



Theoretical and experimental photophysical studies of the tris(4,4,4-trifluoro-1-(1-naphthyl)-1,3-butanedionate) (2,2'-bipyridyl)-europium(III)

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Abstract

The complexes tris(4,4,4-Trifluoro-1-(1-naphthyl)-1,3-butanedionate) (2,2'-bipyridyl) Ln(III), Ln(tan)₃bipy, where Ln(III) = Eu³⁺ and Gd³⁺ have been synthesized, characterized and their photophysical properties (absorption, excitation and luminescence spectra and emission quantum yield) investigated down to 4.2 K. The Eu(tan)₃bipy complex has its molecular structure experimentally determined using X-ray crystallography and theoretically using the SMLC/AM1 method as well as their electronic singlet and triplet states were calculated, using the INDO/S-CI method with a point charge model to represent the Eu³⁺ ion, where two values were adopted, +3.0e and +3.5e, to investigate the imperfect shielding of the 4f shells. The so calculated +3.5e model electronic absorption spectrum and low lying triplet state energies agreed very well with the experimental ones. The emission quantum yield of the Eu³⁺ complex is quite low at room temperature, namely 7%, probably due to the too low lying triplet state, 19,050 cm⁻¹, and increases by a factor of three when the temperature is lowered to 4.2 K. This strong thermal effect indicates the presence of a channel deactivating the main emitting state, what can be due to a LMCT state possibly lying in the same spectral region, as usually found in Eu³⁺ compounds.

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1. Introduction

In recent years there has been an increasing interest in the search for efficient light-converting devices based on rare-earth coordination compounds. Efficient light-conversion molecular devices

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(LCMDs) may find several applications such as luminescent probes in photosensitive bioinorganic compounds [1] and fluoroimmunoassays [2–3], fluorescent lighting [4], luminescent sensors for chemical species [5], electroluminescent devices, UV dosimeters [6], or antireflection coatings for solar cells [7]. In addition to the emission quantum yield of LCMD, other aspects, such as light output, solubility, volatility, photo and thermal stabilities as well as thermodynamic and kinetic stabilities, may be critical to many applications and must be controlled as well.

In order to gain insight into the factors that determine the quantum yield and other relevant properties of lanthanide complexes our group has been investigating the photophysical properties of a number of new lanthanide complexes, using an approach based upon both theoretical and experimental work [8–17]. The results have shown that the quantum yield of a lanthanide complex arises from a balance among the rates of several processes, e.g., ligand to Ln^{3+} energy transfer, multiphonon relaxation, energy back-transfer, crossover to charge-transfer states, etc. The control of these rates, as well as of other relevant physical properties, has been accomplished by a thorough selection of ligands, allowing us to develop some promising LCMDs [8,11–15], with high quantum yields at room temperature, leading to new applications [6,7]. We are now reporting the synthesis, spectroscopic, X-ray characterization, and photophysical investigation, as well as the molecular and electronic structure prediction with emphasis on the ligand-centered triplet energy level of the lanthanide complexes $\text{Ln}(\text{tan})_3\text{bipy}$, where $\text{Ln} = \text{Eu}^{3+}$ or Gd^{3+} ; $\text{tan} = 4,4,4$ -trifluoro-1-(1-naphthyl)-1,3-butanedionate and $\text{bipy} = 2,2'$ -bipyridyl.

2. Experimental procedure

2.1. Synthesis

The starting chemicals were Eu_2O_3 99.9%, Gd_2O_3 99.9%, La_2O_3 99.9%, tan 99%, and bipy 99% all obtained from Aldrich. The above oxides have been converted into their respective chlorides

through addition of HCl (0.7 mol L^{-1}) and successive evaporations in ethanol.

Syntheses of the Eu^{3+} and Gd^{3+} complexes were accomplished by adding a stoichiometric quantity of an ethanolic solution of the anion of tan (3 mmol) and an ethanolic solution of bipy (1 mmol) dropwise to an ethanolic solution of $\text{LnCl}_3 \cdot x\text{H}_2\text{O}$. The reaction was refluxed for 12 h and solid compounds were obtained after solvent evaporation. $\text{Eu}(\text{tan})_3\text{bipy}$ crystals suitable for X-ray structure determination were grown from a $\text{MeOH}/\text{H}_2\text{O}$ mixed solvent. The chemical analytical data of the complexes indicate the formula $\text{Eu}(\text{tan})_3\text{bipy}$ (found: C, 56.16%; H, 3.42%; N, 2.00%; Calc.: C, 56.58%; H, 2.92%; N, 2.54%).

