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ORIGINAL PAPER

Photophysical properties of lanthanide complexes with 5-nitro-1,10-phenanthroline

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Abstract Five novel lanthanide (Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+}, and Gd^{3+}) complexes with 5-nitro-1,10-phenanthroline ($phenNO_2$) have been synthesized and characterized by elemental analysis, IR, UV, and luminescence spectra. The triplet state energy of $phenNO_2$ was determined to be 20,048 cm^{-1} via the phosphorescence spectra of $phenNO_2$ and its gadolinium complex. The photophysical properties of these complexes indicated that the triplet state energy of the ligand is suitable for the sensitization of the luminescence of Eu^{3+} and Sm^{3+}, especially the former.

Keywords Lanthanide complexes · 5-Nitro-1,10-phenanthroline · Fluorescence · Energy transfer

Introduction

Much research has been performed on lanthanide complexes with heterocyclic ligands, such as 1,10-phenanthroline and 2,2′-bipyridine, which strongly absorb ultraviolet light and then effect an intramolecular energy transfer process to central lanthanide ions [1–6]. Moreover, these heterocyclic compounds also act as assistant ligands for some lanthanide complexes of carboxylates or *β*-diketonates by replacing the water molecules in the coordination sphere, which can decrease the nonradiative deactivation originating from the coordinated H_2O to obtain high luminescence [7–10]. 1,10-Phenanthroline can be chemically modified to form substituted heterocyclic ligands such as 1,10-phenanthroline-1-oxide [11], 1,10-phenanthroline-5,6-dione [12], and 5-nitro-1,10-phenanthroline [13]. A few studies on the synthesis and characterization of lanthanide complexes with the first two of these ligands were reported [14–17]. Few investigations have concerned the photophysical properties of lanthanide complexes with 5-nitro-1,10-phenanthroline ($phenNO_2$) except for several related studies concerning mainly the preparation and characterization of complexes with the 3d metal ions [18–20]. The present work explores the photophysical properties of the corresponding complexes with lanthanide ions (Eu^{3+}, Tb^{3+}, Gd^{3+}, Sm^{3+}, and Dy^{3+}) by using UV, IR, phosphorescence, and luminescence spectra.

Results and discussion

The composition of the complex systems was confirmed by chemical analyses as $Ln(phenNO_2)_3Cl_3 \cdot 2H_2O$, where Ln = Eu, Tb, Gd, Sm, and Dy. No AgCl was precipitated with $AgNO_3$ from the ethanol solution of these complexes, which indicates that three Cl^- ions have taken part in the coordination. All the IR spectra of these lanthanide complexes are similar to that of the free ligand $phenNO_2$. Figure 1 gives the IR absorption spectrum of the complex $Eu(phenNO_2)_3Cl_3 \cdot 2H_2O$. The 1,640–1,230 cm^{-1} region could be mainly assigned to the stretch vibration of double bonds (ν(C=C) and ν(C=N)) and the 1,230–1,196 cm^{-1} region could be mainly assigned to the in-plane bending of C–H bonds. At 1,352 and 1,145 cm^{-1}, two strong bands were attributed to $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$, respectively. In comparison with general aromatic nitro compounds, the wavenumbers of these two characteristic bands of NO_2 were obviously decreased by about 200 cm^{-1} [21]. The

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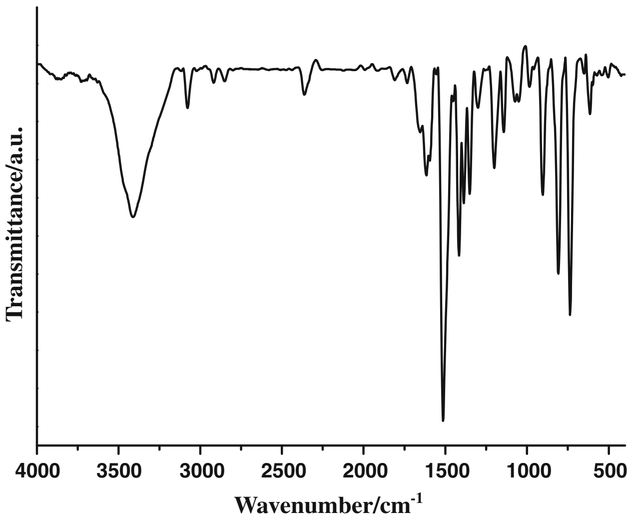

