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Synthesis, structure and fluorescence studies of the lanthanide complexes with 4-fluorobenzoic acid

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ABSTRACT

Tb (**1**) and Eu (**2**) complexes with 4-fluorobenzoic acid have been synthesized by hydrothermal method. The structures of them were established by X-ray crystallography, which revealed that complexes **1** and **2** are isostructural and crystallized into one infinite 1D chains by bidentate bridging carboxyl groups. There are four coordinated and one free H_2O molecules around each Tb^{3+} or Eu^{3+} centers. But the complexes present excellent luminescence under ultraviolet excitation. The photoluminescent properties of the two complexes were investigated by the solid state excitation, the emission spectra and the luminescent decay. The complexes exhibited strong green and red luminescence in visible spectral region on the broad excitation of the ultraviolet ligand absorption, which indicates the antenna effect might have taken place effectively. The overall quantum yields of complexes **1** and **2** are 41% and 14%, respectively, and the sensitization efficiency of the ligand in complex **2** is estimated to be 82%.

1. Introduction

On account of their intrinsic chemical and spectroscopic properties, luminescent lanthanide complexes possess numerous potential applications in lighting, optical communications, analytical chemistry and biomedical devices [1–8]. However, arising from the parity-forbidden 4f–4f transitions, trivalent lanthanide cations have extremely low molar extinction coefficients ($\varepsilon < 1\ M^{-1}cm^{-1}$) [8–10], making the direct lanthanide excitation very inefficient. In order to surmount this predicament, a strongly absorbing organic chromophore is employed as light gatherer to sensitize Ln^{3+} emission in a process known as the antenna effect [9–11], where the organic chromophore absorbs and transfers energy to Ln^{3+}, resulting in more intense lanthanide ion emissions.

By reason of being "hard" Lewis acids, the Ln^{3+} ions exhibit a preference for hard and negatively charged donors atoms such as O and N, particularly for O [8,11]. Aromatic carboxylic acids exhibit particularly attraction by virtue of their excellent capability to absorb energy and to efficaciously transfer the energy to the central lanthanide ions [7,12]. A number of lanthanide benzoate coordination complexes with unique photophysical properties and intriguing structural features have been disclosed in recent decades [13–17]. The benzoate ligands were selected on the basis of the fact that carboxylate groups interact strongly with the lanthanides and the delocalized π-electron system provides a strongly absorbing chromophore. However, the benzoate ligands containing fluorinated groups are studied deficiently, because fluorocarbons are generally difficult to coordinate to metal centers and are resistant to chemical interaction [18]. But, it is interesting to find that the near infrared emission could be significantly enhanced by incorporation of fluorinated organic linkers because the quenching effect of the C–F vibration on the lanthanide emission is much lower than that of the C–H [19]. Therefore, it is a challenge to investigate the lanthanide complexes with fluorides containing ligands. Wong and his coworkers have studied the effect of 4-trifluoromethylbenzoic acid and 4-trifluoromethoxybenzoic acid on the photophysical and magnetic properties of Tb/Eu complexes [13], while the reported two ligands have more steric hindrance and result in relatively shorter lifetimes than the complexes with benzoate ligands. However, the steric hindrance of 4-fluorobenzoic acid (FBA) is not as significant as the above two ligands, yet it still possesses the strong electron withdrawing fluoride atom, therefore, it is chosen as the chromophore in this work. This article works on luminescent properties of Eu (emitting red light due to $^5D_0 \rightarrow {}^7F_2$ transition) and Tb (emitting green light due to $^5D_4 \rightarrow {}^7F_5$ transition) FBA complexes. The two complexes were structurally characterized by single crystal X-ray diffraction and were found to be isostructural and exist as infinite 1D coordination polymers. It is interesting to note that the Tb(III) or Eu(III) centers in complex **1** or **2** are singly bridged by carboxylate groups of the 4-Fluorobenzoic acid ligands and thereby form infinite 1D

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wavelike chains. The other one noteworthy structural feature of these compounds is the presence of free H_2O molecules within the 1D coordination polymer. The photoluminescence (PL) studies demonstrated that Tb(III) and Eu(III) complexes exhibit bright green and red luminescence in the solid state at room temperature. The efficient luminescence are particularly surprising in view of the presence of four coordinated H_2O molecules in the first coordination sphere and one free H_2O molecule, since water molecules typically serve as vibrational deactivators of the excited state of Tb^{3+} and Eu^{3+} ions [20]. Based on the excellent luminescent properties of the Eu(III) and Tb(III) complexes, they could be considered as potential emitting materials for the fabrication of OLEDs.

2. Experimental

2.1. Materials and methods

All chemicals were of AR (analytical reagent) or EP (extra pure) grade and were used without further purification. Eu_2O_3 (99.99%), Tb_4O_7 (99.99%), NaOH (AR), 4-fluorobenzoic acid and nitric acid (AR) were used as starting materials.

Elemental analyses of C, H and N were performed with an Elmentar Vario EL III analyzer. The Fourier Transform Infrared (FTIR) spectra were recorded on a Perkin Elmer spectrum 65 FTIR spectrometer by KBr pelleting technique. The absorbance of the free ligand and complexes were measured by a PERSEE TU-1901 ultraviolet–visible (UV–Vis) spectrophotometer in the range between 200 and 400 nm in methanol solution with the concentration of 10^{-4} M. The photoluminescence excitation (PLE), photoluminescence (PL) spectra and luminescence decay measurements were recorded on an Edinburgh FLS920 fluorescence spectrometer equipped with a 450 W xenon lamp and a pulse xenon lamp as the excitation sources. When recorded the solid-state PLE and PL spectra, the slit was set to be 0.5 nm, which is small for the instrument setup. All the other scanning parameters were kept the same for the two compounds during the spectra recording to make better comparison. The overall quantum yields (Φ_{overall}) of the two complexes were measured by an integrating sphere attachment of FLS920 spectrometer. The powder samples were placed in the integrating sphere and the Xe lamp was employed as the light source to pump the samples. The Φ_{overall} was obtained by comparing the spectral intensities of the light source and the sample emission, as stated in Refs. [21,22].

