

Photoluminescent Tetrazolate-based Eu(III) Complexes: An Outstanding Impact of Aromatic Phosphine Oxide Co-ligands on the Photoluminescence Quantum Yields

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New ternary Eu(III) 5-(2-pyridyl-1-oxide)tetrazolate complexes with phosphine oxide co-ligands have been synthesized and characterized by elemental analysis, and IR and ¹H NMR spectroscopic techniques. The analytical data revealed that these complexes are mononuclear, and the central Eu(III) ion is coordinated by three oxygen and three nitrogen atoms of the tetrazolate and two oxygen atoms from the phosphine oxide ligands. The ancillary ligands increased remarkably the luminescence efficiency of the Eu(III) tetrazolate.

Key words: Europium Tetrazolates, Phosphine Oxides, Photoluminescence, Quantum Yields, Lifetime

Introduction

The unique properties of lanthanide complexes exhibiting narrow emission bands upon excitation, long-living luminescence lifetimes, emission over the visible and near-IR (NIR) regions makes them very attractive materials for various technologies. On account of their high photoluminescence quantum yields, lanthanide complexes can be applied in light-emitting devices [1–3], low-threshold lasers [4], optical amplifiers [5], displays, or biomedical imaging [6, 7]. Bredol and coworkers demonstrated the feasibility to manufacture highly photoluminescent hybrid organic/inorganic materials – sol-gels incorporating photoluminescent lanthanide complexes [8–10].

The limiting features of lanthanide ions themselves are the low absorbance leading to a low value of the molar absorption coefficient and the spin- and parity-forbidden nature of *f-f* transitions that prevent direct excitation. Such problems can be avoided by introducing organic ligands which act as the “antenna”

chromophores by transferring energy from the excited states of the “antenna” to the emissive states of lanthanide ions [11–13]. This process involves excitation of the ligand to a singlet state, radiationless intersystem crossing to the triplet state and energy transfer from the triplet state to the emissive level of the lanthanide cation. Further, the excited lanthanide ions undergo radiative transitions to lower energy states which are responsible for the characteristic multiple narrow band emissions. For such a phenomenon to occur, one must take into account the energy of the excited states of the organic chromophore used, which must be higher as compared to the emissive levels of the lanthanide ions [14–17]. Ligands such as 1,3-diketonates [18–20], carboxylates [21–23], and analogs of 1,3-diketonates (pyrazolonates and isoxazonates) [24, 25], have been extensively studied so far to act as “antenna” for the lanthanide ions. A great number of different chromophores have been investigated and studied to achieve better and brighter lanthanide complex luminescence. The applicability of

lanthanide complexes can be limited by: 1) vibronic quenching of lanthanide complex emission by OH, NH oscillators present in the 1st coordination sphere of the Ln(III) cation, 2) low photoluminescence quantum yield, and 3) low thermodynamic and kinetic stability. To overcome all such problems, ligands bearing suitable chromophores forming thermodynamically stable complexes with lanthanide ions are to be used. Coordinatively unsaturated lanthanide complexes frequently display low photoluminescence quantum yields, due to the presence of quenching molecules (water or alcohol). These quenchers can be replaced by several neutral sensitizing auxiliary ligands. These co-ligands can also act as an additional “antenna” and can enhance the overall photoluminescence quantum yield. A large number of highly coordinated complexes of lanthanide 1,3-diketones containing additional *N*-ligands such as 1,10-phenanthroline, 4,7-disubstituted 1,10-phenanthrolines, 2,2'-bipyridine, 4,4'-disubstituted 2,2'-bipyridines, or 1,4-diaza-1,3-butadienes [18, 26, 27] have been successfully synthesized and used in photophysical studies. Phosphine oxides display particularly high affinity for the complexation of lanthanide cations. The square-antiprismatic structure formed by introducing phosphine oxides into lanthanide complexes also promotes the faster radiative decay of the lanthanide ion, leading to an increase of the photoluminescence efficiencies due to an enhanced $^5D_0 \rightarrow ^7F_2$ transition [28–30].