Fig. 1 IR spectrum of $Eu(phenNO_2)_3Cl_3·2H_2O$

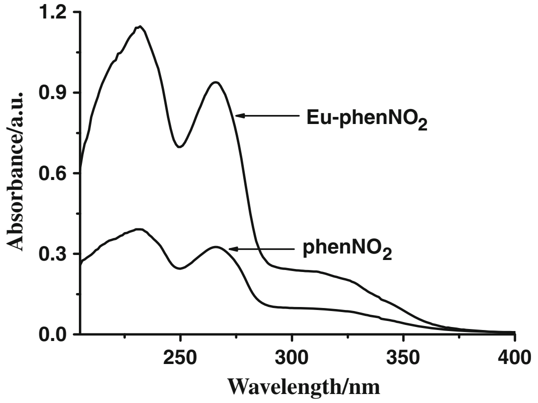

Fig. 2 UV absorption spectra of $phenNO_2$ and $Eu(phenNO_2)_3Cl_3·2H_2O$

Table 1 Absorption data for complexes and $phenNO_2$ in ethanol solution

Compounds	Abs at λ (nm) ε (dm^3 mol^{-1} cm^{-1})
$Eu(phenNO_2)_3Cl_3·2H_2O$	232 (54,510), 266 (46,310), 320 (10,900)
$Tb(phenNO_2)_3Cl_3·2H_2O$	232 (53,810), 266 (49,430), 320 (12,220)
$Sm(phenNO_2)_3Cl_3·2H_2O$	232 (54,820), 266 (44,860), 320 (10,190)
$Dy(phenNO_2)_3Cl_3·2H_2O$	232 (54,180), 266 (43,290), 320 (11,660)
$phenNO_2$	232 (18,210), 265 (15,140), 320 (4,150)

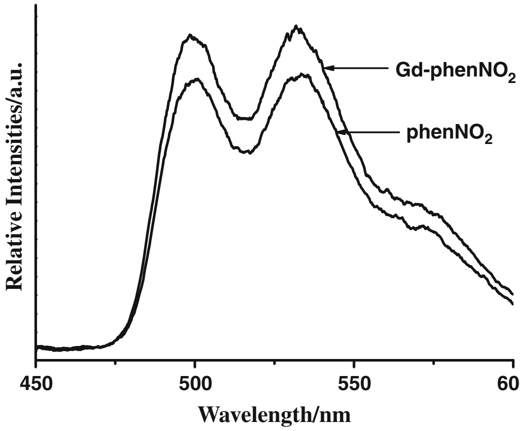

Fig. 3 Phosphorescence spectra of $Gd(phenNO_2)_3Cl_3·2H_2O$ and $phenNO_2$ ligand ($\lambda_{ex} = 265$ nm) at 77 K

out-of-plane rocking of C–H bonds occurred in the 1,087–565 cm^{-1} region. The absorption bands corresponded to the in-plane swing vibration of coordinated H_2O molecules were not observed in the range 605–585 cm^{-1}, which verifies that the water molecule is not coordinated to Ln^{3+} and corresponds to crystal water molecule [22].

The absorption spectrum of a given complex was not significantly modified by changing the metal ion, and each spectrum is very similar to that of the free ligand. This indicates that the absorption depends mainly on the ligand, and $phenNO_2$ is the energy donor and luminescence sensitizer of the lanthanide ion. Figure 2 gives the UV absorption spectra of the free $phenNO_2$ ligand and the corresponding europium complex in ethanol solution. The absorption peaks of $phenNO_2$ in the ultraviolet region appearing at 232 and 265 nm are assigned to the band of π–π* transitions of the aromatic ring, which belongs to the K band [23]. UV–Vis spectroscopic data obtained at room temperature for complexes and $phenNO_2$ are presented in Table 1.

The gadolinium complex was selected for the determination of the triplet state energy of the ligand $phenNO_2$ owing to an enhanced phosphorescence–luminescence ratio ($\Phi_{ph}/\Phi_{fl} > 1$) compared with that of other lanthanide complexes [24]. The phosphorescence spectra of the gadolinium complex with $phenNO_2$ and the free $phenNO_2$ ligand were measured and the triplet state energy of $phenNO_2$, E_T, was determined to be 20,048 cm^{-1} based on both maximum phosphorescence bands around 498 nm (as shown in Fig. 3). It is worth noting that the triplet level of $phenNO_2$ was found to be moderately lower than that of 1,10-phenanthroline (22,075 cm^{-1}) [25], which may be due to the presence of the nitro group on the phenanthroline ring.

