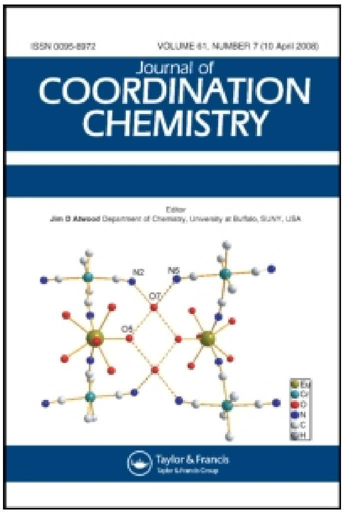

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Synthesis, characterization, solid state and aqueous solution fluorescence study for lanthanide-crown ether-terpyridine complexes

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Synthesis, characterization, solid state and aqueous solution fluorescence study for lanthanide-crown ether-terpyridine complexes

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The complexes [Eu(12-crown-4)(terpy)(H_2O)]3Cl, [Eu(15-crown-5)(terpy)]3Cl, [Tb(12-crown-4)(terpy)(H_2O)]3Cl, [Tb(15-crown-5)(terpy)]3Cl, [Gd(12-crown-4)(terpy)(H_2O)]3Cl and [Gd(15-crown-5)(terpy)]3Cl (terpy = $2,2',6',2''$-terpyridine) were synthesized and characterized by CHN elemental analysis, infrared spectroscopy and fluorescence spectroscopy. Emission spectra were obtained on both, solid state and aqueous solutions for europium and terbium complexes. The complexes exhibit good emission, even in aqueous solution, enhancing their potential for biological applications. The reduction of emission intensity, from solid state to aqueous solution, is lower for europium complexes, in comparison to terbium complexes. The [Eu(12-crown-4)(terpy)(H_2O)] · 3Cl complex exhibits an emission lifetime of 0.64 ms while [Eu(15-crown-5)(terpy)] · 3Cl exhibits a value of 0.38 ms. Furthermore, the 15-crown-5 complex emission intensity is about 3.8 times larger than the emission intensity of the 12-crown-4 complex. This ratio (3.8) is the same as observed for the A_{RAD} and A_{NRAD} for the aqueous solutions: $1225.5/339.5 = 3.6$. The aqueous solution quantum yield is higher for [Eu(12-crown-4)(terpy)(H_2O)]3Cl in comparison with [Eu(15-crown-5)(terpy)]3Cl, suggesting that 12-crown-4 exhibits a more suitable ratio than 15-crown-5.

Keywords: Luminescence; Lanthanides; Crown ether

1. Introduction

Lanthanide complexes with organic ligands are efficient Light Conversion Molecular Devices (LCMD), are an important theme in coordination chemistry and have been investigated by several research groups [1–3]. Efficient LCMDs have potential applications such as luminescent probes, in photosensitive bioinorganic compounds [4], fluoroimmunoassays [5], fluorescent lighting [6], luminescent sensors for chemical species [7] and electroluminescent devices [8].

Since the biological medium is mainly aqueous, water soluble luminescent probes could be very useful as biological chemical sensors. However, in order to penetrate the

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cells, a compound must penetrate a "fatty" layer around the cells. In this connection, crown ethers could be very useful ligands, since they exhibit oxygen atoms that are pointing "inward", providing very stable bonds with metal cations, e.g. alkali metals, as well as methylene groups pointing "outward", making them liposoluble compounds.

This article reports the synthesis, characterization and photoluminescence properties of six new trivalent lanthanide complexes ($Ln^{3+} = Eu$, Tb and Gd) with 12-crown-4 or 15-crown-5 and 2,2′:6′,2″-terpyridine (terpy). Based on the experimental data for $[Eu(12\text{-crown-}4)(terpy)(H_2O)]\cdot 3Cl$ and $[Eu(15\text{-crown-}5)(terpy)]\cdot 3Cl$, the intensity parameters Ω_2 and Ω_4 were calculated. The energy transfer process from the triplet state (T) of ligands to the Eu^{3+} ion, lifetime, radiative and non-radiative rates and quantum efficiency were also investigated.

