

Synthesis and spectroscopic behavior of highly luminescent Eu^{3+} –dibenzoylmethanate (DBM) complexes with sulfoxide ligands

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Abstract

In this paper the synthesis, characterization and photoluminescent behavior of the $[\text{RE}(\text{DBM})_3\text{L}_2]$ complexes ($\text{RE} = \text{Gd}$ and Eu) with a variety of sulfoxide ligands; $\text{L} =$ benzyl sulfoxide (DBSO), methyl sulfoxide (DMSO), phenyl sulfoxide (DPSO) and *p*-tolyl sulfoxide (PTSO) have been investigated in solid state. The emission spectra of the Eu^{3+} – β -diketonate complexes show characteristics narrow bands arising from the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0-4$) transitions, which are split according to the selection rule for C_n , C_{nv} or C_s site symmetries. The experimental Judd–Ofelt intensity parameters (Ω_2 and Ω_4), radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates, and R_{02} for the europium complexes have been determined and compared. The highest value of Ω_2 ($61.9 \times 10^{-20} \text{ cm}^2$) was obtained to the complex with PTSO ligand, indicating that Eu^{3+} ion is in the highly polarizable chemical environment. The higher values of the experimental quantum yield (q) and emission quantum efficiency of the emitter $^5\text{D}_0$ level (η) for the Eu-complexes with DMSO, DBSO and PTSO sulfoxides suggest that these complexes are promising Light Conversion Molecular Devices (LCMDs). The lower value of quantum yield ($q = 1\%$), for the hydrated complex $[\text{Eu}(\text{DBM})_3(\text{H}_2\text{O})]$, indicates that the luminescence quenching occurs via multiphonon relaxation by coupling with the OH-oscillators from water molecule coordinated to rare earth ion. The pure red emission of the Eu-complexes has been confirmed by (x, y) color coordinates.

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1. Introduction

Interest in the photoluminescence (PL) properties of the new coordination compounds containing trivalent rare earth ions (RE^{3+}) have been attracted attention in last decades by their improvement in performance of devices. The RE^{3+} -complexes have been used in the fluorimetric determination, electroluminescent (EL) devices, ultraviolet dosimeters and fluorescent labels, molecular biology, etc. [1–4].

The intraconfigurational 4f–4f transitions in rare earth ions are parity forbidden (Laporte rule), consequently the absorp-

tion and emission spectra of the RE^{3+} ions show weak intensity. However, the population of the excited states of the RE^{3+} ions may be increased by coordination to organic ligands, which act as sensitizers. The ligands that present this property were called by Lehn [5] as “antennas”, that could be seen as light conversion molecular devices (LCMD). In RE^{3+} -complexes, the organic ligands absorb and transfer energy efficiently to the metal ion (intramolecular energy transfer) and consequently increasing their luminescence intensity. One of the many potential advantages of RE^{3+} ions for applications as LCMDs is the narrow bands displayed by the emission spectra of RE-complexes due to the effective shield of the 4f^N orbitals from influence of the chemical environment by the 5s5p orbitals, consequently RE^{3+} -compounds exhibit almost

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pure color (monochromatic behavior). Occasionally the 4f transitions are only slightly shifted in different chemical environment around the metal ion.

Among the RE^{3+} -complexes those using β -diketonate ligands as sensitizers have attracted intense research interest due to their higher luminescence intensity, which can be explained by the high absorption coefficient of this kind of ligand and the very efficient ligand-to-metal ions energy transfer [4–7]. In particular, Eu^{3+} -dibenzoylmethane (Eu^{3+} -DBM) ternary complexes have exhibited appealing and desirable photo and electroluminescent properties [8]. However, in the hydrated Eu^{3+} - β -diketonate complexes the water molecules act as effective luminescence quencher due to OH oscillators. In order to improve the luminescent properties, the water molecules are generally substituted by a second kind of organic ligands such as sulfoxide, phosphine oxide, heteroaromatic that protect the first coordination sphere of solvent molecules in solution minimizing the contribution of the radiationless processes. Besides, these ligands can improve the volatility and carrier-transport ability for application in electroluminescent devices. Gao et al. [9] have prepared the $[\text{Eu}(\text{DBM})_3\text{L}]$ complex, where $\text{L} = 2$ -phenylimidazo[4,5-f]1,10-phenanthroline, that was easily evaporated and presented higher luminescence intensity.

