Luminescence enhancement of the Tb(III) ion with the thenoyltrifluoroacetonate ligand acting as an efficient sensitizer

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The synthesis, structural investigation, and photophysical properties of the complex [Tb(TTA)2(NO3)(TPPO)2] are reported. Unlike the analog tris-diketonate complex [Tb(TTA)3(TPPO)2], the new complex presents abnormally high luminescence intensity centered on the terbium ion. Our results clearly suggest a higher energy transfer efficiency from the TTA antenna ligand to the Tb(III) ion in the bis-diketonate complex compared with that in the tris-diketonate complex. A mechanism involving the increasing of triplet state energy when one TTA ligand is replaced by the NO3 group in the first coordination sphere is suggested and experimentally investigated to explain the anomalous luminescence properties of the new complex [Tb(TTA)2(NO3)(TPPO)2].

A B S T R A C T

The antenna effect in lanthanide coordination compounds depends on the electromagnetic energy absorption from the ligand that transfer energy to the excited 2S + 1LJ states of the Ln(III) ion, which decay radiatively with photon emission. Based on the energy of the triplet state (T) of the organic ligands, there could be four different situations: i) The ligand T state is located below the emitter 2S + 1LJ levels of the Ln(III) ion. In this case, the metal ion cannot easily accept energy from the first excited triplet states (T1) of the organic ligands (diketonates) via the intramolecular ligand-to-metal energy transfer. For example, the Gd(III) ion has its first excited level, 5P7/2, located at one higher than the T state of the organic ligands; ii) The ligand T states have energies very close to the excited 2S + 1LJ states. For this situation, there is a competitive balance between the non-radiative donation and the retrodonation (T ← 2S + 1LJ), which makes the Ln(III) ions exhibit low luminescence intensities; iii) The donor ligand T state is considerably more energetic than the main acceptor excited 2S + 1LJ state of the Ln(III) ion, minimizing the retrodonation (T ← 2S + 1LJ) processes; and iv) The ligand T states have energies largely above the main acceptor excited states of the central metal ion. Some works have determined that the energy gap between the lowest singlet and triplet excited states of the ligand around 5000 cm⁻¹ and the triplet...
state at least 3500 cm\(^{-1}\) more energetic than the acceptor \(^{2S+1}L_\text{J}\) level, is one of the better energetic conditions to obtain the coordination compounds with higher luminescence intensities centered on the Ln(III) ions [9–15].

Several kinds of antenna ligands have been successfully synthesized during the last decade to obtain new, highly luminescent complexes for photonic applications as either optical probes in clinical analyses or emitter layers in organic light-emitting devices (OLEDs). The \(\beta\)-diketone ligands are among the most largely investigated [13–15]. Previous works have shown that \(\beta\)-diketone complexes containing aromatic or a combination of aromatic and aliphatic substituent groups are very efficient antennae for the Eu(III) ion. These include thenoyltrifluoroacetone (TTA), dibenzoylmethanate (DBM), benzylocetate (BA), and naphthylacetates (1NTFA and 2NTFA) [16,17]. For the Tb(III) ion, often the aliphatic diketones are better antennae than the aromatic ones. But, some aromatic diketones with methoxy and fluor substituents can present ideal energy to tune the T states for efficient intramolecular energy transfer from the ligand to the Tb(III) ion [15].

The points discussed above are based on the similarity between the T state energy values in both the \(\text{tris}\) and \(\text{tetrakis}\) diketone complexes. In fact, X-rays of the structures of these lanthanide, coordination compounds have shown that the \(\beta\)-diketone ligands coordinate in an analogous mode. The differences between the Ln(III)–O(\(\beta\)-diketone) distances for these two complexes are around 0.02 Å [18,19]. Consequently, significant changes in the electronic charge distributions between the \(\text{tris}\) and \(\text{tetrakis}\) chelate rings are not expected to take place. However, for some Eu(III) compounds with DBM and TTA ligands, energetic changes considerably [20–22].