2. Experimental

2.1. *Synthesis*

The starting chemicals were $EuCl_3\cdot 6H_2O$, $TbCl_3\cdot 6H_2O$, $GdCl_3\cdot 6H_2O$, 2,2′,6′,2″-terpyridine (terpy), 12-crown-4 and 15-crown-5 (Aldrich). The lanthanide compounds were synthesized from a mixture of 1 : 1 (mol : mol) of $LnCl_3$ and the crown ether (12-crown-4 or 15-crown-5) dissolved in 20 cm^3 of a 1 : 1 (v : v) ethanol/acetone solution. After precipitation of the complex (24 h) 2,2′ : 6′,2″-terpyridine was added (1 : 1). A light yellow precipitate was formed, which was filtered off, washed with cold acetone and dried under vacuum at room temperature.

2.2. *Measurements*

Carbon, nitrogen and hydrogen percentages in the complexes were determined from elemental analyses, using a Perkin-Elmer Model 240 microanalyzer. The spectral analyses (emission spectra) and quantum yield were performed at room temperature and 77 K (N_2) with a Jobin Yvon Ramanor U-1000 spectrometer, using a 450 W Xe lamp. The detector was a RCA C31034 photomultiplier tube or an intensified diode array. Excitation spectra of the complexes were recorded on an ISS K2 Multifrequency Phase Fluorometer. The IR vibrational spectra were obtained on a Bruker IF 566 FTIR spectrophotometer (KBr discs). The emission lifetime measurements were obtained in a SPEX Fluorog F212 spectrofluorimeter with a 150 W Xe lamp.

3. Theoretical

3.1. *Intensities parameters*

From the spectra shown in figure 1, it is possible to calculate the Ω_λ ($\lambda = 2$ and 4) intensity parameters by using the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions. As usual, the procedure is to express the emission intensity as:

$$I_{J-J'} = \hbar\omega_{J-J'} A_{J-J'} N_J \qquad (1)$$

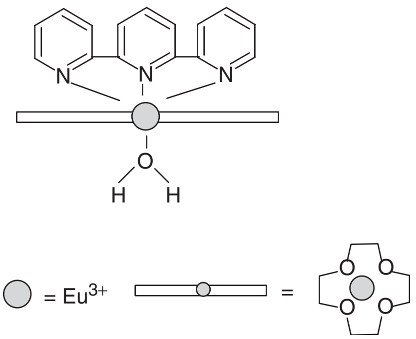

Figure 1. Schematic structure (out of scale) of the complex cation [Eu(12-crown-4)(terpy)(H_2O)].

where $\hbar\omega_{J-J'}$ is the transition energy (J–J'), $A_{J\text{–}J}'$ is the corresponding coefficient of spontaneous emission and N_J is the population of the emitting level (the area under the emission curve). In practice, relative intensities are measured and for the Eu(III) ion, the reference is the magnetic dipole $^5D_0 \rightarrow {}^7F_0$ transition.

The experimental intensity parameter Ω_λ is determined according to equation [9]:

$$\Omega_\lambda = \frac{3\hbar C^3 A_{0-\lambda}}{4e^2\omega^3\chi\langle {}^7F_\lambda \| U^{(\lambda)} \| {}^5D_0\rangle^2} \tag{2}$$

In this procedure, J-mixing is the appropriate reduced matrix element taken from ref. [10]. An average index of refraction equal to 1.5 has been used in the Lorentz local field, which is present in the expressions for the coefficients of spontaneous emission:

$$\chi = \frac{\eta(\eta^2+2)^2}{9} \tag{3}$$

The experimental radiative rate of spontaneous emission, A_{RAD} (table 2) was determined by summing the A_{0-J} (where $J = 1$, 2 and 4) values, obtained by the relation:

$$A_{0-J} = A_{01}\left(\frac{S_{0J}}{S_{01}}\right)\left(\frac{\upsilon_{01}}{\upsilon_{0J}}\right) \tag{4}$$

where S_{01} and S_{0J} are the integrated intensities of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_J$ transitions ($J = 2$ and 4). In this equation, $\upsilon_{01}$and υ_{0J} are the energy barycenters. This relation gives the coefficient of spontaneous emission, A_{01} in equation (2), $A_{01} = 0.31 \cdot 10^{-11}(\eta)^3(\upsilon_{01})^3$, and its value is estimated to be around $50\,\mathrm{s}^{-1}$ [11]. The obtained results are summarized in table 2.

