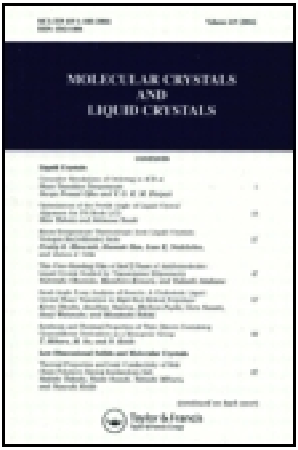

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Optical Properties of the Eu(Thenoyltrifluoroacetonate)$_3$. (Cholesteryl Tetradecanoate or Nonanoate) Complexes

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Optical Properties of the Eu(Thenoyltrifluoroacetonate)$_3$. (Cholesteryl Tetradecanoate or Nonanoate) Complexes

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We report the optical properties study of two new europium coordination complexes Eu(Thenoyltrifluoroacetonate)$_3$. (Cholesteryl Pelargonate), n H_2O (**EuTTA$_3$P**), Eu(Thenoyltrifluoroacetonate)$_3$. (Cholesteryl Myristate), n H_2O (**EuTTA$_3$M**) and of an optically active cholesteric liquid crystal (CLC) mixture obtained doped with these two fluorescent complexes. Refractive indices of these coordination compounds and of the doped cholesteric liquid crystal mixture have been determined. Wavelength-dependent scattering of these doped cholesteric mixtures has been investigated. Optical absorption and luminescence bands of **EuTTA$_3$P** and **EuTTA$_3$M** have been measured and assigned to transitions between the energy levels of Eu^{3+}. From these optical measurements and using Judd-Ofelt theory, intensity parameters Ω_2, Ω_4 and emission cross-section have been estimated.

Keywords: Cholesteric liquid crystal; europium complex; Judd-Ofelt

INTRODUCTION

Recently, we have published the synthesis and the luminescence properties of new Eu^{3+} complexes **EuTTA$_3$P** and **EuTTA$_3$M**, which can be homogeneously added to a CLC mixture[1]. We have introduced 2.5 molar percent of dopants with an empirically determined amount of CLC to obtain an optically active CLC mixture shortly labeled **Eu$_{2.5}$MPN** with a selective reflection band located at 616 nm. The work described in this paper is a part of our investigation of the optical properties of these two new coordination compounds and of the doped CLC mixture. Refractive indices of the two new materials and of the doped CLC mixture have been measured separately using a microellipsometer and a Abbe-refractometer respectively. Wavelength-dependent scattering of **Eu$_{2.5}$MPN** has been investigated. From absorption and luminescence spectra of **EuTTA$_3$P** and **EuTTA$_3$M**, the Judd-Ofelt theory has been successfully used in estimating the intensities of the transitions of the rare earth ion. This theory requires the use of a set of three intensity parameters $\Omega_{t=2,4,6}$ that allow to predict the emission characteristics of Eu^{3+} in peculiar structure of our complexes. The stimulated emission cross sections of Eu^{3+} can be estimated from this study.

EXPERIMENTAL

Used molecular species

In this work, we have used two new cholesteryl alkanoate complexes say **EuTTA$_3$P** and **EuTTA$_3$M**. Let us briefly remind the synthesis process of these molecules. The reaction scheme is given in Fig. 1. For more details, the reader can refer to our previous paper[1].

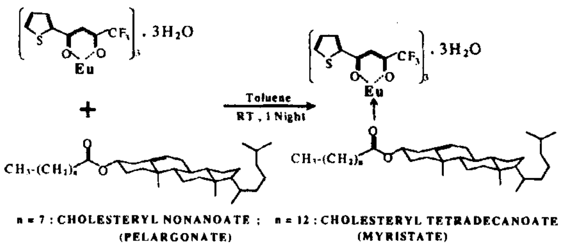


FIGURE 1 Synthesis of the complexes **EuTTA$_3$P** and **EuTTA$_3$M**.

Absorption

The absorption spectra have been recorded at room temperature using a computer controlled Cary 2300 spectrophotometer.

