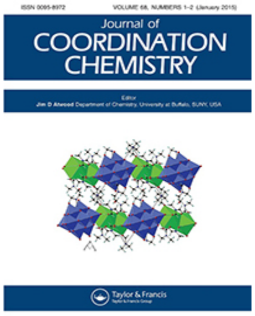

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Strongly photoluminescent Eu(III) tetrazolate ternary complexes with phosphine oxides as powerful sensitizers

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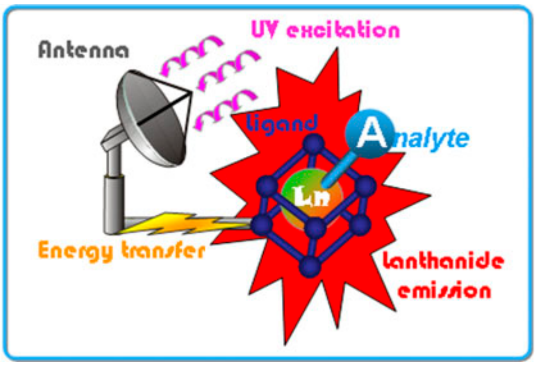

The Eu(III) cation forms electrically neutral photoluminescent complex with 5-(2-pyridyl-1-oxide) tetrazolate (PTO) anion. Although the photoluminescence properties of such tertiary Eu(III) and Tb (III) complexes were not as high (13 and 31% photoluminescence quantum yield, respectively) as reported for other diketonate lanthanide complexes probably because of high number of nitrogen atoms involved in PTO which leads to attachment of water molecules, reducing the luminescence quantum yield with vibrational and rotational quenching. Here, we report the removal of quencher molecules from the coordination sphere of tris-europium tetrazolate oxide complex by replacing them with various phosphine oxides which leads to improved photoluminescence quantum yield for the complexes by acting as auxiliary co-ligands with that of the main antenna 5-(2-pyridyl-1-oxide) tetrazolate. The coordination sphere in these complexes can be complemented by **a**romatic phosphine oxides to provide highly photoluminescent Eu(III) complexes. The highest quantum yield was 38% in **3** $[\mathrm{Eu(PTO)_3\cdot DPEPO}](\mathrm{H_2O})_5$ containing bis(2-(diphenylphosphino)phenyl) ether oxide (DPEPO) as compared to tris–europium complex with 5-(2-pyridyl-1-oxide)tetrazolate.

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Keywords: Europium; Tetrazoles; Phosphine oxides; Photoluminescence; Quantum yields

1. Introduction

Lanthanide complexes give sharp and intense emission lines upon ultraviolet irradiation because of the effective intramolecular energy transfer (ET) from the coordinated ligands to the luminescent central lanthanide ion, which, in turn, undergoes the corresponding radiative process (the so-called antenna effect) [1]. Therefore, they are increasingly used as highly efficient electroluminescent components for light-emitting diodes [2, 3], luminescent probes for analytes [4], labels for proteins and amino acids [5], and molecular recognition and chirality sensing of biological substrates [6]. The major drawback of lanthanide complexes is the luminescent quenching by matrix vibrations such as hydroxyl groups via non-radiative pathways, which decreases their luminescence intensity and limits the application for organic light-emitting devices [7]. Because of low thermal stability of some lanthanide complexes, they are suitable only in an appropriate temperature range for applications. A way to circumvent these difficulties is to use ligands bearing suitable chromophores capable of forming thermally stable complexes with lanthanide ions. These ligands could play the antenna role, absorbing light and transferring excitation energy to the emitting ion. So far, tetrazoles have not been particularly popular as sensitizing ligands for lanthanides emitting in a visible range. Tetrazoles are as acidic as carboxylic acids, but four nitrogens provide multitude of options for coordination bond formation with lanthanide cations. To avoid OH vibronic quenching from the coordination sphere of Eu(III), additional auxiliary ligands such as phosphine oxides or nitrogen containing molecules may complement the coordination sphere. The new complexes with increased coordination number have the effect of protecting metal ions from vibration coupling and increasing their light absorption cross section by the antenna effect [8]. Phosphine oxide ligands in the europium(III) tris(*tetrazolate*) complex can produce a square antiprismatic structure that promotes faster radiation rates and an increased quantum yield because of an increase in the $^5D_0$–$^7F_2$ emissions (electric dipole transitions), related to odd parity [9]. Furthermore, increased quantum efficiencies of the Eu(III) complexes can be expected due to extra sensitization for lanthanide cations via phosphine oxide triplet states. The novel class of heterocyclic molecules such as 5-(2-pyridyl-1-oxide)tetrazole (HPTO) with other auxiliary co-ligands has not been utilized much for the preparation of luminescent materials. Interest in tetrazole and its derivatives has been growing due to success achieved in preparation of a number of highly efficient drugs based on tetrazole [10–15]. They also play exceptional part in the synthetic chemistry for preparation of compounds belonging to various classes [16, 17]. Metal-organic coordination complexes with tetrazolate- or carboxylate-based [18] ligands have been the subject of intense research for decades, owing to their interesting structural topologies and wide physical properties such as molecular magnetism, molecular absorption and recognition, catalysis, non-linear optics and luminescence [19].

