

Energy Transfer Processes in Tb(III)-Dibenzoylmethanate Complexes with Phosphine Oxide Ligands

Francisco A. Silva Jr.,^a Helenise A. Nascimento,^a Dariston K. S. Pereira,^a
Ercules E. S. Teotônio,^{*a} Hermi F. Brito,^b Maria Cláudia F. C. Felinto,^c
José Geraldo P. Espínola,^a Gilberto F. Sá^d and Wagner M. Faustino^a

^aDepartamento de Química, Universidade Federal da Paraíba, 58051-970 João Pessoa-PB, Brazil

^bDepartamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, 05508-900 São Paulo-SP, Brazil

^cInstituto de Pesquisas Energéticas e Nucleares, Av. Prof Lineu Prestes, 2242, Cidade Universitária, 05508-000 São Paulo-SP, Brazil

^dDepartamento de Química Fundamental, Centro de Ciências Exatas e da Natureza (CCEN), Universidade Federal de Pernambuco, 50670-90 Recife-PE, Brazil

Este trabalho relata a síntese, a caracterização e as propriedades luminescentes dos complexos de fórmulas [Tb(DBM)₃L], [Tb(DBM)₂(NO₃)₂L₂] e [Tb(DBM)(NO₃)₂(HMPA)₂] (DBM = dibenzoylmetanato; L: TPPO = óxido de trifenilfosfina ou HMPA = óxido de hexametilfosforamida). Os compostos foram caracterizados por análise elementar (CHN), titulação complexométrica com EDTA e espectroscopia no infravermelho com transformada de Fourier (FTIR), e as propriedades de fotoluminescência foram avaliadas. As energias dos estados tripleto do ligante DBM foram determinadas experimentalmente a partir dos espectros de fosforescência resolvidos no tempo dos compostos análogos do íon Gd³⁺. As energias aumentam em função do número de ânions nitratos que substituem o ligante DBM nos complexos. Ademais, os espectros de luminescência e os tempos de vida dos níveis emissores revelaram que a eficiência de transferência de energia ligante-metal segue a mesma tendência. Ao contrário dos complexos tris-DBM, o bis- e o mono-DBM apresentaram elevada intensidade de luminescência, sendo candidatos promissores para camadas emissoras de luz em dispositivos moleculares conversores de luz (LCMD).

The Tb³⁺-β-diketonate complexes [Tb(DBM)₃L], [Tb(DBM)₂(NO₃)₂L₂] and [Tb(DBM)(NO₃)₂(HMPA)₂] (DBM = dibenzoylmethanate; L: TPPO = triphenylphosphine oxide or HMPA = hexamethylphosphine oxide) were prepared and characterized by elemental analysis (CHN), complexometric titration with EDTA and Fourier transform infrared (FTIR) spectroscopy, and the photoluminescence properties evaluated. The triplet state energies of the coordinated DBM ligands were determined using time-resolved phosphorescence spectra of analogous Gd³⁺ complexes. The results show that the energies increase along with the number of coordinated nitrate anions replacing the DBM ligand in the complexes. The luminescence spectra and emission lifetime measurements revealed that the ligand-to-metal energy transfer efficiency follows the same tendency. Unlike the tris-DBM complexes, bis- and mono-DBM presented high luminescence, and may act as promising candidates for preparation of the emitting layer of light converting molecular devices (LCMDs).

Keywords: terbium(III), β-diketonate, phosphine oxide, energy transfer

Introduction

Several transition metal and lanthanide β-diketonate complexes have been reported in the literature.¹⁻⁴ In

lanthanide compounds, the coordinated ligands play various roles that permit obtaining complexes with high luminescence quantum yields. They can (i) relax the Laport's parity selection rule;⁵⁻⁷ (ii) protect the emitting ion from solvent molecules, that can act as quenchers and (iii) help overcome the low absorption coefficients of

*e-mail: teotonioees@quimica.ufpb.br

intraconfigurational-4f electronic transitions (ϵ ca. 0.01 to 3 L mol⁻¹ cm⁻¹), since the excited organic ligands can transfer energy to a suitable excited energy level of the lanthanide ion.⁷⁻⁹

It is easy to find Ln³⁺- β -diketonate complexes exhibiting quantum yields above 70% in the literature,² in which the efficiency of the β -diketonate-to-Ln³⁺ intra-molecular energy transfer process is largely dependent on the energy difference between the donor state of the ligand and the acceptor state of the Ln³⁺ ion (ΔE).^{10,11} The more operative intra-molecular ligand-to-metal energy transfer is observed in compounds presenting ligand donor states above the lanthanide acceptor energy levels, minimizing the back energy-transfer processes.^{1,10-12} Furthermore, β -diketonate ligands generally have their donor states localized on the chelating ring, shortening the donor-acceptor distance, R_L , and thus enhancing the luminescence quantum yield.^{1,12}

After the pioneering study by Weissman,¹³ a great number of authors have been concerned with elucidating the details of intra-molecular energy-transfer for different lanthanide coordination compounds, particularly Eu³⁺ and Tb³⁺ ones.¹⁴⁻²⁰ The main emitting level of the Tb³⁺ ion, ⁵D₄, is approximately 3250 cm⁻¹ above the main emitting level of the Eu³⁺ ion, ⁵D₀. Therefore, a single β -diketonate ligand is often not optimum to sensitize both ions, since the triplet states are not resonant for both of them.¹⁷

Energy levels of β -diketonate ligands remain essentially the same in tris and tetrakis-complexes such that the ligand-to-metal intra-molecular energy transfers in these complexes are very similar. In the absence of additional luminescence quenching routes, the luminescence quantum yields of tris and tetrakis-complexes are similar suggesting that they are independent of the number of coordinated β -diketonate ligands.^{15-17,21} However, recently our group reported that the luminescence of the complex [Tb(TTA)₂NO₃(TPPO)] is much higher than in its tris and tetrakis analogues.²²⁻²⁵