The main role of the TPPO ligand is to substitute the water molecules in Ln(III) complexes, minimizing the non-radiative processes. It is important to mention that phosphine and phosphine oxides ligands have large cone angles that influence both the number of the ligands around the metal ion and the effectiveness of the overlap between the metal ion and the ligand wave functions. In our previous paper, we determined the energetic positions of the singlet (S) and triplet (T) states arising from the TTA ligand in \(\text{bis}-\text{TTA}\) and \(\text{tris}-\text{TTA}\) complexes of the Gd(III) and Eu(III) ions [20]. The energy values of the TTA triplet states were estimated from the shortest wavelength based on the emission bands corresponding to the \(T\rightarrow S_0\) transitions (0–0 phonon). The energy values of the excited S states were taken as the longest wavelength from the absorption spectra corresponding to the \(S_0\rightarrow S\) transition (0–0 phonon). The data showed that the excited levels of the TTA ligand are higher in \(\text{bis}-\text{TTA}\) complexes than in \(\text{tris}-\text{TTA}\) ones.

In this paper, we describe the synthesis [23,24], characterization [25], structure [26] and optical properties, of a new, unusual, highly luminescent complex of terbium(III) with the thenoyltrifluoroacetone (TTA) and TPO (triphenylphosphine oxide) in a 1:2:2 ratio in methanol [23], while the \(\text{tris}\)-complex \([\text{Tb(TTA)}_3(\text{TPPO})_2]\) was prepared by direct reaction of TbCl\(_3\)·6H\(_2\)O, HTTA (thenoyltrifluoroacetone) and TPPO (triphenylphosphine oxide) in a 1:2:2 ratio in ethanol [24]. The experimental results are in good agreement with the calculated data, confirming that the complexes present the following stoichiometries \([\text{Tb(TTA)}_2(\text{NO}_3)(\text{TPPO})_2]\) and \([\text{Tb(TTA)}_3(\text{TPPO})_2]\).

The IR spectra of the \(\text{Tb(III)}\) complexes show two strong absorption bands at 1688 and 1557 cm\(^{-1}\) attributed to \(\nu_{\text{cis}}(\text{C=O})\) and \(\nu_{\text{as}}(\text{C=O})\) vibrational stretching modes, suggesting that the TTA ligand acts as a chelate ligand. Moreover, the coordination of the TPPO ligand via an oxygen atom to the Tb(III) ion is indicated by the shift of the stretching frequency \(\nu(\text{P=O})\) from 1200 cm\(^{-1}\) in the non-coordinate TPPO to around 1180 cm\(^{-1}\) in the Tb(III) complexes. The IR spectrum of the \([\text{Tb(TTA)}_2(\text{NO}_3)(\text{TPPO})_2]\) complex also displays two absorption bands around 1175 and 1136 cm\(^{-1}\) assigned to the \(\text{NO}_3\) group acting as chelate with the \(C_3\) symmetry.

Single crystals of the \([\text{Tb(TTA)}_2(\text{NO}_3)(\text{TPPO})_2]\) complex grown in hexagonal form were obtained after evaporation of solvents from the mother solution at room temperature (298 K) over 48 h. It is important to report that no sign of deterioration during storage under ordinary laboratory atmospheric conditions was observed. X-ray diffraction data indicate that this coordination compound crystallizes in the triclinic system with the \(P_1\) space group symmetry [26–30]. As can be seen in