Recently, we published tris complexes of pyridineoxidetetrazolate of Eu(III) and Tb(III) complexes showing 13 and 31% photoluminescence quantum yield, respectively [20], without any additional co-ligands in the framework. Herein, we report the synthesis and photophysical properties of new europium(III) complexes of 5-(2-pyridyl-1-oxide)tetrazole (HPTO) with phosphine oxide co-ligands, tri-*n*-octylphosphine oxide (TOPO), triphenylphosphine oxide (TPPO), and bis(2-(diphenylphosphino)phenyl) ether oxide (DPEPO) which not only enhance the photoluminescence quantum yields of Eu(III) as compared to previously reported tris tetrazolate Eu(III) complex (13%) but also lifetimes as well. Additionally, when the Eu(III) cation is coordinatively unsaturated by the original ligands, an additional neutral ligand (respective phosphine oxide) coordinates to the lanthanide center to form a highly coordinated complex, thereby excluding coordination of solvent molecules and leads to improved volatility and thermal stability of the complexes.

2. Experimental

2.1. *Materials*

The following commercially available chemicals were used without purification: europium (III) nitrate hexahydrate, 99.9% (Aldrich); gadolinium(III) nitrate hexahydrate, 99.9% (Aldrich); and terbium(III) nitrate hexahydrate, 99.9% (Aldrich). All other chemicals used were of analytical reagent grade.

2.2. *Instrumentation*

Elemental analyses were performed with a Vario EL III Heraeus instrument. MS spectra were run on an Applied Biosystems 4000 Q TRAP instrument with photospray ionization mode and a Waters Micromass GCT Premier mass spectrometer with field desorption/field ionization–time of flight method. IR spectra were recorded using a Perkin-Elmer 2000 spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ with a Bruker DRX 200 MHz spectrometer using TMS as internal standard. For ^{31}P NMR, Bruker Avance 400 was used. UV–Vis spectra were recorded with a Shimadzu UV-3100 spectrophotometer, and corrected luminescence spectra with a Fluorolog 3 spectrofluorimeter, using quinine sulfate as a reference.

2.3. *Photoluminescence quantum yield determination*

Photoluminescence quantum yields were determined using quinine sulfate as a standard ($\Phi = 0.51$). A methodology described by Williams *et al.* [21] and Eaton [22] was taken into account to measure and to calculate the photoluminescence quantum yields of lanthanide 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. Since Φ_{ST} for the standard sample is known, it is trivial to calculate the Φ_X for the test sample. Φ_X can be calculated using equation (1) as shown below,

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

where Φ_X and Φ_{ST} represent photoluminescence quantum yield of lanthanide complexes (sample) and standard quinine sulfate, respectively, while η_X and η_{ST} represent the refractive index of solvents 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 standard under identical conditions, respectively. F_{ST} and F_X mean fractions of light absorbed by standard and sample. Furthermore radiative and non-radiative constants (A_{RAD} and A_{NR}, respectively) are calculated by equations (2) and (3) where τ represents the photoluminescence decay lifetime.

$$A_{ARD} = \Phi/\tau \quad (2)$$

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

3. Synthetic methodology

3.1. *Synthesis of ligands*

The ligands HPTO and 5-(2-pyridyloxide)tetrazole were synthesized according to figure 1 by two step as reported in our previous publication [20].