In order to transfer the energy from the ligand to the lanthanide ion, the triplet state energy needs to be higher than the resonance level of the metal ion (Eu^{3+}: $^5D_0$, 17,200 cm^{-1}; Tb^{3+}: $^5D_4$, 20,500 cm^{-1}; Sm^{3+}: $^4G_{5/2}$, 17,900 cm^{-1}; Dy^{3+}: $^4F_{9/2}$, 21,000 cm^{-1}), and a difference of 2,500–3,500 cm^{-1} is necessary to sensitize the luminescence of the lanthanide efficiently [22]. In cases where the triplet state and the resonance level of the metal are similar in energy, the energy transfer process becomes reversible due to thermal repopulation of the triplet state [26], and thermally assisted energy back-transfer to the triplet state of the ligand dominates [27]. Therefore, the sensitization of the metal-centered (MC) luminescence is observed for the europium and samarium complexes (Figs. 4, 5) because the $^5D_0$ level of Eu^{3+} and the $^4G_{5/2}$ level of Sm^{3+} are both much lower in energy than E_T ($\Delta E = 2{,}848$ and $2{,}148\ cm^{-1}$ for Eu^{3+} and Sm^{3+}, respectively), whereas the lack of MC luminescence for the terbium and dysprosium complexes is consistent with the fact that the resonance levels of the both metal ions are higher in energy than E_T.

The excitation spectra of $Eu(phenNO_2)_3Cl_3{\cdot}2H_2O$ and $Sm(phenNO_2)_3Cl_3{\cdot}2H_2O$ are similar except for a small difference in band intensities, as shown in Fig. 6. The excitation spectra exhibit a large, broad band between 320 and 400 nm, with a maximum around 368 nm, corresponding to transitions populating ligand-centered excited states. This strongly suggests an efficient sensitization process between the ligand and the lanthanide ions, with the ligand unit acting as an antenna [28]. Figures 4 and 5 give the emission spectra of $Eu(phenNO_2)_3Cl_3{\cdot}2H_2O$ and $Sm(phenNO_2)_3Cl_3{\cdot}2H_2O$, respectively. The europium complex shows five emission peaks of different intensities at 579, 593, 618, 652, and 698 nm, which belong to the transitions of $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ of the Eu^{3+} ion, respectively. The most intense transition in the emission spectrum is the $^5D_0 \rightarrow {}^7F_2$ transition at 618 nm; this is the so-called hypersensitive transition and is responsible for the brilliant red emission color of this complex. For the $Sm(phenNO_2)_3Cl_3{\cdot}2H_2O$ complex, the emission spectrum shows four emission peaks centered at 566, 602, 644, and 707 nm, which can be assigned to the transitions of $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2} \rightarrow {}^6H_{9/2}$, and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ of the Sm^{3+} ion, respectively. The $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition presents the highest relative emission intensity around 602 nm. The values of the emission intensities and the relative luminescence quantum yields of the complexes $Eu(phenNO_2)_3Cl_3{\cdot}2H_2O$ and $Sm(phenNO_2)_3Cl_3{\cdot}2H_2O$ were determined to be 20,190, 14.8% and 13,920, 10.2%, respectively. Considering that all the luminescence spectra have been recorded at the same concentration, we can conclude that the luminescence of the europium complex is stronger than that of the samarium complex, which suggests that the triplet state energy of $phenNO_2$ is more suitable for the sensitization of Eu^{3+} than for Sm^{3+}. Moreover, for the samarium complex, a lot of internal energy levels ($^6F_{11/2}$, $^6F_{9/2}$,…, $^6H_{11/2}$, etc.) exist between the first excited state $^4G_{5/2}$ and the ground state $^6H_{9/2}$ of Sm^{3+}, readily causing some nonradiative energy transfer processes to lose the excited energy, also resulting in the weaker luminescence of Sm^{3+} complex.

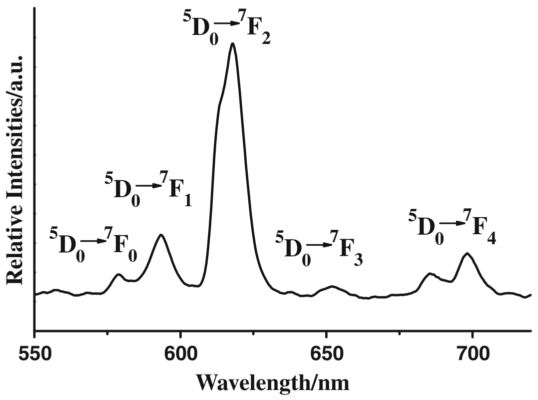

Fig. 4 Emission spectrum of $Eu(phenNO_2)_3Cl_3{\cdot}2H_2O$ ($\lambda_{ex} = 368$ nm)