In this work, our group extends the investigation to the mono-, bis- and tris-DBM complexes, [Ln(DBM)₃L], [Ln(DBM)₂(NO₃)₂L₂] and [Ln(DBM)(NO₃)₂L₂] (DBM = dibenzoylmethanate; L: TPPO = triphenylphosphine oxide or HMPA = hexamethylphosphine oxide; Ln = Tb³⁺ and Gd³⁺), and the study of the dependence of Tb³⁺ luminescence properties as a function of the number of coordinated β -diketonate ligands. The corresponding Gd³⁺ complexes were used to mimic the Tb³⁺ complexes and determine the excited state energies of the coordinated ligand.

Experimental

Reagents and syntheses

Terbium oxide (Tb₄O₇), dibenzoylmethane, phosphine oxide ligands (TPPO and HMPA) as well as the solvents (ethanol and acetone) were purchased from Aldrich Co., and used without any previous treatment. Terbium chloride and nitrate were synthesized as described in the literature.²⁶ The terbium and gadolinium complexes were synthesized in the same way; and the preparation of terbium complexes are given as representative.

Syntheses of the tris-diketonate complexes

Tb(DBM)₃L (L = TPPO or HMPA)

To an ethanol solution containing 1.00 g (4.46 mmol) of DBM, and 0.41 g (1.49 mmol) of TPPO (or 0.29 g of HMPA), a solution of 0.56 g (1.49 mmol) of terbium chloride in 30 mL of ethanol was added dropwise, under stirring. The pH value of the resulting solution was then adjusted to approximately 6.0 using NaOH (0.01 mol L⁻¹) in a 50/50 water/ethanol mixture. The resulting yellow solid was filtered, washed with ethanol and dried under vacuum.

Tb(DBM)₃(TPPO): yield 1.50 g (90.8%); C₆₃H₄₈TbO₇P: calc. C 68.36, H 4.37, Tb 14.36; found C 68.15, H 4.52, Tb 13.97; FTIR (KBr) v/cm⁻¹ 3055 (w), 2923 (w), 1597 (s), 1550 (s), 1519 (s), 1477 (s), 1454 (m), 1404 (s), 1311 (m), 1219 (w), 1168 (s), 1118 (s), 1091 (m), 1068 (w), 1026 (m), 999 (w), 941 (w), 852 (w), 817 (w), 783 (w), 744 (m), 721 (s), 690 (s), 609 (m), 540 (s).

Tb(DBM)₃(HMPA): yield 1.30 g (87.5%); C₅₁H₅₁TbN₃O₇P: calc. C 60.78, H 5.10, N 4.17, Tb 15.77; found C 60.63, H 5.05, N 4.22, Tb 16.09; FTIR (KBr) v/cm⁻¹ 3059 (w), 2927 (w), 1600 (s), 1550 (s), 1520 (s), 1477 (s), 1458 (m), 1411 (s), 1303 (m), 1220 (w), 1157 (s), 1068 (m), 1022 (w), 987 (s), 941 (w), 783 (w), 748 (s), 717 (s), 686 (m), 609 (m), 509 (w).

Gd(DBM)₃(TPPO): yield 1.42 g (85.9%); C₆₃H₄₈GdO₇P: calc. C 68.46, H 4.38, Gd 14.23; found C 68.46, H 4.42, Gd 14.14; FTIR (KBr) v/cm⁻¹ 3059 (w), 3024 (w), 1597 (s), 1546 (s), 1516 (s), 1476 (s), 1456 (m), 1404 (s), 1307 (m), 1281 (w), 1223 (w), 1168 (s), 1119 (s), 1095 (m), 1064 (w), 1022 (m), 999 (w), 941 (w), 852 (w), 810 (w), 783 (w), 745 (m), 721 (s), 691 (s), 609 (m), 540 (m), 509 (w).

Gd(DBM)₃(HMPA): yield 1.38 g (91.7%); C₅₁H₅₁GdN₃O₇P: calc. C 60.48, H 5.11, N 4.18, Gd 15.63; found C 60.53, H 5.15, N 4.02, Gd 15.58; FTIR (KBr) v/cm⁻¹ 3059 (w), 2922 (w), 1597 (s), 1551 (s), 1519 (s), 1477 (s), 1458 (m), 1412 (s), 1304 (m), 1219 (w), 1180 (s), 1064 (m), 1022 (w), 988 (s), 941 (w), 783 (w), 748 (s), 718 (s), 687 (m), 609 (m), 509 (w).

Syntheses of the bis-diketonate complexes

[Tb(DBM)₂(L)₂(NO₃)₂]

1.00 g (4.46 mmol) of DBM and 1.24 g (4.46 mmol) of TPPO (or 0.87 g of HMPA) were dissolved in 30 mL of ethanol and added dropwise under stirring to 30 mL of an ethanol solution containing 0.56 g (1.49 mmol) of terbium chloride. The pH value of the resulting mixture was adjusted to 1.0 with concentrated HNO₃ solution and then to 6.0 using NaOH (0.01 mol L⁻¹) in a 50/50 water/ethanol mixture. The yellow solid was filtered, washed with ethanol and dried under vacuum.