Emission

The fluorescence has been excited using the 488nm line of an Ar^+ Coherent Radiation Innova 300 CW laser. The corresponding spectra have been recorded using a computer controlled SOPRA model F1500 spectrometer equiped with a 600 groves mm^{-1} grating, a Hamamatsu R928 photomultiplier and a Stanford Research model SR830 Lock-in amplifier.

Refractive indices

The refractive indices have been measured with a conventional Abbe-refractometer at the wavelenght of a He-Ne laser (632.8 nm) or by using a Jobin-Yvon microellipsometer.

RESULTS AND DISCUSSION

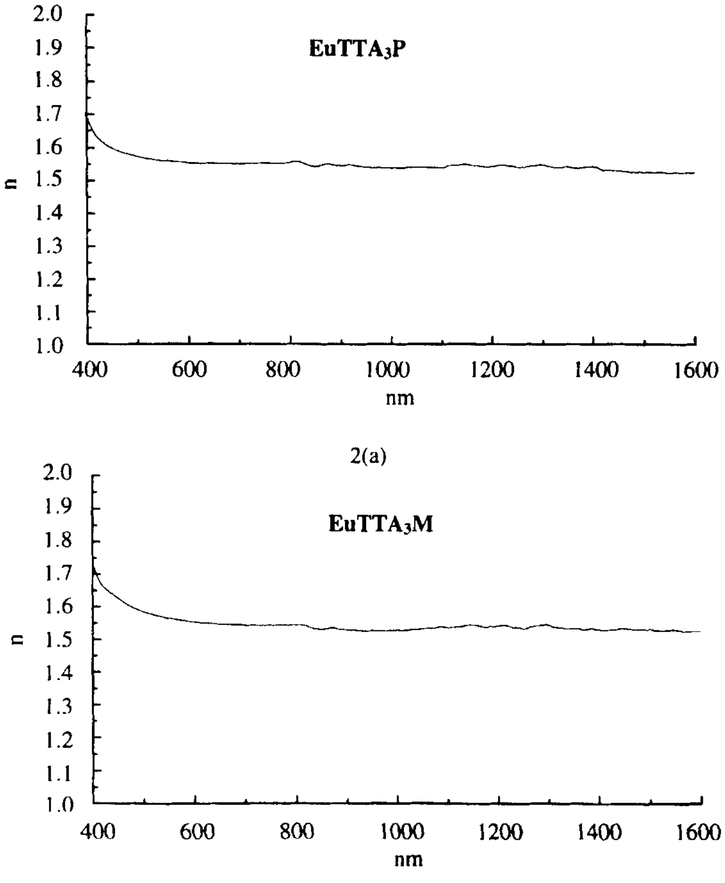
Realization of a doped cholesteric liquid crystal mixture.

To realize an aggregate free doped cholesteric liquid crystal mixture with a selective reflection band located in the visible or near infrared regions and to prevent any crystallisation at room temperature, the $EuTTA_3P$ and $EuTTA_3M$ molecules were blended with an empirically determined mixture of Pelargonate, Myristate and ZLI 1083 Nematic liquid crystals.

In the case of this study, 2.5 molar percents of dopants were blended with 27.8% of Pelargonate, 8.1% of Myristate and 61.6% of Nematic. Finally a doped mixture **$Eu_{2.5}MPN$** still presenting the liquid crystal phase at room temperature with a selective reflective band located at 616 nm has been obtained.

Refractive indices measurement of $Eu_{2.5}MPN$.

The refractive indices of **$EuTTA_3P$**, **$EuTTA_3M$** have been determined by using a microellipsometer. The obtained dispersion curves are shown in (Fig. 2(a) and 2(b)).



2(b)

FIGURE 2 Dispersion curves of **EuTTA$_3$P** and **EuTTA$_3$M**.

The refractive index of **Eu$_{2.5}$MPN** has been measured using a computer controlled conventional Abbe refractometer at the wavelength of a HeNe laser[2]. The **Eu$_{2.5}$MPN** mixture was introduced by capillarity in a cell made up of a corning prism and a glass slide. The facing planar surfaces were preliminarly cleaned with methanol and rubbed with diamond paste (0.25 μm grain size) to obtain a planar orientation of the doped CLC sample (Fig. 3).