Since the position of the triplet states (T) of the ligands play an important role in the intramolecular energy transfer process of the RE^{3+} -complexes, the DBM ligand acts as a good “antenna” for the Eu^{3+} and Sm^{3+} ions, considering that its lowest excited triplet state is found at around $21,600\text{ cm}^{-1}$ [9–11]. Generally, in Eu^{3+} -coordination compounds the energy transfer occurs from triplet state (T) of the organic ligand to the excited $^5\text{D}_J$ level ($J = 0, 1, 2$). Therefore, the energy transfer probability from T state to $^5\text{D}_0$ level is very small, except when the ligand triplet state is located between the $^5\text{D}_1$ and $^5\text{D}_0$ states. Particularly, the Eu -DBM complexes present the resonance conditions favoring the ligand-to-metal energy transfer $\text{T} \rightarrow ^5\text{D}_1$. Moreover, the effect of anisotropic DBM polarizability on the intensity parameters for Eu -DBM complexes have been reported [12,13]

In this work, we have synthesized and characterized novel highly luminescent europium complexes containing dibenzoylmethane and sulfoxide as ligands (Fig. 1). The T states of the DBM ligand are determined based on the phosphorescent

spectra of the trivalent gadolinium complexes. The ligand-to-metal energy transfer ($\text{L} \rightarrow \text{Eu}^{3+}$) and the experimental intensity parameters are investigated. The emission quantum efficiency of the emitting $^5\text{D}_0$ level of the Eu^{3+} -complexes are discussed and compared with the experimental quantum yield.

2. Experimental

$\text{RECl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{RE}^{3+} = \text{Eu}$ and Gd) were prepared from RE_2O_3 (from Aldrich) and hydrochloride acid (from Merck). The dibenzoylmethane (from Merck) and sulfoxide ligands: methyl sulfoxide (DMSO), benzyl sulfoxide (DBSO), phenyl sulfoxide (DPSO) and *p*-tolyl sulfoxide (PTSO) were purchased from Aldrich and used as received. The $[\text{RE}(\text{DBM})_3 \cdot \text{H}_2\text{O}]$ complex utilized as precursors were synthesized according to the reference [14]. In the preparation of the $[\text{RE}(\text{DBM})_3 \cdot \text{L}_2]$ complexes with sulfoxide ligands the precursor hydrated complex and sulfoxide ligand were separately dissolved in acetone and mixed in 1:2 (hydrated complex:sulfoxide ligand) molar ratio. After evaporation of the solvent a viscous product was produced, which was dried under vacuum in presence of phosphorus pentoxide as secant agent in desiccator.

The carbon and hydrogen contents were determined from elemental analyses, using a Perkin–Elmer model 240 micro-analyzer, while the RE^{3+} contents (Eu and Gd) were performed by complexometric titration with EDTA [15]. The infrared absorption spectra of the free ligands (DBM, DMSO, DBSO, DPSO and PTSO) and complexes in KBr pellets were recorded in the spectral range of $400\text{--}4000\text{ cm}^{-1}$ on a Bomen model MB-102 spectrophotometer.

The X-ray powder diffraction patterns from 10 to 60° (2θ) were recorded on a Zeiss Jena diffractometer model URD-6 using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405\text{ \AA}$) at 40 kV and 40 mA . Thermogravimetric (TG) curves of the complexes were recorded with a TG-50 thermobalance (Shimadzu), using Pt crucibles with mass sample around 6 mg , under dynamic condition of N_2 atmosphere (50 mL min^{-1}) and heating rate of $10^\circ\text{C min}^{-1}$.

The measurement of refraction index of the $[\text{Eu}(\text{DBM})_3(\text{PTSO})_2]$ complex was obtained by measuring

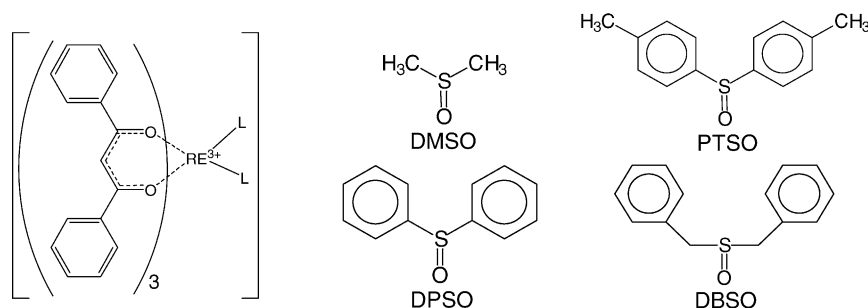


Fig. 1. Structural formulas for $[\text{Eu}(\text{DBM})_3(\text{L})_2]$, where $\text{L} = \text{DBSO}$, DMSO , DPSO and PTSO .

the Brewster angle condition of the thin film using the Abelès–Hacskalylo technique [16].

The excitation and emission spectra of the solid state samples at room (~ 298 K) and liquid nitrogen temperatures were collected at an angle of 22.5° (front face) in a spectrofluorimeter (SPEX-Fluorolog 2) with double grating 0.22 m monochromator (SPEX 1680), and a 450 W Xenon lamp as excitation source. To eliminate the second-order diffraction of the source radiation, a cut-off filter was used in the measurements. All spectra were recorded using a detector mode correction. The luminescence decay curves of the emitting levels were measured using a phosphorimeter SPEX 1934D, which was coupled to the spectrofluorometer. The spectral intensities were automatically corrected for the photomultiplier response.