[Tb(DBM)₂(TPPO)₂(NO₃)₂]: yield 2.27 g (83.4%); C₆₆H₅₂TbNO₉P₂: calc. C 64.76, H 4.28, N 1.14, Tb 12.98; found C 64.16, H 4.30, N 1.84, Tb 13.26; FTIR (KBr) v/cm⁻¹ 3055 (m), 2920 (w), 1597 (s), 1550 (s), 1520 (s), 1477 (s), 1454 (s), 1404 (s), 1311 (m), 1219 (w), 1165 (s), 1118 (s), 1092 (w), 1068 (w), 1026 (m), 999 (w), 941 (w), 852 (w), 817 (w), 783 (w), 744 (m), 721 (s), 690 (s), 609 (m), 540 (s).

[Tb(DBM)₂(HMPA)₂(NO₃)₂]: yield 1.96 g (86.0%); C₄₂H₅₈TbN₇O₉P₂: calc. C 49.18, H 5.70, N 9.56, Tb 15.49; found C 49.72, H 5.90, N 8.76, Tb 15.52; FTIR (KBr) v/cm⁻¹ 3059 (w), 2924 (m), 1597 (s), 1550 (s), 1516 (s), 1477 (s), 1458 (m), 1408 (s), 1300 (m), 1219 (w), 1161 (s), 1068 (m), 1026 (w), 987 (s), 941 (w), 783 (w), 744 (s), 721 (s), 686 (m), 609 (m), 509 (w), 478 (w).

[Gd(DBM)₂(TPPO)₂(NO₃)₂]: yield 2.34 g (85.4%); C₆₆H₅₂GdNO₉P₂: calc. C 64.85, H 4.29, N 1.15, Gd 12.86; found C 64.23, H 4.32, N 1.62, Gd 12.61; FTIR (KBr) v/cm⁻¹ 3055 (m), 2920 (w), 1593 (s), 1551 (s), 1520 (s), 1477 (s), 1453 (s), 1404 (s), 1312 (m), 1219 (w), 1168 (s), 1119 (s), 1092 (w), 1072 (w), 1026 (m), 999 (w), 941 (w), 852 (w), 814 (w), 783 (w), 745 (m), 721 (s), 691 (s), 609 (m), 540 (s), 447 (w).

[Gd(DBM)₂(HMPA)₂(NO₃)₂]: yield 2.08 g (90.5%); C₄₂H₅₈GdN₇O₉P₂: calc. C 49.26, H 5.71, N 9.57, Gd 15.35; found C 49.12, H 5.66, N 9.67, Gd 15.93; FTIR (KBr) v/cm⁻¹ 3059 (w), 2924 (m), 2897 (m), 2808 (m), 1597 (s),

1554 (s), 1516 (s), 1477 (s), 1454 (m), 1408 (s), 1304 (m), 1219 (w), 1192 (s), 1161 (s), 1068 (m), 1026 (w), 987 (s), 941 (w), 818 (w), 783 (w), 748 (s), 721 (s), 687 (m), 610 (m), 505 (w), 478 (w).

Syntheses of the mono-diketonate complexes

[Tb(DBM)(HMPA)₂(NO₃)₂]

Mono-dibenzoylmethanate complex was obtained only with HMPA as neutral ligand. The synthetic route for this complex was similar to that used for [Tb(DBM)₂(HMPA)(NO₃)₂], but using the 1:2:1 molar ratio of DBM:HMPA:Tb³⁺. An ethanol solution (ca. 20 mL) of terbium nitrate (1.66 g, 4.44 mmol) was added to 20 mL of an ethanol solution containing a mixture of 1.00 g (4.46 mmol) of DBM and 1.61 g (8.92 mmol) of HMPA. After ca. 24 h, the yellow single crystals were filtered, washed with ethanol and dried in a desiccator under vacuum.

[Tb(DBM)(HMPA)₂(NO₃)₂]: yield 2.90 g (75.0%); C₂₇H₄₇TbN₈O₁₀P₂: calc. C 37.51, H 5.48, N 12.96, Tb 18.38; found C 37.28, H 5.31, N 10.48, Tb 18.32; FTIR (KBr) v/cm⁻¹ 3062 (w), 2935 (m), 1597 (s), 1554 (s), 1523 (s), 1481 (s), 1384 (s), 1300 (s), 1230 (w), 1188 (s), 1165 (s), 1138 (s), 1068 (m), 1029 (w), 991 (s), 817 (w), 756 (s), 721 (m), 690 (w), 609 (w).

[Gd(DBM)(HMPA)₂(NO₃)₂]: yield 3.15 g (81.4%); C₂₇H₄₇GdN₈O₁₀P₂: calc. C 37.58, H 5.49, N 12.99, Gd 18.22; found C 37.40, H 5.28, N 12.88, Gd 17.80; FTIR (KBr) v/cm⁻¹ 3059 (w), 2997 (m), 2891 (m), 2854 (m), 2816 (m), 1601 (s), 1558 (s), 1524 (s), 1481 (s), 1458 (s), 1385 (s), 1300 (s), 1238 (w), 1161 (s), 1138 (s), 1061 (m), 1030 (w), 984 (s), 941 (w), 818 (w), 756 (s), 721 (m), 687 (w), 605 (w), 521 (w), 482 (w).

Apparatus

The elemental analyses of carbon, hydrogen and nitrogen in the tris-, bis- and mono-diketonate complexes were performed using a Perkin-Elmer model 2400 microanalyzer, whereas the Tb³⁺ ion contents were determined by complexometric titration with EDTA.²⁷ Infrared absorption spectra were recorded in the range of 400 up to 4000 cm⁻¹ in KBr pellets using a Shimadzu FTIR spectrophotometer model IRPRESTIGE-21.

