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Systematic study of luminescent properties of new lanthanide complexes using crown ethers as ligand

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ABSTRACT

This is a report on the synthesis, characterization and spectroscopic study of 24 lanthanide-crown ether coordination compounds, where Eu(III), Tb(III) and Gd(III) were complexes to 12-crown-4 (12C4), 15-crown-5 (15C5), 1,10-phenanthroline (phen) and 2,2′-dipyridyl (dipy). The compounds were synthesized in an ethanol/acetone solution at room temperature and analyzed using CHN elemental analysis and infrared, absorption and emission spectroscopies. The polarizability that the ligand exerts on the emission process was verified and found remarkable. The Eu-15C5-phen complex showed the highest quantum efficiency (71.6%) because of its low non-radiative rate and highest polarizability with reference to the ligands system.

1. Introduction

Lanthanide coordination compounds are widely known for their interesting luminescent properties, which arise from their f–f transitions with narrow emission lines, making them useful for various applications [1–14].

A suitable choice of ligands produces efficient effects, since the excited state of the lanthanide ion is characterized by intramolecular energy transfer of its ligands system, which acts as a sensitizer (antenna effect) [15,16]. Although different types of chelating agents can be used for the preparation of these complexes, the N-heterocyclic aromatic ring (dipyridine and phenanthroline) units commonly improve the sensitization of the luminescence of the Eu(III) and Tb(III). This is due to its efficient contribution to ligand-to-metal energy transfer [17–19]. Although crown ethers (CE) are used in this current work, their presence, as ligand, increases the solubility and stability (macrocycle effect) of the complexes [20]. Lanthanide-crown ether complexes have also been extensively studied [21,22]. Interest in their important role is because of their spectroscopic behavior, a result of the interplay between Ln(III) ions luminescent properties and the encapsulation process provided by crown ether.

The synthesis, characterization and spectroscopic study of new lanthanide-crown ether complexes is reported in this work. Their proposed formulae is $[Ln(CE)(L)_n]Cl_3$, were Ln=Eu(III), Tb(III) and Gd(III), CE=12-crown-4 and 15-crown-5 and L=H_2O ($n=4$); 2,2′-dipyridyl ($n=1$) and 1,10-phenanthroline ($n=2$). The intensity and *R*02 parameters were determined from luminescence spectra of the Eu(III) complexes [23–25]. In addition, the radiative and non-radiative rates and experimental emission quantum efficiencies were also investigated.

2. Experimental details

The lanthanide chlorides $EuCl_3 \cdot 6H_2O$, $TbCl_3 \cdot 6H_2O$ and $GdCl_3 \cdot 6H_2O$, crown ethers 12-crown-4 (12C4) and 15-crown-5 (15C5), and 2,2′-dipyridyl (dipy) and 1,10-phenanthroline (phen) ligands, supplied by Aldrich, were all used without further purification.

Crown ether coordination compounds were synthesized starting from 1:1 stoichiometric ratio mixtures of $LnCl_3 \cdot 6H_2O$ (Ln(III): Eu(III), Tb(III) and Gd(III)) and crown ethers (12C4 and 15C5), which were dissolved in 50 mL of a 3:1 (v:v) ethanol/acetone solution and kept under stirring at room temperature for 24 h. The resulting solid Ln(III)/crown ether was filtered, washed with cold acetone and dried under vacuum.

These precursors complexes were dissolved in ethanol and the dipy and phen ligands were added at a stoichiometric ratio of 1:2. The resulting complexes (precipitate in solution) were formed after stirring for 24 h at room temperature. The solvent was removed and the resulting solids were washed with cold ethanol and dried under vacuum.

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The elemental compositions of all coordination compounds were determined on a Perkin-Elmer 240 CHN analyzer. UV–vis absorption spectra were acquired on a Perkin-Elmer lambda 6 spectophotometer using tungsten and deuterium lamps, within the 190–900 nm range from ethanolic solutions. Infrared spectra were acquired from KBr pellets, in a FT-IR Perkin-Elmer spectrophotomer, IF6 model, in the 4000–400 cm^{-1} range, at a 4 cm^{-1} spectral resolution and 32 acquisitions per spectrum.