The Ω_2 and Ω_4 values indicate that the dynamic coupling mechanism is operative and possibly dominant with respect to the forced electric dipole mechanism. This may be explained by the fact that the atoms, or groups of atoms, to which the Eu^{3+} ion is coordinated, are highly polarizable [12].

Based on the emission spectrum and lifetime of the $^5D_0$ emitting level ($\tau = 0.64$ and 0.38 ms, for the 12-crown-4 and 15-crown-5 complexes, respectively) the emission quantum efficiency (η) of the europium ion in the compounds was calculated. First, the coefficients A_{02} and A_{04} of the forced electric dipole transitions $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$, respectively, were calculated taking the magnetic dipole of the

$^5D_0 \rightarrow {}^7F_1$ transition. By the relation between the lifetime of the emitting state and the total decay rate, $A_{\mathrm{total}} = 1/\tau = A_{\mathrm{RAD}} + A_{\mathrm{NRAD}}$, where A_{RAD} and A_{NRAD} are the radiative and non-radiative rates, respectively, the η value can be calculated by the following equation:

$$\eta = \frac{A_{\mathrm{RAD}}}{A_{\mathrm{total}}}. \tag{5}$$

3.2. *Quantum yield*

The quantum yields are determined according to equation 6 [ref. 9]

$$\Phi_x = \Phi_{\mathrm{ref}}\left(\frac{S_x}{S_{\mathrm{ref}}}\right)\left(\frac{A_{\mathrm{ref}}}{A_x}\frac{(\lambda_{\mathrm{ref}})}{(\lambda_x)}\right)\left(\frac{I^{\mathrm{exc}}}{I^{\mathrm{exc}}}\frac{(\lambda_{\mathrm{ref}})}{(\lambda_x)}\right)\left(\frac{\eta_x^2}{\eta_{\mathrm{ref}}^2}\right) \tag{6}$$

where Φ_{ref} is the quantum yield of the reference (tris(2,2′-bipyridyl)dichlororuthenium(II) = 2.8%), S corresponds to the area under the emission spectra curve (reference or sample), $A(\lambda)$ is the absorption maximum in λ, $I(\lambda)$ is maximum excitation in λ, and η is the refraction index.

The quantum yield measurements were performed with samples in aqueous solution ($3.3 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$).

4. Results and discussion

The CHN elemental analysis results, in good agreement with the proposed formulas, are summarized in table 1.

Table 1. Elemental analysis results for the synthesized Ln-crown ether complexes. Calculated values are in parenthesis.

Complex	C (%)	H (%)	N (%)
[Eu(12-crown-4)(terpy)(H_2O)] · 3Cl	38.8 (39.0)	3.9 (4.0)	5.9 (6.0)
[Eu(15-crown-5)(terpy)] · 3Cl	40.7 (41.0)	4.1 (4.2)	6.5 (6.7)
[Tb(12-crown-4)(terpy)(H_2O)] · 3Cl	37.6 (38.0)	4.1 (4.1)	5.8 (5.9)
[Tb(15-crown-5)(terpy)] · 3Cl	39.8 (40.0)	4.6 (4.2)	5.5 (5.7)
[Gd(12-crown-4)(terpy)(H_2O)] · 3Cl	38.5 (38.9)	4.3 (4.0)	5.9 (6.0)
[Gd(15-crown-5)(terpy)] · 3Cl	39.4 (40.0)	4.4 (4.2)	5.7 (5.7)

Table 2. Experimental value for the radiative (A_{RAD}) and non-radiative (A_{NRAD}) rates, quantum efficiency (η), intensities parameters (Ω_2 and Ω_4), lifetime (τ) and quantum yield (Φ) for the europium-crown ether complexes.

Complex	A_{RAD} (s^{-1})	A_{NRAD} (s^{-1})	η (%)	Ω_2 ($10^{-20}\,cm^2$)	Ω_4 ($10^{-20}\,cm^2$)	τ (ms)	Φ (%)*
[Eu(12-crown-4)(terpy)(H_2O)] · 3Cl	339.5	1225.2	22	4.8	1.1	0.64	7.4
[Eu(15-crown-5)(terpy)] · 3Cl	221.2	44.3	83	3.0	5.5	0.38	4.3

*Quantum yields in water ($3.3 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$).

