



Hydrothermal synthesis and luminescence of lanthanide complexes sensitized with dpphen



Hongzhen Xie^{a,b}, Guanzhong Lu^{a,*}

^a Key Laboratory for Advanced Materials and Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, PR China

^b State Key Laboratory Base of Novel Functional Materials and Preparation Science, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo, Zhejiang 315211, PR China

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ABSTRACT

Three new lanthanide complexes $[\text{Ln}(\text{dpphen})(\text{L})(\text{NO}_3)]$ ($\text{Ln}=\text{Tb}(\mathbf{1})$, $\text{Eu}(\mathbf{2})$, $\text{Nd}(\mathbf{3})$, $\text{H}_2\text{L}=\text{glutaric acid}$, $\text{dpphen}=4,7\text{-diphenyl-1,10-phenanthroline}$) have been synthesized hydrothermally by the reaction of H_2L , dpphen and $\text{Ln}(\text{III})$ ions. The X-ray diffraction analysis reveals that three coordination polymers have similar structures. The $\text{Ln}(\text{III})$ ions are nine coordinated and glutarate ligands bridge $\text{Ln}(\text{III})$ to form 1D polymer chains. The solid-state luminescence of complexes $\mathbf{1}$ and $\mathbf{2}$ was investigated at room temperature. The complexes $\mathbf{1}$ and $\mathbf{2}$ exhibited strong green and red luminescence under ultraviolet light. The ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$ ($j=6, 5, 4$ and 3) transition emissions of $\text{Tb}(\text{III})$ and the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j=0\text{--}4$) transition emissions of $\text{Eu}(\text{III})$ were observed in their emission spectra. The strong luminescence of complexes $\mathbf{1}$ and $\mathbf{2}$ demonstrates that luminescence of lanthanide coordination polymers is sensitized by an effective energy-transfer from dpphen ligand to $\text{Ln}(\text{III})$ ions. Moreover, the magnetic properties of complexes $\mathbf{1}\text{--}\mathbf{3}$ were also investigated.

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1. Introduction

In recent years, the studies on the efficient luminescent lanthanide complexes are continually one of the hot research topics, and mainly focused on the design and synthesis of fluorescent rare earths complexes [1–3]. Many rare earth complexes have been developed as the emitters in organic photoluminescence and electroluminescence devices [4–6]. Generally, the $\text{Ln}(\text{III})$ ions show very weak absorption in the visible region, because dielectric transitions between states of the same f configuration are strictly parity-forbidden by the Laporte rule. Therefore, the $\text{Ln}(\text{III})$ ions often require the application of strongly absorbing “antennae” for light harvesting to obtain efficient photoluminescence. That is to say, the selection of ligands plays a key role in improving the luminescence intensity of rare earth complexes [7–9]. These organic ligands with the ability to promote ligand-mediated energy transfer can suppress the environmental vibronic quenching. The polypyridyl N-donor ligands, such as 2,2':6',2''-terpyridine, 2,3,4,5-tetrakis(2-pyridyl)pyrazine, 1,10-phenanthroline-5,6-dione, 2,2'-dipyridylamine, 1,10-phenanthroline or 2,2'-bipyridine, can coordinate metals by either σ or π -electron donation from the ligand to metal center [10–13]. Moreover, these polypyridyl

lanthanide complexes frequently exhibit a strong absorption band in the visible region, due to the metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT). Recently, we paid attention to the assembly reaction between lanthanide metal ion and two types of ligands to synthesize lanthanide complexes with dpphen (4,7-diphenyl-1,10-phenanthroline) and glutaric acid as ligands, to develop the novel solid-state rare earths luminescence materials. Herein, we report the hydrothermal synthesis, crystal structures, thermal stabilities, magnetic properties and luminescence of three new lanthanide complexes, namely $[\text{Ln}(\text{dpphen})(\text{L})(\text{NO}_3)]$ ($\text{Ln}=\text{Tb}$ ($\mathbf{1}$), Eu ($\mathbf{2}$), Nd ($\mathbf{3}$), $\text{H}_2\text{L}=\text{glutaric acid}$, $\text{dpphen}=4,7\text{-diphenyl-1,10-phenanthroline}$).

2. Experimental section

2.1. Materials and synthesis of the complexes $\mathbf{1}\text{--}\mathbf{3}$

Except $\text{Tb}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ and $\text{Eu}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ prepared in our laboratory, all chemicals of reagent grade were commercially available (Aladdin) and used without further purification.