Emission spectra were measured at 298 K in the 450–700 nm range for terbium and 570–720 nm for europium complexes. The Gd-phosphorescence spectra were measured at 77 K (N_2) in the 400–700 nm range. Data acquisitions were carried out in solid state using a Jobin-Yvon Ramanor U1000 model H-10, with a RCA C31034-02 photomultiplier as a detector and a Spectralink interface for data processing. The luminescence decay curves of the emitting levels were measured using a phosphorimeter SPEX 1934D accessory coupled to the spectrofluorometer.

Table 1
Elemental analysis data (theoretical and experimental) of the complexes.

Complexes	C (%)		H (%)		N (%)	
	E	*T*	*E*	*T*	*E*	*T*
$[Eu(12C4)(H_2O)_4]Cl_3$	18.88	18.90	4.68	4.70	0	0
$[Eu(15C5)(H_2O)_4]Cl_3$	21.79	21.80	5.07	5.10	0	0
$[Tb(12C4)(H_2O)_4]Cl_3$	18.68	18.69	4.69	4.70	0	0
$[Tb(15C5)(H_2O)_4]Cl_3$	21.47	21.50	5.00	5.00	0	0
$[Gd(12C4)(H_2O)_4]Cl_3$	18.76	18.77	4.68	4.69	0	0
$[Gd(15C5)(H_2O)_4]Cl_3$	21.57	21.60	5.02	5.04	0	0
$[Eu(12C4)(phen)_2]Cl_3$	47.98	48.00	3.99	4.00	7.08	7.10
$[Eu(15C5)(phen)_2]Cl_3$	48.59	48.60	4.29	4.30	7.00	7.00
$[Tb(12C4)(phen)_2]Cl_3$	47.99	48.00	3.99	3.40	7.00	7.00
$[Tb(15C5)(phen)_2]Cl_3$	44.97	45.00	3.78	3.80	6.98	7.00
$[Gd(12C4)(phen)_2]Cl_3$	47.98	48.00	3.87	3.90	7.00	7.00
$[Gd(15C5)(phen)_2]Cl_3$	44.98	45.00	3.79	3.80	6.57	6.60
$[Eu(12C4)(dipy)(H_2O)_2]Cl_3$	34.53	34.56	3.17	3.20	4.48	4.50
$[Eu(15C5)(dipy)(H_2O)_2]Cl_3$	36.76	36.80	4.60	4.60	4.19	4.20
$[Tb(12C4)(dipy)(H_2O)_2]Cl_3$	33.99	34.00	5.87	5.90	4.39	4.40
$[Tb(15C5)(dipy)(H_2O)_2]Cl_3$	36.36	36.40	4.49	4.50	4.18	4.20
$[Gd(12C4)(dipy)(H_2O)_2]Cl_3$	33.99	34.00	3.78	3.80	4.47	4.50
$[Gd(15C5)(dipy)(H_2O)_2]Cl_3$	44.98	45.00	4.48	4.50	7.08	7.10
$[Eu(12C4)(dipy)(phen)]Cl_3$	47.00	47.00	4.08	4.10	7.27	7.30
$[Eu(15C5)(dipy)(phen)]Cl_3$	43.99	44.00	4.38	4.40	6.88	6.90
$[Tb(12C4)(dipy)(phen)]Cl_3$	45.96	46.00	4.07	4.10	7.18	7.20
$[Tb(15C5)(dipy)(phen)]Cl_3$	46.68	46.70	4.36	4.40	6.77	6.80
$[Gd(12C4)(dipy)(phen)]Cl_3$	45.98	46.00	4.09	4.10	7.17	7.20
$[Gd(15C5)(dipy)(phen)]Cl_3$	43.99	44.00	3.88	3.90	6.78	6.80

*E=Experimental and T=Theoretical.