2.2. Syntheses of lanthanide complexes

The synthesis procedure of complexes **1** and **2** is described in Scheme 1. $LnNO_3 \cdot 6H_2O$ (Ln = Tb and Eu) were prepared by dissolving the corresponding lanthanide oxide (Tb_4O_7 and Eu_2O_3) with concentrated nitric acid, and the solution was heated tenderly to dryness. This process was repeated several times until the pH value of the solution was near 7. In a typical procedure, an aqueous solution of $Tb(NO_3)_3 \cdot 6H_2O$ (1 mmol) was added to an aqueous solution of 4-fluorobenzoic acid (3 mmol) in the presence of NaOH (2.5 mmol). Precipitation took place immediately, and the reaction mixture was stirred subsequently for 1 h at 50 °C. Thereafter, the mixture was transferred to a 50 mL Teflon reactor and kept at 160 °C for 80 h under autogenous pressure. After it was cooled to room temperature, the colorless block single crystals of complex **1** was obtained. *Anal.* Calc. for $C_{21}H_{22}F_3O_{11}Tb$: C, 37.84; H, 3.00. Found: C, 39.98; H, 3.36%. IR (KBr pellet): 3433, 1552, 1429, 1385, 1241, 1152, 780, 616 cm^{-1}.

The synthesis procedure of complex **2** is similar to those of **1** except $Tb(NO_3)_3 \cdot 6H_2O$ was replaced by $Eu(NO_3)_3 \cdot 6H_2O$. However, crystals suitable for single-crystal X-ray diffraction experiments had not been directly obtained from the Teflon reactor. The ultimate mixture in the Teflon reactor was filtrated, and the colorless block single crystals of complex **2** was obtained by slow evaporation of the filtrate at room temperature. *Anal.* Calc. for $C_{21}H_{22}F_3O_{11}$ Eu: C, 38.20; H, 3.03. Found: C, 41.52; H, 3.12%. IR (KBr pellet): 3398, 1552, 1431, 1242, 1152, 781, 616 cm^{-1}.

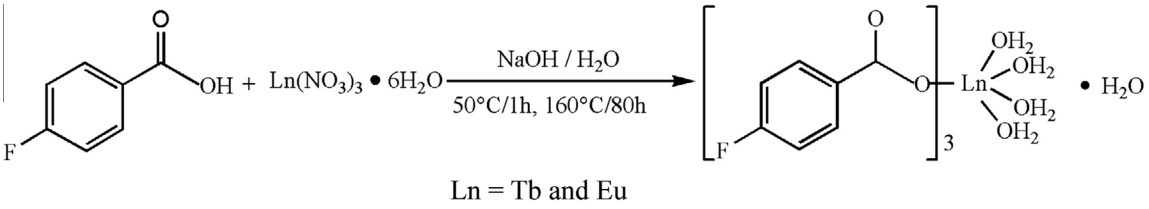
2.3. X-ray crystallography

Two suitable crystals with dimensions of 0.42 mm × 0.32 mm × 0.28 mm for complex **1** and 0.29 mm × 0.23 mm × 0.2 mm for **2** were selected for X-ray diffraction studies. The diffraction data were collected at 170 and 293 K on a Oxford Xcalibur (Atlas Gemini ultra) diffractometer equipped with a low-temperature device and a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation source. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2 using the SHELXTL-97 program. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned geometrically (C–H, 0.95 Å).

3. Results and discussion

3.1. FTIR results and analysis

The FTIR spectra of the complexes and the ligand are displayed in Fig. S1. The 4-fluorobenzoic acid ligand exhibits the intense C=O stretching vibration band at 1683 cm^{-1}, which disappears in the spectra of complex **1**–**2**, indicating the coordination of the 4-fluorobenzoic acid ligand to the respective Ln^{3+} ions. It is known that the $\Delta\nu(COO^-)$ value of 150 cm^{-1} is associated with ideal symmetric carboxylate groups (C_{2v}) resulting from bridging and chelating coordination modes. Distortion caused by uneven coordination, such as binding selectively to one carboxylate oxygen, usually leads to smaller $\Delta\nu$ values [14,15]. In complex **1**, the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands locate at 1552 cm^{-1} and 1429 cm^{-1} respectively. The difference between the asymmetric and symmetric stretching vibration $\Delta\nu(COO^-) = \nu_{as} - \nu_s$ is 123 cm^{-1}, suggesting the presence of asymmetric carboxylate groups [23], which is in accordance with the X-ray analysis results. On the other hand, the asymmetric and symmetric stretching vibration modes of the carboxyl groups are assigned to $\nu_{as}(COO^-)$: 1552 cm^{-1} and $\nu_s(COO^-)$: 1431 cm^{-1} in complex **2**. The difference between the asymmetric and symmetric stretching vibration modes ($\Delta\nu(COO^-) = \nu_{as} - \nu_s$) is 121 cm^{-1}, which implies that the carboxyl



Scheme 1. Synthesis procedure of complexes **1** and **2**.