

Research Article

Factors Affecting the Efficiency of Excited-States Interactions of Complexes between Some Visible Light-Emitting Lanthanide Ions and Cyclophanes Containing Spirobiindanol Phosphonates

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The efficiency of excited-states interactions between lanthanide ions Tb³⁺ and Eu³⁺ and some new cyclophanes (I, II, and III) has been studied in different media. High luminescence quantum yield values for terbium and europium complexes in DMSO and PMMA were obtained. The photophysical properties of the green and red emissive Tb³⁺ and Eu³⁺ complexes have been elucidated, respectively.

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1. INTRODUCTION

Lanthanide ions, particularly Tb³⁺ and Eu³⁺, are popular luminescent probes for the development of fluoroimmunoassays [1–6]. Their photophysical properties, narrow line luminescence with long lifetimes, are attractive in comparison with the broad luminescence of the organic fluorescent dyes. The disadvantage of low absorption coefficients of the lanthanides can be overcome by the introduction of ligands that act as light-harvesting centers (LHCs) to sensitize the lanthanide emission [7–13]. Chelating agents commonly used for enhancement of lanthanides include bidentate ligands, such as β -diketonates [14–17], tridentate pyridines, such as an amide-based open-chain crown ether ligand [18], and open-chain carboxylate crown ether ligands [19]. In addition, the energy transfer (ET) from donor ligands to acceptor lanthanide ions in macrocyclic polyether complexes of lanthanides has been studied [20–23]. In these complexes, the excitation energy (excitation of the ligand in the first excited singlet state) either in the ultraviolet or in the visible region is converted to a narrow band 4f/4f emission of the acceptor rare earth (RE) ions. The energy transfer (ET) could take place through the singlet state [24] or the lowest

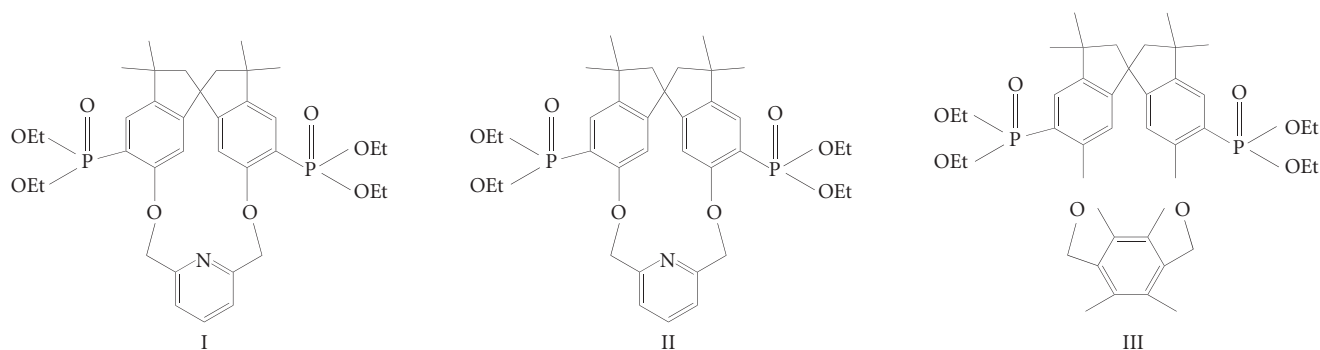
triplet (T₁) state [25–27] of an aromatic unit acting as ligand.

Chiral cyclophanes containing ancillary groups are able to act as powerful binding sites for large variety of natural guests in polar solvents. These compounds found to have a cavity not large enough to include bulk guests [28].

In the present paper, the absorption and the emission spectroscopic properties of new cyclophanes containing spirobiindanol phosphonates derivatives (I, II, and III) and their Ln(III) complexes in different solvents were studied and discussed. Also, the sensitization of Ln(III) by this new type of ligands in solution and in thin films of polymer matrix was investigated.

2. EXPERIMENTAL

The metal nitrates (Aldrich, 99.99%) were used as received. Pure grade (Aldrich) solvents were used. Cyclophanes containing spirobiindanol phosphonates derivatives (I, II, and III) were synthesized according to methods described before [29]. The solutions of complexes were prepared by the addition of metal nitrate (typical concentration: 8×10^{-5} M) to 2×10^{-5} M of cyclophanes in different solvents.



