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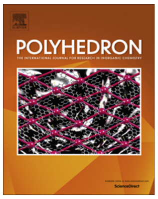

# Luminescent mononuclear Eu(III) and Tb(III) complexes with bipyridyl-tetrazolate tridentate ligands

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ABSTRACT

A new series of four luminescent mononuclear Eu(III) and Tb(III) complexes with bipyridyl tetrazolate tridentate chelates, $[Ln(tbpy)_2(DMF)(H_2O)_2](NO_3)$ and $[Ln(tmbpy)_2(DMF)(NO_3)]$ (Ln = Eu(III) and Tb(III), DMF = N,N-dimethylformamide, tbpy and tmbpy denote the deprotonated 6-(1*H*-tetrazole-5-yl)-2,2′-bipyridine and 6-(1*H*-tetrazole-5-yl)-4,4′-dimethyl-2,2′-bipyridine, respectively), have been synthesized and characterized. Each Ln(III) ion displays a distorted tricapped trigonal prism with two mono-anionic tridentate chelating ligands, originating from the N–H deprotonation of the tetrazolyl ring, and the introduction of two methyl groups into the 2,2′-bipyridyl ring has a significant impact on the coordination environment of the Ln(III) core, exhibiting that two coordinated water molecules are displaced by one chelating nitrate anion. Two types of Ln(III) complexes are all emissive in solution and solid states at room temperature. It is shown that the introduction of two electron-donating methyl groups into the 2,2′-bipyridyl ring has a major effect on the photoluminescence of Ln(III) complexes, and it is favorable for improving the luminescence efficiencies of Ln(III) species.

## 1. Introduction

There has been a rapid increasing interest in synthesizing new lanthanide complexes, particularly europium(III) and terbium(III) species, owing to their excellent luminescence properties and extensive potential applications in lighting, display, telecommunication, analytical sensor, anti-counterfeiting tag, security ink, and biomedical imaging [1–13]. Trivalent lanthanide ions are attractive candidates for the more commonly used organic fluorophores, because their derivatives are photochemically stable and show long lifetime, line-like emission spectra as a result of forced electric-dipole transitions [14]. Since lanthanide f–f transitions are Laporte-forbidden, direct excitation of electrons in trivalent lanthanide ions is usually difficult and weak. One method to overcome this shortcoming and achieve bright emission is to use a sensitizing chromophore or antenna as a ligand in a lanthanide complex, which harvests light and transfers the electronic energy to the lanthanide ion [15–19].

The selection of the suitable ligand for efficient energy transfer to the lanthanide ion after excitation has received much attention. "Hard" lanthanide ions prefer "hard" oxygen ligands, as confirmed by a recent survey of 1391 crystal structures, among which 42% contain exclusively Ln–O bonds while 78% include at least one Ln–O bond [20]. In particular, water strongly coordinates to the lanthanide ion and readily quenches the luminescence by nonradiative energy transfer to high-energy O–H oscillators of water [21,22]. However, the nature of the donor atom is not the only criterion, many stable lanthanide complexes are reported with mixed N,O- or even all-N-donor ligands. "Soft" anionic nitrogen ligands with deprotonated arylamide [23,24], triazole [25–28] or tetrazole [29–46] groups are shown to generate the moisture- and air-stable lanthanide complexes with the Ln–N bonds. Moreover, the binding ability, electronic absorption properties, absence of high-frequency vibrations, and location of donor excited states of the ligands are important criteria to be considered [47–49]. Aromatic pyridine ligands are competent candidates as the sensitizing agents for enhancing lanthanide ion emission, because of their good binding ability to the lanthanide ion and strong UV absorption [50].