Steady state excitation and emission spectra of the solid complexes were recorded at liquid nitrogen temperature, using a Fluorolog-3 spectrofluorometer (Horiba) equipped with 0.22 m excitation and emission double grating monochromators, a 450 W Xenon lamp as the excitation

source, and an R928P PMT photomultiplier as detector. All spectra were recorded using detector mode correction. The second-order diffraction of the source radiation was eliminated by using a cut-off filter. Time-resolved luminescence spectra of the Gd³⁺-complexes and the luminescence decay curves of the Tb³⁺-complexes were recorded at 77 K using the same equipment, but operating in phosphorescence mode with a pulsed Xenon lamp as the excitation source. A time delay of 0.100 ms was applied. The luminescence instruments were fully controlled by the FluorEssence program. All luminescence data were obtained from samples contained in a 2 mm diameter quartz tube.

Results and Discussion

Characterization of the complexes

The elemental analysis (C, H and N) and the complexometric titration data indicated that complexes presenting the formulas [Ln(DBM)₃L], [Ln(DBM)₂(NO₃)L₂] and [Ln(DBM)(NO₃)₂(HMPA)₂] (Ln = Gd³⁺ and Tb³⁺; DBM = dibenzoylmethanate; L: TPPO = triphenylphosphine oxide or HMPA = hexamethylphosphine oxide) were obtained. The tris- and bis-diketonate complexes of either HMPA or TPPO were easily obtained. However, it was not possible to obtain the mono-diketonate with TPPO, even after many attempts. This is probably due to the lower donor capacity and steric hindrance of TPPO when compared to HMPA, which allows coordination of more than one DBM ligand to the lanthanide ion.

The coordination modes of the dibenzoylmethanate, phosphine oxide and nitrate ligands were investigated based on their characteristic FTIR absorption bands (Figure S1 in the Supplementary Information (SI) section). The FTIR spectra exhibited strong bands at around 1600 cm⁻¹ that might be assigned to $\nu(\text{C}=\text{O})$ coupled with $\nu(\text{C}=\text{C})$ of the DBM ligand. These bands are shifted to a lower wavenumber in comparison with the free ligand, indicating that DBM is coordinated to the metal ion in chelating mode.²⁸ The spectra also show strong bands around 1160 cm⁻¹, which might be assigned to $\nu(\text{P}=\text{O})$ of the phosphine oxide ligands (TPPO and HMPA). These bands are also shifted to lower wavenumbers in comparison with the respective free ligands. Two absorption bands were also observed around 1180 and 1036 cm⁻¹ which may be assigned to $\nu_a(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$ modes, indicating that the NO₃⁻ is chelated and has C_{2v} symmetry.^{28,29} Furthermore, the two characteristic bands assigned to $\nu_1 + \nu_4$ combination modes (1820 and 1767 cm⁻¹) are separated about 55 cm⁻¹, reinforcing the implication that nitrate is coordinated as a bi-dentate ligand.²⁸

Luminescent properties of the Tb³⁺-DBM complexes

According to the intra-molecular energy transfer mechanism suggested by the experimental data and theoretical models,^{1,12,14} the excited T₁ states of the ligands play a critical role in defining the Ln³⁺ β -diketonate complexes. In order to estimate these energy levels in the Tb³⁺ complexes, phosphorescence spectra of equivalent Gd³⁺ complexes that do not present intraconfigurational-4f transitions in the visible region were recorded.¹ Figures 1a and 1b show the steady state emission spectra of the [Gd(DBM)₃L], [Gd(DBM)₂(NO₃)L₂] and [Gd(DBM)(NO₃)₂(HMPA)₂] complexes with excitation at 370 nm. These spectra are characterized by one very low intensity broad band in the spectral range of 420–455 nm and the strongest bands are in the spectral range of 460–700 nm, which are assigned to the S₁ → S₀ and to the T₁ → S₀ transitions of the DBM ligand, respectively.

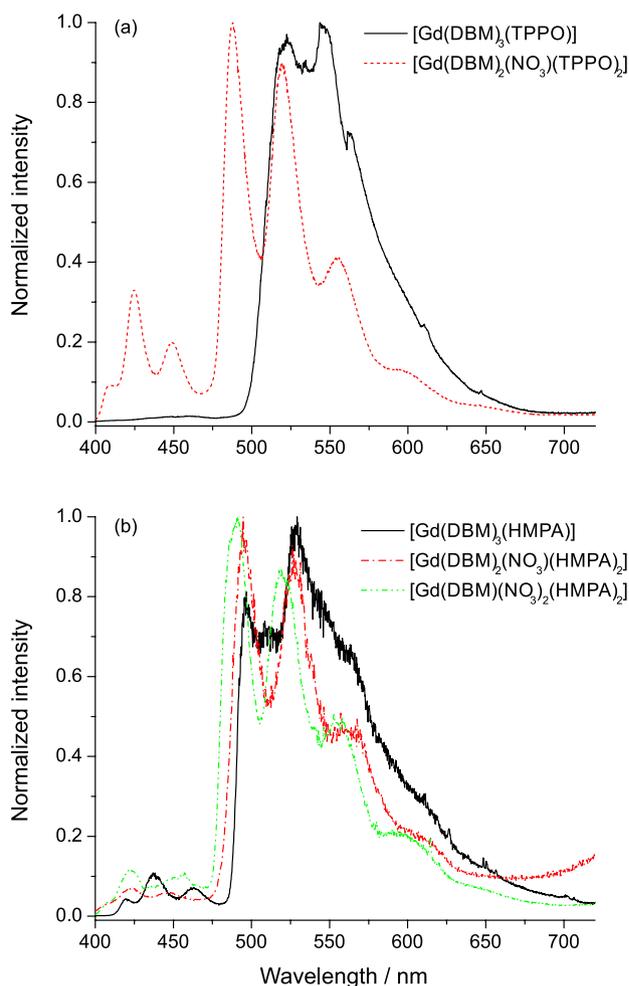


Figure 1. Steady state emission spectra of the tris-, bis- and mono-dibenzoylmethanate recorded at 77 K under excitation at 370 nm: (a) [Gd(DBM)₃(TPPO)₂] and [Gd(DBM)₂(NO₃)(TPPO)₂], and (b) [Gd(DBM)₃(HMPA)₂], [Gd(DBM)₂(NO₃)(HMPA)₂] and [Gd(DBM)(NO₃)₂(HMPA)₂].