SCHEME 1

Polymethylmethacrylate (PMMA) was used as received. PMMA matrix was prepared by dissolving 5 gm PMMA in 25 ml CHCl_3 at 30°C with vigorous stirring for 15 minutes, then Eu and Tb-cyclophanes complexes were incorporated into PMMA matrix at 30°C under vigorous stirring for 15 minutes. The PMMA matrix was left to dry for two days at room temperature to obtain PMMA thin film. The thickness of the thin film was measured by micrometer and it was equal to 0.25 mm. (The concentration of the complexes in the matrix were not determined.)

UV and visible absorption spectra were measured at room temperature using λ -Helios SP Pye-Unicam spectrophotometer.

Luminescence spectra were measured using Shimadzu RF5301 (PC) spectrofluorophotometer. Luminescence quantum yield (Φ_L) determinations in different solvents were obtained using the following equation: [30]

$$\Phi_L = \left[\frac{(F_{(v')} * A_{\lambda_e}^0 * n^2)}{(F_{(v')} * A_{\lambda_e} * n_0^2)} \right] * \Phi_L^0, \quad (1)$$

where $A_{\lambda_e}^0$, $F_{(v')}^0$, n_0^2 , and Φ_L^0 are the absorbance at the exciting wavelength, the area under the emission spectrum, the refractive index of the solvent (quinine sulfate in 0.5 M H_2SO_4 ($n = 1.338$) and rhodamine101 in ethanol ($n = 1.329$)), and quantum yield (1 for rhodamine101 in ethanol and 0.546 for quinine sulphate in 1 M H_2SO_4) of the reference, respectively. A_{λ_e} , $F_{(v')}$, n^2 , and Φ_L are the absorbance at the excitation wavelength, the area under the emission spectrum, the refractive index of the solvent, and quantum yield of the unknown, respectively.

Estimation of the apparent association constant (K_{app}) of (Tb^{3+} and Eu^{3+} with I, II, and III) complexes in DMSO using Benesi-Hildebrand-type plot (see [31]):

$$\frac{1}{A_{\text{obs}} - A_0} = \frac{1}{A_c - A_0} + \frac{1}{K_{\text{app}}(A_c - A_0)[M]}, \quad (2)$$

where A_0 , A_c , A_{obs} , K_{app} , and $[M]$ are the absorbance of the ligand, the absorbance of the complex, the absorbance of the ligand at various concentrations of the metal ion, the formation constant, and the concentration of the metal ion, respectively.

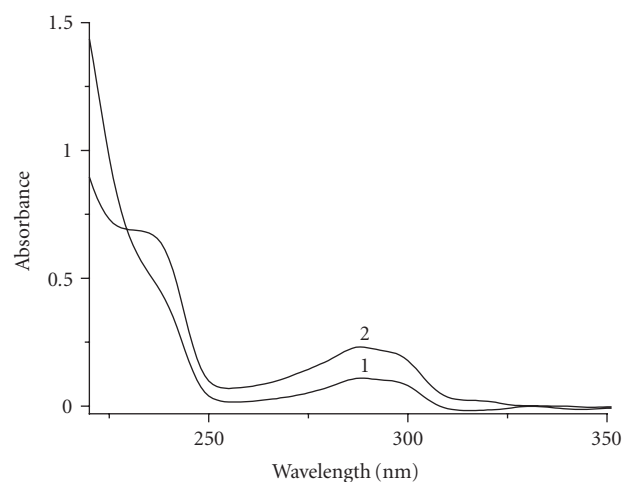


FIGURE 1: Absorption spectra of (1) 2×10^{-5} M of (II) in methanol and (2) 2×10^{-5} M of (II) in the presence of 8×10^{-5} M of Eu^{3+} .

3. RESULT AND DISCUSSION

3.1. Absorption spectra

The absorption spectra of 2×10^{-5} M for the ligands (I, II, and III) in methanol show shoulder in the UV at 240 nm, with molar absorptivity coefficient ($\epsilon = 11850, 11500$, and $8600 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. These bands are attributed to π - π^* transitions in pyridine, benzene, and *o*-xylene moieties, respectively. The longest wavelength at 290 nm may be due to n - π^* transition in the ligands. Upon complexation of lanthanide ion, no red shift is observed in n - π^* transition (Figure 1), indicating a very weak ion-dipole interaction in this solvent between lanthanide ion and the oxygen atoms in the ring of cyclophanes [32].

The ion titration revealed that the complex formed M : L (4 : 1) for compound I and II and 5 : 1 for compound III, which indicates that the metal may coordinate to the ligand from different coordination sites and not only through oxygen of the cage.