2.1.1. Synthesis of $\text{Tb}(\text{dpphen})(\text{C}_5\text{H}_6\text{O}_4)(\text{NO}_3)$ ($\mathbf{1}$)

White $\text{Tb}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ was obtained by slow evaporation of a solution of Tb_4O_7 (0.0187 g, 0.025 mmol) dissolved in HNO_3 under water boiling condition. $\text{Tb}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, glutaric acid (0.0132 g,

* Corresponding author. Tel.: +86 21 64253703; fax: +86 21 64253824.
E-mail address: gzhlu@ecust.edu.cn (G. Lu).

0.100 mmol) and dpphen (4,7-diphenyl-1,10-phenanthroline, 0.0322 g, 0.100 mmol) were dissolved in deionized water (15 mL) and adjusted to pH 6.00 by adding NaOH aqueous solution dropwise under stirring. Then the above mixture was sealed in a 23 mL Teflon-lined stainless autoclave, which was heated at 170 °C for three days. After slowly cooling the autoclave at 10 °C/h to room temperature, the colorless crystals of **1** were collected by filtration. Yield: 60% based on Tb(III). IR (KBr pellet, cm^{-1}): 3442s, 3052w, 1604vs, 1556w, 1410m, 1354w, 1287w, 1154w, 1027w, 1020w, 843m, 812w, 748m, 702m, 621w, 593m, 571 w. Elemental Anal. (%) Calcd for **1**: C, 50.96; H, 3.25; N, 6.15. Found: C, 50.91; H, 3.29; N, 6.09.

2.1.2. Synthesis of $\text{Eu}(\text{dpphen})(\text{C}_5\text{H}_6\text{O}_4)(\text{NO}_3)$ (**2**)

The colorless crystals of **2** were prepared with the similar preparation method as **1** by using Eu_2O_3 (0.0176 g, 0.050 mmol) instead of Tb_4O_7 . Yield: 45% based on Eu(III). IR (KBr pellet, cm^{-1}): 3445s, 2830m, 1598vs, 1416m, 1355m, 1271w, 1153w, 841m, 767m, 745w, 702m, 626w, 572w. Elemental Anal. (%) Calcd for **2**: C, 51.49; H, 3.28; N, 6.21. Found: C, 51.47; H, 3.26; N, 6.16.

2.1.3. Synthesis of $\text{Nd}(\text{dpphen})(\text{C}_5\text{H}_6\text{O}_4)(\text{NO}_3)$ (**3**)

$\text{Nd}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (0.045 g, 0.1 mmol) was dissolved in an aqueous solution of glutaric acid (0.0132 g, 0.100 mmol) and dpphen (0.0322 g, 0.100 mmol). The obtained mixture was adjusted to pH 6.00 by adding NaOH aqueous solution dropwise under stirring and then sealed in a 23 mL Teflon-lined stainless autoclave. This autoclave was heated at 170 °C for 3 days, and then cooled slowly at 10 °C/h to room temperature. The pale purple crystals of **3** were obtained after filtration. Yield: 54% based on Nd(III). IR (KBr pellet, cm^{-1}): 3442s, 2933m, 1598vs, 1558w, 1406m, 1302w, 1278m, 1155w, 833m, 747m, 704m, 659m, 571w. Elemental Anal. (%) Calcd for **3**: C, 52.08; H, 3.32; N, 6.29. Found: C, 52.05; H, 3.36; N, 6.20.

2.2. Characterization of sample

Elemental analyses of C, H, and N were performed on a Perkin-Elmer 2400II CHNS/O full automatic analyzer. The FT-IR spectra of samples were recorded on a Shimadzu FT-IR-8900 spectrometer, and the sample to be measured was ground with KBr and pressed into thin wafer. Powder X-ray diffraction (PXRD) of sample was performed on a Bruker D8 Advance diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Thermogravimetric analysis (TG) of sample was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer under nitrogen at a heating rate of 10 °C/min from room temperature to 800 °C. Solid-state power luminescence spectra of samples were recorded on an F-4600 (Hitachi) fluorescence spectrofluorimeter. The magnetic susceptibility data were collected in the temperature range of 2–300 K at a magnetic field of 2 T on a Quantum Design PPM9 VSM magnetometer.

Suitable single crystals of complexes **1–3** were used for single crystal X-ray diffraction analysis. Data collections were performed at 298(2) K on a RIGAKU RAXIS-RAPID diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All calculations were carried out with SHELXTL-97 programs [14,15]. The structure was refined by full matrix least squares with anisotropic displacement parameters for non-hydrogen atoms. All the other H atoms were generated geometrically and treated as riding. Details of crystal data, collection and refinement of the three complexes are summarized in Table 1. The selected bond distances and angles for complex **1–3** are listed in Table S1–S3.