![Fig. 1. (a) ORTEP drawing (50% of probability) displaying the X-ray structure of \([\text{Tb(TTA)}_2(\text{NO}_3)(\text{TPPO})_2]\) complex; (b) coordination polyhedron of \(\text{Tb}^{3+}\) ion: Bond lengths: \(\text{Tb}-\text{O1} 2.235(4), \text{Tb}-\text{O2} 2.278(4), \text{Tb}-\text{O3} 2.342(4), \text{Tb}-\text{O4} 147.16(13), \text{Tb}-\text{O5} 80.57(15), \text{Tb}-\text{O6} 71.98(14), \text{Tb}-\text{O7} 2.453(4), \text{Tb}-\text{O8} 2.454(4). \text{Bond angles:}\ (\text{O1}-\text{Tb}-\text{O2} 155.89(12), \text{O1}-\text{Tb}-\text{O3} 79.90(15), \text{O2}-\text{Tb}-\text{O5} 80.57(15), \text{O1}-\text{Tb}-\text{O6} 95.01(15), \text{O2}-\text{Tb}-\text{O7} 92.25(14), \text{O3}-\text{Tb}-\text{O4} 71.98(14), \text{O1}-\text{Tb}-\text{O4} 93.44(14), \text{O2}-\text{Tb}-\text{O4} 95.34(14), \text{O5}-\text{Tb}-\text{O4} 147.16(13), \text{O6}-\text{Tb}-\text{O4} 140.86(13), \text{O1}-\text{Tb}-\text{O3} 82.00(15), \text{O2}-\text{Tb}-\text{O3} 79.57(14), \text{O3}-\text{Tb}-\text{O4} 75.60(13), \text{O6}-\text{Tb}-\text{O4} 147.45(12).

\(\text{(a)}\) Part of the crystal structure of the \([\text{Tb(TTA)}_2(\text{NO}_3)(\text{TPPO})_2]\) complex, showing the crystal chain in the [010] direction. (d) Part of the crystal structure of \([\text{Tb(TTA)}_2(\text{NO}_3)(\text{TPPO})_2]\), showing the crystal growth in the [001] direction.\)
The Tb(III) ion is coordinated by eight oxygen atoms belonging to two monodentate TPPO ligands, two bidentate TTA\(^{-}\) anions and one bidentate nitrate group. There are no significant structural differences between the [Ln(TTA)\(_2\)(NO\(_3\))(TPPO)\(_2\)] complexes containing Sm(III), Eu(III) and Tb(III) ions owing to the closeness of their ionic radii of 1.079, 1.066 and 1.040, respectively [18,20]. The shortest Tb–O distance (Fig. 1b) occurs with the oxygen atom of the TPPO ligand and the longest with the oxygen atom of the TTA ligand. One interesting feature is that the values of the two distances Tb–O for the same TTA molecule are very close. These X-ray data are different from those for the tris-complex [Ln(TTA)\(_3\)(TPPO)\(_2\)] in which the Ln–O distances close to the thiyophen substituent group are much longer than those close to the CF\(_3\). This behavior apparently mimics the greater steric effect between TTA and TPPO ligands compared with the \(\text{bis}\)-complex [Tb(TTA)\(_2\)(NO\(_3\))(TPPO)\(_2\)]. Fig. 1b displays the coordination polyhedron TbO\(_8\) for the [Tb(TTA)\(_2\)(NO\(_3\))(TPPO)\(_2\)] compound containing a distorted dodecahedron geometry with the D\(_{2d}\) point group.

This crystal structure contains no classical hydrogen bonds. However, this system has other interactions, such as the S–H...F, C–H...F and CH...O interactions, which define its crystal growth. In a first substructure, a molecular interaction between the S and F atoms is observed. Indeed, the S1A atom in the molecule at (x, y, z) acts as a hydrogen bond donor to the F5 atom in the molecule at (x−1, +y−1, +z−1) with an S...F distance of 3.159 Å generating a chain growing in the [101] crystallographic direction (Fig. 1c). In a second substructure, the C29 atom in the molecule acts as a hydrogen bond donor to the O7 atom in the symmetrically-related molecule (x−1, +y−1, +z, symmetry operation) with a C...O distance of 3.216 Å; simultaneously, the C30 atom makes a hydrogen bond with the F6 atom with a C...F distance of 3.263 Å. These interactions are generated along the [001] direction (Fig. 1d).