Considering the formation thermodynamics and large coordination number (usually 8–10) of Ln(III) complexes, anionic polydentate chelating ligands are a preferred alternative, particularly mono-anionic tridentate chelates, which saturate the coordination sphere of the Ln(III) ions if the formation of tris complexes and

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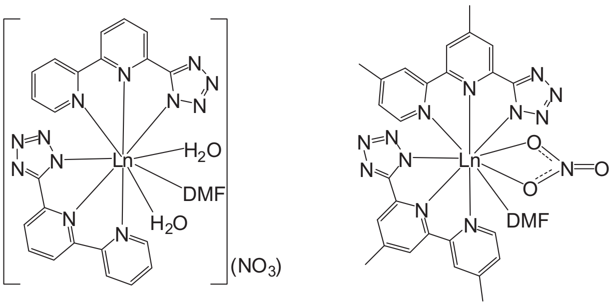
completely compensate the charge, an advantage for application in optical devices. Bipyridyl-tetrazole chelates are an alternative class of N-heterocyclic ligands since they are easily modified and form strong bonding with transition metals, giving robust complexes serve as mono-anionic tridentate chelating ligands via the N–H deprotonation of the tetrazolyl ring [40,51,52].

Herein, we report the syntheses, crystal structures and photophysical properties of a new series of mononuclear Ln(III) complexes with bipyridyl-tetrazolate tridentate ligands, $[Ln(tbpy)_2(DMF)(H_2O)_2](NO_3)$ and $[Ln(tmbpy)_2(DMF)(NO_3)]$ (Ln = Eu and Tb; DMF = N,N-dimethylformamide; tbpy and tmbpy denote the deprotonated 6-(1*H*-tetrazole-5-yl)-2,2′-bipyridine and 6-(1*H*-tetrazole-5-yl)-4,4′-dimethyl-2,2′-bipyridine, respectively) (Scheme 1). It is demonstrated that these mononuclear Ln(III) complexes are all emissive in solution and in the solid state at ambient temperature, and structural modification of the 2,2′-bipyridyl ring, such as introducing two methyl groups at the 4 and 4′-positions of the 2,2′-bipyridyl ring, has a great effect on the structural features and luminescence properties of Ln(III) species. Moreover, $[Ln(tmbpy)_2(DMF)(NO_3)]$ exhibits a markedly enhanced luminescence efficiency compared to $[Ln(tbpy)_2(DMF)(H_2O)_2](NO_3)$, owing to two water molecules bound to the Ln(III) ion replaced by one chelating nitrate anion, as a result of the introduction of two electron-donating methyl groups into the 2,2′-bipyridyl ring.

## 2. Experimental

### 2.1. Materials and instrumentation

All the chemicals used for synthesis were of analytical grade and commercially available. The tbpyH and tmbpyH ligands were synthesized according to the literature methods [40,51]. Infrared (IR) spectra were recorded on a Bruker Optics ALPHA FT-IR spectrometer using KBr pellets. Powder X-ray diffraction (PXRD) (Fig. S1) was recorded on an Empyrean (PANalytical B.V.) diffractometer for a Cu-target tube and a graphite monochromator. Simulation of the PXRD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program version 3.0 available free of charge *via* the Internet at http://www.iucr.org. UV–Vis absorption spectra in DMF solution were measured on a Shimadzu UV-2550 spectrometer. The luminescence properties of **1**–**4** in solution and solid states were determined on an Edinburgh analytical instrument (F900 fluorescence spectrometer) with a thermoelectrically cooled Hamamatsu R3809 photomultiplier tube. An integrating sphere (Lab sphere) was applied to measure the emission quantum yield in the solid state.



Ln = Eu (**1**)
Tb (**3**)

Ln = Eu (**2**)
Tb (**4**)

**Scheme 1.** Molecular structures of Ln(III) complexes **1**–**4**.

### 2.2. Synthesis of Ln(III) complexes **1**–**4**

#### 2.2.1. Synthesis of $[Eu(tbpy)_2(DMF)(H_2O)_2](NO_3)\cdot 2H_2O$ (**1**)

An ethanol solution (8 mL) of $Eu(NO_3)_3\cdot 6H_2O$ (43 mg, 0.096 mmol) and tbpyH (67.0 mg, 0.299 mmol) was refluxed for 12 h, affording a white precipitate. The precipitate was collected by filtration, washed with diethyl ether and dried under vacuum. Colorless crystals of **1** were grown via slow diffusion of $CH_3CN$ into the DMF solution after 5 days. Yield: 33.0 mg, 0.041 mol, 42.5%. *Anal.* Calc. for $C_{25}H_{29}EuN_{14}O_8$: C, 37.27; H, 3.63; N, 24.34. Found: C, 37.20; H, 3.67; N, 24.38%. Selected IR data (KBr, $cm^{-1}$): 3454 m, 3414(m, sh), 3249w, 1668 m, 1602 m, 1466 m, 1431 m, 1383 s, 1242w, 1190w, 1010w, 792w, 759w, 690w.