Table 1
Crystal data and structure refinements for complexes **1–3**.

Compounds	1	2	3
Formula	$\text{C}_{58}\text{H}_{44}\text{N}_6\text{O}_{14}\text{Tb}_2$	$\text{C}_{58}\text{H}_{44}\text{N}_6\text{O}_{14}\text{Eu}_2$	$\text{C}_{58}\text{H}_{44}\text{N}_6\text{O}_{14}\text{Nd}_2$
Formula mass	1366.83	1352.91	1337.47
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$\text{P}2_1/\text{n}$	$\text{P}2_1/\text{n}$	$\text{P}2_1/\text{n}$
<i>a</i> (Å)	9.265(2)	9.369(2)	9.457(3)
<i>b</i> (Å)	8.915(2)	8.759(2)	8.912(3)
<i>c</i> (Å)	32.546(7)	32.489(7)	32.84(1)
β (deg)	95.44(3)	94.89(3)	94.370(3)
Volume (Å ³)	2676.0(9)	2565.4(9)	2759.7(2)
<i>Z</i>	2	2	2
<i>D</i> _{calcd.} (g cm ⁻³)	1.696	1.691	1.610
μ (mm ⁻¹)	2.696	2.414	1.933
<i>F</i> (0 0 0)	1352	1344	1332
2 θ range (deg)	3.04–27.38	2.32–27.46	2.29–27.56
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0326, 0.0634	0.0627, 0.1722	0.0941, 0.2083
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0539, 0.0861	0.0667, 0.1738	0.1051, 0.2129
GOF	1.137	1.274	1.241

$$^a wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

3. Results and discussion

3.1. Description of the structures

Hydrothermal reactions of $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ with dpphen and glutaric acid give complexes **1**, **2** and **3**. Crystallographic analysis reveals that complexes **1–3** are isostructural. Due to the similarity of **1–3**, the crystal structure of **1** has been described in detail as a representative.

An asymmetric unit of the complex **1** contains one Tb(III) ion, one glutarate ligand, one nitrate ion and one dpphen ligand. Each Tb(III) ion is nine-coordinated in a distorted monocapped square-antiprismatic coordination polyhedron. The coordination environment of Tb(III) ion consists of four oxygen atoms from three different glutarate ligands, three oxygen atoms from two nitrate ions, two nitrogen atoms from one dpphen ligand (Fig. 1). The Ln–O bond distance is 2.341(6)–2.561(7) Å for **1**, 2.371(7)–2.588(6) Å for **2**, 2.419(9)–2.656(9) Å for **3**, respectively; the Ln–N bond distance is 2.557(7) Å and 2.602(5) Å for **1**, 2.584(4) Å and 2.645(7) Å for **2**, 2.65(1) Å and 2.68(1) Å for **3** (Tables S1, S2 and S3). These bond distances increase with the ionic radius increase from Tb(III) ion to Nd(III) ion, which agree with the lanthanide contraction.

For glutarate dianion, the aliphatic carbon backbone may be present in three conformations: anti-anti, anti-gauche and gauche-gauche [16]. In complexes **1–3**, the glutarate ligand adopts

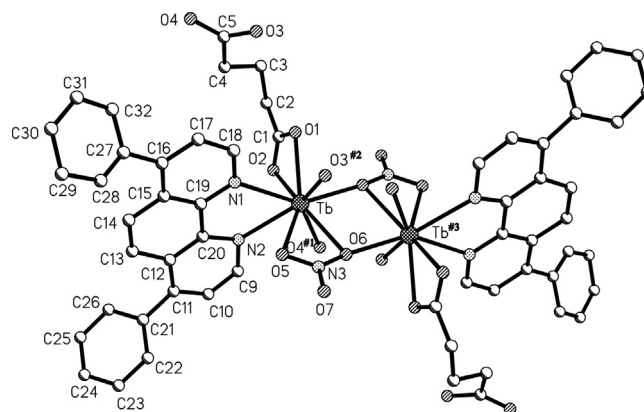


Fig. 1. The coordination environment of Tb(III) in complex **1**. (All hydrogen atoms are omitted for clarity, symmetry transformations: #1 = $-x - 1, y, z$; #2 = $-x + 1, -y, -z$; #3 = $-x, -y, -z$).

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