TABLE 1: Estimation of apparent formation constant of Tb^{3+} and Eu^{3+} in the presence of I, II, and III using Benesi-Hildebrand plot in methanol at 25°C .

Lanthanide ion	Compound	$K_{\text{app}} \text{ K M}^{-1}$
Tb^{3+}	I	2.90
	II	6.50
	III	10.8
Eu^{3+}	I	1.10
	II	3.20
	III	7.40

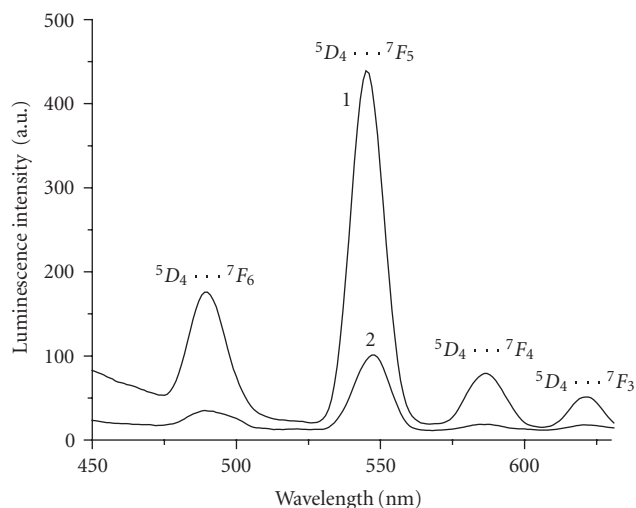


FIGURE 2: Luminescence emission spectra of $8 \times 10^{-5} \text{ M}$ of Tb^{3+} in the presence of $2 \times 10^{-5} \text{ M}$ of (I) in (1) DMSO and (2) ethylacetate at $\lambda_{\text{ex}} = 330 \text{ nm}$.

The unusual stability of lanthanide ions with diethoxyphosphonate cyclophanes that have one or two binding sites is dominated by two primary factors: (1) ion-dipole interaction between metal ion and cyclophanes donating oxygens, and (2) long-range interaction between metal ion and ethoxy group [32]. It can be considered that the outer-sphere interaction between ethoxy group and metal ion can contribute to the complexation stability.

Absorption at wavelength = 290 nm, as a measure of the complex concentration, increases with metal ion concentration and high $K_{\text{formation}}$ values in case of Tb^{3+} (small size = 1.0 Å) compared with Eu^{3+} (large size = 1.066 Å) and $[\text{M}^{n+}] = 8 \times 10^{-5} \text{ M}$; see Table 1 and [33].

3.2. Solvent effect on the luminescence spectra of lanthanide ion crown ether complexes

Figures 2 and 3 show the emission spectra of Tb^{3+} -(I) and Eu^{3+} -(II) complexes in DMSO at $\lambda_{\text{ex}} = 330 \text{ nm}$. The emission

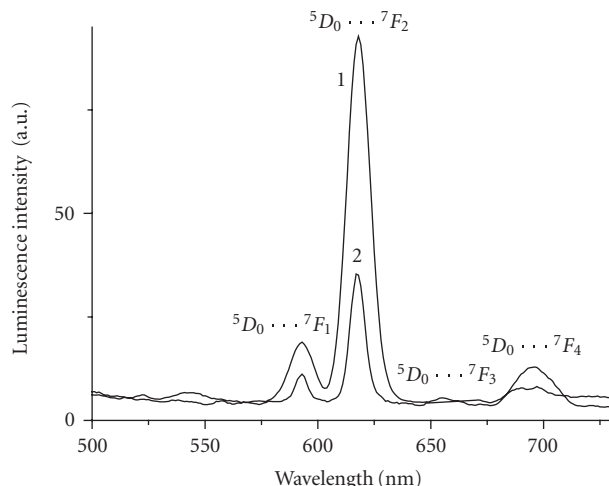


FIGURE 3: Luminescence emission spectra of $8 \times 10^{-5} \text{ M}$ of Eu^{3+} in the presence of $2 \times 10^{-5} \text{ M}$ of (II) in (1) DMSO and (2) acetonitrile at $\lambda_{\text{ex}} = 330 \text{ nm}$.

bands using Tb^{3+} and Eu^{3+} are attributed to different transitions from ($^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$, and $^5\text{D}_4 \rightarrow ^7\text{F}_3$) and ($^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$, and $^5\text{D}_0 \rightarrow ^7\text{F}_4$), respectively; see Table 2. Table 3 lists the values of the luminescence quantum yield in a variety of solvents.