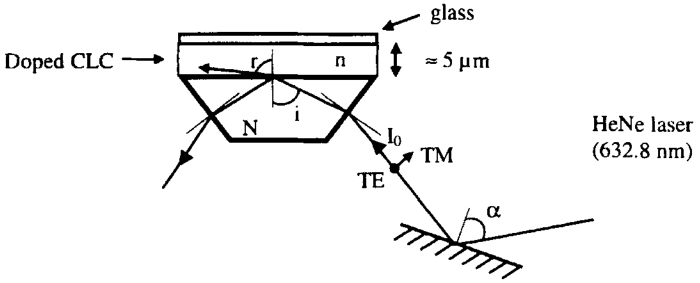
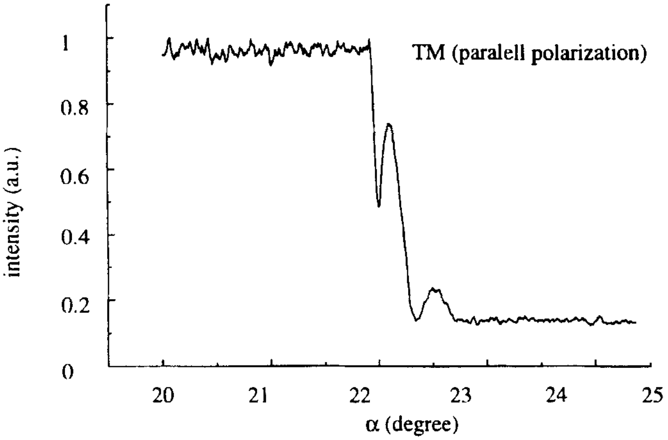
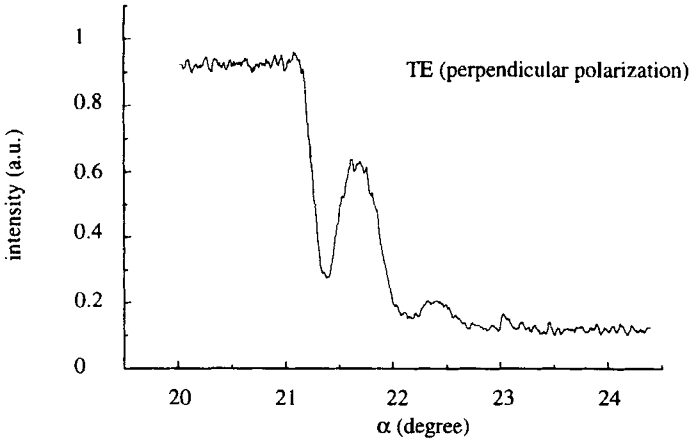


FIGURE 3 Experimental arrangement.

The two reflectivity curves corresponding to the TM and TE polarizations are presented in Fig. 4(a) and 4(b).



4(a)



4(b)

Figure 4 Reflectivity curves of **$Eu_{2.5}$MPN** for the TM and TE polarizations.

The principle of the Abbe refractometer rests on the on measurement of the boundary angle of total reflection. The value of this angle is derived from the reflectivity curves 4(a) and 4(b) for the TM and TE polarization respectively. As it is well known, for a cell containing a CLC, the total reflection occurs for an incident angle [3]: $i_{TM} = \sin^{-1}(n_{TM}/N)$

for the TM polarization, and for an incident angle :

$$i_{TE} = \sin^{-1}(n_{TE}/N)$$

for the TE polarization. We consider N = 1.88 for the corning prism.

And for a CLC, we have the extraordinary an ordinary indices [4]:

$$n_{e,ch} = n_{TM}$$

$$n_{o,ch} = \sqrt{1/2\left(n_{TM}^2 + n_{TE}^2\right)}$$

Finally, we obtain :

$$n_{o,ch} = 1.503$$

$$n_{e,ch} = 1.511$$

with a mean refractive index : $\bar{n} = (n_{o,ch} + n_{e,ch})/2 = 1.507$.

Light scattering measurement for Eu$_{2.5}$MPN.