3.1.1. Synthesis of 5-(2-pyridyl)tetrazole. Yield = 85%, m.p. = 220 °C. ^{1}H NMR (250 MHz, $CDCl_3$, TMS) ppm: 7.59–8.76 m (4H arom), MS: *m/z* = 147.

3.1.2. Synthesis of 5-(2-pyridyl-1-oxide)tetrazole (HPTO). Yield = 85%, m.p. = 245 °C. ^{1}H NMR (250 MHz, $CDCl_3$, TMS) ppm: 7.59–8.76 m (4H arom), CHN anal. Calcd for $C_6H_5N_5O$: C, 44.17; H, 3.08; N, 42.92. Found: C, 44.07; H, 3.23; N, 42.96%. IR (KBr) ν_{max}: 3100, 1496, 1245, 1100, 750, 510 cm^{-1}.

3.2. *Synthesis of the Ln(III) complexes*

Complexes **4** and **5** were synthesized by the same procedure as described in our previous publication as shown in figure 2 [20]. These were used for further analyses and photophysical studies.

3.2.1. $Eu(PTO)_3(H_2O)_{3.5}$ (4). m.p. > 300 °C Elemental analysis (%): Calcd for $C_{18}H_{19}EuN_{15}O_{6.5}$ (701): C, 30.81; H, 2.71; N, 29.95. Found: C, 30.61; H, 2.47; N, 29.67. IR (KBr) ν_{max}: 3300,1600, 1490, 1248, 1030, 755, 510 cm^{-1}.

3.2.2. $Gd(PTO)_3(H_2O)_8$ (5). Elemental analysis (%): Calcd for $C_{18}H_{28}GdN_{15}O_{11}$ (787.76): C, 26.08; H, 3.65; N, 26.65. Found: C, 25.77; H, 3.82; N, 26.40. IR (KBr) ν_{max}: 3310, 1608, 1498, 1248, 998, 755 cm^{-1}.

3.3. *Synthesis of [Eu(PTO)$_3$·(TPPO)$_2$](H$_2$O)$_3$(CH$_3$OH)$_2$ (1)*

Complexes **1** and **2** with corresponding phosphine oxides were prepared by stirring 1 : 2 ratio of europium 1 : 3 complex [Eu(PTO)$_3$·(H$_2$O)$_{3.5}$] with corresponding phosphine oxide and **3** by equimolar solutions of europium 1 : 3 complex [Eu(PTO)$_3$·(H$_2$O)$_{3.5}$] with DPEPO in methanol for 24 h at 70 °C. The solid product was filtered, washed with ethanol, water, and then ethanol (figure 3), dried and stored in a desiccator over P_2O_5. ^{1}H NMR (250 MHz, DMSO-d$_6$) ppm: 7.21–7.69 m broad (all aromatic); El. Anal. Calcd for $C_{56}H_{56}EuN_{15}P_2O_{10}$ (1313.05): C, 51.22; H, 4.30. Found: C, 51.27; H, 4.53. IR (KBr) ν_{max}: 3300, 1700, 1490, 1260, 1148, 1090, 750, 450, 400 cm^{-1}.

3.4. *[Eu(PTO)$_3$·(TOPO)$_2$](H$_2$O)$_4$ (2)*

^{1}H NMR (250 MHz, DMSO-d$_6$) ppm: 7.21, broad m (4H arom), 1.23–1.53 (t, –CH$_2$, 36H), 1.04–1.14 (h, –CH$_2$ near to CH$_3$, 6H), 0.84 (t, CH$_3$, 9H), El. Anal. (%): Calcd for $C_{66}H_{122}EuP_2N_{15}O_9$ (1483.68): C, 53.42; H, 8.28. Found: C, 53.17; H, 8.29. IR (KBr) ν_{max}: 3300, 1690, 1488, 1255, 1205, 1094, 755, 450, 400 cm^{-1}.