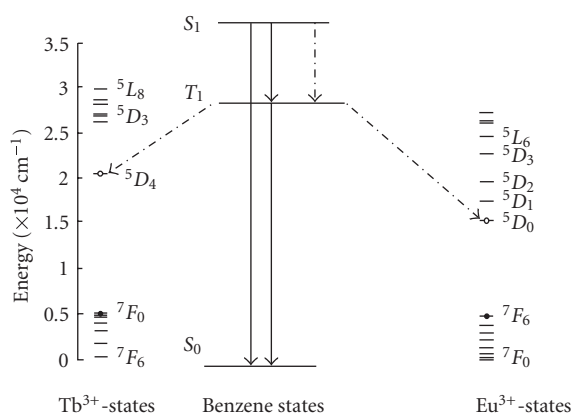
It has found that the values of quantum yield of Tb^{3+} and Eu^{3+} complexes are consistent with the observed K_{app} values, that is, the luminescence quantum yield follows the order M-(III) > M-(II) > M-(I). This behavior can be explained on the fact that the largest heavy atom effect ($\text{Tb}^{3+} > \text{Eu}^{3+}$) results when the metal ion perturber is located along the out-of-plane axis originating from the center of the benzene chromophore which applies in the case of benzene crown ether metal ion (Tb^{3+} and Eu^{3+}) [34]. This in turn was attributed to the symmetry restrictions which enter the spin-orbit matrix elements via the overlap integrals between π electrons of benzene and p orbitals of the heavy atom [35–38]. According to this effect, the triplet (T_1) population and radiative decay of the T_1 state should be a maximum in III due to the heavy atom perturbation [37–40].

The enhanced emission of Tb^{3+} -cyclophanes and Eu^{3+} -cyclophanes in DMSO, DMF, and CH_3CN can be attributed to the formation of anhydrous solvates, Tb^{3+} -cyclophanes $\cdot n$ (solvent), and Eu^{3+} -cyclophanes $\cdot n$ (solvent). Introducing solvent molecules in the first coordination sphere of Tb^{3+} -cyclophanes and Eu^{3+} -cyclophanes leads to the enhancement of the intensity of all transitions especially $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transitions in Eu^{3+} and Tb^{3+} , respectively.

By increasing the radiative rate, Tb^{3+} and Eu^{3+} excited states will become less sensitive to deactivation processes, ultimately resulting in a more efficiently emissive Tb^{3+} and Eu^{3+} complexes [39]. It can be seen that the luminescence intensities for the complexes in DMSO, DMF, and CH_3CN solutions are stronger than in methanol as hydroxy solvent. This is attributed to vibrational energy transfer to the

TABLE 2: The typical emission bands of the lanthanide ions Eu^{3+} and Tb^{3+} in solution.

Ion	Transition	Emission	Ion	Transition	Emission
Eu^{3+}	$^5\text{D}_0 \rightarrow ^7\text{F}_0$	580 nm	Tb^{3+}	$^5\text{D}_4 \rightarrow ^7\text{F}_6$	490 nm
	$^7\text{F}_1$	590 nm		$^7\text{F}_5$	545 nm
	$^7\text{F}_2$	613 nm		$^7\text{F}_4$	590 nm
	$^7\text{F}_3$	650 nm		$^7\text{F}_3$	620 nm
	$^7\text{F}_4$	700 nm		$^7\text{F}_2$	650 nm
	$^7\text{F}_5$	750 nm		—	—

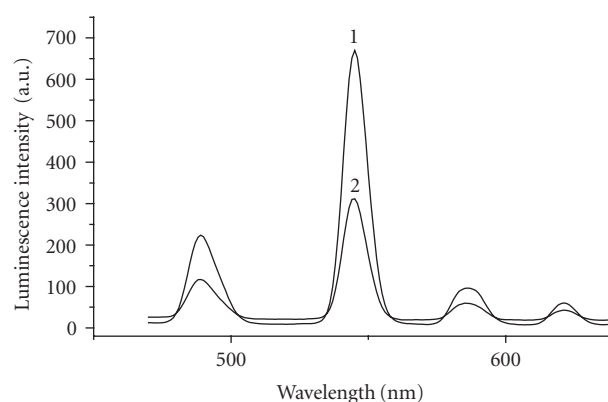
FIGURE 4: Energy level diagram for the system of cyclophane complex with $\text{Tb}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$ showing the likely routes of ET.

solvent molecules. It is well known that the excited state of the lanthanide ions is efficiently quenched by interactions with high-energy vibrations like O–H groups thereby the luminescence of these complexes in –OH containing solvents can be quenched easily because of the O–H oscillators [40].