Excitation spectra of the [Tb(TTA)\(_2\)(NO\(_3\))(TPPO)\(_2\)] and the [Tb(TTA)\(_3\)(TPPO)\(_2\)] complexes recorded at 77 K in the range 250–590 nm, under emission on the \(^{5}\!\!\!\!\!D_4\rightarrow^{7}\!\!\!\!\!F_2\) transition at 545 nm, are given in Fig. 2a. The spectrum of the [Tb(TTA)\(_2\)(NO\(_3\))(TPPO)\(_2\)] compound contains two, overlapped, intense, broaden bands corresponding to the \(S_0\rightarrow S_1\) transition of the TTA ligands. Excitation of the spectrum also displays weak narrow absorption bands in the spectral range from 450 to 500 nm that are assigned to the 4f\(^n\)-intraconfigurational transitions: \(^{7}\!\!\!\!\!F_6\rightarrow^{5}\!\!\!\!\!L_6\) (339 nm), \(^{7}\!\!\!\!\!F_6\rightarrow^{5}\!\!\!\!\!L_9\) (350 nm), \(^{7}\!\!\!\!\!F_6\rightarrow^{5}\!\!\!\!\!L_{10}\) (369 nm), \(^{7}\!\!\!\!\!F_6\rightarrow^{5}\!\!\!\!\!G_6\) (376 nm), \(^{7}\!\!\!\!\!F_6\rightarrow^{3}\!\!\!\!\!D_2\) (380 nm) and \(^{7}\!\!\!\!\!F_6\rightarrow^{5}\!\!\!\!\!D_4\) (488 nm). These optical data show that the TTA ligand must also be considered an efficient antenna for sensitizing the luminescence intensity of the Tb(III) ion in the \(\text{bis}\)-complex.

![Fig. 1 (continued).](image)

![Fig. 2.](image) Excitation spectra of the (a) [Tb(TTA)\(_2\)(NO\(_3\))(TPPO)\(_2\)] and (b) [Tb(TTA)\(_3\)(TPPO)\(_2\)] complexes in solid state recorded at liquid nitrogen temperature with emission monitored at 550.8 nm.
The excitation spectrum of the [Tb(TTA)3(TPPO)2] complex (Fig. 2b) at liquid nitrogen temperature also displays the absorption bands corresponding to the $S_0 \rightarrow S_1$ transition. This band is observed because the thermal quenching of the emitting state decreases when the temperature is lowered.

The emission spectrum of the [Tb(TTA)2(NO3)(TPPO)2] complex in the solid state, recorded in the range of 420 to 720 nm at liquid nitrogen temperature under excitation at the TTA transitions (350 nm), is shown in Fig. 3a. This emission spectrum exhibits characteristic narrow emission bands that are assigned to the $4f^8 \rightarrow 4f^8$ transitions of the Tb(III) ion, emanating from the emitting $^5D_4$ level to the $^7F_J$ ($J=0, 1, 2, 3, 4, 5$ or $6$) levels, where the most intense corresponds to the $^5D_4 \rightarrow ^7F_5$ transition taking place around 545 nm. An important feature to be observed is the nonexistence of broad bands arising from the TTA-centered transitions, indicating that intramolecular energy transfer from the TTA ligands to the Tb(III) ion is operative.

The more significant photoluminescent property difference observed between the complexes studied in this work is that the [Tb(TTA)2(NO3)(TPPO)2] compound in the solid state exhibits strong green luminescence under UV radiation at room temperature, whereas the [Tb(TTA)3(TPPO)2] complex shows a very weak intensity (Fig. 3b). The latter only shows significant luminescence intensity at a low temperature (77 K), probably because of the decreasing thermal deactivation processes. Another distinction between the bis and tris-TTA complexes is that the emission spectrum of the [Tb(TTA)3(TPPO)2] complex at low temperature displays a broad band assigned to the phosphorescence of the TTA ligand.