Coordination of the ligands to the lanthanide ions was investigated comparing infrared spectra of the complexes with the spectra of the free ligands. The infrared spectra of the crown ethers have a strong band around 1120 cm^{-1} attributed to the ν_S(C–O–C) vibrational modes. In infrared spectra of the Ln^{3+} complexes this band is shifted to 1065 cm^{-1}, indicating that the oxygen atoms of the ether ring are involved in coordination. The infrared spectrum of terpyridine exhibits a strong band around 1420 cm^{-1} attributed to the ν_S(C=N) vibrational modes. In the complexes this band is shifted to 1406 cm^{-1}, indicating that terpyridine is coordinated to the lanthanide ion as a chelate through the nitrogen atom. The infrared spectra of the 12-crown-4 complexes exhibit a very broad band around 3300 cm^{-1} assigned to ν(O–H), in agreement with the presence of a water molecule in the coordination sphere. As an illustrative example of the proposed general coordination features of the synthesized

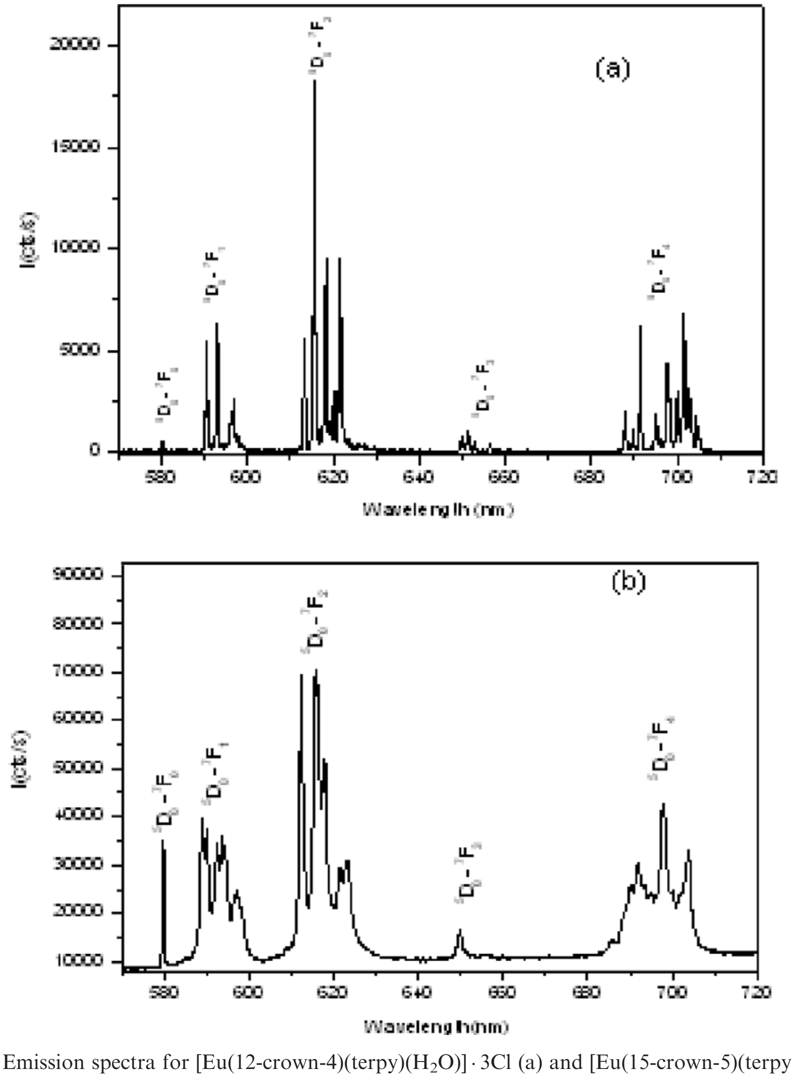

Figure 2. Emission spectra for [Eu(12-crown-4)(terpy)(H_2O)] · 3Cl (a) and [Eu(15-crown-5)(terpy)] · 3Cl (b).

compounds, a schematic structure of the complex cation [Eu(12-crown-4)(terpy)(H_2O)] is shown in figure 1.

The emission spectra were recorded in the range 570–720 nm and 450–700 nm for terbium and europium complexes respectively, at 298 and 77 K (liquid N_2), with a excitation wavelength of 350 nm. The emission spectra for solid gadolinium complexes were obtained at 77 K. Such spectra are shown in figures 2–4.