Furthermore, the luminescence intensity and the quantum yield values of terbium complexes are higher than those of europium complexes in all solvents. This attributed to the fact that the luminescence of Ln^{3+} -chelates is related to the efficiency of the intramolecular energy transfer between the triplet level of ligand and the emitting level of the ions, which depends on the energy gap between the two levels. In the organic solvents, probably the energy gap between the ligand triplet levels and the emitting level of the terbium favors to the energy transfer process for terbium as shown in Figure 4 and Table 2 [41].

3.3. Effect of polymer matrix

To study the effect of rigidity on the efficiency of energy transfer from the ligands (I, II, and III) to Tb and Eu ions, the complexes were incorporated in PMMA matrix. The luminescence quantum yields of the complexes in PMMA are depicted in Table 3. Comparing the luminescence quantum yield values of the complexes with the highest values

FIGURE 5: Luminescence emission spectra of 3×10^{-4} M of Tb^{3+} in the presence of (1) 8×10^{-5} M of (I) and (2) 8×10^{-5} M of (II) in [PMMA= 4 gm/25 ml at $\lambda_{\text{ex}} = 300$ nm].

obtained in DMSO solution it can be seen that the quantum yield increased scientifically for complexes with cyclophanes I and II, while it did not change with cyclophane III. This suggests that energy transfer in PMMA is more efficient than in any of the studied solvents. The relatively rigid matrix structure has inhibited the vibration of the ligand around Tb^{3+} and Eu^{3+} bringing about a longer luminescence lifetime and as a result the luminescence quantum yield increases in PMMA as shown in Figure 5 and Table 3; see [42]. However, the quantum yield values obtained for Tb^{3+} or Eu^{3+} complexes showed no change with cyclophane III. This can be rationalized as a decrease in the rotation of the molecule in the matrix making it improbable to host Tb^{3+} or Eu^{3+} .

3.4. Luminescence mapping

A three-dimensional plot is required for a complete description of the luminescence; see Figures 6 and 7. It may be presented as a so-called excitation/emission matrix [43, 44]. Furthermore, connection of data points with the same luminescence intensity (i.e., same height) by lines results in tomograms of two-dimensional representation (luminescence mapping). Such diagrams always represent a top view [45]. This method seems to be useful as a qualitative tool. In particular, the location and relative intensity of peaks are suitable parameters for pattern recognition analysis as well as a useful new method in clinical chemistry and biochemistry [46–48].

TABLE 3: Quantum yield values of 8×10^{-5} M of Tb^{3+} and Eu^{3+} in the presence of 2×10^{-5} M of ligands (I, II, and III) in different media, Φ ($\pm 5\%$).

Complex	Methanol	Acetonitrile	DMSO	DMF	Ethylacetate	PMMA
Tb(I)	0.003	0.015	0.071	0.014	0.007	0.137
Tb(II)	0.041	0.057	0.075	0.058	0.055	0.116
Tb(III)	0.054	0.064	0.109	0.059	0.067	0.110
Eu(I)	0.002	0.010	0.068	0.010	0.003	0.125
Eu(II)	0.011	0.025	0.070	0.047	0.045	0.106
Eu(III)	0.038	0.058	0.089	0.057	0.056	0.099

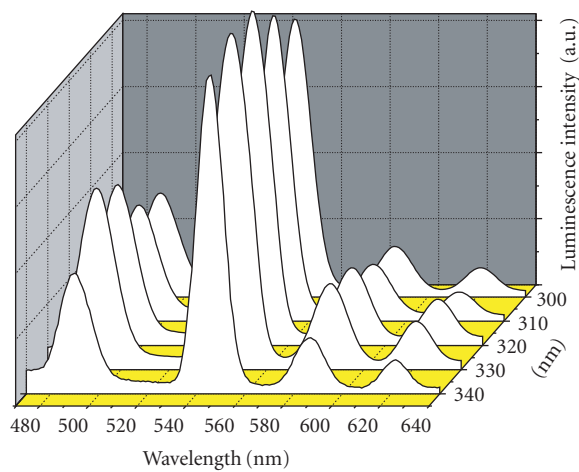


FIGURE 6: 3D view of the emission spectra of Tb^{3+} ion in Tb-(III) complex at different excitation wavelengths in DMSO.