3.5. *[Eu(PTO)$_3$·DPEPO](H$_2$O)$_5$ (3)*

El. Anal. (%): Calcd for $C_{54}H_{50}EuP_2N_{15}O_{11}$ (1298.98): C, 53.42; H, 8.28. Found: C, 53.17; H, 8.29. IR (KBr) ν_{max}: 3290, 1710, 1500, 1260 1165, 1105, 746, 450, 400 cm^{-1}.

4. Results and discussion

4.1. *Synthesis and IR spectroscopy*

The ligand and the complexes were synthesized according to figures 1–3. Microanalysis of each complex shows the combination ratio of metal, PTO, and corresponding phosphine oxide ligand in 1 : 3 : 2, 1 : 3 : 2, and 1 : 3 : 1, respectively, for **1**, **2,** and **3**. The presence of water or solvent molecules was confirmed by IR spectroscopy which shows a broad band between 3000 and 3500 cm^{-1}. The presence of water or solvent molecules in the lattice is reported for such tetrazolate complexes [23–25]. Shifts in the P=O stretching frequencies of phosphine oxide molecules in **1** (from 1143 to 1148 cm^{-1}), **2** (from 1182 to 1205 cm^{-1}), and **3** (from 1158 to 1165 cm^{-1}) show the involvement of phosphoryl oxygen in complex formation with Eu(III) ion, which is absent in [Eu(PTO)$_3$·(H$_2$O)$_{3.5}$]. The disappearance of N–H peak at 1640 cm^{-1} for all synthesized complexes confirms the coordination of N with

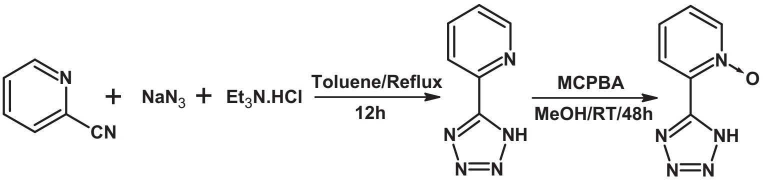
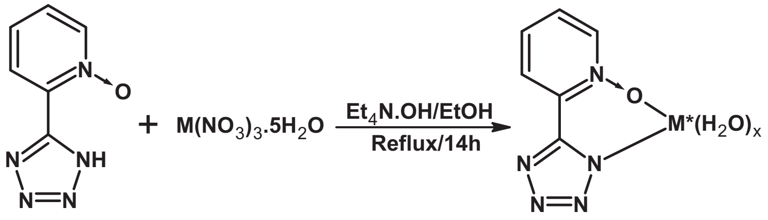
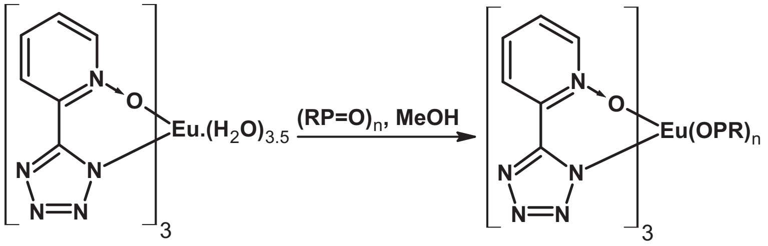


Figure 1. Synthesis of 5-(2-pyridyloxide)tetrazole.



M = Eu(III), Gd(III)

Figure 2. Synthesis of Eu(III) and Gd(III) complexes with HPTO.