To obtain quantitative information about the luminescence of the [Tb(TTA)2(NO3)(TPPO)2] complex, the experimental, luminescence quantum yield ($q_x$) was determined with the method developed by Brill and Veenis at Philips Research Laboratories [31, 32]. The standard phosphor used was sodium salicylate, whose emission spectrum contains a large broad band around 425 nm, with a $q$ value of 60%. Based on this method, the emission quantum yield of [Tb(TTA)2(NO3)(TPPO)2] is 38.5% ($\pm 10\%$). Actually, the emission quantum yield for the [Tb(TTA)3(TPPO)2] complex was not determined owing to its very weak luminescence intensity at room temperature. These data clearly demonstrate that there is a considerable increase of the luminescence intensity for the Tb(III) bis-TTA complex compared with the tris-TTA one. According to our previous work [20], this behavior may be explained by the energy gap between the ligand centered triplet state and the metal center, which is higher in the bis-TTA complex ($\Delta E \approx 1200$ cm$^{-1}$) than in the similar tris-TTA complexes ($\Delta E \approx 160$ cm$^{-1}$). Consequently, the retrodonation $T \leftarrow 2S + 1L_J$ processes play a minor role in the non-radiative, relaxation pathways of the emitting level of the [Tb(TTA)2(NO3)(TPPO)2] compound, producing a strong green luminescence emission. Fig. 4 shows the energy level diagram including the triplet state energy of the TTA ligand in the bis and tris complexes and the main energy transfer pathway from the TTA ligand to the Tb(III) ion [33]. The photographs in Fig. 4 show the luminescence of the bis and tris complexes at room temperature under irradiation at around 390 nm with a UV lamp.

The increase in the triplet state energy observed for the [Ln(TTA)2(NO3)(TPPO)2] complexes, where Ln = Eu(III), Gd(III) and Tb(III), is

![Energy level diagram for the TTA ligand and lanthanide ions (Gd$^{3+}$ and Tb$^{3+}$) in the [Tb(TTA)2(NO3)(TPPO)2] and [Tb(TTA)3(TPPO)2] complexes showing the most probable intramolecular ligand-to-metal energy mechanism. The photographs were obtained after UV irradiation.](image-url)
probably because the shorter Ln–O(β-diketonate) distances tend to decrease the electronic conjugation of the chelate ring, improving the energy match between the excited T state of the TTA ligand and the emitting D levels of the Tb(III) ion.

Another remarkable characteristic of the [Tb(βdTTA)(NO3)(TPPO)2]3 complex is its triboluminescence trait of exhibiting green emission light when its crystals are triturated. This spectroscopic behavior occurs by indirect excitation of the ligands as follows: i) breaking of the crystals, ii) excitation of the ligand, and iii) transfer of energy from the ligand to the Tb(III) ion and iv) emission from the terbium ion [20]. In summary, the optical data of the [Tb(βdTTA)(NO3)(TPPO)2]3 complex demonstrated that the TTA ligand efficiently sensitizes the luminescence of the Tb(III) ion in the β-diketonate form. The Ln–O(β-diketonate) bond distances obtained for the bis and tris-TTA complexes reflect their energy gap between the ligand centered, triplet level and the D levels of the Tb(III) ion and, consequently, their luminescent properties. The photoluminescent properties of the [Tb(βdTTA)(NO3)(TPPO)2]3 complex in a solid state at room temperature indicate that this coordination compound can be used as a green luminescent layer in organic light emitting devices (OLEDs), among other photonic devices.

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Appendix A. Supplementary material

The crystallographic data of the [Tb(βdTTA)(NO3)(TPPO)2]3 complex has been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 770932. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336-033; E-mail:deposit@ccdc.cam.ac.uk]. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2010.07.043.