The wavelength-dependence of the light scattering coefficient of **Eu$_{2.5}$MPN** is shown in Fig. 5. Determination of this scattering is realized using the transmission technique[5]. Two cells with different thicknesses d and 2d (with d = 6 μm), with planar alignment of the doped CLC, were realized. The two transmissions of these cells were taken at a wavelength λ :

$$\begin{cases} T_1 = \dfrac{I_{t1}}{I_0} = t_1^2 \cdot t_2^2 \cdot e^{-\alpha d} \cdot e^{-\beta d} \\ T_2 = \dfrac{I_{t2}}{I_0} = t_1^2 \cdot t_2^2 \cdot e^{-\alpha 2d} \cdot e^{-\beta 2d} \end{cases},$$

where α is the absorption coefficient and β the scattering coefficient at the wavelength λ, t_1 and t_2 the Fresnel's coefficients at the entrance and at the exit of the cell respectively. The ratio represents the normalized transmittance of the CLC layer of thickness d: $\dfrac{T_1}{T_2} = e^{(\alpha+\beta)d}$

where α representing the absorption is small at room temperature compared with β representing the scattering. The coefficient of scattering β at the wavelength λ, is calculated according the relation : $\beta = \dfrac{1}{d} \ln \dfrac{T_1}{T_2}$

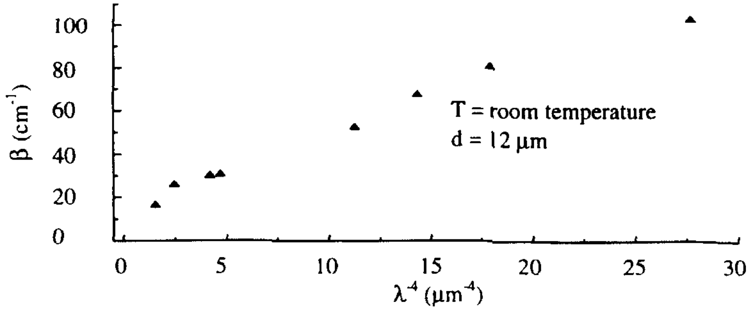
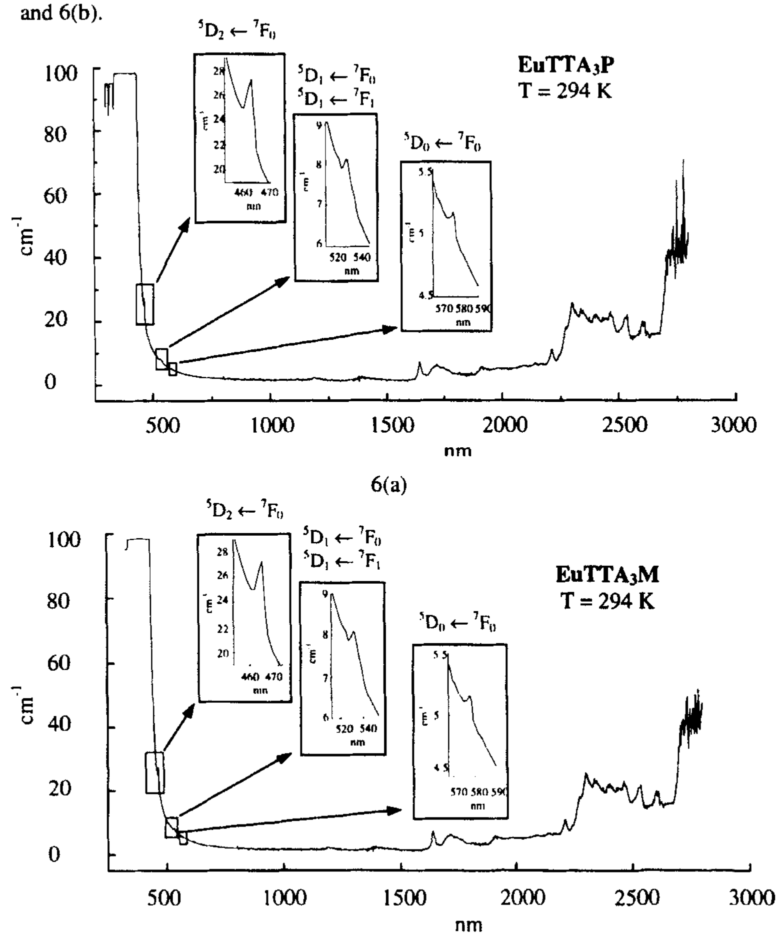


FIGURE 5 Wavelength dependence of the light scattering of **Eu$_{2.5}$MPN**.