3. Results and discussion

As it can be seen in Table 1 the elemental analysis data are in good concordance with the general formulas $[\text{RE}(\text{DBM})_3(\text{H}_2\text{O})]$ and $[\text{RE}(\text{DBM})_3(\text{L})_2]$ (where $\text{L} = \text{DMSO}$, DPSO , DBSO and PTSO). It is observed that two sulfoxide ligands are coordinated to trivalent rare earth ions, indicating the higher coordinating ability of the sulfoxide ligands that overcome the steric interactions as compared with the water molecule.

The IR spectral data presented a displacement of the $\text{C}=\text{O}$ stretching from 1560 cm^{-1} in the free DBM ligand to 1520 cm^{-1} for the complexes, suggesting that this ligand is coordinated to the rare earth ion through the oxygen atoms. It is also observed that the band assigned to the $\text{S}=\text{O}$ stretching at around 1032, 1024, 1038 and 1038 cm^{-1} in the free DBSO, DMSO, DPSO and PTSO ligands are displaced to 1026, 1018, 1022 and 1028 cm^{-1} in the RE^{3+} -complexes, respectively; indicating that the coordination of the sulfoxide ligands to metal ion occurs through the oxygen atom, which reduced strongly the double bond character of the $\text{S}-\text{O}$ bond. These results reflect the high affinity of rare earth ions by hard base. Furthermore, the absence of a broad band around

3500 cm^{-1} confirms that the compounds with sulfoxide ligands are anhydrous.

TG and DTG curves of $[\text{RE}(\text{DBM})_3(\text{H}_2\text{O})]$ complexes ($\text{RE}^{3+} = \text{Eu}$ and Gd) (figure not shown) presented weight loss of $\sim 2.5\%$ in the range of $70\text{--}240^\circ\text{C}$, which is associated to loss of one water molecule, corroborating the elemental analysis data. It was also observed in the TG/DTG curves that the decomposition of the organic ligands (DBM and sulfoxides) occurs simultaneously in the temperature interval of $120\text{--}700^\circ\text{C}$. Based on the TG/DTG curves, the complexes presented the following order of thermal stability with ligands: $\text{H}_2\text{O} < \text{DPSO} < \text{DBSO} < \text{DMSO} < \text{PTSO}$.

The X-ray powder diffraction patterns (figure not shown) of the $[\text{RE}(\text{DBM})_3(\text{L})_2]$ complexes suggest different crystalline forms among complexes containing different ligands. On the other hand, the Eu and Gd complexes with the same ligand exhibit similar X-ray patterns, which allow grouping them in the same isomorphic series.

3.1. Photoluminescent study

The emission spectra of the Gd^{3+} -DBM complexes recorded from 400 to 750 nm, at 77 K, with excitation monitored at ligand $\text{S}_0 \rightarrow \text{S}_1$ transition around 350 nm are showed in Fig. 2a–e. In particular, the emission spectra of the Gd^{3+} complexes are appropriate to obtain information on the energy levels of the organic ligands, considering that the first excited ${}^6\text{P}_{7/2}$ level of the trivalent gadolinium ion is around $32,000\text{ cm}^{-1}$ above the ${}^8\text{S}_{7/2}$ ground state [17]. Generally, the triplet states of organic ligands are located below the ${}^6\text{P}_{7/2}$ level from Gd^{3+} ion, hindering the intramolecular energy transfer from organic ligands to gadolinium ion.

The emission spectra of the Gd-complexes (Fig. 2a–e) exhibit intense broad bands in the spectral range from 480 to 720 nm with a maximum at about 544 nm assigned to the phosphorescence from $\text{T} \rightarrow \text{S}$ transition centered in the DBM ligand. These spectra also display a very weak band from 400 to 480 nm, which could be associated to fluorescence from excited singlet states of the DBM ligand.

Fig. 3a–e show the excitation spectra of the Eu^{3+} -complexes obtained at liquid nitrogen temperature in the spectral range from 250 to 590 nm, under emission on hypersensitive ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition at 612 nm. The spectra display a broad high intensity band in the range 250–500 nm, which is attributed to the DBM centered transition, evidencing that the excitation of Eu^{3+} ion is caused by an indirect process via an efficient intramolecular energy transfer from DBM to this metal ion. It is also showed in (Fig. 3a–e) that these broad bands from the ligands are overlapped with the sharp peaks assigned to the intraconfigurational-4f transitions arising from the ground state ${}^7\text{F}_0$ to the following excited levels: ${}^4\text{G}_6$ (361 nm), ${}^5\text{H}_4$ (374 nm) and ${}^5\text{L}_6$ (394 nm). Other narrow bands corresponding to the Eu^{3+} ion centered ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ (464 nm), ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ (532 nm) and ${}^7\text{F}_0 \rightarrow {}^4\text{G}_6$ (578 nm) transitions are also observed [18,19].