Tetrazoles display pK_a values in the range of 4.2–4.4, similarly to carboxylic acids [31]. They are excellent ligands for metal ion coordination [32, 33]. The water binding at lanthanide ions is prevented by introducing multidentate tetrazole-based ligands containing terpyridine or bipyridine chromophores, providing luminescent lanthanide complexes with good photoluminescence quantum yields [34, 35]. Quite recently, much higher photoluminescence quantum yields have been reported in solution and in the solid state for Eu(III) and Tb(III) complexes containing tri-

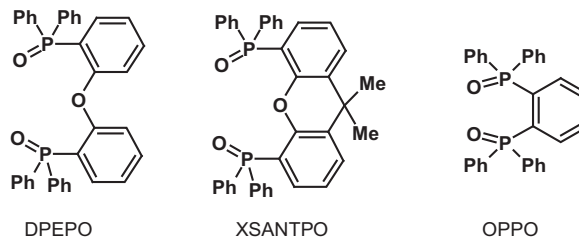


Fig. 1. The phosphine oxides used as co-ligands.

dentate pyridine-tetrazolates as analogs of dipicolinate ligands [36].

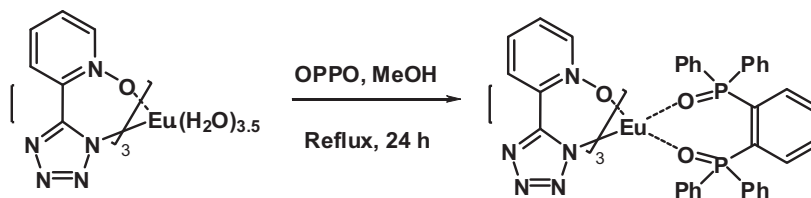
In a previous paper [37] we described the photoluminescence properties of europium and terbium tetrazolates. Herein we report the synthesis and photophysical studies of Eu(III) complexes with 5-(2-pyridyl-1-oxide)tetrazole (HPTO) and phosphine oxides as co-ligands: 4,8-bis(diphenylphosphino)-9,9-dimethyl-xanthene dioxide (XANTPO), 1,2-bis(diphenylphosphino)benzene dioxide (OPPO) and 2,2'-bis(diphenylphosphino)-diphenylether dioxide (DPEPO). The choice of these auxiliary ligands is due to their strong coordination ability with the lanthanide ions and their structural rigidity. These ligands are shown in Fig. 1.

Result and Discussion

Syntheses and characterization of complexes

The ligand HPTO and its neutral complex **1** were synthesized according to our previous work [37]. The complexes with the *P*-oxide co-ligands were synthesized according to Scheme 1.

Microanalysis of the products confirmed the proposed stoichiometry. The bands observed at 3000–3300 cm^{-1} in the IR spectra of all complexes confirms the presence of water molecules, also reported for other tetrazole-containing complexes. The water molecules are hydrogen-bonded to the tetrazole



Scheme 1. Synthesis of ternary complexes.