As seen in Fig. 5, the scattering coefficient is inversely proportionnal to the fourth power of the wavelength for **Eu$_{2.5}$MPN** as generally described in the literature on the liquid crystals[6].

Spectroscopic study of EuTTA$_3$P and EuTTA$_3$M.

The absorption spectra of **EuTTA$_3$P** and **EuTTA$_3$M** are shown in Figs.6(a) and 6(b).



6(a)

6(b)

FIGURE 6 Absorption spectra of **EuTTA$_3$P** and **EuTTA$_3$M**.

The Judd-Ofelt analysis is based on measured absorption line strengths at sufficiently high temperature (in general at room temperature) to provide a significant population of the various Stark levels of the ground state. Details on the theory have been well described earlier[7,8] ; hence, only a brief presentation of the method will be given here. First all, in calculating the line strengths, the selection rules for electric dipole and magnetic dipole transitions must be considered.

The selection rules for electric dipole transitions are :

$$\Delta\ell = \pm 1,\ \Delta S = 0,\ |\Delta L|,\ |\Delta J| \le 2\,\ell$$

where, for the lanthanides, $\ell = 3$.

The selection rules for magnetic dipole transitions are :

$$\Delta S = \Delta L = 0,\ \Delta J = 0, \pm 1 \text{ (but } 0 \leftrightarrow 0 \text{ is forbiden).}$$

According the Judd-Ofelt theory, the electric dipole line strength for a transition from a level J to a level J' is given by :

$$S_{ed}^{J'\leftarrow J} = \sum_{t=2,4,6} \Omega_t \left|\left\langle \Psi J \left\| U^{(t)} \right\| \Psi' J' \right\rangle\right|^2$$

The matrix elements $U^{(t)}$ used in the present work, were calculated by Carnall, Fields and Rajnak[9]. These matrix elements only depend on the rare earth ion which is considered. The host dependent part of the line strengths is contained in the so called Judd-Ofelt intensity parameters Ω_t. To perform the treatment we need to know how to calculate the line strengths from the recorded absorption spectra and this is made possible by use of the following relation[7,8] :

$$S_{ed}^{meas}(J' \leftarrow J) = \frac{9n}{\left(n^2+2\right)^2}\left[\frac{3hc}{8\pi^3}\frac{1}{e^2}\frac{2J+1}{N}\frac{1}{\bar{\lambda}}\int_{J'\leftarrow J} k(\lambda)d\lambda - nS_{md}\right]$$

where n stands for the refractive index of the material, N the Eu^{3+} number density, $\bar{\lambda}$ the mean wavelength of the $J' \leftarrow J$ transition, $k(\lambda)$ the measured absorption and S_{md} the magnetic dipole line strenght.

The existence of transitions between the $^7F_0$, $^7F_1$ ground levels and the upper level is indicative of two thermally populated ground states. The energy level differences of the Eu^{3+} ^7F_J ground levels are on the order of kT, where k is Boltzmann's constant and T is the absolute temperature. Thereby, the various ^7F_J ground levels are thermally populated at room temperature. So, we must consider the fractional populations of the Eu^{3+} levels to estimate S_{ed}. The value of S_{ed} for each transition and the different parameter used in their estimation are given in Tabl. 1(a) and 1(b).