2.2. Spectroscopic measurements

The UV-Vis absorption spectra were recorded with a Perkin-Elmer Lambda 6 spectrophotometer using 10^{-5} M ethanolic solutions of the complexes. Diffuse reflectance spectra of the powder samples were recorded with a Perkin-Elmer Lambda 7 spectrophotometer equipped with an integration sphere. The IR absorption spectra were measured on a Bruker IF566 FTIR spectrophotometer using the KBr pellet technique.

The luminescence spectrum of the Eu^{3+} complex at 77 K was obtained under excitation at 370 nm, by using a 150 W Xe lamp and a Jobin–Yvon 0.25 m monochromator. The luminescence was dispersed by a Jobin–Yvon double monochromator (model V-1000) and the signal was detected by a water-cooled RCA C31034-02 photomultiplier. Excitation of the Gd^{3+} complex was accomplished with a laser science model VSL-337ND laser at 330 nm.

Excitation and luminescence spectra were also obtained by using a Spex Fluorolog DM3000F spectrofluorometer with double-grating 0.22 m Spex 1680 monochromators and a 450 W Xe lamp as the excitation source. This setup is equipped with an Oxford LF205 liquid helium flow cryostat, allowing for measurements down to 4.2 K. The spectra were corrected for the instrumental response.

Excited state decay-time measurements were performed at 298 and 77 K using the third

harmonic of an Nd–YAG laser (10 Hz) as the excitation source. The emission was detected with a modified IP28 photomultiplier tube after dispersion through a 0.25 m monochromator. A filter was used to cutoff any residual laser light. The signal was then analyzed on a Boxcar system (EG&G Princeton applied research). The temporal resolution of the overall system is ca. 50 ns.

The emission quantum yield, q , defined as the ratio between the number of photons emitted by the Eu^{3+} ion and the number of photons absorbed by the ligand, was measured according to the method described in detail elsewhere [10], which has an accuracy of 10%.

The crystal structure was elucidated by X-ray diffraction analysis. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer, using $\text{MoK}\alpha$ radiation (graphite monochromator) in the $\varpi - 2\theta$ scan mode, at room temperature. Data were corrected for absorption using Ψ -scan [18] ($T_{\text{max}} = 0.9999$, $T_{\text{min}} = 0.9847$). The structure was solved by SIR92 [19] and refined by SHELXL-97 [20].

3. Theoretical procedure

The molecular structure of $\text{Eu}(\text{tan})_3\text{bipy}$ was obtained with the SMLC II (Sparkle Model for lanthanide compounds–parameterization scheme II) method [21–23] implemented within the MO-PAC93 program [24]. Two starting geometries were used in the optimization procedure, namely, the experimental X-ray (structure 1) and a model structure (structure 2) constructed from a similar compound of known structure.

The absorption transitions as well as the triplet state energy levels, both ligand-centered, were calculated with the INDO/S-CIS (Intermediate neglect of differential overlap/spectroscopy parameterization–configuration interaction singly excitations) method [25,26]. The Eu^{3+} ion is replaced by a [27] $+3e$ and a [28] $+3.5e$ point charge. This method considers all configurations obtained by singly electron replacements (CIS) of the reference determinant within an active space. The variable point charge value is intended to investigate the imperfect shielding of the 4f shells from the

coordinated carbonyl groups affecting the position of the $\text{C}=\text{O}$ centered $\pi \rightarrow \pi^*$ states and subsequently the triplet state energies [28].

For the $\text{Eu}(\text{tan})_3\text{bipy}$ compound, an active space of 28 occupied and 16 unoccupied molecular orbitals (MOs) yielded converged results for the calculated absorption spectrum (transition energies and oscillator strengths). In order to better compare the calculated spectrum with the experimental one, a Lorentzian lineshape with a 30 nm bandwidth has been adjusted to the calculated results [27].