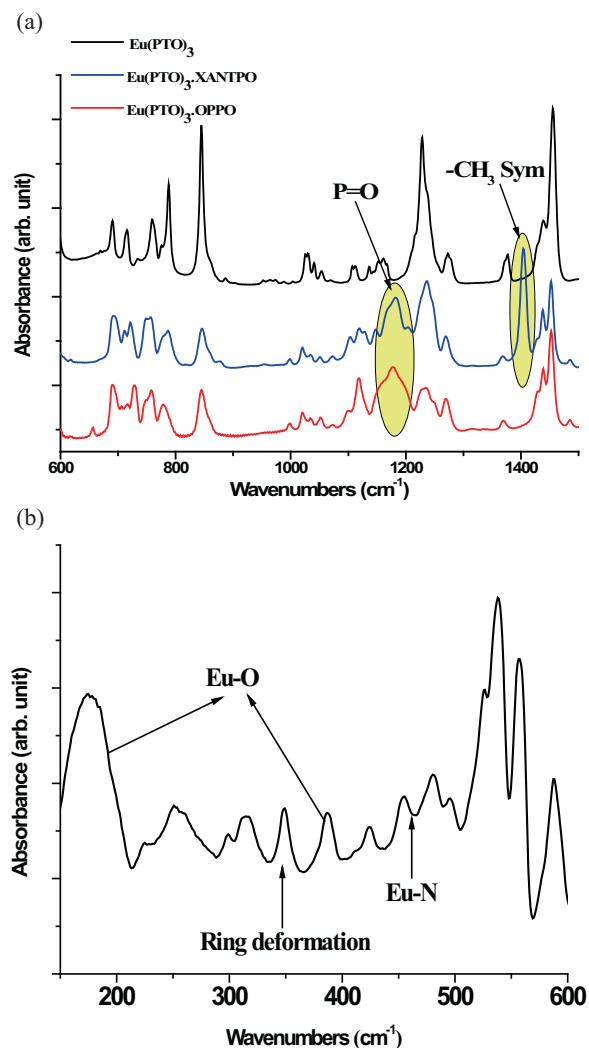


Fig. 2 (color online). Mid- and far-IR spectra of complexes 1–3 (A) and of complex 1 (B).

units, but not to the metal ions [38–40]. The shifts in the P=O stretching frequencies of the phosphine oxide molecules in the presented complexes (from 1135 to 1150 cm^{-1} in **2**, from 1155 to 1178 cm^{-1} in **3** and from 1135 to 1165 cm^{-1} in **4**) show the involvement of the phosphoryl oxygen atoms in the complex formation with the Eu(III) ion. The shift of the band at 1265 cm^{-1} of the N–O stretching to 1360 cm^{-1} indicates that the N–O group is engaged in complex formation with the Eu(III) ion. The far-IR spectra reveal the coordination of the Eu(III) ion with the nitrogen atoms of tetrazole and the oxygen atoms of pyridine

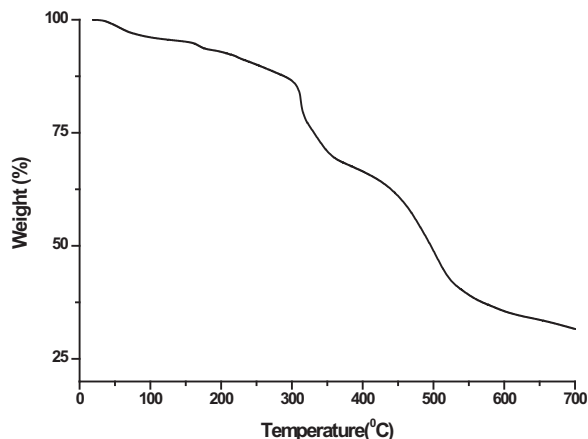


Fig. 3. Thermogravimetric curve for complex **2**.

oxide by the sharp bands at 450 and 400 cm^{-1} , respectively (Fig. 2).

The proton NMR spectra of complexes **1–4** showed all the expected peaks of the PTO ligand. The signals of the pyridine protons have been shifted upfield upon coordination with the metal ion for complexes **1–4**. The TGA analysis shows the loss of water molecules below 70 °C (4.1%, 6% and 3% for **2**, **3** and **4**, respectively) confirming their presence in the outer coordination sphere, followed by the loss of the respective phosphine oxides and tetrazoles, which at last leads to the formation of europium oxide (Fig. 3).

Molecular structure modeling of complexes by the MOPAC/AM1 model

We have tried to optimize the molecular structure of the synthesized europium(III) complexes by using the MOPAC/AM1 model with parameters for europium [41]. The central Eu(III) ion in complexes **2–4** possesses an eight-fold coordination environment, and the geometry can be described as a square antiprism. Lanthanide complexes with seven-, eight- or nine-fold coordination are well documented [42, 43]. Short P=O–Eu bonds (2.324–2.333 Å) were calculated for these complexes. They are distinctly shorter than those found in the crystal structure of gadolinium 5-(2-pyridyl-1-oxide)tetrazolate between Gd–OH₂ (coordinated water, 2.450 Å) [41]. That suggests stronger interactions of the phosphine oxides with the Eu(III) ion. Fig. 4 represents the calculated structure of the tetrazolate complex with the XANTPO co-ligand.