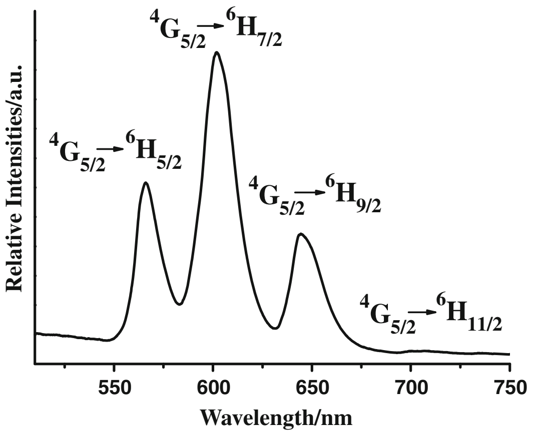

Fig. 5 Emission spectrum of $Sm(phenNO_2)_3Cl_3{\cdot}2H_2O$ ($\lambda_{ex} = 368$ nm)

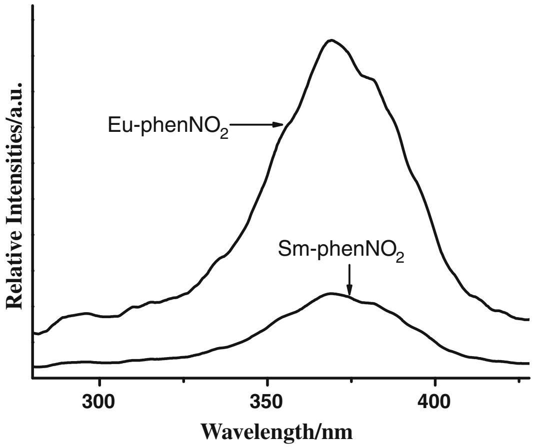

Fig. 6 Excitation spectra of $Eu(phenNO_2)_3Cl_3{\cdot}2H_2O$ ($\lambda_{em} = 618$ nm) and $Sm(phenNO_2)_3Cl_3{\cdot}2H_2O$ ($\lambda_{em} = 602$ nm)

In summary, five lanthanide (Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+}, and Gd^{3+}) complexes with 5-nitro-1,10-phenanthroline ($phenNO_2$) were synthesized and characterized. The triplet state energy of phenNO_2 was determined to be 20,048 cm^{-1} via the phosphorescence spectra of phenNO_2 and its gadolinium complex, which is much higher in energy than the resonance levels of Eu^{3+} and Sm^{3+} ions, but lower than those of Tb^{3+} and Dy^{3+} ions. So it can be predicted that phenNO_2 is able to sensitize the luminescence of Eu^{3+} and Sm^{3+}. The values of the emission intensities and the relative luminescence quantum yields for these two luminescent complexes, determined to be 20,190, 14.8% and 13,920, 10.2%, respectively, indicate that the europium complex shows stronger luminescence compared with the samarium complex, which suggests that the triplet state energy of phenNO_2 is more suitable for the sensitization of Eu^{3+} than for Sm^{3+}.

Experimental

The purity of lanthanide oxides used (Eu_2O_3, Tb_4O_7, Gd_2O_3, Sm_2O_3, and Dy_2O_3) exceeded 99.99%. Other chemicals were analytical grade and used as received. Elemental analyses (C, H, N) were performed with a Flash-EA1112 elemental analyzer, and lanthanide ions were analyzed by complexometric titration with EDTA; the results were found to be in good agreement with the calculated values. ^1H NMR spectra were collected on a Bruker-400 spectrometer. Mass spectra were measured on an Aligent 5975 spectroscopy. Infrared spectra of KBr pellets were measured at room temperature in the 400–4,000 cm^{-1} region by using a Bruker Tensor 27 FT-IR spectrophotometer. UV spectra of 2.0×10^{-5} mol dm^{-3} solutions in ethanol were obtained by a Perkin-Elmer Lambda 25 spectrophotometer. Luminescence and phosphorescence spectra of 5.0×10^{-4} mol dm^{-3} solutions in ethanol were recorded in an Hitachi F-4500 spectrophotometer equipped for both room temperature and 77-K measurements. The luminescence quantum yields were measured by using quinine sulfate in 1.0 M H_2SO_4 ($\Phi = 54.6\%$) as reference [29].