4. Results and discussions

It is observed that the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretching bands shift from 1577 cm^{-1} and 1558 cm^{-1} , respectively, in the free bipy ligand, to 1595 cm^{-1} and 1569 cm^{-1} in the complexes. These observations provide evidence that the metal ion is coordinated through the nitrogen atoms [29]. Another good evidence for the complexation is obtained by observations of the $\text{C}=\text{O}$ stretching band. It is a large band in the free tan ligand (enolic and diketone forms are possible) at 1600 cm^{-1} and becomes narrower in the complexes (just enolic form is expected) at 1610 cm^{-1} .

The crystal structure of the $\text{Eu}(\text{tan})_3\text{bipy}$ complex has been elucidated by X-ray crystallography [30] (Fig. 1) and yielded the empirical formula $\text{EuC}_52\text{H}_{32}\text{O}_6\text{N}_2\text{F}_9$, which is consistent with the microanalytical results. This complex crystallizes in a primitive cell with four molecules per unit cell and a monoclinic crystalline system with a symmetry spatial group $P2_1/c$, which is detailed in Table 1.

The luminescence spectrum of $\text{Gd}(\text{tan})_3\text{bipy}$ at 4.2 K, presented in Fig. 2, was measured in order to determine the excited energy levels of the organic ligands that could participate in the energy transfer process to the Eu^{3+} in the $\text{Eu}(\text{tan})_3\text{bipy}$ compound. The maximum occurs at 525 nm ($19,050\text{ cm}^{-1}$) and since the correspondent 77 K measured decay time was 330 μs , this emission was ascribed to a triplet state. In this way, this peak is chosen as the experimental estimate of the lowest triplet energy level of the whole ligand system.

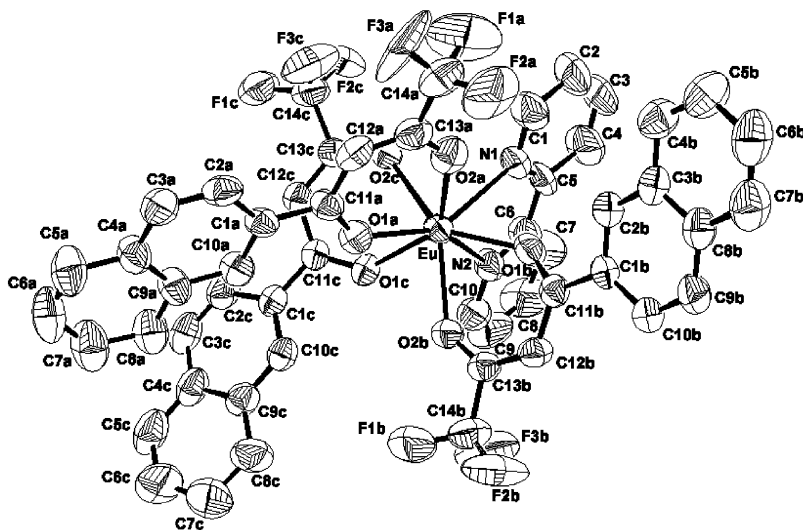


Fig. 1. ORTEP drawing of the $\text{Eu}(\text{tan})_3\text{bipy}$ complex crystallographic structure (50.0% probability ellipsoids, except for the hydrogen atoms).

Table 1

Crystallographic data for $\text{Eu}(\text{tan})_3\text{bipy}$

Chemical formula:	Formula weight: 1106.78
$\text{EuC}_{52}\text{H}_{35}\text{O}_6\text{N}_2\text{F}_9$	
crystal system: monoclinic	Space group: $P2_1/c$ (No. 14)
$a = 11.307(1) \text{ \AA}$	$T = 293(2) \text{ K}$
$b = 23.497(2) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$c = 17.961(2) \text{ \AA}$	$\rho_{\text{calc}} = 1.553 \text{ g/cm}^3$
$\beta = 97.10(1)^\circ$	$\mu = 14.12 \text{ mm}^{-1}$
$V = 4735.1(8) \text{ \AA}^3$	$R(F^2) = 0.0445^a$
$Z = 4$	$R_w(F^2) = 0.0865^b$

$$^a R(F^2) = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}$$

$$^b R_w(F^2) = \left[\frac{\sum w (|F_o| - |F_c|)^2}{\sum w |F_o|^2} \right]^{1/2}$$