The spectrum of the europium complexes shows the $^5D_0 \rightarrow {}^7F_J$ transitions ($J = 0$, 1, 2, 3 or 4) containing ($2J + 1$)-components, suggesting the presence of only one site

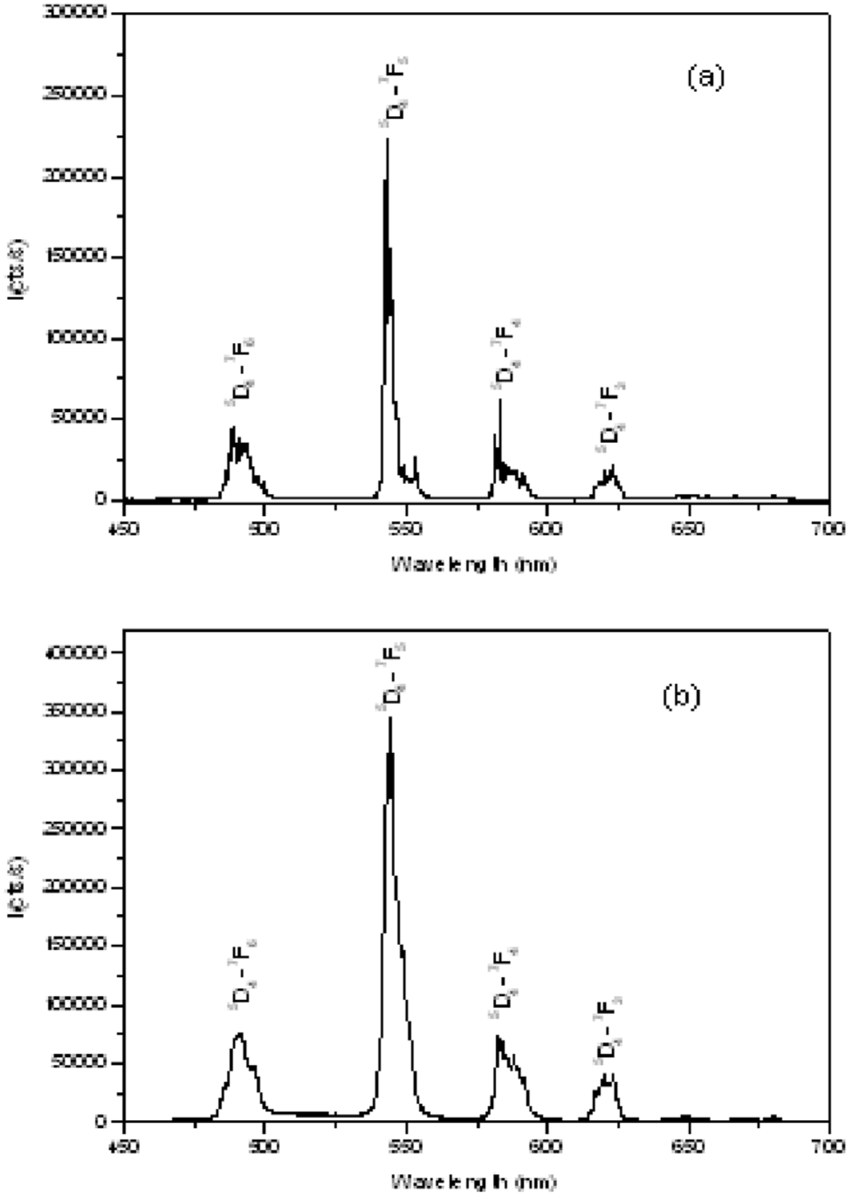

Figure 3. Emission spectra for [Tb(12-crown-4)(terpy)(H_2O)] · 3Cl (a) and [Tb(15-crown-5)(terpy)] · 3Cl (b).

symmetry for the Eu(III) ion (figure 2). Also we observe in the spectrum the presence of the $^5D_0 \rightarrow {}^7F_0$ transition, indicating low symmetry, C_n, C_{nv} or C_s.

Spectra of the terbium complexes are shown in figure 3 with $^5D_4 \rightarrow {}^7F_J$ transitions, where $J = 6$, 5, 4 or 3. All the complexes had solubility and luminescence in water. A bigger intensity of emission in the terbium complexes indicates applicability in immunoassays.