In order to determine the exact position of 0-0 phonon transitions, the time-resolved luminescence spectra (Figures 2a and 2b) were recorded using a time delay of 0.100 ms. As can be seen, these spectra present only those broad bands that may be attributed to the triplet to singlet transitions. The T_1 state energies determined as the shortest wavelength phosphorescence bands for the complexes are [Gd(DBM)₃(TPPO)] (20325 cm⁻¹), [Gd(DBM)₃(HMPA)] (20660 cm⁻¹), [Gd(DBM)₂(TPPO)₂(NO₃)] (21186 cm⁻¹), [Gd(DBM)₂(HMPA)₂(NO₃)] (21142 cm⁻¹) and [Gd(DBM)(NO₃)₂(HMPA)₂] (21231 cm⁻¹).

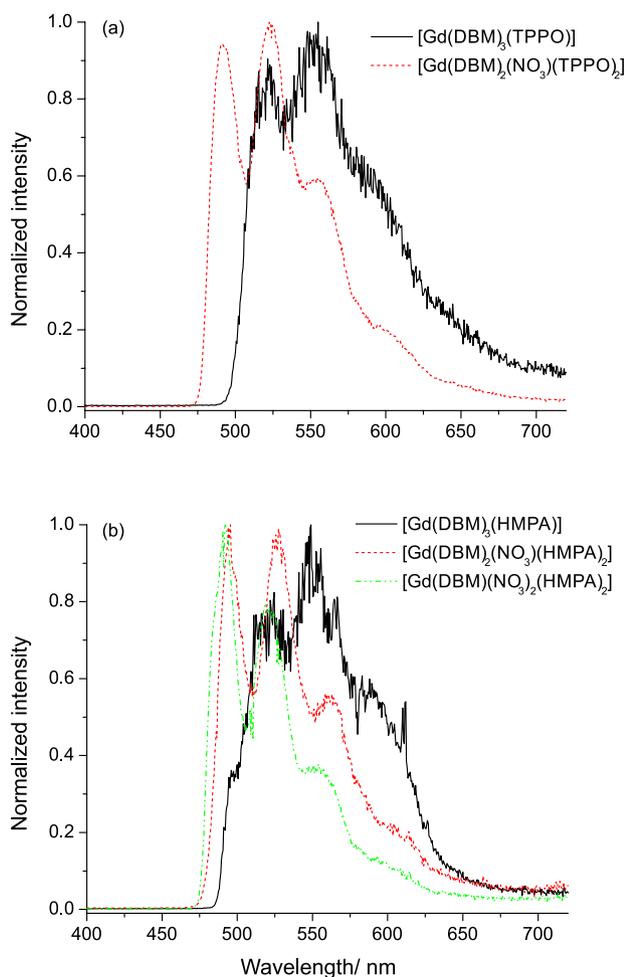


Figure 2. Time-resolved emission spectra of tris-, bis- and mono-dibenzoylmethanate recorded at 77 K, under excitation at 370 nm with a delay time of 0.100 ms: (a) [Gd(DBM)₃(TPPO)] and [Gd(DBM)₂(NO₃)(TPPO)₂] and (b) [Gd(DBM)₃(HMPA)], [Gd(DBM)₂(NO₃)(HMPA)₂] and [Gd(DBM)(NO₃)₂(HMPA)₂].

A significant increase in the T_1 state energies is observed when changing the inner coordination sphere (around the lanthanide ion) from tris- to either bis- or mono-DBM complexes. This is in agreement with results previously observed for Gd(III)-TTA-phosphine oxide complexes^{22,26} and suggests that the inter-ligand interactions

play an important role in the energy level structures of Ln³⁺ diketonate complexes.

Figure 3 shows the excitation spectra of the [Tb(DBM)₂(NO₃)L₂] and [Tb(DBM)₃L] complexes recorded at 77 K in the 250-520 nm range, monitoring the emission from the ⁵D₄ → ⁷F₅ transition at around 545 nm. The broad bands that can be attributed to S₀ → S₁ transitions centered on the DBM ligands. This result indicates a luminescent sensitization of the Tb³⁺ ion via antenna effect. Some narrow bands in the excitation spectra due to the intraconfigurational-4f⁸ transitions ⁷F₆ → ⁵L₆ (339 nm), ⁷F₆ → ⁵L₉ (350 nm), ⁷F₆ → ⁵L₁₀ (369 nm), ⁷F₆ → ⁵G₆ (376 nm), ⁷F₆ → ⁵D₃ (380 nm) and ⁷F₆ → ⁵D₄ (488 nm) centered on the Tb³⁺ ion are also observed.³⁰ The comparison of the relative intensities for the bands in the excitation spectra reveals a significant intensification on the DBM centered transitions from tris- to mono-diketonate complexes. These results suggest higher luminescence sensitizing of the Tb³⁺ ion in those complexes.