Table 1

Analytical data for hydrated and $[\text{RE}(\text{DBM})_3(\text{L})_2]$ complexes, where $\text{L} = \text{DBSO}$, DMSO , DPSO and PTSO

Compound	%RE		%C		%H	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
$[\text{Eu}(\text{DBM})_3(\text{H}_2\text{O})]$	18.10	18.08	64.37	64.28	4.20	4.36
$[\text{Eu}(\text{DBM})_3(\text{DMSO})_2]$	15.48	15.54	60.18	59.93	4.64	4.46
$[\text{Eu}(\text{DBM})_3(\text{DPSO})_2]$	12.28	12.39	67.58	67.28	4.36	4.57
$[\text{Eu}(\text{DBM})_3(\text{DBSO})_2]$	11.87	11.85	68.37	67.73	4.79	4.84
$[\text{Eu}(\text{DBM})_3(\text{PTSO})_2]$	11.57	11.85	68.37	68.26	4.79	4.94
$[\text{Gd}(\text{DBM})_3(\text{H}_2\text{O})]$	18.63	18.61	63.96	63.98	4.17	4.25
$[\text{Gd}(\text{DBM})_3(\text{DMSO})_2]$	16.09	15.99	59.86	60.15	4.61	4.55
$[\text{Gd}(\text{DBM})_3(\text{DPSO})_2]$	12.28	12.39	67.29	66.97	4.34	4.48
$[\text{Gd}(\text{DBM})_3(\text{DBSO})_2]$	11.98	12.21	68.09	67.88	4.77	4.93
$[\text{Gd}(\text{DBM})_3(\text{PTSO})_2]$	12.21	12.07	68.09	68.45	4.77	4.82

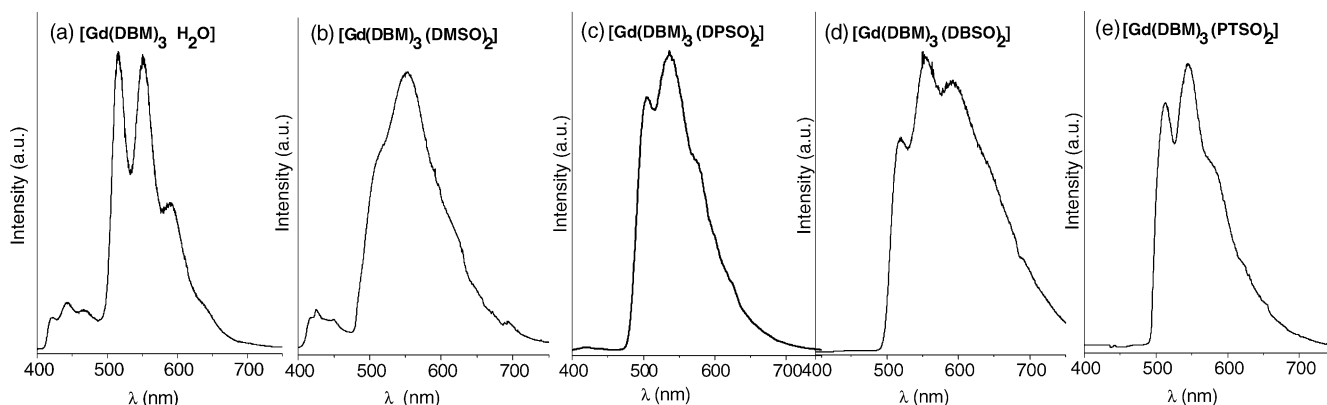


Fig. 2. Emission spectra of the hydrated and $[\text{Gd}(\text{DBM})_3(\text{L})_2]$ complexes at 77 K recorded from 400 to 750 nm, at 77 K, with excitation monitored at 350 nm, containing the following ligands: (a) H_2O , (b) DMSO, (c) DPSO, (d) DBSO and (e) PTSO.

The emission spectra of the trivalent europium complexes recorded in the range of 450–720 nm, at 77 K, under excitation at around 395 nm are presented in Fig. 4a–e. The emission spectra obtained at room temperature (figure not shown) present similar profiles as those recorded at 77 K, but with lower resolutions, indicating that there is no structural change with temperature reduction. The emission spectrum of the hydrated precursor (Fig. 4a) presents similar spectral profile as compared with that reported by Kirby and Richardson [12], corroborating that the hydrated complex synthesized presents the formula $[\text{Eu}(\text{DBM})_3\text{H}_2\text{O}]$.

When examining the luminescence spectra of Eu^{3+} complexes in Fig. 4a–e the intense broad band is not displayed in the interval of 480–700 nm arising from phosphorescence of the organic ligands exhibited for the Gd^{3+} -complexes (Fig. 2a–e). These spectral data indicate that the energy transfer from lowest triplet state of the DBM ligands to europium ion is very efficient. Since the fluorescence bands (400–470 nm) from singlet state of the DBM ligand are not presented in the emission spectra of the Eu^{3+} -complexes, the intramolecular energy transfer can also be occurring from the S_1 state to the excited $^5\text{D}_4$ or $^5\text{L}_6$ levels of the Eu^{3+} ion.