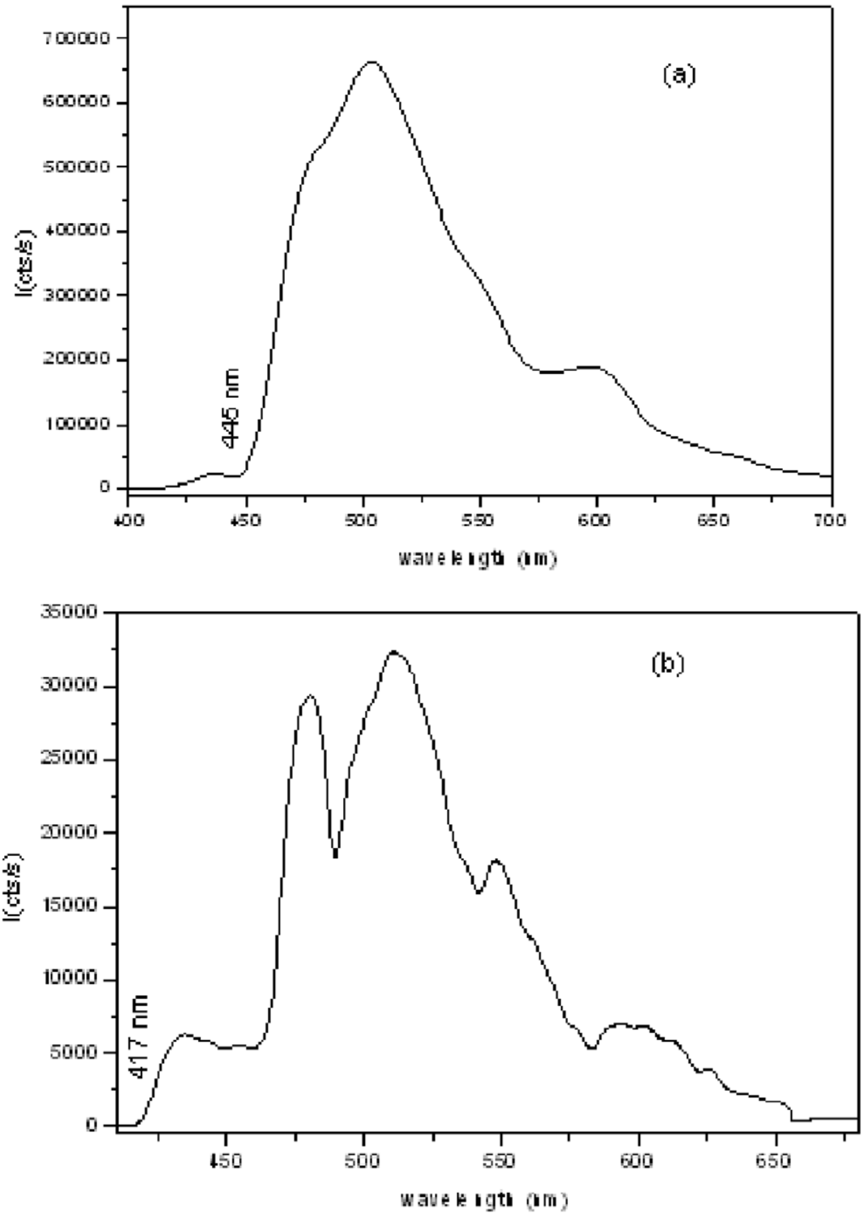

Figure 4. Emission spectra for [Gd(12-crown-4)(terpy)(H$_2$O)] · 3Cl (a) and [Gd(15-crown-5)(terpy)] · 3Cl (b).

The zero-phonon lines of the higher energy emission bands are observed at 445 nm (22,472 cm^{-1}) and 417 nm (23,981 cm^{-1}) for [Gd(12-crown-4)(terpy)(H_2O)] · 3Cl and [Gd(15-crown-5)(terpy)] · 3Cl, respectively (figure 4), suggesting that the energy transfer process is more effective in terbium complexes ($^5D_4 \rightarrow {}^7F_J$; E = 21,000 cm^{-1}). Decay time measurements for Gd(III) complexes provide evidence for the existence of emitting