3. Results and discussion

The precursors and dipy complexes were white solids while the samples containing phen were yellow. The synthesis procedures shown were reproducible, and the yields within the 85–87% range. Chemical analysis results are all in good agreement (within an 1% error) with theoretically expected values (see Table 1).

Crown ether complexation to Ln(III) ions shifts the C–O–C vibration mode in the infrared spectra (not shown) from 1100 cm^{-1}, in the free ligand, to 1064 cm^{-1} (coordinated form) [26]. The complexation of the dipy and phen ligands can be followed by a dislocation of the $\nu C{=}N$ band of the pyridine ring for the lower frequencies (1398 cm^{-1}). The OH stretching mode appears at 3300 cm^{-1}, which means that water is present in the Ln(III) coordination sphere in the dipy complex.

The solvents used for synthesis were ethanol/acetone (3:1), affording an optimal conformation of the ligand oxygen atoms (crown ethers), which contributes to the stabilization of the coordination sites. Even though the chemical equation used in the synthesis process of the dipy complexes should have been 1:2 (precursor complex—dipy ligand), it was not possible to get this proportion because the distance between the nitrogen atom donors of the ligand caused a steric block, thus restricting the addition of a second dipy-type ligand.

In Fig. 1 the excitation spectra of $[Eu(CE)(H_2O)_4]Cl_3$ are shown. The $^7F_0 \rightarrow {}^5L_6$, $^7F_0 \rightarrow {}^5D_2$ and $^7F_0 \rightarrow {}^5D_3$ transitions dislocated for the minor energy in the $[Eu(15C5)(H_2O)_4]Cl_3$ complex indicate a decrease in the polarizability of the chemical environment around the metallic ion, when compared to the $[Eu(12C4)(H_2O)_4]Cl_3$ complex. The other complexes showed broad bands related to the ligands structures, whose maximum values were 356, 348 and 350 nm for the dipy, dipy–phen and phen complexes, respectively.

The emission spectra of $[Ln(12C4)(H_2O)_4]Cl_3$ (Ln-12C4) and $[Ln(15C5)(H_2O)_4]Cl_3$ (Ln—Eu, Tb) complexes are presented in Figs. 2 and 3, respectively, in which the typical transitions from europium and terbium ions can be observed.

Eu(III) ion transitions, observed in the emission spectra, occur via three main mechanisms: forced electric dipole, magnetic dipole and dynamic coupling [15]. The relationship between the magnetic ($^5D_0 \rightarrow {}^7F_1$) and electric ($^5D_0 \rightarrow {}^7F_2$) parcel gives informations about the symmetry surrounding ion. The europium complexes manifest an intensity ratio of $^5D_0 \rightarrow {}^7F_1 / {}^5D_0 \rightarrow {}^7F_2 < 1$, suggesting that the