EuTTA$_3$P

Transition	$\bar{\lambda}$ (nm)	n	J	N (10^{20}ions/cm^3)	$\lvert\langle U^2\rangle\rvert^2$	$\lvert\langle U^4\rangle\rvert^2$	$\lvert\langle U^6\rangle\rvert^2$	$\int k(\lambda)d\lambda$ (nm cm^{-1})	S^{ed}_{mes} (10^{-20} cm^2)
$^5D_0 \leftarrow {}^7F_0$	577.1	1.557	0	4.11	0	0	0	0.46	0.0014
$^5D_1 \leftarrow {}^7F_0$	524.7	1.565	0	4.11	0	0	0	0.21	0.0000
$^5D_2 \leftarrow {}^7F_0$	464.5	1.587	0	4.11	0	0	0	13.43	0.0513
$^5D_1 \leftarrow {}^7F_1$	533.8	1.563	1	1.89	0.0025	0	0	4.02	0.0885

1(a)

EuTTA$_3$M

Transition	$\bar{\lambda}$ (nm)	n	J	N (10^{20}ions/cm^3)	$\lvert\langle U^2\rangle\rvert^2$	$\lvert\langle U^4\rangle\rvert^2$	$\lvert\langle U^6\rangle\rvert^2$	$\int k(\lambda)d\lambda$ (nm cm^{-1})	S^{ed}_{mes} (10^{-20} cm^2)
$^5D_0 \leftarrow {}^7F_0$	577.7	1.556	0	3.89	0	0	0	0.46	0.0015
$^5D_1 \leftarrow {}^7F_0$	524.7	1.573	0	3.89	0	0	0	0.23	0.0000
$^5D_2 \leftarrow {}^7F_0$	463.7	1.609	0	3.89	0	0	0	13.63	0.0542
$^5D_1 \leftarrow {}^7F_1$	533.8	1.569	1	1.83	0.0025	0	0	3.93	0.0893

1(b)

TABLE 1 Measured line strengths of Eu^{3+} in **EuTTA$_3$P** and **EuTTA$_3$M**.

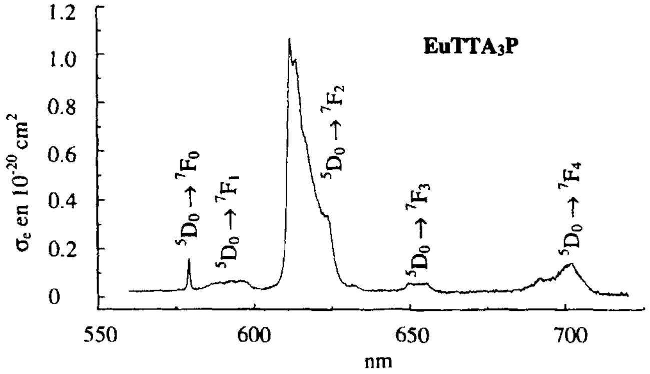
Subsequently these results are used to obtain the Ω_2 intensity parameter (Tabl. 2).

Compound	Judd-Ofelt intensity parameters (10^{-20} cm^2)		
	Ω_2	Ω_4	Ω_6
$EuTTA_3P$	35.43	—	—
$EuTTA_3M$	35.72	—	—

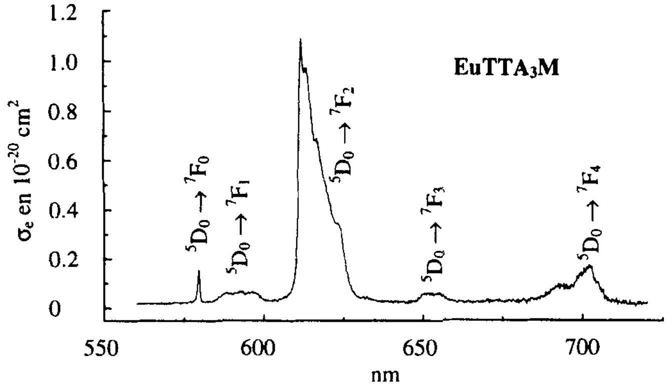
TABLE 2 Measured intensity parameters Ω_t.

The Ω_4 and Ω_6 intensity parameters cannot be calculated because the $U^{(t)}$ matrix elements for the corresponding transition are zero.