The principal features appearing in the emission spectra of the Eu^{3+} -complexes (Fig. 4a–e) are the presence of the narrow bands that are attributed to the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ transitions ($J=0-4$), which are dominated by the so-called hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. The weak emission bands arising from $^5\text{D}_1 \rightarrow ^5\text{F}_J$ transitions ($J=0, 1$ and 2) at 526, 535 and 553 nm, respectively, have been observed (inset Fig. 4a–e).

The presence of only one peak corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition around 579 nm (Fig. 4a–e) suggests the existence of one local site of symmetry for the Eu-complexes. The monoexponential behavior of the luminescence decay curves of the emitting $^5\text{D}_0$ level for the Eu^{3+} -complexes are in agreement with one chemical environment (figure not shown). Additionally, the presence of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition for all complexes suggests that the europium ion reside at C_s , C_n or C_{nv} site symmetries. Besides, the $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ transitions are split in their maximum number of $(2J+1)$ -components (Table 2) exhibiting different spectral profiles, except for the complexes with DMSO and DBSO that present similar profile (Fig. 4b and d) indicating that the Eu^{3+} -coordination unit possesses similar point-group symmetry.

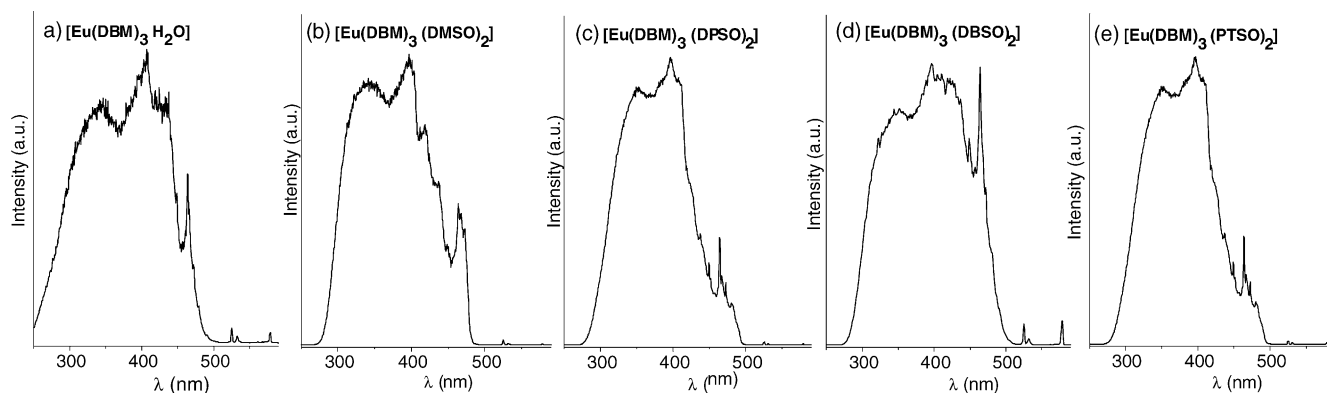


Fig. 3. Excitation spectra of the hydrated and $[\text{Eu}(\text{DBM})_3(\text{L})_2]$ complexes recorded from 400 to 750 nm, at 77 K, with excitation monitored on hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at around 612 nm, containing the following ligands: (a) H_2O , (b) DMSO, (c) DPSO, (d) DBSO and (e) PTSO.