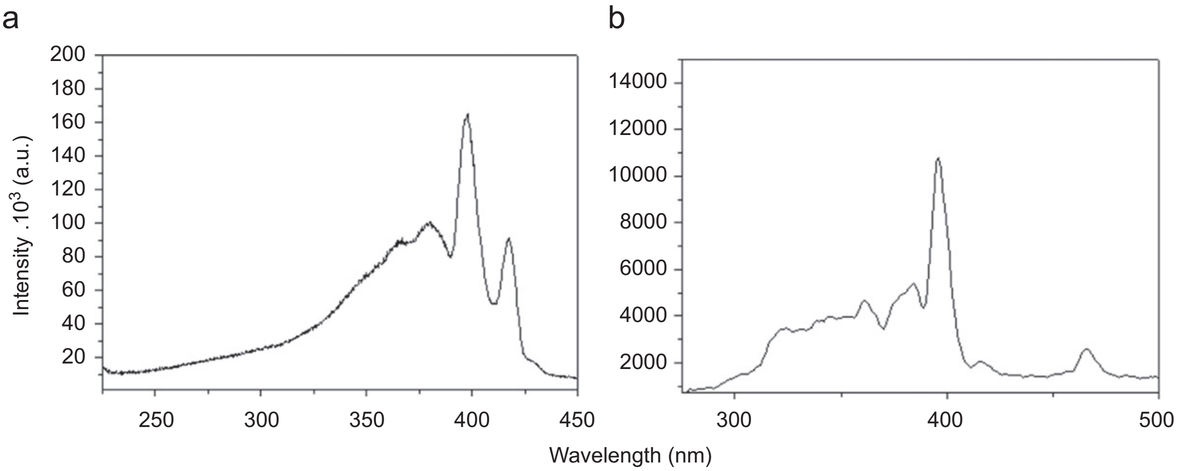

Fig. 1. Excitation spectra of (a) $[Eu(12C4)(H_2O)_4]Cl_3$ and (b) $[Eu(15C5)(H_2O)_4]Cl_3$ complexes.

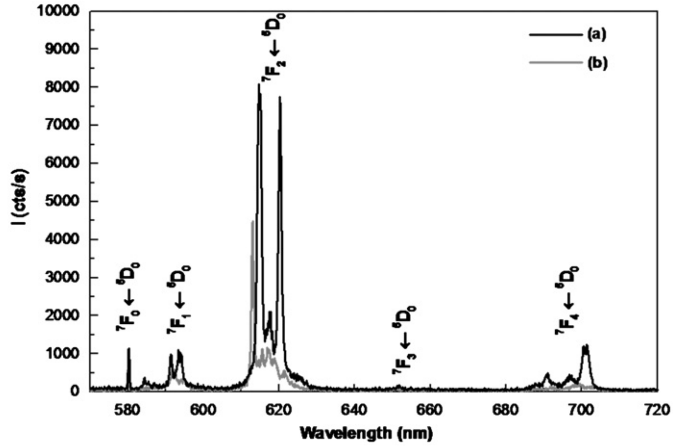

Fig. 2. Emission spectra of (a) $[Eu(12C4)(H_2O)_4]Cl_3$ and (b) $[Eu(15C5)(H_2O)_4]Cl_3$ complexes.

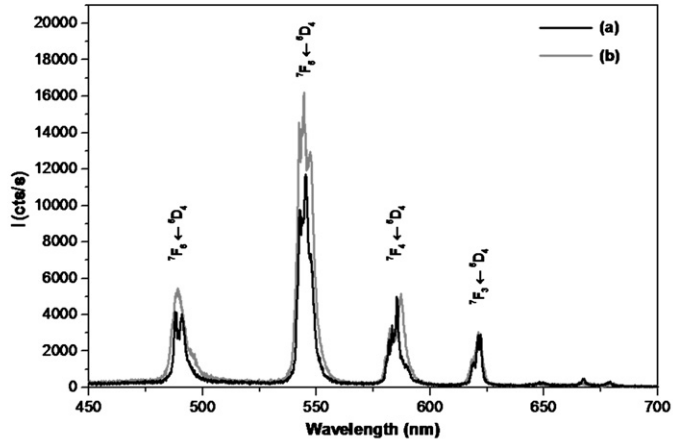

Fig. 3. Emission spectra of (a) $[Tb(12C4)(H_2O)_4]Cl_3$ and (b) $[Tb(15C5)(H_2O)_4]Cl_3$ complexes.

Eu(III) ions occupy a low symmetry environment (C_n, C_{nv} or C_s, where $n < 4$). Despite the fact that the crown ether ligand antennas were not acceptable, since there are no groups of chromophores, the complex showed high luminescence intensity when compared to typical cases in the literature [23]. There is an evidence for a change in the environment around the europium ion (III) when the $^5D_0 \rightarrow {^7F_2}$ transition is compared for all complexes, on observing variations in their maximum and *J* splitting. The Eu-12C4 complex manifested high intensity luminescence when compared with Eu-15C5, but an inverse behavior was observed when it was compared to terbium complexes.