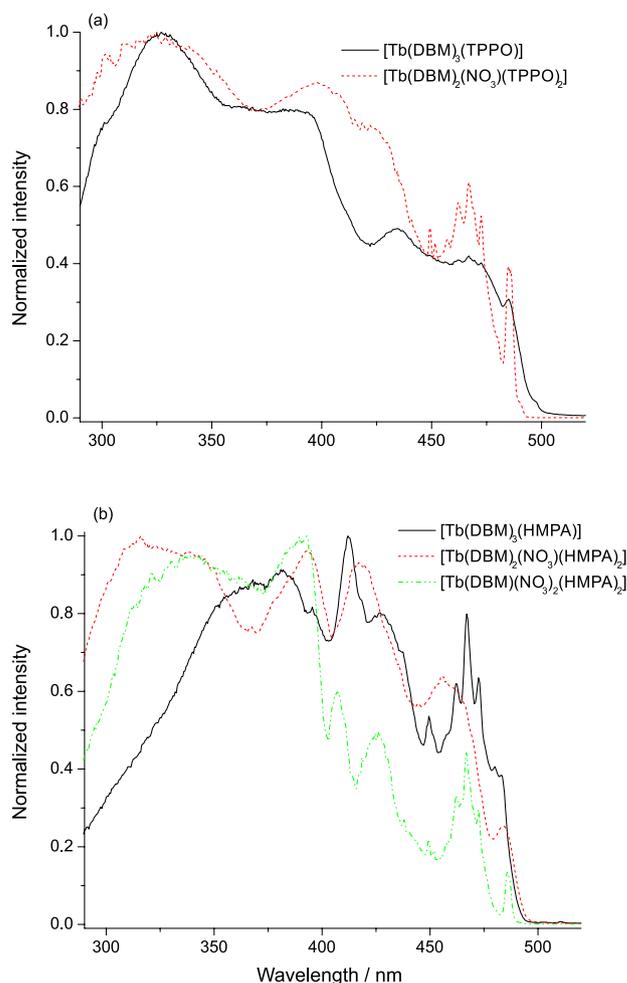


Figure 3. Excitation spectra of tris-, bis- and mono-dibenzoylmethanate recorded at 77 K under excitation at 545 nm: (a) [Tb(DBM)₃(TPPO)] and [Tb(DBM)₂(NO₃)(TPPO)₂], and (b) [Tb(DBM)₃(HMPA)], [Tb(DBM)₂(NO₃)(HMPA)₂] and [Tb(DBM)(NO₃)₂(HMPA)₂].

The emission spectra of the Tb³⁺-DBM complexes in solid state were recorded in the range of 420 to 720 nm at 77 K, upon excitation in an absorption band of the DBM ligand around 370 nm (Figure 4). These spectra present characteristic narrow bands assigned to the intraconfigurational ⁵D₄ → ⁷F_j transitions of Tb³⁺ ion: ⁵D₄ → ⁷F₆ (492 nm), ⁵D₄ → ⁷F₅ (545 nm), ⁵D₄ → ⁷F₄ (589 nm), ⁵D₄ → ⁷F₃ (625 nm), ⁵D₄ → ⁷F₂ (651 nm), ⁵D₄ → ⁷F₁ (662 nm) and ⁵D₄ → ⁷F₀ (680 nm). All spectra present the band due to the ⁵D₄ → ⁷F₅ transition as the most intense one. In addition to intraconfigurational ⁵D₄ → ⁷F_j transitions, broad emission bands in the 470-720 nm range assigned to the phosphorescence from the DBM ligands can also be observed. However, the intensity of the phosphorescence bands decreases significantly from tris- to bis-diketonate (Figures 4a and 4b), for both TPPO and HMPA complexes. Although the band in the [Tb(DBM)₃(TPPO)] complex (Figure 4a) exhibits lower intensity than in the similar tris-DBM complex with HMPA (Figure 4b), both are not luminescent at room temperature. The lowest relative intensity of the phosphorescence band was obtained for mono-diketonate [Tb(DBM)(NO₃)₂(HMPA)₂] (Figure 4b), that presents the strongest green luminescence at room temperature under UV

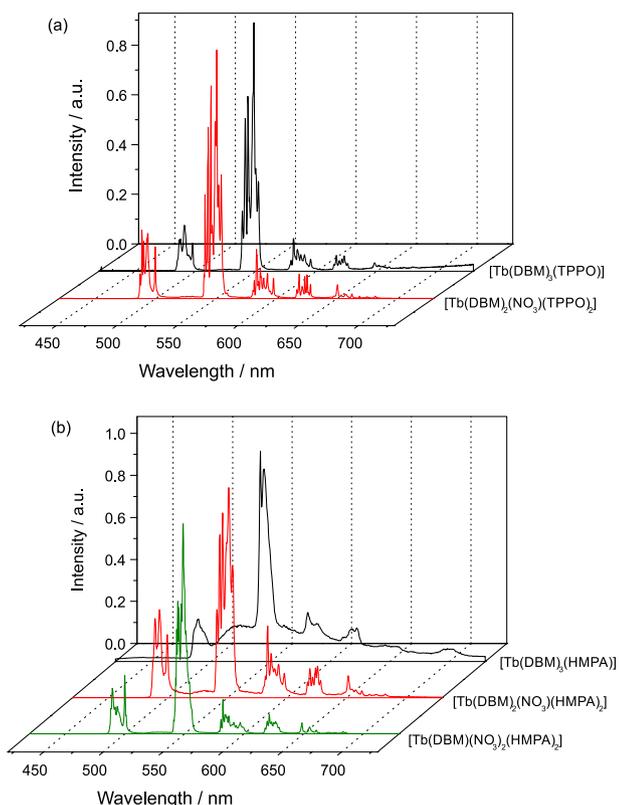


Figure 4. Emission spectra of tris-, bis- and mono-dibenzoylmethanate recorded at 77 K under excitation at 370 nm: (a) [Tb(DBM)₃(TPPO)₂] and [Tb(DBM)₃(NO₃)(TPPO)₂], and (b) [Tb(DBM)₃(TPPO)₂], [Tb(DBM)₂(NO₃)(TPPO)₂] and [Tb(DBM)(NO₃)₂(TPPO)₂].