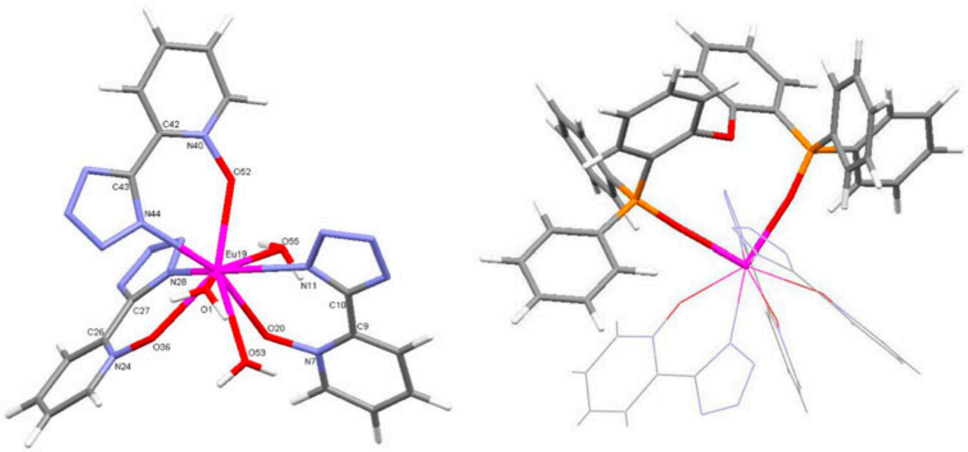
(RP=O) = TPPO, TOPO, DPEPO

Figure 3. Synthesis of ternary europium complexes with TPPO, TOPO, and DPEPO.

Eu(III). The shifted band at 1260 cm^{-1} of N–O from 1360 cm^{-1} (in free HPTO) also indicates the environment of N–O in the complex formation with Eu(III) (supporting information figure S1, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.987765). Far-IR spectrum reveals the coordination of Eu(III) ion with N of tetrazole and O of pyridine oxide with sharp bands at 450 and 400 cm^{-1}, respectively (supporting information figure S2).

4.2. *NMR spectroscopy*

Due to less solubility of the synthesized ternary europium complexes (**1–3**) in organic solvents, ^{1}H and ^{31}P NMR spectrum of all ternary complexes are made in DMSO-d_6. The ^{1}H NMR spectra of all complexes bears the respective peaks for HPTO and corresponding phosphine oxide. Complex **1** clearly shows the multiplet mixed peaks for all aromatic hydrogens of HPTO and TPPO. In **2,** the respective band of all alkyl protons of TOPO phosphine oxides is little shifted as compared to free TOPO phosphine oxide (0.86–1.58 to 0.84–1.53 ppm) due to complexation with Eu(III). A broad peak at 7.21 ppm, which is similar to that of tris–(PTO) europium complex **1**, displays the pyridine oxide protons. As DMSO-d_6 also has coordination ability with the lanthanide cations, there will be competition between the large quantity of DMSO-d_6 solvent and small quantity of respective phosphine oxides (compared to solvent) in the synthesized ternary complexes. In the ^{31}P NMR spectrum, we observed one sharp peak at 27 ppm for **1** and poorly resolved peak at 35 ppm for **2**, due to its poor solubility in DMSO-d_6. For the respective triphenylphosphine oxide (TPPO) used to synthesize ternary tetrazolate Eu(III) complex, the chemical shift for the ^{31}P NMR signal in DMSO-d_6 solvent is 39 ppm [26]. Therefore, it indicates that at least **1** is stable in DMSO-d_6 solvent (supporting information figures S3–S6).



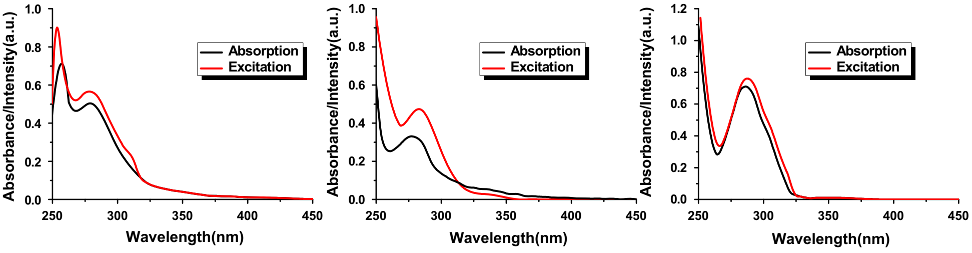
4

3

Figure 4. Optimized molecular structure of **4** and **3** by MOPAC/AM1 modeling**.**