The emission spectra of dipy, dipy–phen and phen complexes are as shown in Figs. 4, 5 and 6, respectively. The 12C4 complexes were more luminescent than 15C5 complexes, corroborating observed precursor complexes. For all the complexes, the Eu-12C4–dipy–phen complex showed high intensity luminescence. In the case of terbium complexes, a behavior opposite to the europium complexes was observed, explained by analyzing the gadolinium complexes phosphorescence spectra.

The gadolinium complexes were synthesized in order to obtain information about ligand electronic states. Fig. 7 shows the determinated energy levels in comparison to those of the europium and terbium free ion states.

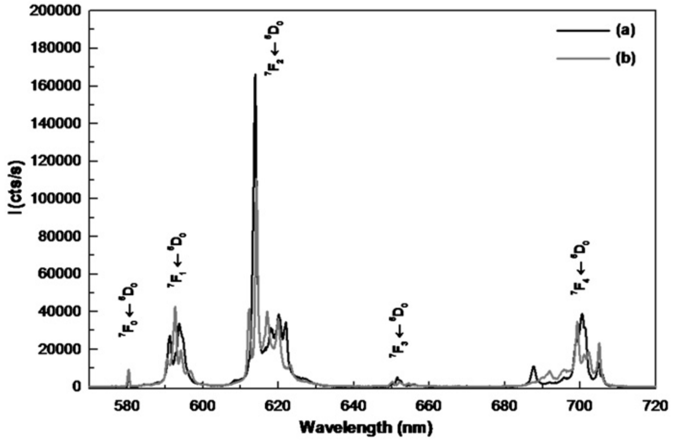

Fig. 4. Emission spectra of (a) $[Eu(12C4)(dipy)(H_2O)_2]Cl_3$ and (b) $[Eu(15C5)(dipy)(H_2O)_2]Cl_3$ complexes.

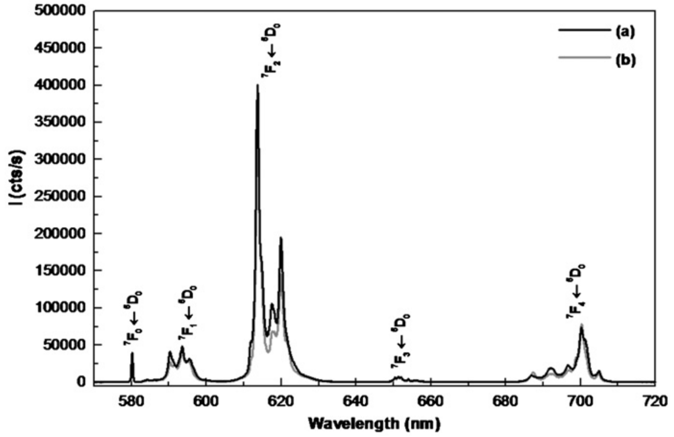

Fig. 5. Emission spectra of (a) $[Eu(12C4)(dipy)(phen)]Cl_3$ and (b) $[Eu(15C5)(dipy)(phen)]Cl_3$ complexes.