References


Synthesis of the Tb(βdTTA)(NO3)(TPPO)2 complex

One equivalent of Tb(NO3)3·6H2O (0.61 g, 1.7×10−3 mol) in 10 mL of methanol was added to a solution containing three equivalents of HTTA (1.00 g, 6.7×10−3 mol) and two equivalents of TPPO in 40 mL of methanol by dropping (under stirring). The resulting solution was in state for two days, forming crystals, which were filtered, washed with cooled methanol to remove the excess of ligand and dried in a vacuum desicator with an 80% yield of the [Tb(βdTTA)(NO3)(TPPO)2]3 complex. C26H24F8O18P2Tb3 (1319.85 g/mol) calcld: Tb3+, 13.07; C, 49.67; H, 3.51; F, 13.07; N, 2.90. IR (KBr, cm−1): 3058 (w), 1625 (s), 1561 (s), 1537 (s), 1502 (s), 1464 (s), 1439 (m), 1341 (s), 1385 (w), 1360 (s), 1346 (m), 1230 (m), 1161 (s), 1138 (s), 1104 (m), 1028 (m), 930 (w), 880 (w), 785 (m), 731 (s), 692 (m), 642 (w), 579 (m), 540 (s).

Synthesis of the Tb(TTA)3(TPPO)2 complex

Terbium chloride (0.56 g, 1.5 mmol) aqueous solution was added to a solution containing three equivalents of HTTA (1.00 g, 6.7×10−3 mol) and six equivalents of TPPO in 40 mL of methanol and by dropping (under stirring). The formed precipitate was washed with 10 mL of ethanol and dried in a vacuum. C26H24F8O18P2Tb3 (1319.85 g/mol) calcld: Tb3+, 11.52; C, 52.66; H, 3.07; Eu3+, 11.23; C, 52.02; H, 3.16, IR (KBr, cm−1): 3058 (w), 1614 (s), 1574 (m), 1537 (s), 1477 (s), 1458 (m), 1414 (s), 1381 (w), 1354 (m), 1308 (s), 1232 (m), 1124 (s), 1063 (m), 932 (w), 856 (m), 738 (m), 748 (m), 721 (s), 692(m), 642 (w), 579 (m), 540 (s).

Experimental elemental analysis of the carbon, hydrogen and nitrogen of the complexes were performed on a Perkin-Elmer model 2400 microanalyzer. The Ln3+ ion contents were identified by complexometric titration with EDTA. Infrared spectra were recorded in KBr pellets on a Bomen model MB-102 spectrophotometer in the range of 4000 to 400 cm−1. Steady-state excitation and emission spectra at room temperature were recorded at an angle of 22.5° (front face) with a spectrofluorimeter (SPEX-Fluorolog 2) with a double grating 0.22 mm monochromator (SPEX 1680) and a 450 W Xenon lamp as an excitation source. All spectra were recorded using a detector mode correction. The luminescence decay curves of the emitting levels were measured using a phosphorimeter SPEX 1934D accessory coupled to the spectrofluorimeter. The TL spectrum measured at room temperature was recorded with a USB4800 spectrometer fitted with a grating blazed at 500 nm with 600 grooves per mm, 3648-element linear CCD-array detector (Ocean Optics, Inc.).

Crystallographic data for Tb(TTA)3(TPPO)2 complex

Crystal data for Tb(TTA)3(TPPO)2: Empirical formula C26H24F8O18P2Tb3. Formulation weight = 1219.81, Temperature (K) = 293(2), Wavelength (Å) = 0.71073, Crystal system, space group Triclinic, P1, Unit cell dimensions a = 10.9224(7), b = 11.6539(7), c = 12.4000(8), β = 102.481(5), γ = 102.285(6), V = 1173.00(19) Å3. Absorption coefficients = 0.04 mm−1. Crystallographic data were collected on an X-ray diffractometer (Unicam 3500) equipped with a graphite monochromator Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. The orientation matrix and cell dimensions were determined by least-square refinement of the angular positions of all reflections. Data were collected for absorption and Lorentz polarization effects. The structure of the [Tb(βdTTA)(NO3)(TPPO)2] complex solved by the standard Patterson function technique. Space group, structure solution, refinement, molecular graphics and geometrical calculation were published in out with the SHIELXL-97 [27], ORTEP 3 [28], Mercury [29] and PARST [30] programs.