4.3. *Molecular structure modeling of 1–3 by the MOPAC/AM1 model*

We optimized the molecular structures of all synthesized europium(III) complexes using the MOPAC/AM1 model with parameters for europium [27] (figure 4). In **4,** the central Eu(III) is coordinated with three nitrogens of tetrazole, three oxygens of pyridine oxide, and three water molecules giving nine-coordinate lanthanide complex with approximately tricapped trigonal-prismatic geometry. In **1**–**3** Eu(III) is eight-coordinate and the structure can be assigned as antisymmetrical square antiprism. Lanthanide complexes with seven, eight, or nine coordination are well documented [28, 29]. The coordinated water molecules in **4** are replaced by phosphine oxide TPPO, TOPO, and DPEPO in **1**, **2,** and **3**, respectively. The closer proximity of the phosphine oxide bond with Eu(III) (2.304, 2.312 Å and 2.301, 2.311 Å, respectively) observed in **1–3** as compared to the coordinated water for **4** (2.496 Å) suggests the strong interaction of phosphine oxides with Eu(III) [30]. The torsional angle strain produced between HPTO and phosphine oxide (DPEPO) gives indication of distortion of planarity around Eu(III) by the introduced phosphine oxide which leads to non-planar geometry of the complexes. The distortion is greater in **3** with DPEPO generating more asymmetry around Eu(III).



Complex **1**

Complex **2**

Complex **3**

Figure 5. UV absorption and normalized excitation spectra of **1–3** in acetonitrile at room temperature.

4.4. *UV absorbance and photoluminescence studies*

The room temperature absorption and normalized excitation spectra of **1–3** are shown in figure 5. The excitation spectra were obtained by monitoring the emission wavelength of Eu(III) at 612 nm ($^5D_0$–$^7F_2$ transition). The excitation spectra of the complexes exhibit a broad excitation band between 250 and 325 nm, which can be assigned to π–π* transitions of the ligands.

From the photophysical point of view, there are two distinct problems to overcome to achieve intense and long-lived luminescence. The problems are: (i) to overcome the low value of ε of lanthanides by introducing suitable antenna chromophores and (ii) to prevent the rapid deactivation of the excited state by vibrations of the ligands and/or solvent molecules. The introduction of HPTO and neutral auxiliary co-ligands (TPPO, TOPO, and DPEPO) increased the molar absorption coefficient (table 1) and replaced the quenchers (water or solvent molecules) from the inner coordination sphere of Eu(III) in **4**, thus enhancing the photoluminescence.

The room temperature-normalized emission spectra of **1, 2** and **3** (in acetonitrile solution) under the excitation wavelength (284, 270, and 271 nm, respectively, for **1–3**) that maximizes the Eu(III) emission intensity are shown in figure 6. The emission spectra of the complexes display characteristic sharp peaks from 575 to 725-nm associated with the $^5D_0$–^7F_J transitions of Eu(III). The five expected peaks of the $^5D_0$–$^7F_{0–4}$ transitions are well resolved, and the hypersensitive $^5D_0$–$^7F_2$ transition is very intense, pointing to a highly polarizable chemical environment around Eu(III), responsible for the brilliant red emission of these complexes.

To describe ET process, the phosphorescence spectrum of $Gd(PTO)_3(H_2O)_x$ was measured at 77 K to calculate the triplet state of PTO ligand. As $^6P_{7/2}$ of Gd(III) is too high in energy to accept energy from ligand, the data obtained from phosphorescence spectrum revealed the emissive triplet state of PTO (supporting information figure S7). Singlet state estimation of PTO was done by referencing its absorption edge which is 29,100 cm^{-1}. The triplet energy ($^3\pi\pi$*) level of HPTO was calculated as 21,312 cm^{-1} (supporting information figure S8). The observed single sharp emission band of $^5D_0$–$^7F_0$ for ternary europium(III) complex **1** (half band width 1 nm for **1**) proves the existence of a single chemical environment around Eu(III). Because the intensity of $^5D_0$–$^7F_0$ transition is generally low, it is difficult to conclude from insets for these transitions in case of **2** and **3**, whether Eu(III) is in a single chemical environment, or there is electronic noise, when magnifying this transition.