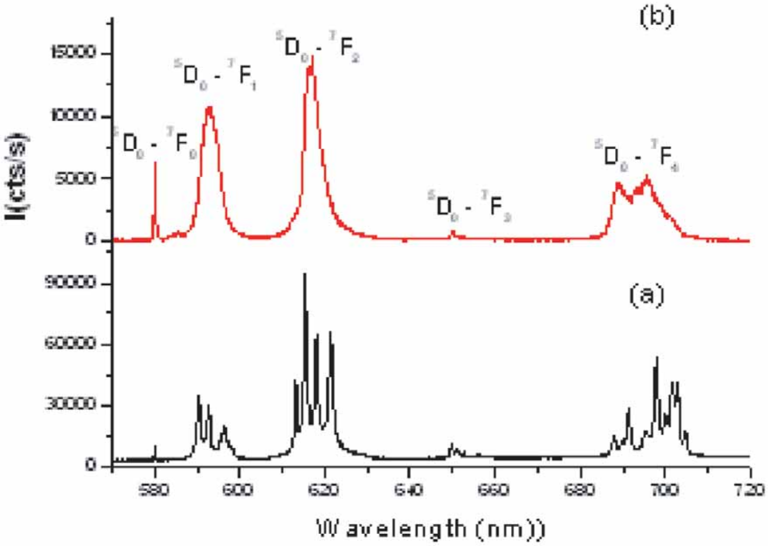

Figure 5. Emission spectra for [Eu(12-crown-4)(terpy)H_2O] · 3Cl in the solid state (a) and aqueous solution (b).

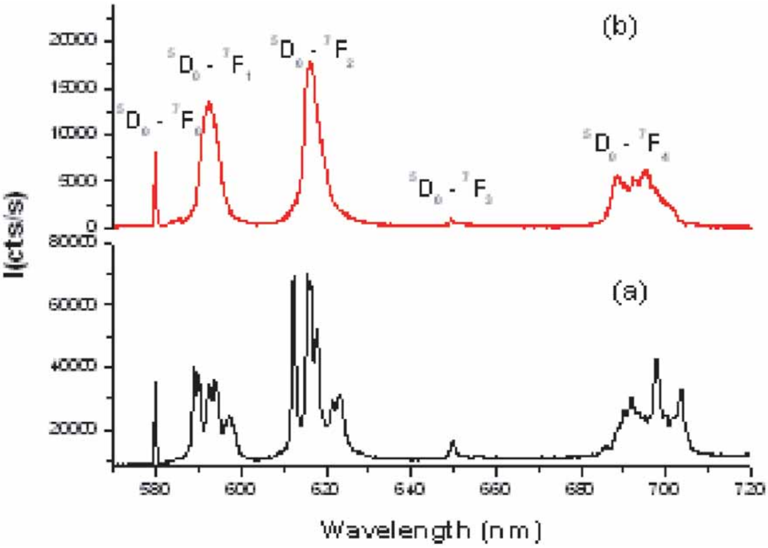

Figure 6. Emission spectra for [Eu(15-crown-5)(terpy)] · 3Cl in the solid state (a) and aqueous solution (b).

state triplets. For all the gadolinium complexes, the triplet level is resonant with $^5D_4$ of the terbium ion, giving an increase of the luminescence intensity.

The solid state and aqueous solution emission spectra for europium and terbium complexes are shown in figures 5–8. The complexes exhibit good emission, even in aqueous solutions (the crown ether-Ln and terpyridine-Ln bonds are very stable. So, it is inferred that the complex cations still remain in aqueous solution) enhancing their potential for possible biological applications. Reduction of the emission intensity

