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Synthesis and Fluorescence Properties of Europium, Terbium Doped Zn^{2+}, Cd^{2+} and Cr^{3+} Complexes

Wen Xiaochun (温孝春)[1], Zhao Yongliang (赵永亮)[1,2*], Wang Lianmeng (王连蒙)[1], Zhang Mei (张 梅)[1], Gao Deqing (高德青)[3]

(1. College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China; 2. State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing 100871, China; 3. Wuppertal University, Wuppertal 42119, Germany)

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Abstract: Europium and terbium complexes with strong fluorescence intensity and long fluorescence lifetime were prepared. By replacing half of the europium or terbium ion with M (M = Zn^{2+}, Cd^{2+}, and Cr^{3+}) using the doped method, and then incorporating it with 18-crown-6 ether and terephthalic acid, six heteronuclear samples $EuZnLL'Cl_3 \cdot 3H_2O$(1), $EuCdLL_2'Cl_3 \cdot 5H_2O$(2), $EuCrLL'Cl_4 \cdot 4H_2O$(3), $TbZnLL'Cl_3 \cdot 4H_2O$(4), $TbCdLL'_2Cl_3 \cdot 4H_2O$(5), and $TbCrLL'_2Cl_4 \cdot 4H_2O$(6) (L = terephthalic acid, L' = 18-Crown-6 ether) were obtained. The elemental analysis, molar conductivities, rare earth complexometry, Fourier Transform Infrared Spectroscopy (FT-IR), ultraviolet (UV), TGA, fluorescence intensity, and fluorescence lifetime of the samples were measured. The results showed that there were good luminescence properties for heteronuclear complexes (1), (2), (4), and (5), which were even stronger than those of the homonuclear complexes $Eu_2LL'_2Cl_4 \cdot 4H_2O$ and $Tb_2LL'_2Cl_4 \cdot 4H_2O$, but the luminescence properties of $EuCrLL'Cl_4 \cdot 4H_2O$, $TbCrLL'Cl_4 \cdot 4H_2O$ were very weak. A possible luminescence mechanism was suggested by the organic-inorganic doped mechanism and the law of intramolecular energy transfer.

Key words: europium complex; terbium complex; terephthalic acid; crown ether; rare earths

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Luminescent lanthanide complexes have found wide applications in luminescent display phosphorescence, laser, electroluminescent optical devices, and in probes of chemical and biological molecules, because their luminescence exhibits high fluorescent efficiency, with very sharp emission bands, and excellent monochromatocity[1]. Rare earth complexes with organic ligands, especially those containing Eu^{3+} and Tb^{3+}, often display efficient luminescence because of the strong absorption of the organic ligands and efficient energy transfer from the triplet state of ligands to rare earth ions[2]. During the last decade, the interest in doped complexes has been growing on account of their enhanced fluorescent properties. Many investigations have been reported on the energy match and energy transfer between the triplet state energy of β-diketones and the resonant energy level of the central rare earth ions in the rare earth β-diketones[3]. However, little attention has been paid to the rare earth complexes that doped the transition metals with aro-

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* **Corresponding author**(E-mail: nmgzyl100@163.com)

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Biography: Wen Xiaochun (1978-), Female, Master; Research field: Rare earth luminescence materials matic carboxylic acids[4]. The rare earth complexes of aromatic carboxylic acids have higher stability than those of β-diketones because of their infinite chain structure of chelation[5]. On the other hand, the existence of an OH group will result in a luminescence quenching action[6,7]. To overcome this negative influence, second ligand 18-crown-6 ether was added. Regarding the role of the introduced Zn^{2+} or Cd^{2+}, the dope made the ligands twice that of the rare earth ions in mole ratio, which means that the triplet level energy from terephthalic acid is double compared to the pure europium or terbium complexes. In this article, four excellent luminescent hybrid complexes of Eu^{3+} or Tb^{3+}, low-cost M^{2+}(Zn, Cd), and two weaker luminescent hybrid complexes of Eu^{3+} or Tb^{3+} and Cr^{3+} were prepared successfully.

1 Experimental

1.1 Preparation

The materials $EuCl_3$ and $TbCl_3$ were prepared and crystallized from the corresponding rare earth oxides of high purity (99.99%); other reagents (A. R.) were obtained commercially. In principle, the adopted preparation method for the complexes was very similar to the previous studies[8].