This state is usually considered the main channel for energy transfer to the lanthanide $^5\text{D}_j$ states. However, in this case, the energy level of this triplet state is quite low and, thus it is not in optimal resonance conditions with the Eu^{3+} emitting levels ($^5\text{D}_j$) in the energy transfer process. This statement is corroborated by the low quantum yields measured for this compound as shall be discussed below. Furthermore, the $\text{Gd}(\text{tan})_3\text{bipy}$ luminescence spectrum presents a well resolved vibrational progression, where the shortest wave-

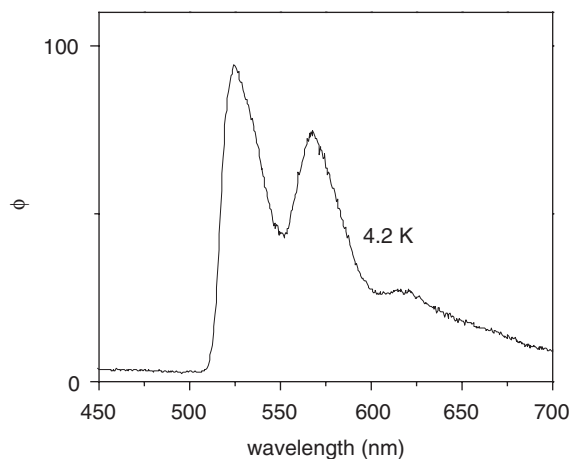


Fig. 2. Luminescence spectrum of $\text{Gd}(\text{tan})_3\text{bipy}$ at 4.2 K, upon ligand excitation (330 nm). ϕ gives the radiant power per constant wavelength interval in arbitrary units.

length band, the band maximum at 525 nm, is assigned to the 0–0 phonon line, whereas the two following bands with decreasing intensities, at 565 and 625 nm, are assigned to the 0–1 and 0–2 phonon lines, respectively. This spectrum is characteristic of an emitting excited state with a energy potential curve that has little displacement of its minimum in comparison to the ground state

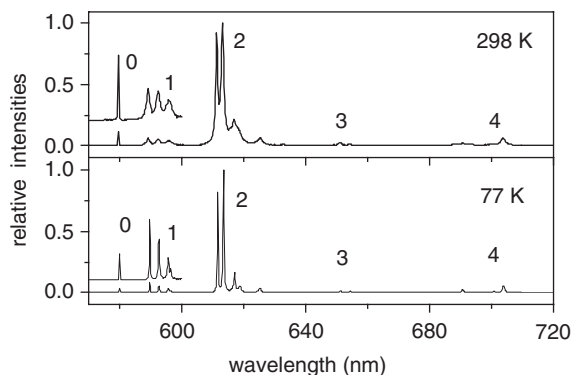


Fig. 3. Luminescence spectra of the powdered $\text{Eu}(\text{tan})_3\text{bipy}$ complex at 298 and 77 K excited at 370 nm. The labels refer to the J values of the final level of the emission transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$. The insets show the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0,1}$ region magnified.

potential curve minimum, which would correspond to a small Huang–Rhys coupling constant, S [31], commonly used in the solid state literature, $S \sim 1$ (weak-to-intermediate coupling case). This behavior will be, as seen below, important in the nonradiative deactivation of the $\text{Eu}(\text{tan})_3\text{bipy}$ compound luminescence at room temperature.

The luminescence spectra at 298 and 77 K of the powdered $\text{Eu}(\text{tan})_3\text{bipy}$ complex are presented in Fig. 3. The emission lines of Eu^{3+} complex were attributed to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition presents three large bands where one of them is split, possibly due to a vibronic effect. The hypersensitive transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ shows best resolution at 77 K as is shown in Fig. 3.

The luminescence spectrum at 298 K of the $\text{Eu}(\text{tan})_3\text{bipy}$ in the single-crystalline material is similar to that of the powdered. The spectrum of the crystal was also measured at 77 K (Fig. 3), and indicates the existence of a low symmetry but a single site for the Eu^{3+} ion, which was previously observed by X-ray diffraction analysis.