However, we have an another possibility to obtain Ω_4. Indeed, from the emission spectra of **$EuTTA_3P$** and **$EuTTA_3M$** we can determine the experimental intensity parameters Ω_2 and Ω_4 by using the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively. To calibrate the emission spectra, the $^5D_0 \leftrightarrow {}^7F_0$ transition was taken as a reference, because this transition is observed both in the absorption and emission spectra. These spectra are shown in Fig. 7(a) and 7(b) as a plot of the emission cross section σ_e versus wavelength.



7(a)



7(b)

FIGURE 7 Wavelength dependence of the emission cross sections of **EuTTA$_3$P** and **EuTTA$_3$M**.

The results of the measured line strengths from the emission spectra are given in Tabl. 3(a) and 3(b).

EuTTA$_3$P

Transition	$\bar{\lambda}$ (nm)	n	J	N (10^{20}ions/cm^3)	$\lvert<U^2>\rvert^2$	$\lvert<U^4>\rvert^2$	$\lvert<U^6>\rvert^2$	$\int k(\lambda)d\lambda$ (nm cm^{-1})	S^{ed}_{meas} (10^{-20} cm^2)
$^5D_0 \rightarrow {}^7F_0$	579.6	1.557	0	6.11	0	0	0	0.69	0.0014
$^5D_0 \rightarrow {}^7F_1$	592.6	1.556	0	6.11	0	0	0	2.51	0.0000
$^5D_0 \rightarrow {}^7F_2$	616.8	1.553	0	6.11	0.0032	0	0	54.84	0.1100
$^5D_0 \rightarrow {}^7F_3$	653.0	1.552	0	6.11	0	0	0	1.81	0.0034
$^5D_0 \rightarrow {}^7F_4$	699.4	1.552	0	6.11	0	0	0.0023	9.31	0.0164

3(a)

EuTTA₃M									
Transition	$\bar{\lambda}$ (nm)	n	J	N (10^{20}ions/ cm^3)	$\lvert\langle U^2\rangle\rvert^2$	$\lvert\langle U^4\rangle\rvert^2$	$\lvert\langle U^6\rangle\rvert^2$	$\int k(\lambda)d\lambda$ (nm cm^{-1})	S^{ed}_{meas} (10^{-20} cm^2)
$^5D_0 \rightarrow {}^7F_0$	579.2	1.556	0	5.82	0	0	0	0.69	0.0015
$^5D_0 \rightarrow {}^7F_1$	592.5	1.553	0	5.82	0	0	0	2.72	0.0000
$^5D_0 \rightarrow {}^7F_2$	617.2	1.550	0	5.82	0.0032	0	0	52.88	0.1090
$^5D_0 \rightarrow {}^7F_3$	652.7	1.545	0	5.82	0	0	0	1.56	0.0031
$^5D_0 \rightarrow {}^7F_4$	698.9	1.543	0	5.82	0	0	0.0023	10.12	0.0174

3(b)

TABLE 3 Measured line strengths of **EuTTA₃P** and **EuTTA₃M** derived from the emission spectra

The corresponding Judd-Ofelt intensity parameters of these two fluorescent compounds are listed in Tabl. 4.

Compound	Judd-Ofelt intensity parameters (10^{-20} cm^2)		
	Ω_2	Ω_4	Ω_6
EuTTA₃P	34.45	7.13	—
EuTTA₃M	34.29	7.63	—

TABLE 4 Measured intensity parameters Ω_t of **EuTTA₃P** and **EuTTA₃M** from emission spectra.

The Ω_6 intensity parameter was not included in this study since the $^5D_0 \rightarrow {}^7F_6$ transition could not be observed.

CONCLUSION

In this work we have characterized and studied the optical and spectroscopic properties of two new Eu^{3+} coordination compounds. The main features are the highly luminescent of **$EuTTA_3P$** and **$EuTTA_3M$** under blue excitation, and the high value of the Ω_2 intensity parameter derived from the emission spectra of the Eu^{3+} ion in both compounds as previously observed elsewhere[10]. This later characteristic reflects the hypersensitive behavior of the $^5D_0 \rightarrow {}^7F_2$ transition and indicates that the europium ion is in a highly polarizable chemical environnment [11].

Acknowledgments

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