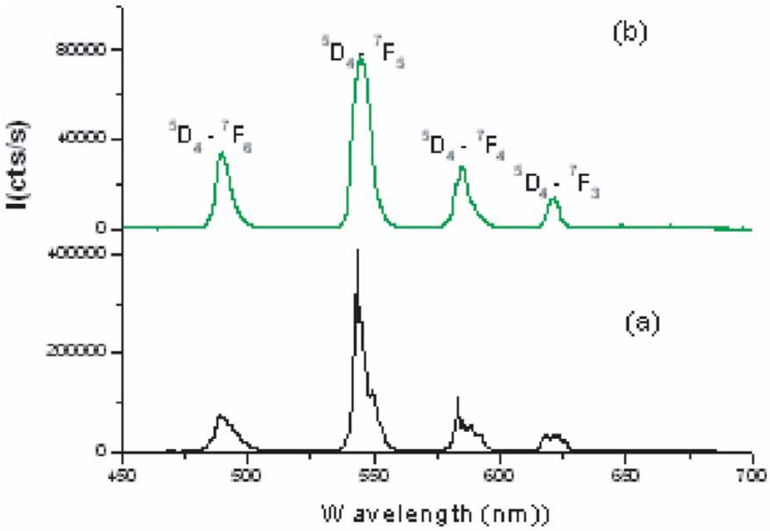

Figure 7. Emission spectra for [Tb(12-crown-4)(terpy)(H_2O)]·3Cl in the solid state (a) and aqueous solution (b).

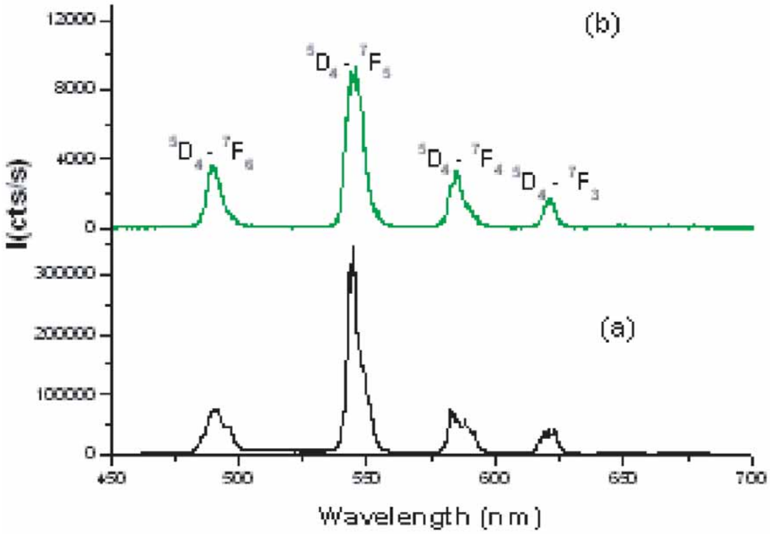

Figure 8. Emission spectra for [Tb(15-crown-5)(terpy)]·3Cl in the solid state (a) and aqueous solution (b).

for solid state to aqueous solution, is lower for europium complexes, in comparison with terbium complexes.

The obtained intensity parameters, quantum efficiency and quantum yields are summarized in table 2. The Ω_2 and Ω_4 values of the [Eu(12-crown-4)(terpy)(H_2O)] · 3Cl complex, suggest that the environment is more polarizable compared with [Eu(15-crown-5)(terpy)] · 3Cl.

The [Eu(12-crown-4)(terpy)(H_2O)] · 3Cl complex exhibits an emission lifetime of 0.64 ms while the [Eu(15-crown-5)(terpy)] · 3Cl exhibits a value of 0.38 ms. Despite the longer lifetime exhibited by 12-crown-4 it exhibits a low quantum efficiency due to the larger values of non-radioactive rate, compared with the radioactive rate (about four times larger). Furthermore, comparing the spectra shown in figure 2 and the data in table 2, 15-crown-5 complex emission intensity is about 3.8 times larger than the emission intensity of the 12-crown-4 complex. This ratio (3.8) is also observed for the A_{RAD} and A_{NRAD} for the aqueous solution complexes: $1225.5/339.5 = 3.6$. Such facts are probably related with the presence of one water molecule in the coordination sphere of the 12-crown-4 complex, resulting in a low quantum efficiency. Furthermore, the quantum efficiency relation for such compounds is $83/22 = 3.8$.

Inspection of table 2 data, show that the aqueous solution quantum yield is higher for Eu(12-crown-4)(terpy)(H_2O)] · 3Cl than [Eu(15-crown-5)(terpy)] · 3Cl, probably related to the crown ether ratio; 12-crown-4 exhibits a more suitable ratio in comparison with 15-crown-5.

5. Conclusions

(a) The water-soluble Eu^{3+} and Tb^{+3} crown ether-terpyridine complexes (Eu^{3+}, mainly) are possible chemical probes for biological applications, taking into account their luminescent properties.

(b) For possible biological applications, and taking into account the water solution quantum yields for europium complexes, 12-crown-4 exhibits a more suitable ratio in comparison with 15-crown-5.

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