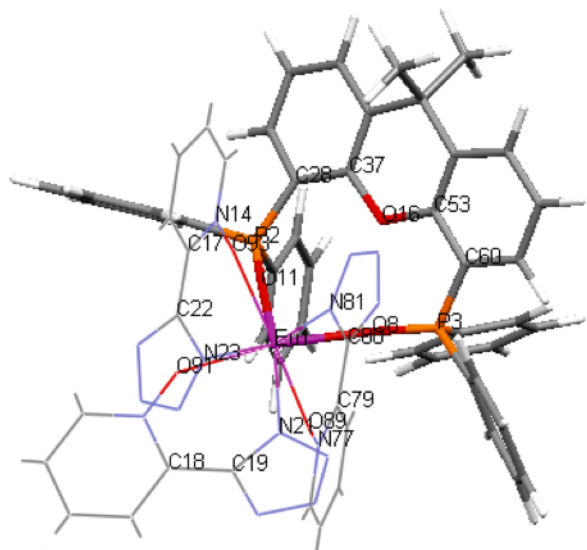


Fig. 4 (color online). Optimized molecular structure of complex **2**.

The observed torsion angle in-between the PTO and the phosphine oxide ligand suggests a distortion around the Eu(III) ion by the introduced phosphine oxide.

Photoluminescence properties of the Eu(III) complexes

The room-temperature absorption and normalized excitation spectra of complexes **2–4** are shown in Fig. 5. The excitation spectra were obtained by monitoring the emission wavelength of Eu(III) at 612 nm by using a xenon lamp. The excitation spectra of the complexes exhibit a broad band between 250 and 325 nm, which can be assigned to π - π^* electron transitions of the ligands. The shape of the excitation spectra of the complexes comply with that of the absorption spectra, confirming the environment of Eu(III) by the main ligand PTO and the corresponding phosphine oxides used.

This is diagnostic of the typical sensitization of the Eu(III) ion by ligands instead of direct excitation of the lanthanide ion. The molar absorption coefficient values for complexes **3** and **4** were found much higher than for complex **1** (Table 1). This confirms that the sensitization of the Eu(III) ion by the ligands is very significant and prevents the rapid deactivation of the excited