As mentioned above, at temperatures lower than 120 K the Gd^{3+} complex shows a broadband green luminescence upon UV excitation (Fig. 2), which is ascribed to the triplet ligand states. This emission is completely absent in the Eu^{3+} complex, even at 4.2 K, indicating the occurrence of ligand to Eu^{3+} energy transfer. Nevertheless, the quantum yield of the Eu^{3+} emission in the

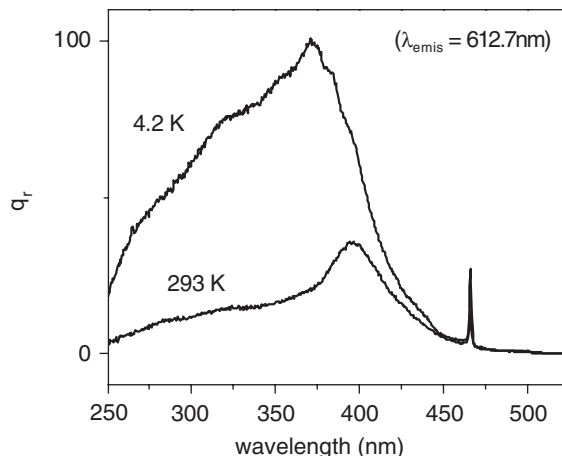


Fig. 4. Excitation spectra of the Eu^{3+} luminescence (emission wavelength at 612.7 nm) in $\text{Eu}(\text{tan})_3\text{bipy}$ complex at 293 and 4.2 K. q_r gives the relative external quantum yield.

$\text{Eu}(\text{tan})_3\text{bipy}$ complex is rather low at 300 K (viz. 7%). It is probably due to the too low energy of the triplet ligand state, namely $19,050 \text{ cm}^{-1}$, poorly resonant with the ${}^5\text{D}_2$ state ($21,000 \text{ cm}^{-1}$) of the Eu^{3+} ion, which is believed, as it was recently proposed [32], to be the most important channel for an efficient luminescence via the exchange mechanism. Another interesting aspect is that the quantum yield of the Eu^{3+} emission increases by a factor of three (7–21%) when the temperature is lowered to 4.2 K (Fig. 4). This observation implies the existence of a quenching state whose population is strongly temperature dependent. Usually, the crossover from the ${}^5\text{D}_0$ emitting state (or from its feeding levels) to a charge transfer (CT) state involves an energy barrier and it is therefore strongly dependent on the temperature [9]. The charge transfer state will then be depopulated via nonradiative decay to the ground state, therefore, resulting in quenching of the Eu^{3+} luminescence [9,31,33]. Since the available thermal energy at 4.2 K is small, it seems likely that the crossover rate to the CT state would be very slow at this temperature, thus this quenching channel would not be significant. However, at higher temperatures the thermally activated crossover to the CT state becomes faster, therefore, leading to a larger degree of quenching and a lower emission

quantum yield. Other important nonradiative losses of the system are through ion states ($4f-4f$ transition) or via the lowest ligand triplet level after an energy back-transfer Eu^{3+} -to-ligand process. Among these processes, the last one involves an energy barrier, as in the CT case, and is exponentially dependent upon temperature. Based on these statements, we suggest that the reasons for this large decrease of the quantum yield through lowering the temperature are two-fold: (i) a significant energy back-transfer from the Eu^{3+} states to the ligand states, which being ligand-centered decay nonradiatively and; (ii) energy transfer from either ligand or Eu^{3+} states to the LMCT states that acts as quencher states due to nonradiative decay.

Fig. 4 shows that the dependence of the Eu^{3+} luminescence quenching with the temperature is not the same for all the excitation wavelengths, being more pronounced for wavelengths shorter than ca. 400 nm. We can assume that the energy back-transfer from the Eu^{3+} to the ligand states mechanism is weakly dependent upon the excitation wavelength, whereas the opposite behavior is expected for the energy transfer from the ligand to the LMCT states, since LMCT states with higher energies would become viable. Thus, for excitation wavelengths shorter than 400 nm it is expected that the quenching through LMCT states dominate. Whereas, for excitation wavelengths longer than 400 nm it is expected a competition between these two mechanisms. Also, the $^5\text{D}_0$ lifetime is not strongly temperature dependent, changing from 447 μs at 300 K to 432 μs at 77 K. This suggests that there should not be any LMCT states with energies near the $^5\text{D}_0$ one and that the nonradiative depopulation of the $^5\text{D}_0$ state via back-energy transfer to the ligand triplet states should be negligible. As a result, we can infer that the LMCT states have energies larger than $25,000\text{ cm}^{-1}$, that is $\lambda > 400\text{ nm}$, and they are the dominating states for luminescence quenching in the $\text{Eu}(\text{tan})_3\text{bipy}$ complex at any temperature and excitation wavelength.