#### 2.2.2. Synthesis of $[Eu(tmbpy)_2(DMF)(NO_3)]\cdot 2THF\cdot DMF$ (**2**)

Complex **2** was prepared following the procedure for **1**, using $Eu(NO_3)_3\cdot 6H_2O$ (75.4 mg, 0.169 mmol) and tmbpyH (128.2 mg, 0.508 mmol). Colorless crystals of **2** were afforded by slow diffusion of THF into the DMF solution after 6 days. Yield: 70.2 mg, 0.075 mol, 44.4%. *Anal.* Calc. for $C_{36}H_{44}EuN_{15}O_6$: C, 46.25; H, 4.74; N, 22.48. Found: C, 46.30; H, 4.70; N, 22.44%. Selected IR data (KBr, $cm^{-1}$): 3413w, 1653 m, 1618 s, 1566w, 1481w, 1441w, 1384 s, 1296w, 1242w, 1009w, 939w, 874w, 837w, 792w, 513w.

#### 2.2.3. Synthesis of $[Tb(tbpy)_2(DMF)(H_2O)_2](NO_3)\cdot 2H_2O$ (**3**)

Complex **3** was prepared following the procedure for **1**, using $Tb(NO_3)_3\cdot 6H_2O$ (70.3 mg, 0.155 mmol) and tbpyH (104.6 mg, 0.466 mmol). Colorless crystals of **3** were afforded by slow diffusion of THF into the DMF solution after 6 days. Yield: 57.8 mg, 0.071 mol, 45.8%. *Anal.* Calc. for $C_{25}H_{29}TbN_{14}O_8$: C, 36.96; H, 3.60; N, 24.13. Found: C, 36.90; H, 3.65; N, 24.18%. Selected IR data (KBr, $cm^{-1}$): 3452 m, 3252w, 1664 s, 1603 m, 1468 m, 1430 s, 1383 s, 1242w, 1187w, 1009w, 790w, 758w, 689w.

#### 2.2.4. Synthesis of $[Tb(tmbpy)_2(DMF)(NO_3)]\cdot 2THF\cdot DMF$ (**4**)

Complex **4** was prepared following the procedure for **1**, using $Tb(NO_3)_3\cdot 6H_2O$ (50.4 mg, 0.111 mmol) and tmbpyH (84.2 mg, 0.334 mmol). Colorless crystals of **4** were afforded by slow diffusion of THF into the DMF solution after 6 days. Yield: 43.6 mg, 0.046 mol, 41.4%. *Anal.* Calc. for $C_{36}H_{44}TbN_{15}O_6$: C, 45.91; H, 4.71; N, 22.31. Found: C, 45.97; H, 4.67; N, 22.26%. Selected IR data (KBr, $cm^{-1}$): 3416w, 1656 m, 1619 s, 1565w, 1484 s, 1387 s, 1295w, 1241w, 1011w, 939w, 837w, 791w, 513w.

### 2.3. Crystallographic data and structure refinements

Single-crystal X-ray diffraction data of **1**–**4** were collected on a Bruker D8 QUEST diffractometer at room temperature using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The program *Crystalclear* [53] was used for integration of the diffraction profiles. The structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares methods using the SHELXTL-97 program package [54]. The heavy atoms were located from the *E*-maps and other non–hydrogen atoms were located in subsequent difference Fourier syntheses and refined with anisotropic thermal parameters on $F^2$. The hydrogen atoms of the ligands and the solvent molecules were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The crystallographic data and structure refinement detail of **1**–**4** are summarized in Table 1, and the selected bond lengths and angle for **1**–**4** are listed in Table 2.