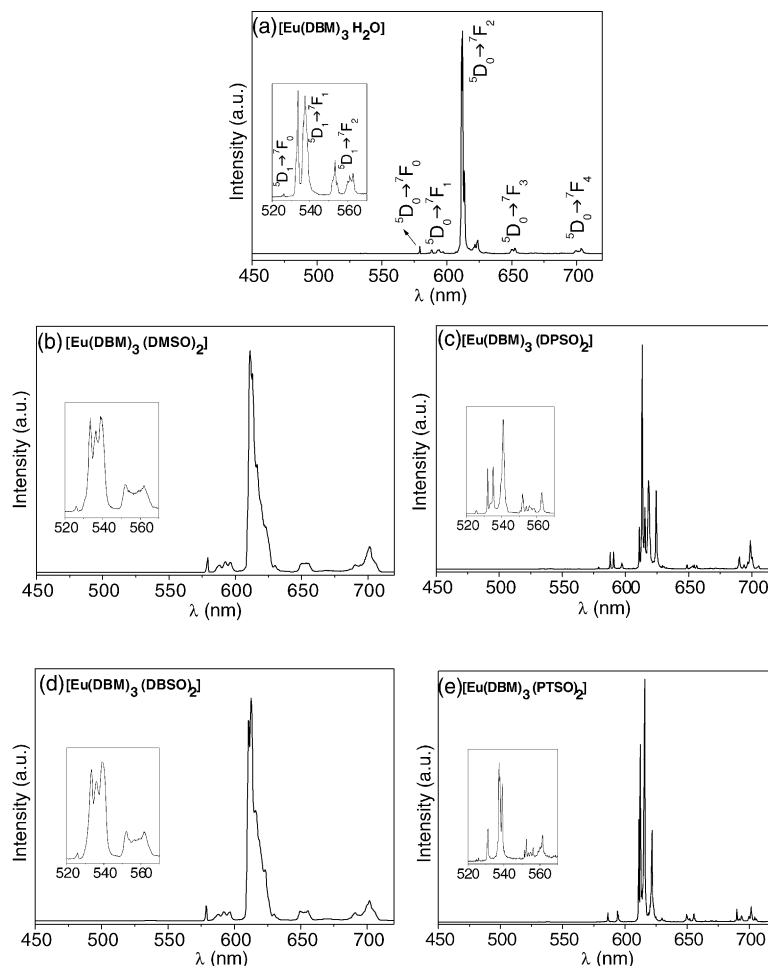


Fig. 4. Emission spectra of the hydrated and $[\text{Eu}(\text{DBM})_3(\text{L})_2]$ complexes at 77 K recorded from 400 to 750 nm, at 77 K, under excitation at around 395 nm, containing the following ligands: (a) H_2O , (b) DMSO, (c) DPSO, (d) DBSO and (e) PTSO.

According to the emission spectral data of the $[\text{Eu}(\text{DBM})_3(\text{L})_2]$ complexes, where L is a sulfoxide ligand, display unusually high intense $^5\text{D}_0 \rightarrow ^7\text{F}_3$ transition, which was found to be somewhat stronger than it was observed for most other luminescent Eu^{3+} coordination compounds [12]. This behavior indicates that there is a significant J – J' mixing in order for the $^5\text{D}_0 \rightarrow ^7\text{F}_3$ transition to acquire dipole strength.

Spectroscopic studies [12,20] have showed that the major contribution to $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}_3$ electric dipole strength are “borrowed” from the strongly forced electric dipole allowed $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, considering that there is a regard crystal-field induced mixing of the $^7\text{F}_0$ and $^7\text{F}_3$ intermediate-coupling states with components of the $^7\text{F}_2$ state. Generally, the magnitude of the J – J' mixing effect (where $J=0$ and $J'=2$) is determined from the R_{02} experimental parameter, which is defined as the ratio between the intensities of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions [20]. The R_{02} values for the complexes following the order (Table 3): $\text{PTSO} < \text{DBSO} < \text{DMSO} < \text{DPSO} < \text{H}_2\text{O}$. These values show that the sulfoxide complexes present mi-

nor values of R_{02} parameter than hydrated one, suggesting a much lower magnitude of the J -mixing effect.

The standard theory of 4f–4f intensities gives the intensity Ω_λ parameters (where $\lambda=2$ and 4), which is the integrated coefficient of spontaneous emission (radiative) of a transition between two manifolds J and J' . These parameters contain the contributions from the forced electric dipole and dynamic coupling mechanisms. Since the radiative decay rate of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ allowed by magnetic dipole transition is almost independent of the crystal field environment around the europium ion (A_{01} value is estimated to be around 50 s^{-1}), this transition can be taken as a internal standard one in order to determine the radiative decay rates assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_{2,4}$ transitions (A_{02} and A_{04}). The coefficient of spontaneous emission A is given by:

$$A = \frac{4e^2\omega^3}{3\hbar c^3} \chi \sum_{\lambda=2,4} \Omega_\lambda \langle ^5\text{D}_0 || U^{(\lambda)} || ^7\text{F}_J \rangle^2 \quad (1)$$

where $\chi = n_0(n_0^2 + 2)^2/9$ is a Lorentz local field correction. The square reduced matrix elements are $\langle ^5\text{D}_0 || U^{(2)} || ^7\text{F}_2 \rangle^2 =$

Table 2

Energy levels of the $^5D_{0,1} \rightarrow ^7F_{0-4}$ manifolds (cm^{-1}) observed in the emission spectra of hydrated and $[\text{Eu}(\text{DBM})_3(\text{L})_2]$ complexes, where L = DBSO, DMSO, DPSO and PTSO