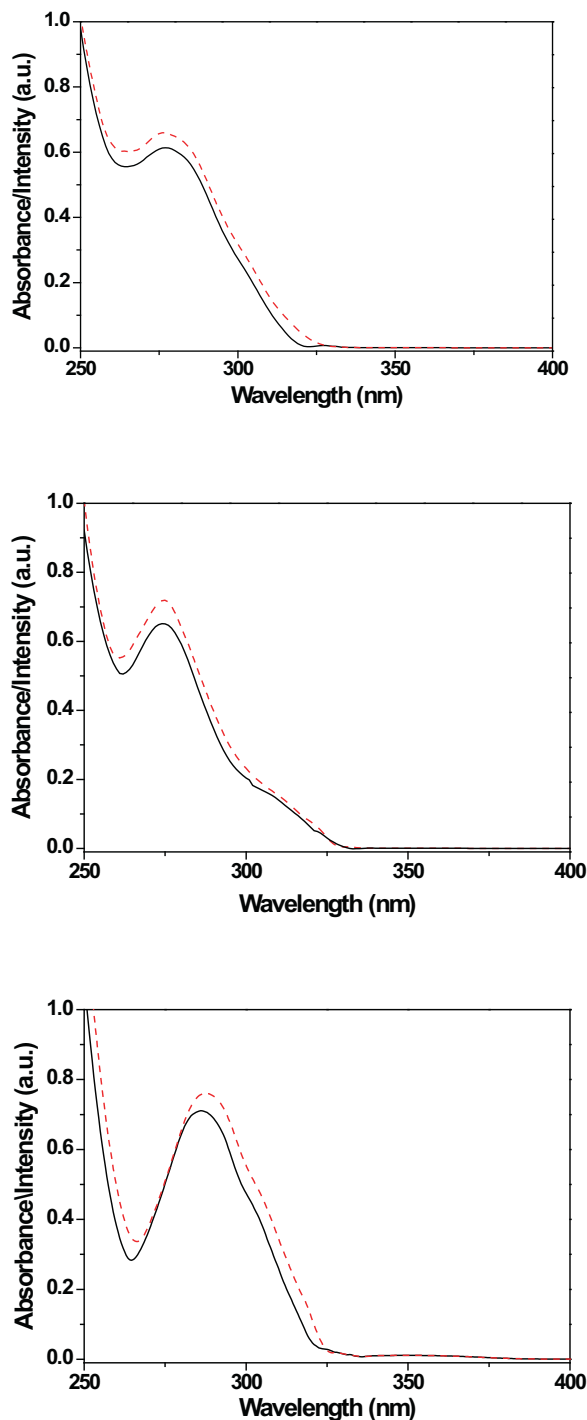


Fig. 5 (color online). UV/Vis absorption (solid line) and excitation spectra ($\lambda_{em} = 612$ nm) (dashed line) of complexes **2** (top), **3** (middle) and **4** (bottom) in acetonitrile solution at room temperature.

Table 1. Absorption wavelength maxima (λ in nm) and molar absorption coefficients (ϵ in $\text{cm}^{-1} \text{mol}^{-1}$) for complexes **1–4** in acetonitrile solution.

Complex	Wavelength (nm)	Molar absorption coefficient ($\text{cm}^{-1} \text{mol}^{-1}$)
1	272	27 400
	253	43 000
2	276	54 730
	244	126 430
3	274	40 960
	240	111 085
4	289	47 260
	241	90 700

state by the vibrations of the ligands and/or solvent molecules.

The room temperature-normalized emission spectra of the europium(III) complexes **1–4** under the excitation wavelengths 262, 260 and 271 nm are shown in Fig. 6. The emission spectra exhibit the characteristic sharp peaks in the 575–725 nm region associated with the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions of the Eu(III) ion. The five major peaks of the $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ transitions are resolved, and the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is very intense, pointing to a highly polarizable chemical environment around the Eu(III) ion, which is responsible for the brilliant-red emission of these complexes [43]. The absence of a broad emission band resulting from organic ligands in the blue region indicates the effective energy transfer from the ligands to the central Eu(III) ion. The absence of any absorption band due to the $f-f$ transitions of the Eu(III) ion proves that luminescence sensitization *via* ligands is

Table 2. Excitation wavelengths (λ_{exc}), $^5\text{D}_0$ lifetimes (τ_{obs}), photoluminescence quantum yields (Φ), K_{RAD} and K_{NR} for complexes **1–4** in acetonitrile solution at room temperature.

Complex	λ_{exc} (nm)	Φ (%)	τ_{obs} (ms)	K_{RAD} (ms^{-1})	K_{NR} (ms^{-1})
1	284	13	0.66	0.21	1.30
2	262	73	1.99	0.37	0.14
3	260	36	1.59	0.23	0.40
4	271	38	1.45	0.26	0.43

more effective than direct excitation of the metal ion. The presence of a single emission band of $^5\text{D}_0 \rightarrow ^7\text{F}_0$ for the europium(III) complexes proves the existence of a single chemical environment around the Eu(III) ion at a low symmetry site. The $^7\text{F}_1$ level shows three main overlapping components of almost equal intensity at 588–598 nm that can be assigned to the allowed magnetic dipole transitions, while the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition gives rise to a strong band at 699 and two smaller ones at 696 and 694 nm, attributed to the electric dipole transitions. Furthermore, the transitions from the excited $^5\text{D}_1$ state to the $^7\text{F}_J$ ($J = 0, 1, 2$) state (538 nm, 556 nm) were also evident (Fig. 6). The luminescence decay of the europium(III) complexes **1–4** was measured in acetonitrile solution at the $^7\text{F}_2$ site upon ligand excitation at room temperature and derived by fitting as a mono-exponential function. The calculated values of luminescence decay for complexes **1–4** are presented in Table 2. The longer lifetime observed for the ternary complexes **2–4**, in contrast to complex **1**, confirms the replacement of water from the inner coordination sphere of the Eu(III) ion. The shorter decay