The absorption spectrum of the $\text{Eu}(\text{tan})_3\text{bipy}$ complex in ethanolic solution is presented in Fig. 5 together with the theoretical predictions. It can be seen three broad bands with maxima at 257, 289

and 334 nm, the second one being the least intense. These bands have been assigned to $\pi \rightarrow \pi^*$ like ligand-centered transitions.

The ligand-centered absorption spectra of the $\text{Eu}(\text{tan})_3\text{bipy}$ complex has been calculated with the INDO/S-CIS method using both a +3.0 and +3.5 point charge representing the lanthanide ion [28]. The reasoning for using a larger than +3.0 point charge has been discussed elsewhere [28], and as it can be seen from Fig. 5, the spectrum calculated with the +3.5 point charge is in better agreement with the experimental one than that using a +3.0 point charge. It should also be noted that there are no significant differences between the calculated spectra of the structures 1 (X-ray) and 2 (model), except near 240 nm, where structure 2 yields a small shoulder, which is absent in the spectrum of structure 1. These results show that despite the differences in the starting structures, the SMLC II method is quite robust and yields optimized structures that have almost identical absorption spectra. In Table 2 the comparison between the calculated and experimental data regarding the energy levels of the $\text{Eu}(\text{tan})_3\text{bipy}$ complex is presented and it can be observed a very good agreement between the experimental and theoretical energy levels. The experimental absorption

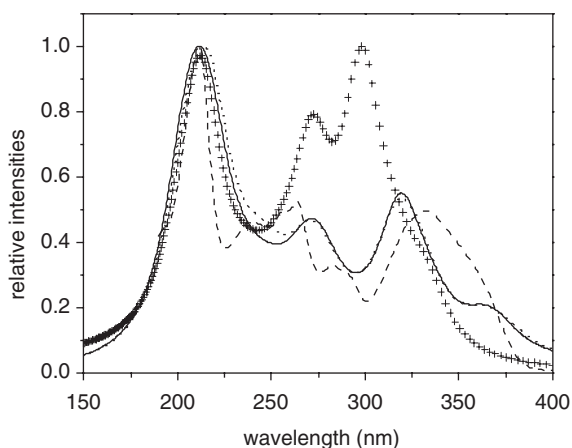


Fig. 5. Experimental ethanolic solution (dashed line) and theoretical absorption spectra of the $\text{Eu}(\text{tan})_3\text{bipy}$ complex obtained with a +3.0 point charge with structure 1 (+ + +), a +3.5 point charge with structure 1 (solid line) and a +3.5 point charge with structure 2 (dotted line).

Table 2
Theoretical (+3.5e point charge) and experimental ligand-centered energy levels

Structure	Singlet			Triplet energy (cm ⁻¹)	
	Experimental	Theoretical	Oscillator strengths	Experimental	Theoretical
	Energy (cm ⁻¹)	Energy (cm ⁻¹)			
1 (X-ray)	30,303	31,553	1.92	19,050	
		29,953	0.32		18964
	27,397	27,796	0.2		18746
		27,123	0.25		18297
2 (model)	30,303	30,459	0.33	19,050	
		29,977	0.19		19016
		27,914	0.25		18797
	27,397	27,471	0.12		18723
		26,447	0.2		

spectrum presents only a maximum at 30,303 cm⁻¹ and a large shoulder at longer wavelength 27,397 cm⁻¹. From Table 2 it can be observed that the largest theoretical oscillator strengths are found at the same region. Also in Table 2, a good agreement can be observed between the experimental and the theoretical triplet energy levels, which is slightly red shifted.

5. Conclusions

Insights into the electronic structure of the Eu(tan)₃bipy complex, focusing the role of the ligand triplet state in the energy transfer process, as well as the temperature dependence of its luminescence quantum yield based on the presence of a LMCT state have been provided. The experimental and theoretical calculations are consistent and could help to improve the design of new luminescent materials and to understand the ligand-lanthanide energy transfer process at the electronic level.

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