Transitions	H ₂ O	DBSO	DMSO	DPSO	PTSO
$^5D_1 \rightarrow ^7F_0$	19,004	19,011	19,033	19,019	18,825
	18,734	18,748	18,797	18,741	18,615
$^5D_1 \rightarrow ^7F_1$	18,643	18,636	18,727	18,657	18,601
	18,608	18,553	18,685	18,553	18,546
	18,077	18,116	18,173	18,109	18,136
$^5D_1 \rightarrow ^7F_2$	18,038	17,825	18,044	17,806	18,096
	17,857	17,794	17,992	17,794	17,979
	17,825	–	17,908	–	17,857
	17,775	–	17,768	–	17,813
$^5D_0 \rightarrow ^7F_0$	17,265	17,265	17,277	17,271	17,289
	17,001	17,007	17,007	17,013	17,059
$^5D_0 \rightarrow ^7F_1$	16,835	16,869	16,932	16,892	16,835
	16,750	16,773	16,745	16,756	16,812
	16,356	16,361	16,367	16,377	16,361
$^5D_0 \rightarrow ^7F_2$	16,335	16,313	16,308	16,324	16,329
	16,297	16,223	16,250	16,234	16,244
	16,088	16,134	16,176	16,166	16,234
	16,031	16,046	16,021	16,046	16,082
	15,389	15,390	15,413	15,399	15,394
$^5D_0 \rightarrow ^7F_3$	15,366	15,366	15,309	15,375	15,380
	15,328	15,305	15,281	15,309	15,333
	15,216	15,277	15,235	15,263	15,253
	–	15,263	–	–	–
	14,302	14,480	14,489	14,472	14,493
$^5D_0 \rightarrow ^7F_4$	14,286	14,405	14,413	14,249	14,455
	14,245	14,397	14,351	–	14,422
	14,213	14,261	14,310	–	14,409
	–	14,249	14,278	–	14,290
	–	–	14,196	–	14,253
	–	–	14,176	–	14,192
	–	–	–	–	14,168

0.0032 and $\langle ^5D_0 || U^{(4)} || ^7F_4 \rangle^2 = 0.0023$ in Eq. (1), and an average index of refraction experimentally determined as 1.65 was used. In this case the A values are obtained by using the relation: $A = A_{01} \sum_{\lambda} S_{0\lambda} \sigma_1 / S_{01} \sigma_{\lambda}$ where $S_{0\lambda}$ is the area under the emission curve related to the $^5D_0 \rightarrow ^7F_{\lambda}$ transitions, σ_{λ} is the energy barycenter of these transitions. The Ω_6 intensity parameter was not included in this calculation since the $^5D_0 \rightarrow ^7F_6$ (around 850 nm) could not be observed. The lifetime (τ), non-radiative (A_{nrad}) and radiative (A_{rad}) rates are related through the following equation

$A_{\text{tot}} = 1/\tau = A_{\text{rad}} + A_{\text{nrad}}$, where the A_{rad} rate was obtained by summing over the radiative rates A_{0J} for each $^5D_0 \rightarrow ^7F_J$ transitions ($A_{\text{rad}} = \sum_J A_{0J}$). The emission quantum efficiency of the emitting 5D_0 level is given by:

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nrad}}} \quad (2)$$

The experimental intensity parameters (Table 3) give the influence of the DBM and sulfoxides ligands on the europium luminescence behavior by determining the radiative contribution for the depopulation of the emitting level, 5D_0 , and the emission quantum efficiency.

A point to be noted is that the Ω_2 values (Table 3) are higher for the Eu^{3+} -complexes with sulfoxide ligands than for the monohydrated complex (except in the case of the $[\text{Eu}(\text{DBM})_3(\text{DBSO}_2)]$). This result is associated with the higher polarizability of the oxygen sulfoxide ligands as compared with the oxygen belong to the water molecule. The lowest value of the Ω_2 parameter for the $[\text{Eu}(\text{DBM})_3(\text{DBSO}_2)]$ is probable due to the different positions of ligand atoms with respect to the Eu^{3+} ion (i.e. the geometry of the complex). One interesting feature of the Ω_2 parameter is that the highest value ($\Omega_2 = 61.9 \times 10^{-20} \text{ cm}^2$) was found for the $[\text{Eu}(\text{DBM})_3(\text{PTSO}_2)]$ complex, which indicates the highest hypersensitive behavior of the $^5D_0 \rightarrow ^7F_2$ transition, which reflects the most polarizable chemical environment of the Eu^{3+} ion. These data are consistent with the high contribution of the *p*-tolyl substitute group in the sulfoxide ligand and that increases the polarizability of the sulfoxide oxygen. Also are noted that the highest value of the Ω_4 parameter was obtained to the $[\text{Eu}(\text{DBM})_3(\text{PTSO}_2)_2]$ complex, indicating the highest sensitive behavior of the $^5D_0 \rightarrow ^7F_4$ transition possibly as a consequence of the basicity of the oxygen donor.