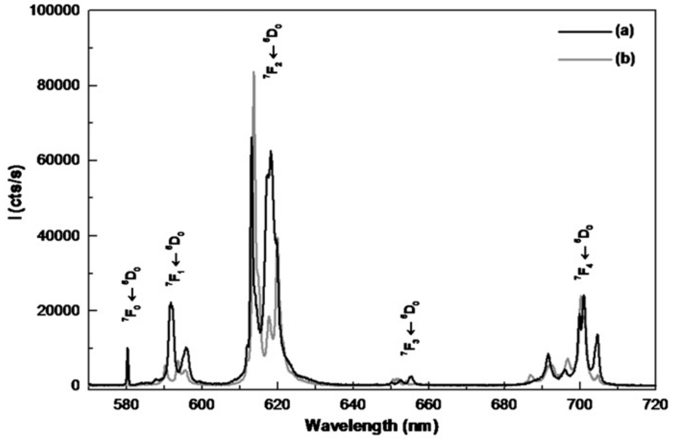

Fig. 6. Emission spectra of (a) $[Eu(12C4)(phen)_2]Cl_3$ and (b) $[Eu(15C5)(phen)_2]Cl_3$ complexes.

The Gd–dipyphen complex phosphorescence is at 17.746 cm^{-1}, which indicates a more efficient energy transfer process for the $^5D_0$ state located in the Eu(III) ion. Triplet states with high energy were observed for the Gd–15C5–phen complex, suggesting that the energy transfer process is more efficient for the terbium ion. For all Eu(III) complexes, the main acceptor level in the energy transfer process is the $^5D_1$ ($\sim$19,000 cm^{-1}), via the exchange mechanism [27]. These data agree with the emission intensities observed.

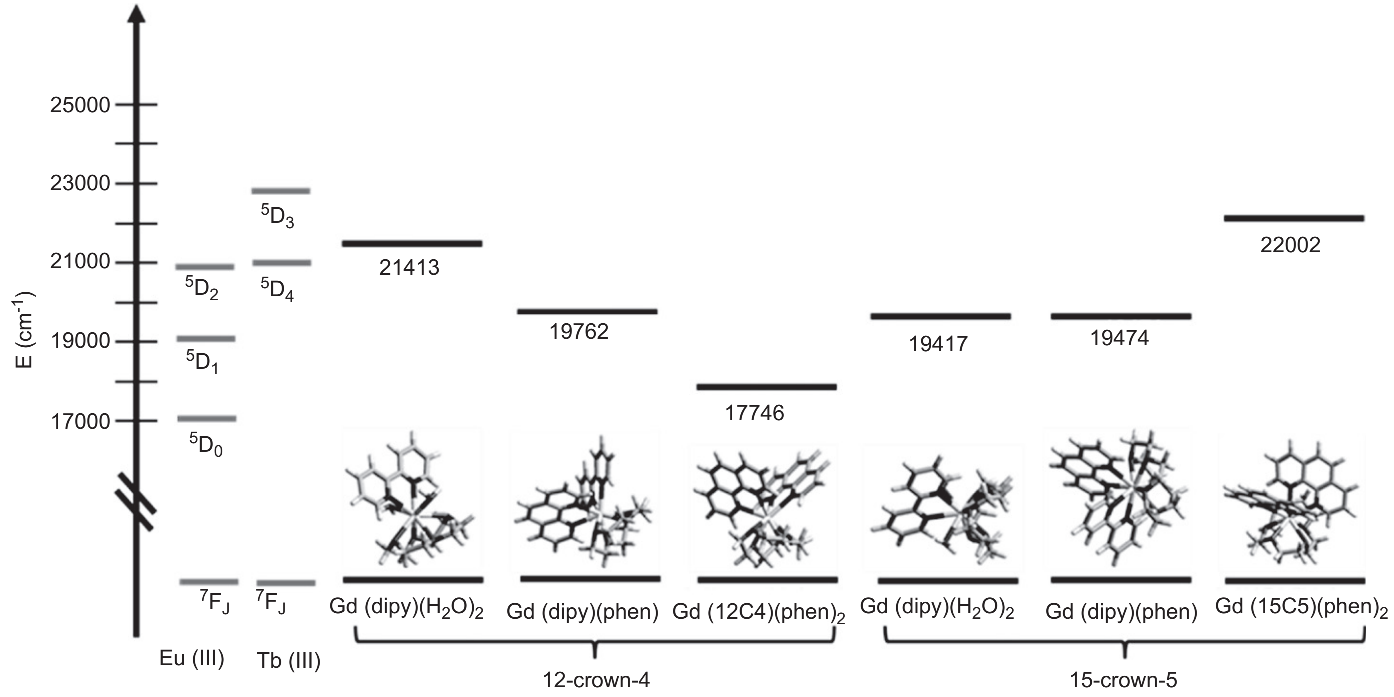

Fig. 7. Energy levels of ligands, determined from the gadolinium complexes, in comparison to the free europium and terbium ions states.