radiation, which is unlike most Tb³⁺ complexes containing aromatic diketonates as ligands reported in the literature.¹⁵⁻¹⁷

An energy level diagram to rationalize the photophysical properties of the synthesized complexes was built (Figure 5). The energy gap values ΔE (T – ⁵D₄) were calculated as the difference between the energies corresponding to the 0-0 phonon transitions from the phosphorescence spectra of the Gd-complexes (Figure 2a and 2b), and the main emitting energy level ⁵D₄ of the Tb³⁺ ion at 20492 cm⁻¹.³⁰ The values of ΔE (T – ⁵D₄) for tris-, bis- and mono-dibenzoylmethanate complexes are [Gd(DBM)₃(TPPO)] (-167 cm⁻¹), [Gd(DBM)₃(HMPA)] (168 cm⁻¹), [Gd(DBM)₂(TPPO)₂(NO₃)] (694 cm⁻¹), [Gd(DBM)₂(HMPA)₂(NO₃)] (650 cm⁻¹) and [Gd(DBM)(NO₃)₂(HMPA)₂] (740 cm⁻¹). The values for bis- and mono-dibenzoylmethanate compounds are high enough to permit considerable intramolecular DBM-to-Tb³⁺ ion energy transfer.

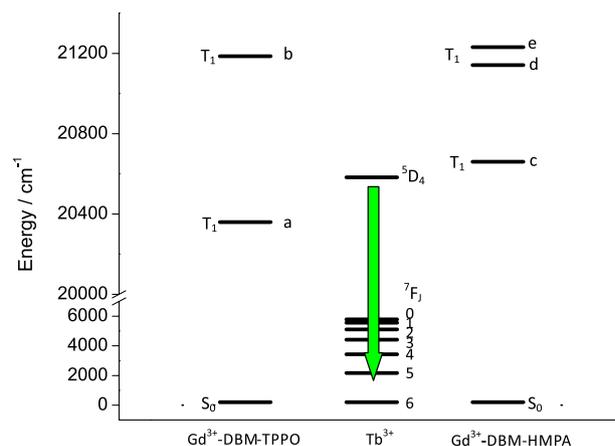


Figure 5. Partial energy level diagram presenting excited triplet (T₁) states of the DBM ligand in the Gd³⁺-complexes (a: [Gd(DBM)₃(TPPO)₂], b: [Gd(DBM)₂(NO₃)(TPPO)₂], c: [Gd(DBM)₃(HMPA)₂], d: [Gd(DBM)₂(NO₃)(HMPA)₂] and e: [Gd(DBM)(NO₃)₂(HMPA)₂]) and the energy levels of the Tb³⁺ ion. The singlet ground states are represented by S₀.

In order to obtain evidence for the relationship between the T₁ state position and the luminescent intensity of the Tb³⁺ ion in the tris-, bis- and mono-dibenzoylmethanate complexes, the luminescence decay curves were measured (Figures S2 and S3 in the SI section). The decay curves for bis- and mono-dibenzoylmethanate complexes were adjusted with a single exponential function and the lifetime values (τ) of the ⁵D₄ emitting level were found to be: 0.4948 ms for [Tb(DBM)₂(NO₃)(TPPO)₂], 0.6661 ms for [Tb(DBM)₂(NO₃)(HMPA)₂], and 0.6847 ms for [Tb(DBM)(NO₃)₂(HMPA)₂]. The luminescence decay curves for tris-DBM complexes were better adjusted by a bi-exponential function (τ₁ = 0.8946 ms, τ₂ = 0.0214 ms) for [Tb(DBM)₃(TPPO)], and (τ₁ = 1.0499 ms, τ₂ = 0.0508 ms)

for [Tb(DBM)₃(HMPA)], and indicate that both the DBM ligand and Tb³⁺ ion are acting as emitting species with lifetimes of τ_1 and τ_2 , respectively. The values of τ for the mono- and bis-dibenzoylmethanate complexes are higher than the values of τ_2 for the tris-dibenzoylmethanate complexes. The results suggest that the emitting ⁵D₄ level of the Tb³⁺ ion is efficiently deactivated in the tris-dibenzoylmethanate complexes. This is consistent with the energy level diagram presented in Figure 5, that shows T₁ states for [Tb(DBM)₃(TPPO)] and [Tb(DBM)₃(HMPA)], below and a little above of the ⁵D₄ level, respectively.

Conclusions

In this work, three series of Tb³⁺-diketonate complexes containing DBM, and phosphine oxide ligands were successfully synthesized and characterized. These compounds with general formulas [Tb(DBM)₃L], [Tb(DBM)₂(NO₃)L] and [Tb(DBM)(NO₃)₂L] (L = TPPO or HMPA) exhibit different luminescence properties under excitation at DBM transitions. This is in contrast with Tb³⁺ tris-DBM compounds, and most of the Tb³⁺-diketonate complexes reported in the literature, which display only very weak luminescence intensities. Bis- and mono-dibenzoylmethanate forms are characterized by strong green luminescence arising from the Tb³⁺ ion. Notably, the luminescent sensitizer activity of the DBM ligands for the Tb³⁺ center in these complexes increases when the number of the DBM ligand in the first coordination sphere decreases. In mono- and bis-DBM complexes, both stronger DBM-metal interactions and conformational changes of DBM ligand due to the replacement of other coordinated DBM by nitrate ion probably play the main role in increasing the energies of remaining DBM ligand triplet states, thus intensifying the antenna effect. This behavior emphasizes the importance of the inter-ligand interactions on the T₁ state energy, and consequently on the efficiency of T₁ → ⁵D₄ energy transfer process. Finally, the experimental results reveal that mono- and bis-DBM complexes of the Tb³⁺ ion are promising candidates for light converting molecular devices (LCMD).

