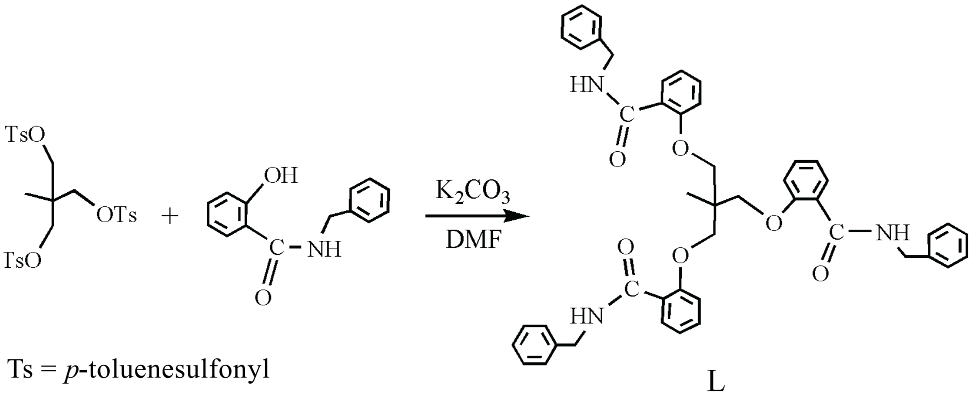

Figure 1. Preparing of ligand L.

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The ligand could be easily prepared by a similar procedure to that reported earlier [7], but the central skeleton material was replaced into 1,1,1-tris(*p*-tosyloxymethyl)-ethane (Figure 1). All the complexes of rare earth were synthesized by the reaction of hydrated metal salt $Ln(NO_3)_3 \cdot 6H_2O$ with ligand L in molar ratio 1:1 in ethyl acetate.

Analytical data of the complexes are listed in Table 1. The elemental analytic data and the content of metal show that the complexes have the composition of $LnL(NO_3)_3$.

The most important IR assignments in the spectra of ligand and complexes can be summarized as follows. Free ligand exhibits two absorption bands at about 1638 cm^{-1} (C=O) and 1110 cm^{-1} (Ar–O–C). The complexes also exhibit these two bands, but only the high-energy band (C=O) has a significant red shift, suggesting that only the O atoms of C=O take part in coordination to the metal ions. At the same time, bands at about 1490 (ν_1) and 1290 (ν_4) cm^{-1} indicate that nitrate groups (C_{2v}) are coordinated [8]. The separation of the two bands (about 200 cm^{-1}) confirms the bidentate coordination style of all the nitrate groups [9].

The molar conductivity of the complexes is about 60 $S \cdot cm^2 \cdot mol^{-1}$ in methanol at 25°C, indicating no free nitrate group existed (<80 $S \cdot cm^2 \cdot mol^{-1}$) [10].

Table 1. Analytical data of the complexes.

Complexes	Content of metal found % (Calc.)	IR (cm^{-1}) C=O	IR (cm^{-1}) Ar–O–C	Λ_m ($S \cdot cm^2 \cdot mol^{-1}$) ($CH_3OH$, 25°C)
L		1638	1110	
Eu $(NO_3)_3 \cdot L$	13.5 (14.0)	1607	1110	59.8
Tb $(NO_3)_3 \cdot L$	14.2 (14.5)	1606	1109	54.4

As the ligand can activate both Eu^{3+} and Tb^{3+} to give out their characteristic lights, their intensity of luminescence can be compared. Excited by the absorption band at 325 nm at the same conditions, the luminescence spectra of the two complexes (Figure 2) revealed that both complexes exhibit strong luminescence. But the complex of Tb^{3+} has stronger luminescence than that of Eu^{3+}, indicating the triplet-state level of the ligand matches much better with the lowest excited state level of Tb^{3+} than that of Eu^{3+}.

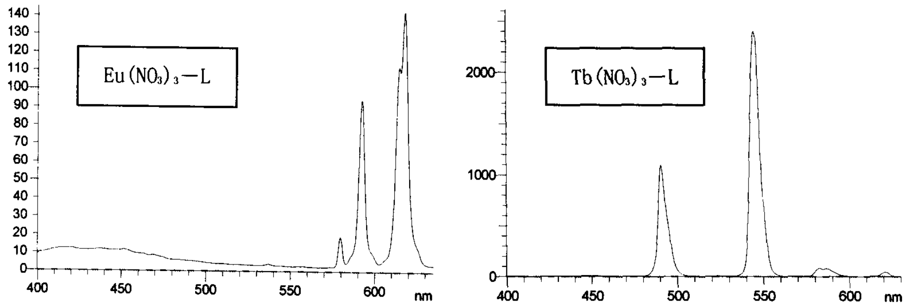
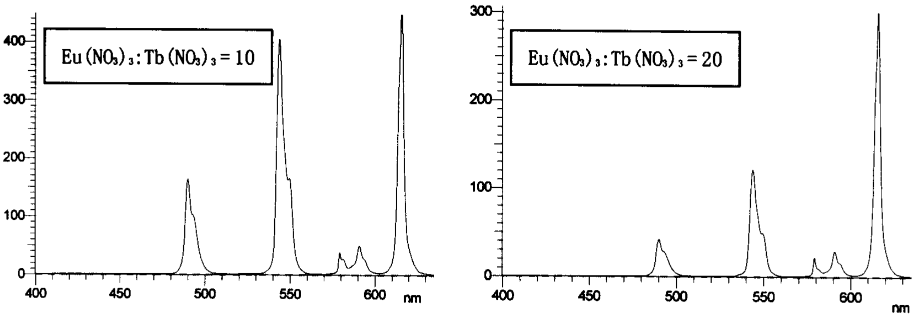


Figure 2. Emission spectra of complexes in solid state (excited at 325 nm).



a b

Figure 3. Emission spectra of mixed-metal complexes in solid state (excited at 325 nm).

On the other hand, the ions Eu^{3+} and Tb^{3+} have the same valence and similar radius. So they have similar coordination properties. By controlling the molar ratio of $Eu(NO_3)_3$ and $Tb(NO_3)_3$ when preparing complexes, a series of complexes with different ratio of metal ions have been synthesized. Although it is very hard to confirm the accurate contents of two metal ions in these mixed-metal complexes, the satisfied result is that they can exhibit different color luminescence light from red to green under UV light. For example, if the value of $Eu(NO_3)_3/Tb(NO_3)_3$ is 10 (Figure 3a), the complex give out yellow luminescence light. On the other hand, if the value is 20, the complex with orange luminescence can be obtained (Figure 3b). To the best of our knowledge, this is the first report of adjustable luminescence property of rare earth complexes through controlling the ratio of two different active metal ions.

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