Table 2
Data of radiative (A_{rad}) and non-radiative (A_{nrad}) rates, quantum efficiency (η), $R02$ and intensity (Ω_λ; where λ=2 or 4) parameters for the Eu(III) complexes.

Complexes	$R02$	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	η (%)	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)
[Eu(12C4)(H$_2$O)$_4$]Cl$_3$	**0.0240**	424.5	2278.2	15.7	9.88	5.13
[Eu(15C5)(H$_2$O)$_4$]Cl$_3$	0.0467	303.6	516.1	37.0	6.33	2.70
[Eu(12C4)(phen)$_2$]Cl$_3$	0.0105	387.9	1430.3	21.3	8.11	6.27
[Eu(15C5)(phen)$_2$]Cl$_3$	**0.0078**	**746.3**	**295.4**	**71.6**	**13.87**	**15.64**
[Eu(12C4)(dipy)(H$_2$O)$_2$]Cl$_3$	0.0163	383.8	1838.4	17.2	**4.93**	**4.60**
[Eu(15C5)(dipy)(H$_2$O)$_2$]Cl$_3$	0.0082	298.0	1426.1	17.3	5.62	5.30
[Eu(12C4)(dipy)(phen)]Cl$_3$	0.0148	420.8	1465.9	22.3	9.32	6.05
[Eu(15C5)(dipy)(phen)]Cl$_3$	0.0109	413.8	**2631 .6**	**13.6**	9.06	5.76

The europium complexes data of radiative (A_{rad}) and non-radiative (A_{nrad}) rates, quantum efficiency (η), $R02$ and intensity (Ω_λ; where λ=2 or 4) parameters are shown in Table 2.

The high non-radiative rate shown through complexes (except in the case of [Eu(15C5)(phen)$_2$]Cl$_3$ complex) suggests that crown ethers ligands are not good antenna (energy transfer). The 15C5 complexes present the best quantum efficiency when compared to 12C4 complexes (except for the dipy–phen complex), indicating that the macrocyle effect in this case minimizes the non-radiative rate of the system. The [Eu(15C5)(phen)$_2$]Cl$_3$ complex manifested a higher quantum efficiency when compared to 12-crown-4, which had a smaller cavity for ion adjustment. This was probably due to the absence of coordination water and a macrocycle effect.

The intensity parameters (Ω_2 and Ω_4) suggest that low polarizability causes loss in the quantum efficiency, as corroborated by the emission spectra of the europium complexes [23,24]. The $R02$ parameters suggest that minor quantum efficiency is associated with greater effect in the mixture of J.

4. Conclusions

All complexes showed quantum efficiency, an unexpected result, since crown ether does not act as a good antenna due to lack of the chromophores group. This present study, involving these ligands, was motivated by an attempt to contribute to the discussion about these systems, to provide a more adequate description of the synthesis and possible applications, such as luminescent devices. The 12-crown–4 ligand, despite its small cavity, showed certain stability in the formation of the complex with the lanthanide ions, whereas even when replaced by stronger ligands, it did not cause the crown ether to release. The appropriate solvent choice was based on a procedure that enabled the exposure of electron donor oxygens without compromising the optimal crown ether cavity size; for this purpose, a suitable composition (ethanol:acetone) was used as the reactional medium. The terbium complex had the highest intensity of emission in most cases, probably due to the fact that these compounds have less affinity for water molecules (less hygroscopic nature), which enable a quenching event.

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