1.2 Spectroscopy measurements

The determinations of C and H were performed by a PE-2400 elemental analysis instrument and the contents of rare earth elements were obtained by EDTA titration. Molar conductivities were measured using DDS-11A and DJS-1 Pt electrode at room temperature, with DMF as the solvent (1 mmol · L^{-1}). Luminescence spectra were measured on a Shimadzu RF-5301PC spectrophotometer, using the xenon lamp as the excitation source. The luminescence lifetimes were recorded by an Edinburgh Analytical Instrument F-900; FT-IR spectra were measured in the 4000 ~ 400 cm^{-1} region on a Nexus 670 FT-IR spectrophotometer with KBr pellet technique; UV spectra were recorded on a Tu-1901 spectrophotometer, using DMF as the solvent; TGA was recorded by the Shimadzu DTG-50 thermal analysis instrument, the heating rate was 10 ℃ · min^{-1}.

2 Results and Discussion

2.1 Characterization of complexes

The compositions of the complexes were confirmed by C, H elemental analysis and rare earth complexometry (Table 1).

FT-IR spectra data of these complexes are recorded in Table 2, and they are similar. The 1550 and 1405 cm^{-1} peaks are assigned to asymmetric stretching vibrations $\nu_{as}(COO^-)$ and symmetric stretching vibrations $\nu_s(COO^-)$ of COO^- respectively, which are explained by the existence of bidentate coordination forms of the COO^- group[9,10]. The split at 1112 ~ 1073 cm^{-1} ν_{as}(C-O-C) and 960 cm^{-1} ν_s(C-O-C) indicated that metal ions were loaded on complexes and coordinated by crown ethers, and both the RE and Zn^{2+}, Cd^{2+} or Cr^{3+} ions coordinated with the ligands. Based on the earlier results, it could be seen that they were 3:1 or 4:1 style electrolytes from molar conductivities[11]. UV spectra of the complexes were similar, the UV spectra of terephthalic acid and the complex (1) are given in Fig. 1. The spectrum of terephthalic acid exhibited two major bands, the absorption peaks at 264.3 and 281.7 nm corresponded to $\pi \rightarrow \pi^*$ transition. Moreover, it was noteworthy that the absorption intensity of these complexes was stronger than that of terephthalic acid. The peak moved to 264.1 nm, and the 281.7 nm peak disappeared, that is, it contributed to the rise of π^* energy after the carbonyl groups cooperated with the metal ions. The different spectra indicated that the coordination reactions had taken place between terephthalic acid and rare earth ions. The TG-DTA curves (the determination range of temperature was 20 ~ 600 ℃) showed that the complexes were stable below 300 ℃, when the temperature rose to over 330 ℃, where decomposition and oxidization occurred.

2.2 Fluorescence properties

The excitation spectrum of the $Tb^{3\bullet}$ series complexe shows a wide band from 230 to 340 nm with a maximum peak at 302 nm, up to the Eu^{3+} series complexes, for which the band is from 220 to 330 nm and the maximum peak is at 271 nm, which is assigned to the ligand - metal energy transfer band through the

Table 1 Composition analysis and molar conductivities λ_m ($S \cdot cm^2 \cdot mol^{-1}$, 25 ℃) of complexes

Complexes	C/%		H/%		RE/%		λ_m
	Found	Cal.	Found	cal.	Found	Cal.	Found
$Eu_2LL'_2Cl_4 \cdot 4H_2O$	31.92	31.74	4.89	4.94	25.11	25.49	166
$EuZnLL'Cl_3 \cdot 3H_2O$	29.55	29.79	4.29	4.22	26.92	26.54	145
$EuCdLL'_2Cl_3 \cdot 5H_2O$	32.97	33.05	4.86	4.97	22.91	22.93	169
$EuCrLL'Cl_4 \cdot 4H_2O$	28.64	28.38	4.22	4.25	24.41	24.11	151
$Tb2LL'_2Cl_4 \cdot 4H_2O$	30.98	31.38	4.96	4.90	26.03	25.95	176
$TbZnLL'Cl_3 \cdot 4H_2O$	29.15	28.89	4.41	4.33	26.95	26.96	163
$TbCdLL'_2Cl_3 \cdot 4H_2O$	32.99	33.11	4.78	4.94	23.57	23.77	180
$TbCrLL'Cl_4 \cdot 4H_2O$	28.02	28.14	4.54	4.22	24.71	24.76	155