Table 3 presents the values of emission quantum efficiency (η) for the hydrated $[\text{Eu}(\text{DBM})_3\text{H}_2\text{O}]$ and $[\text{Eu}(\text{DBM})_3(\text{L})_2]$ complexes. As can be observed the substitution of the water molecule in the first coordination sphere of the Eu^{3+} ion by sulfoxide ligands increase the emission quantum efficiency (η), reflecting a significant decrease in the non-radiative rates from hydrated compound ($A_{\text{nrad}} = 3093 \text{ s}^{-1}$) to sulfoxide complexes ($A_{\text{nrad}} = 2000 \text{ s}^{-1}$). This behavior is a consequence of the absence of water molecules coordinated to the Eu^{3+} ion in the complexes with sulfoxide ligands, considering that the H_2O molecule acts as efficient luminescence intensity quencher via non-radiative processes due to an ef-

Table 3

Experimental intensity parameters (A_{nrad} , A_{rad} , A_{total} , Ω_{λ} , R_{02}), lifetime (τ), emission quantum efficiency (η) and emission quantum yield (q) for hydrated and $[\text{Eu}(\text{DBM})_3\text{L}_2]$ complexes, where L = DBSO, DMSO, DPSO and PTSO, at room temperature

Ligand	$A_{\text{rad}} (\text{s}^{-1})$	$A_{\text{nrad}} (\text{s}^{-1})$	$A_{\text{total}} (\text{s}^{-1})$	$\Omega_2 (10^{-20} \text{ cm}^2)$	$\Omega_4 (10^{-20} \text{ cm}^2)$	R_{02}	τ (ms)	η (%)	q_x (%)
H ₂ O	1200	3093	4293	37.0	1.6	0.0180	0.233	37	1
DPSO	1508	1754	3262	42.9	11.1	0.0090	0.307	62	16
DBSO	1217	1204	2421	33.8	10.7	0.0025	0.413	67	62
DMSO	1538	1887	3425	44.7	9.7	0.0084	0.292	60	49
PTSO	2098	1763	3861	61.9	12.8	0.0004	0.259	72	70

efficient coupling between the 5D_0 emitting level and the O–H oscillators of higher energy.

3.1.1. Experimental emission quantum yield (q)

The emission quantum yield (q), is defined as the ratio between the number of photons emitted by the rare earth ion and the number of photons absorbed by the ligand. Following the method developed by Bril and Veenis [21].

The experimental emission quantum yield q_x of a sample is thus determined as follows:

$$q_x = \left(\frac{1 - r_{ST}}{1 - r_x} \right) \left(\frac{\Delta\Phi_x}{\Delta\Phi_{ST}} \right) q_{ST} \quad (3)$$

where r_{ST} and r_x are the amounts of exciting radiation reflected by the of the standard and by the sample, respectively, and q_{ST} is the quantum yield of the standard phosphor. The terms $\Delta\Phi_x$ and $\Delta\Phi_{ST}$ give the integrated photon flux (photons s^{-1}) for sample and standard phosphor, respectively. In this work the standard phosphor was sodium salicylate, which exhibits broad emission band with a maximum at 450 nm and $q_{ST} = 55\%$, at room temperature. A detail description of this method has been reported elsewhere in reference [22].

The values of emission quantum yield (q_x) for Eu–DBM complexes synthesized present the following order: $H_2O < DPSO < DMSO < DBSO < PTSO$. This behavior shows that the substitution of water molecule by sulfoxide ligands increases the emission quantum yield values as well as occurs with the emission quantum efficiency (η). The high difference between the values of q and η for the hydrated and $[Eu(DBM)_3(DPSO)_2]$ complexes (Table 3) may be probably due to the energy back-transfer global from the rare earth to ligand.

The higher values of the emission quantum efficiency (η) and quantum yield (q) for the $[Eu(DBM)_3(L)_2]$ (Table 3) (where $L = DMSO, DBSO$ and $PTSO$) suggesting that in these complexes the organic ligands may act efficient antenna.

Based on emission spectra of Eu-complexes, the (x, y) color coordinates were determined. The values of coordinates (around $x = 0.66$ and $y = 0.33$) are located in the red vertex in the Commission Internationale l'Eclairage (CIE) chromaticity diagram, indicating that the red emission of the Eu^{3+} –DBM compounds exhibit monochromatic color [23].

4. Concluding remarks

In the $RE(DBM)_3(L)_2$ complexes synthesized (where $RE = Eu^{3+}, Gd^{3+}$ and $L = DBSO, DMSO, DPSO$ and $PTSO$), the metal–ligand interaction occurs through the oxygen atoms. The Eu-complexes exhibit characteristic bright luminescence under ultraviolet radiation by the organic ligand followed by energy transfer to the europium ion. The only one peak exhibited by the $^5D_0 \rightarrow ^7F_0$ transition and the monoexponential behavior for the decay curve of emitter 5D_0 level indicate the presence of only one Eu^{3+} site in the chemical

environment. The $[Eu(DBM)_3(PTSO)_2]$ showed higher value of the Ω_2 parameter than other complexes in this work, which reflects a highly polarizable chemical environment around the Eu^{3+} ion in the complex. The higher values q and η for the Eu-complexes with DMSO, DBSO and PTSO sulfoxides suggesting that these new complexes are promising Light Conversion Molecular Devices (LCMDs), such as in electroluminescence devices. The (x, y) chromaticity coordinates of the Eu-complexes are excellent as a red luminescent material when compared to the $Y_2O_2S:Eu^{3+}$ phosphor.

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