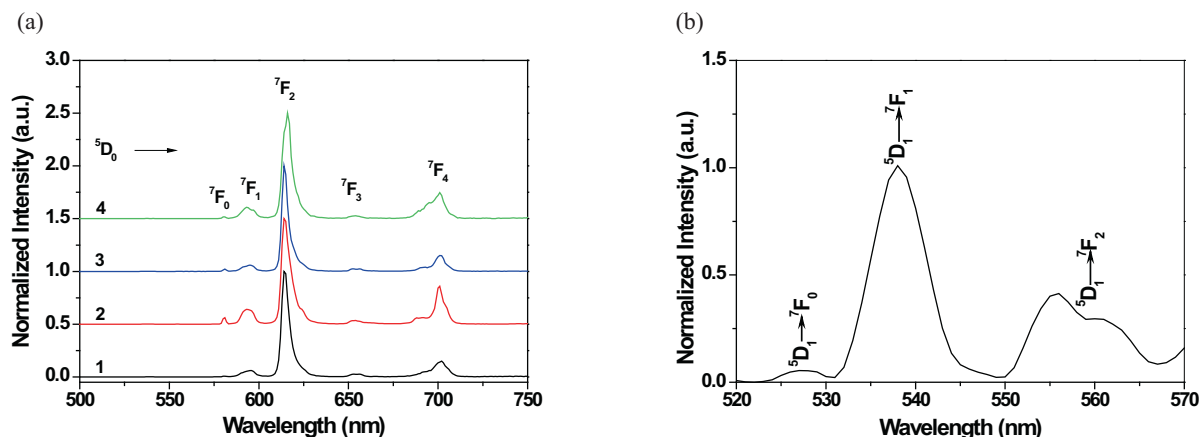


Fig. 6 (color online). Emission spectra of Eu(III) complexes **1–4** recorded in acetonitrile solution at room temperature for $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0-4$) transitions (a), and $^5\text{D}_1 \rightarrow ^7\text{F}_J$ ($J = 0-2$) transitions for complex **2** (b).

lifetime observed for complex **1** can be attributed to the vibronic oscillations shown by the coordinated water molecules which promote the non-radiative decay as it is well described for the tetrazole-containing hydrated complexes [34–36].

Table 2 gives data for the radiative (K_{RAD}) and non-radiative decay (K_{NR}), the photoluminescence quantum yields (Φ) for the $^5\text{D}_0$ europium(III) ion excited state and the luminescence decay lifetime (τ) for complexes **1–4**. Complex **1** exhibited a lower photoluminescence efficiency due to quenching by vibronic oscillations of coordinated water molecules in the 1st coordination sphere of the Eu(III) ion. Complexes **2**, **3** and **4** exhibit photoluminescence efficiencies by the six- to three-fold higher than that of complex **1**.

The low symmetry of the proposed square-antiprismatic structure of the complexes with the phosphine oxide co-ligands also enhances the radiative rates and quantum efficiencies by increasing the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission related to the odd parity factor [42]. In the present study, complex **2** exhibited a photoluminescence efficiency (73 %) which is the highest reported to date for tetrazolate Eu(III) complexes. From our previous experimental data the singlet and triplet state energy values of the PTO ligand were calculated from the phosphorescence spectra of the $\text{Gd}(\text{PTO})_3 \cdot (\text{H}_2\text{O})_x$ complex [37]. On this basis we propose an energy transfer diagram for the ternary Eu(III) tetrazolate complexes, in which the energy migration takes place from the PTO ligand and the corresponding phosphine oxides to the emissive level of the europium ion. Based on Reinholdt's empirical rule [44] the intersystem crossing process will be effective when ΔE ($S_1 - T_1$) is at least 5000 cm^{-1} for all kinds of ligands. The triplet states of the ligands thus play an important role in the energy transfer process which is also confirmed by experimental evidences, such as back-energy transfer reported for cases where there is a small energy gap between the lowest triplet state of the chromophore and the lanthanide emissive levels. Latva *et al.* supported this suggestion by his extensive study on terbium complexes giving an empirical rule stating that ligand-to-metal energy transfer takes place only when ΔE ($T_1 - ^5\text{D}_j$) is greater than 2000 cm^{-1} , which results in a higher photoluminescence quantum yield [45]. Phosphine oxide ligands fulfill the required two conditions for an effective energy transfer (Fig. 7, XANTPO ligand shown, but analogous energy flow for DPEPO). The energy diagram shows the effective and predomi-