Supplementary Information

FTIR spectra of the Tb³⁺-dibenzoylmethanate compounds are available free of charge at <http://jbcs.sbq.org.br> as PDF file.

Acknowledgments

This work was supported by the Brazilian agencies CNPq (Conselho Nacional de Desenvolvimento Científico

e Tecnológico), INCT-INAMI (CNPq), CNPq-FACEPE-PRONEX, CAPES and FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo).

References

- de Sá, G. F.; Malta, O. L.; Donegá, C. M.; Simas, A. M.; Longo, R. L.; Santa-Cruz, P. A.; Silva Jr., E. F.; *Coord. Chem. Rev.* **2000**, *196*, 165.
- Brito, H. F.; Malta, O. L.; Felinto, M. C. F. C.; Teotonio, E. E. S. In *The Chemistry of Metal Enolate*; Zabicky, J., ed.; John Wiley & Sons: Chichester, England, 2009, ch. 3.
- Bünzli, J. C. G.; Choppin, G. R., eds.; *Lanthanide Probes in Life, Chemical and Earth Sciences – Theory and Practice*; Elsevier: Amsterdam, Holland, 1989, ch. 7.
- Bünzli, J. C. G.; *Chem. Soc. Rev.* **2005**, *34*, 1048.
- Judd, B. R.; *Phys. Rev.* **1962**, *127*, 750.
- Ofelt, G. S.; *J. Chem. Phys.* **1962**, *37*, 511.
- Malta, O. L.; Carlos, L. D.; *Quim. Nova* **2003**, *26*, 889.
- Mason, S. F.; Peacock, R. D.; Stewart, B.; *Mol. Phys.* **1975**, *30*, 1829.
- Judd, B. R.; *J. Chem. Phys.* **1979**, *70*, 4830.
- Latva, M.; Takalo, H.; Mikkala, V. M.; Marachescu, C.; Rodríguez-Ubis, J. C.; Kankare, J.; *J. Lumin.* **1997**, *75*, 149.
- Felinto, M. C. F. C.; Tomiyama, C. S.; Brito, H. F.; Teotonio, E. E. S.; Malta, O. L.; *J. Solid State Chem.* **2003**, *171*, 189.
- Faustino, W. M.; Junior, S. A.; Thompson, L. C.; de Sá, G. F.; Malta, O. L.; Simas, A. M.; *Int. J. Quantum Chem.* **2006**, *103*, 572.
- Weissman, S. I.; *J. Chem. Phys.* **1942**, *10*, 214.
- Silva, F. R. G. E.; Malta, O. L.; *J. Alloys Compd.* **1997**, *250*, 427.
- Sata, S.; Wada, M.; *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1955.
- Sager, W. F.; Filipescu, N.; Serafin, F. A.; *J. Phys. Chem.* **1965**, *69*, 1092.
- Filipescu, N.; Sager, W. F.; Serafin, F. A.; *J. Phys. Chem.* **1964**, *68*, 3324.
- Kokko, T.; Kokko, L.; Soukka, T.; *J. Fluoresc.* **2009**, *19*, 159.
- Blomberg, K.; Hurskainen, P.; Hemmila, I.; *Clin. Chem.* **1999**, *45*, 855.
- Richardson, F. S.; *Chem. Rev.* **1982**, *82*, 541.
- Bruno, S. M.; Ferreira, R. A.; Paz, F. A. A.; Carlos, L. D.; Pillinger, M.; Ribeiro-Claro, P.; Gonçalves, I. S.; *Inorg. Chem.* **2009**, *48*, 4882.
- Teotonio, E. E. S.; Silva Jr., F. A.; Pereira, D. K. S.; Santos, L. M.; Brito, H. F.; Faustino, W. M.; Felinto, M. C. F. C.; Santos, R. H.; Moreno-Fuquen, R.; Kennedy, A. R.; Gilmore, D.; *Inorg. Chem. Comm.* **2010**, *13*, 1391.
- Teotonio, E. E. S.; Fett, G. M.; Brito, H. F.; Faustino, W. M.; de Sá, G. F.; Felinto, M. C. F. C.; Santos, R. H.; *J. Lumin.* **2008**, *128*, 190.

24. Steblevskaya, N. I.; Karasev, V. E.; Shchelokov, R. N.; *Russ. J. Inorg. Chem.* **1984**, *29*, 2230.
25. Karasev, V. E.; Botova, I. N.; *Russ. J. Inorg. Chem.* **1988**, *33*, 2257.
26. Teotonio, E. E. S.; Fett, G. M.; Brito, H. F.; Trindade, A. C.; Felinto, M. C. F. C.; *Inorg. Chem. Comm.* **2007**, *10*, 867.
27. Teotonio, E. E. S.; Espinola, J. G. P.; Brito, H. F.; Malta, O. L.; Oliveira, S. F.; de Faria, D. L. A.; Izumi, C. M. S.; *Polyhedron* **2002**, *21*, 1837.
28. Nakamoto, K.; *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Willey-Interscience Publication: New York, USA, 1986.
29. Fu, Y. J.; Wong, T. K. S.; Yan, Y. K.; Hu, X.; *J. Alloys Compd.* **2003**, *358*, 235.
30. Carnall, W. T.; Crosswhite, H.; *Energy Levels Structure and Transition Probabilities of the Trivalent Lanthanides in LaF₃*; Argonne National Laboratory Report: USA, 1977.

Submitted: September 10, 2012

Published online: March 27, 2013

FAPESP has sponsored the publication of this article.