The lifetime values (δ_{obs}) of the $^5D_0$ level determined from the luminescence decay profiles for **1–3** at room temperature by fitting with a monoexponential curve are depicted in table 2. As from our previous measurements, 1 : 3 complex of europium(III) with PTO has PL lifetime of 0.350 ± 0.0105 ms, but with co-ligands TPPO, TOPO, and DPEPO it is

Table 1. Absorption wavelength maxima (λ) in nm and molar absorption coefficient (ε) in cm^{-1} M^{-1} for **1, 2,** and **3**.

Complex	Wavelength (nm)	Molar absorption coefficient (cm^{-1} M^{-1})
1	272	27,400
	253	43,000
2	278	38,130
	241	99,900
3	289	47,260
	241	90,700

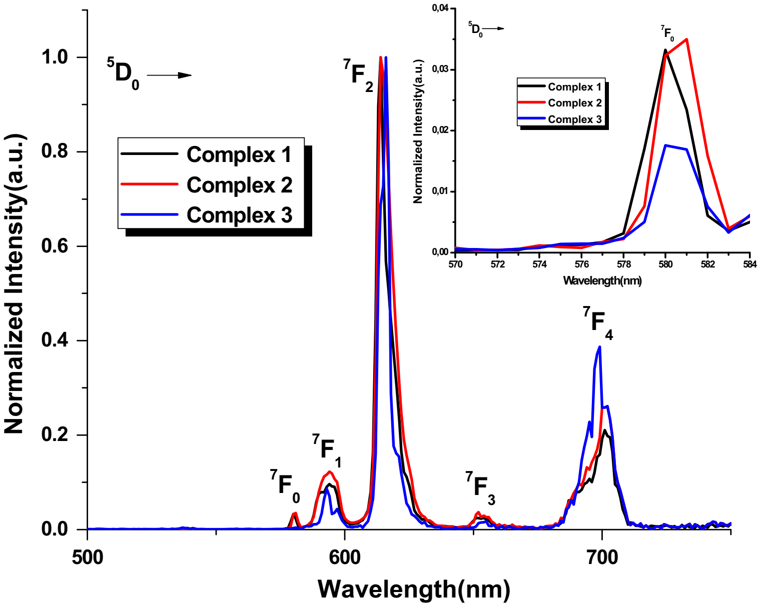


Figure 6. Normalized emission spectra of **1–3** in acetonitrile at room temperature.

Table 2. Experimental photoluminescence parameters. Excitation wavelength (λ_{exc} nm). $^5D_0$ Lifetime (τ_{obs}) (error: 3%), intrinsic quantum yields (Φ in %), A_{RAD} and A_{NR} represent the radiative and non-radiative decay constants, respectively, non-radiative for **1–3** in acetonitrile solution at 303 K.

Complex	λ_{exc} (nm)	Φ (%)	τ_{obs} (ms)	A_{RAD} (ms^{-1})	A_{NR} (ms^{-1})
1	284	15	0.660 ± 0.0198	0.212	1.303
2	270	19	0.590 ± 0.0177	0.254	1.441
3	271	38	0.60 ± 0.0180	0.533	1.133

increased to 0.660 ± 0.0198 ms. A recent study on measurement of photoluminescence decay time reveals that it also depends on excitation wavelength of the complex [31]. We observed maximum photoluminescence decay time at the particular excitation wavelength mentioned in table 2. The shorter decay lifetime observed for tris–pyridinetetrazolate Eu (III) complex **4** can be attributed to the vibronic oscillations shown by coordinated water which promotes the faster non-radiative decay.