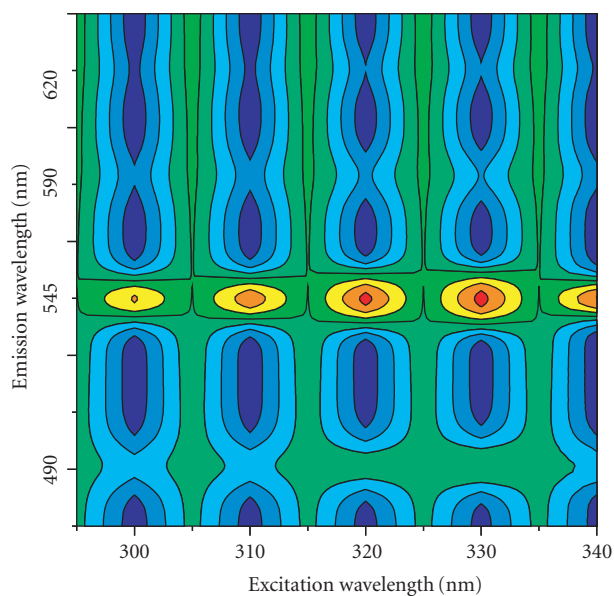


FIGURE 7: Contour view of the emission spectra of Tb^{3+} ion in Tb-(III) complex at different excitation wavelengths in DMSO.

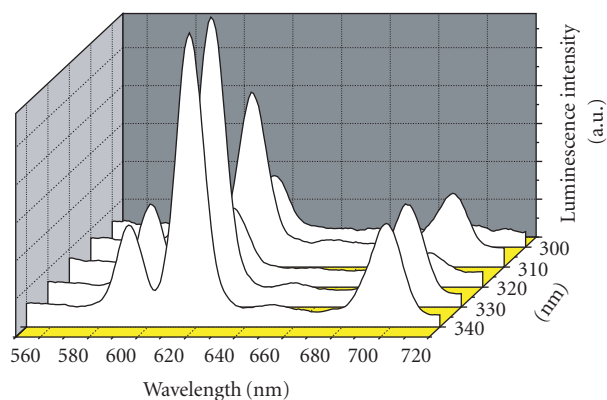


FIGURE 8: 3D view of the emission spectra of Eu^{3+} ion in Eu-(III) complex at different excitation wavelengths in DMSO.

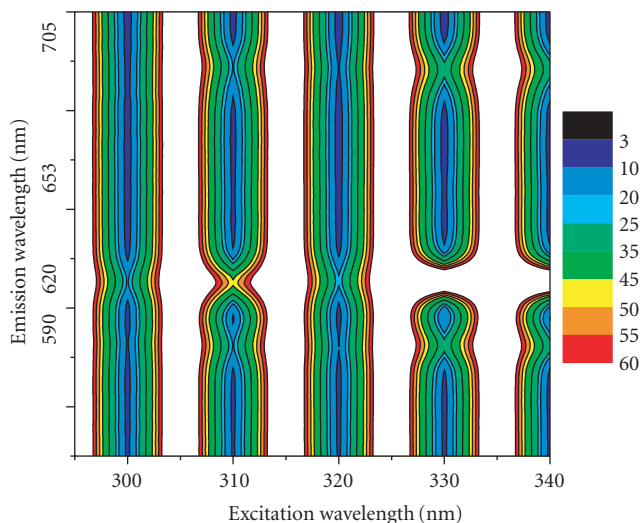


FIGURE 9: Contour view of the emission spectra of Eu^{3+} ion in Eu-(III) complex at different excitation wavelengths in DMSO.

The excitation/emission matrix represents the fingerprint of metal ions (Tb^{3+} and Eu^{3+} ions), which is different according to different excitation wavelengths; see Figures 8 and 9.

4. CONCLUSION

Cyclophanes containing spirobiindanol phosphonates have been proven to be efficient light sensitizers for the studied

lanthanide ions Tb^{3+} and Eu^{3+} . The luminescence intensities for the complexes in DMSO, DMF, and CH_3CN solutions are stronger than those in hydroxy solvents as methanol solutions. The further enhancement of the luminescence intensity observed in rigid PMMA reflects the much higher energy transfer from the ligand to the metal ion due to the hindrance of vibrational/torsional deactivation channel.

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