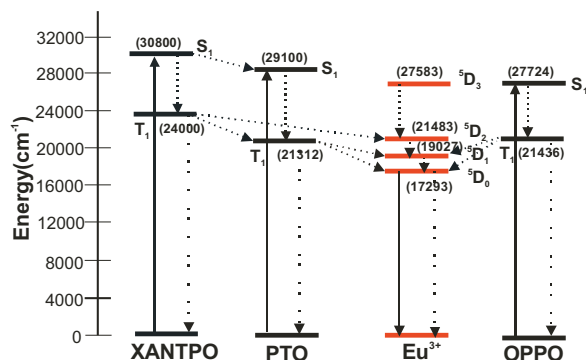


Fig. 7 (color online). Proposed energy transfer diagram in ternary complexes.

nant energy transfer from the triplet state of the ligands to the $^5\text{D}_1$ and $^5\text{D}_0$ emissive levels of the Eu(III) ion as proven by the emission spectra (Fig. 6).

Conclusions

Tetrazoles are a promising class of heterocyclic ligands that can sensitize effectively the luminescence of lanthanide ions upon UV excitation. The coordination of phosphine oxide expels water molecules from the first coordination sphere, leading to highly improved photoluminescence of the ternary complexes. The proposed intra-molecular energy migration diagram indicates an energy transfer from the triplet state of the ligand to the $^5\text{D}_1$ and $^5\text{D}_0$ levels of the Eu(III) ion. The photoluminescence quantum yields and decay lifetimes of the complexes vary according to the nature of the co-ligand. The highest values of photoluminescence quantum yield and decay lifetime have been observed for complex **2** (73 %, 1.99 ms). Thus our results suggest that the XANTPO-coordinated 5-(2-pyridyl-1-oxide)tetrazolate-europium(III) complex may find an application in organic photonics and electronics.

Experimental Section

Phosphines from Aldrich were used without further purification. Solvents were of analytical reagent grade. IR spectra were recorded using a Perkin-Elmer 2000 spectrometer. ^1H NMR spectra were recorded in CDCl_3 or $[\text{D}_6]\text{DMSO}$ with a Bruker DRX 250 MHz spectrometer using TMS as internal standard. Elemental analyses were performed with a Vario EL III Heraeus instrument. TG-DSC measurements were carried out by using a TG-DSC 111 instrument (Setaram France).

Synthesis of 5-(2-pyridyl-1-oxide)tetrazole (HPTO) and Eu(PTO)₃·(H₂O)_{3.5} (1)

The synthesis of HPTO and its europium complex were carried out as described previously by us [31].

Synthesis of the phosphine oxides

The phosphine oxides were synthesized by oxidation of the corresponding phosphines. Calculated amounts of H₂O₂ (30%) were added slowly to the vigorously stirred THF solution of the respective phosphine. Stirring was maintained at room temperature for 2 h. After evaporation of THF, the residue was treated with acetone-ethyl acetate to obtain the respective phosphine oxide product as a precipitate. The precipitates thus obtained were filtered off and dried in a vacuum. All melting points were above 360 °C with decomposition.

XANTPO: ¹H NMR (250 MHz, CDCl₃): δ = 7.59–7.62 (d, 2H, Phen-H), 7.24–7.48 (m, 20H, Phen-H), 6.94–7.20 (t, 2H, Phen-H), 6.74–6.84 (m, 2H, Phen-H), 1.70 (s, 6H, 2Me). – MS (EI): *m/z* = 610. Yield 77%.

OPPO: ¹H NMR (250 MHz, CDCl₃): δ = 7.19 (m, 8H, Phen-H), 7.35 (m, 12H, Phen-H), 7.57 (t, 2H, Phen-H), 7.75 (m, 2H, Phen-H). – MS (EI): *m/z* = 478. Yield 82%.

DPEPO: ¹H NMR (250 MHz, CDCl₃): δ = 7.75–7.64 (m, 9H, Phen-H), 7.42 (m, 13H, Phen-H), 7.05–7.04 (t, 2H, Phen-H), 7.07 (t, 2H, Phen-H), 7.08 (t, 2H, Phen-H). – MS (EI): *m/z* = 570. Yield 84%.