The complexes were stable at room temperature as none of them show photobleaching when they are continuously excited (1 h) and emission was measured at different intervals of time (supporting information figure S9 for **3**, $^5D_0$–$^7F_2$ transition). In order to validate **1–3**, the photoluminescence quantum yield (Φ) has been determined upon ligand excitation (table 2). The low photoluminescence quantum yield obtained for Eu(PTO)$_3$ (13% in solution) is enhanced three times for **3** (38% in solution), which is the maximum reported for such tetrazolate lanthanide complexes. Although there are other lanthanide complexes reported in the literature with greater PLQY such as diketonates, dicarboxylates, and other ternary complexes, in the field of tetrazolates, this work is novel which can replace carboxylates as ligands. Further study to enhance the PLQY is still under investigation with other co-ligands (phosphine oxides and N-containing molecules).

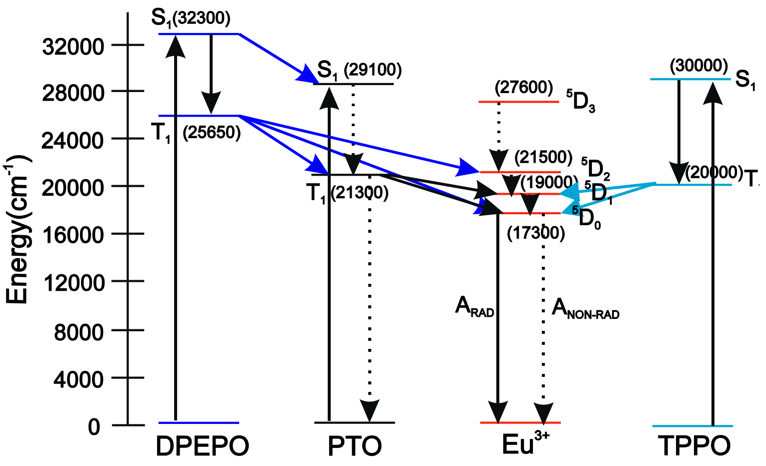


Figure 7. Proposed ET mechanism for ternary europium complexes.

The ET mechanism diagrams of corresponding complexes are shown in figure 7. The S_1 and T_1 energy levels of the ligands are indicated as well as the respective emissive levels of Eu(III), $^5D_2$, $^5D_1$, and $^5D_0$. On the basis of energy levels of triplet and singlet states of ligands (calculated from Gd complex) and higher energy levels of metal, we propose the ET diagram for ternary Eu(III) tetrazolate complexes, in which the energy is transferred not only via PTO triplet state to the emissive level of Eu(III), but also via triplet state of TPPO, TOPO to mainly $^5D_1$ and partially $^5D_0$ states of Eu(III). In the case of DPEPO, the ET is much more effective, having energy gap between ^1S (DPEPO)-^1S (PTO) > 3000 cm^{-1} and ^1T (DPEPO)-^1T (PTO) > 4000 cm^{-1} which can transfer energy not only via triplet state but also through singlet level from ^1S (DPEPO) to ^1S (PTO) and further to the $^5D_{J\ (J\,=\,0,\ 1)}$ of Eu(III) ions via ^1T state of PTO. Due to more efficient ET, complexes of Eu(PTO)$_3$ with phosphine oxides such as TPPO, TOPO, and DPEPO show high photoluminescence quantum yield ranging from 15 to 38% in acetonitrile solution.

5. Conclusion

Tetrazolate ligands effectively sensitize the visible emission of selected lanthanide ions. These complexes are not susceptible to photobleaching and air oxidation, as for 1,3-diketonates. The use of phosphine oxides proved to have a beneficial effect on enhancement of the photoluminescent properties. Phosphine oxides form strong complexes with lanthanide cations. It seems that there is still unexplored field to tailor phosphine oxide auxiliary ligands with the triplet states optimized to have a profound impact on the photoluminescence quantum yields of ternary Eu(III) complexes. Work in this direction is in progress.

Funding

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Supplementary data

The supplementary data are related to mid-IR and far-IR spectra of **1–3**, luminescence measurement of PTO, and ^{1}H and ^{31}P NMR spectra of these complexes. Supplemental data for this article can be accessed http://dx.doi.org/10.1080/00958972.2014.987765.

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