5-Nitro-1,10-phenanthroline

The directions given by Hammett et al. [13] were used with the following modifications. To a stirred solution of 10.0 g 1,10-phenanthroline (55.6 mmol) in 15 cm^3 of 95% sulfuric acid was added a mixture of concentrated nitric acid/95% sulfuric acid (1:1, 60 cm^3) at such a rate that the temperature approached but did not exceed 170 °C. Heating was then continued for 3 h at reflux. The mixture was then cooled, poured on ice, and neutralized with 30% sodium hydroxide solution. The precipitate was filtered, washed with cold water, and dried. Crystallization from ethanol yielded 9.8 g (86%) of a light yellow crystalline solid, m.p. 201.8–202.3 °C (Ref. [13] m.p. 202 °C). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.37$ (dd, $J = 4.34$, 1.71 Hz, 1H), 9.31 (dd, $J = 4.26$, 1.58 Hz, 1H), 9.01 (dd, $J = 8.62$, 1.60 Hz, 1H), 8.69 (s, 1H), 8.45 (m, 1H), 7.82 (m, 2H) ppm; IR (KBr): $\bar{\nu} = 3{,}414$, 3,080, 1,618, 1,519, 1,419, 1,386, 1,353, 1,202, 1,145, 1,045, 986, 906, 809, 734, 623 cm^{-1}; EIMS (70 eV): m/z (%) = 225 (64, M^+), 179 (100), 167 (37), 152 (24), 125 (17), 99 (10), 75 (13).

Preparation of the complexes

Lanthanide oxides (Eu_2O_3, Gd_2O_3, Sm_2O_3, and Dy_2O_3) were converted to their chlorides by treatment with concentrated hydrochloric acid and evaporated just to dryness. For the preparation of the terbium chloride, whose oxides contain the lanthanide in a higher oxidation state (Tb_4O_7), hydrogen peroxide was used as the reductant. The corresponding lanthanide complexes with the ligand phenNO_2 were prepared by the same method described below.

To a stirred solution of lanthanide chloride (2 mmol) in 15 cm^3 of deionized water was added a solution of 1.35 g phenNO_2 (6.0 mmol) in 100 cm^3 of 95% C_2H_5OH. The reaction mixture was stirred at 80 °C for 10 h and then concentrated under reduced pressure to about 25 cm^3. After cooling to room temperature the precipitate was filtered off, washed with water (2×10 cm^3) and ethanol (2×10 cm^3), dried, and stored over silica gel.

Trichlorotri(5-nitro-1,10-phenanthroline)europium(III) dihydrate ($C_{36}H_{25}Cl_3N_9O_8Eu$)

Yield: 1.35 g (70%); IR (KBr): $\bar{\nu} = 3{,}412$, 3,079, 1,621, 1,520, 1,420, 1,383, 1,352, 1,200, 1,145, 1,044, 986, 905, 809, 732, 622 cm^{-1}.

Trichlorotri(5-nitro-1,10-phenanthroline)terbium(III) dihydrate ($C_{36}H_{25}Cl_3N_9O_8Tb$)

Yield: 1.32 g (68%); IR (KBr): $\bar{\nu} = 3{,}418$, 3,082, 1,621, 1,521, 1,420, 1,384, 1,353, 1,201, 1,145, 1,044, 987, 906, 807, 732, 621 cm^{-1}.

Trichlorotri(5-nitro-1,10-phenanthroline)samarium(III) dihydrate ($C_{36}H_{25}Cl_3N_9O_8Sm$)

Yield: 1.44 g (75%); IR (KBr): $\bar{\nu} = 3{,}421$, 3,085, 1,621, 1,518, 1,419, 1,385, 1,354, 1,202, 1,144, 1,044, 986, 907, 807, 733, 621 cm^{-1}.

Trichlorotri(5-nitro-1,10-phenanthroline)dysprosium(III) dihydrate ($C_{36}H_{25}Cl_3N_9O_8Dy$)

Yield: 1.32 g (72%); IR (KBr): $\bar{\nu} = 3{,}420$, 3,083, 1,621, 1,519, 1,419, 1,386, 1,355, 1,200, 1,143, 1,045, 987, 906, 807, 731, 622 cm^{-1}.

Trichlorotri(5-nitro-1,10-phenanthroline)gadolinium(III) dihydrate ($C_{36}H_{25}Cl_3N_9O_8Gd$)

Yield: 1.45 g (75%); IR (KBr): $\bar{\nu} = 3{,}419$, 3,081, 1,620, 1,520, 1,419, 1,386, 1,354, 1,201, 1,144, 1,045, 986, 908, 806, 732, 622 cm^{-1}.

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