Synthesis of the ternary complexes

All complexes were prepared by stirring equimolar amounts of europium 5-(2-pyridyl-1-oxide)tetrazolate with the corresponding phosphine oxide in methanol for 24 h at 70 °C. The products were obtained after solvent evaporation and recrystallization from an ethanol-hexane mixture. All melting points were above 300 °C with decomposition.

Eu(PTO)₃·XANTPO·(H₂O)₃ (2)

IR (KBr): ν = 3310 (O–H), 1460 (N=N), 1400 (CH₃), 1270 (N–O), 1150 (P=O), 1025 (N–N), 746 (C–H), 550 (P–C), 450 (Eu–N), 400 (Eu–O) cm⁻¹. – ¹H NMR (250 MHz, [D₆]DMSO): δ = 6.59–7.95 (broad m, arom.), 1.56 (s, Me). – C₅₇H₅₀EuP₂N₁₅O₉: calcd. C 52.54, H 3.87, N 16.12; found C 52.20, H 3.93, N 16.23. Yield 67%.

Eu(PTO)₃·OPPO·(H₂O)₄ (3)

IR (KBr): ν = 3305 (O–H), 1452 (N=N), 1370 (N–C), 1270 (N–O), 1178 (P=O), 1030 (N–N), 750 (C–H), 560 (P–C), 450 (Eu–N), 400 (Eu–O) cm⁻¹. – ¹H NMR (250 MHz, [D₆]DMSO): δ = 6.92–7.71 (broad m, arom.). – C₄₈H₄₄N₁₅EuP₂O₉: calcd. C 48.49, H 3.73, N 17.67; found C 48.30, H 3.55, N 17.95. Yield 72%.

[Eu(PTO)₃·DPEPO·(H₂O)₂] (4)

IR (KBr): ν = 3290 (O–H), 2988 (C–H arom.), 1500 (N=N), 1260 (N–O), 1165 (P=O), 1026 (N–N), 746 (C–H), 570 (P–C), 450 (Eu–N), 400 (Eu–O) cm⁻¹. – ¹H NMR (250 MHz, [D₆]DMSO): δ = 6.67–7.75 (broad m, arom.). – C₅₄H₄₄N₁₅EuP₂O₈: calcd. C 52.10, H 3.56, N 16.88; found C 52.17, H 3.29, N 16.97. Yield 79%.

Photophysical properties

UV/Vis spectra were recorded with a Shimadzu UV-3100 spectrophotometer and corrected luminescence spectra (excitation, emission and decay lifetime) with a Fluorolog 3 spectrofluorimeter using acetonitrile of spectral grade as solvent at room temperature. *Calculations and measurements*: Photoluminescence quantum yields were determined to quantify the complexes by using quinine sulfate as a standard ($\Phi = 0.52$). A methodology described by Williams *et al.* [46] and Eaton [47] was taken into account to measure and to calculate the photoluminescence quantum yields of the complexes in solution. It involves the use of well characterized standard samples with known Φ_{ST} values.

Essentially, solutions of the standard and test samples with identical absorbance at the same excitation wavelength can be assumed to be absorbing the same number of photons. Hence, a simple ratio of the integrated fluorescence intensities of the two solutions (recorded under identical conditions) will yield the ratio of the quantum yield values. Φ_X can be calculated by using Eq. 1,

$$\Phi_X = \Phi_{ST} (I_X/I_{ST}) \left(\eta_X^2/\eta_{ST}^2 \right) (F_{ST}/F_X) \quad (1)$$

where Φ_X and Φ_{ST} represent photoluminescence quantum yield of lanthanide complexes (sample) and standard quinine sulfate, respectively. The terms I_X and I_{ST} represent the integrated emission intensity of the complex and of the standard under identical conditions, respectively. F_{ST} and F_X mean fractions of light absorbed by standard and sample. Radiative and non-radiative constants (K_{RAD} and K_{NR} , respectively) were calculated by Eqs. 2 and 3.

$$K_{RAD} = \Phi/\tau \quad (2)$$

$$1/\tau = K_{RAD} + K_{NR} \quad (3)$$

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