

Photoluminescence of the $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$ coordination compound: the spectroscopy, kinetic and efficiency

Bordian Olga, Verlan Victor, Culeac Ion, Iovu Mihail
Institute of Applied Physics of Moldova
5 Academy Str. , Chisinau MD-2028, Republic of Moldova
vverlan@gmail.com

Zubareva Vera
Institute of Chemistry of Moldova
3 Academy Str. , Chisinau MD-2028, Republic of Moldova
verzub@mail.ru

Malahov Ludmila
Institutul de Matematică și Informatică al Republicii Moldova
5 Academy Str. , Chisinau MD-2028, Republic of Moldova
lmalahov@gmail.com

ABSTRACT – a tris (2-thenoyltrifluoroacetato (TTA)) (monophenanthroline (Phen)) Europium (III) ($\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$) organic compound was synthesized. Upon excitation with ultraviolet light the material has an abundant photoluminescence (PL) in the red field of spectrum. The experimental results of PL and its kinetics were analyzed using the theory of Judd-Ofelt's parametric method and from which were obtained the lifetime τ , the efficiency η and the probability transitions of the electrical dipoles.

I. INTRODUCTION

Rare earth ions have low PL efficiency, but luminescence intensity can be significantly increased when they coordinate with organic ligands with high absorption and form complex compounds with rare earths. Amplification of PL in coordinating compounds is attributed to the transfer of energy from organic ligands to rare earth ions, and so the fluorescence of the latter improves [1-2]. The direct excitation of Eu^{3+} ions is insignificant, because the cross-section of the ion to the absorbs light is small. The orbital $4f$ of ion is shielded by filled orbits $5s^2$ and $5p^6$ with electrons with higher energy levels. This leads to the insignificant influence of the outer environment of the coordinating compound and crystalline symmetry on the $4f$ transitions of Eu^{3+} ion. One way to overcome the problem of poor absorption of Europium ions and achieve good emissions is to surround the ion with compatible organic ligands that are capable of absorbing light and then transfer the energy absorbed to the states $4f$ of ion. At the same time, the surrounding ligands provides a rigid coordination protection to minimize deactivation of luminescent transitions [3,4-8]. The saturation of the Eu^{3+} ion coordination sphere with ligands allows it protecting from action of water molecules or other materials which turn off the luminescence [9]. We developed novel technology for synthesis of organic coordination compound (OCC) $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$ with down conversion of light with high yield and extended absorption spectral response to UV. As optimal ionic and neutral ligands were used TTA and Phen.

II. EXPERIMENTAL DETAILS

Optical transmission ($T = f(\lambda)$) in the spectral range of 300-800 nm were measured with the monochromator SPECORD UV-Vis (Carl Zeiss Jena). PL spectra and their kinetic were measured under excitation of a laser beams 337 or 405 nm using a MDR-23 monochromator and a photon counting module H9319-12 connected to a PC.

Characterizations of the physical properties of $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$ compound were made by UV, Vis and IR spectroscopy, as well as by X-ray diffraction.

III. SYNTHESIS OF $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$

In order to promote the properties luminescence of the OCC Eu (III) ion, we designed, synthesized and investigated a $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$ (Fig. 1). The ligands which were chosen for synthesis are required to control the luminescence properties by transferring energy and increasing the compatibility of dissolution in different solvents of the $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$. The synthesis of coordinated compound of tris(thenoyltrifluoroacetato)bis(triphenylphosphine oxide)Europium(III) [$\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$] was carried out after the scheme described in [10] with some modifications.

Synthesis: 0,66 g (3 mmol) of thenoyltrifluoroacetone and 0,56 g (2 mmol) triphenylphosphine oxide were dissolved in 10 ml of warm 96% ethanol and 3 ml of 1N solution of sodium hydroxide were added. The mixture was stirred, while 1 mmol of Europium chloride in 5 ml of water was added dropwise. A type of light pink precipitate formed immediately. The precipitate was filtered off, washed with small portions of ethanol and diethyl ether, dried thoroughly in air, and the solid of the complex was obtained. Yield was 0.68 g.

For $\text{C}_{60}\text{H}_{42}\text{F}_9\text{EuO}_8\text{P}_2\text{S}_3$ calcd, %: C = 52.53; H = 3.09.

Found, %: C = 52.37; 52.28; H = 3.18; 2.98.

The chemical schema of the $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$ molecule is presented on Fig. 1.

IV. RESULTS

Transmission spectra $T(\lambda)$ of the solutions with different $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$ concentrations in the ultraviolet domain (UV) clearly show absorption bands peaking at 3.39, 4.56, 5.37, and 6.14 eV. A sharp absorption threshold is present in the 370–380 nm spectral range. The band-gap energy $\Delta E_{\text{HL}} = \text{LUMO} - \text{HOMO}$, (where HOMO is the energy of the highest occupied molecular orbital, and LUMO is the energy of the lowest unoccupied molecular orbital), which is obtained from 80% of the absorption threshold $T(\lambda)$, are in a range of 3.14–3.16 eV. This probably is caused by the absorption of the coordinating ligand TTA incorporated in the organic compound.

The spectra of absorption and photoluminescence (PL) were identified the cascade of energy transfer from LUMO energy levels of ligands to the energetic levels of 4f electronic shell of the Eu^{3+} ion. The energy of singlet (S) and triplet (T) levels of ligands in OCC are located higher than the energies of PL of Eu^{3+} ion.

The photoluminescence spectra show a strong emissions of 5 bands centered at 579, 590, 619, 650, 687 nm, which are associated with the transitions ${}^5D_0 \rightarrow {}^7F_i$ ($i = 0, 1, 2, 3, 4$) in the 4f shell of the Eu^{3+} ion. There is a big emission peak in domain 612–615 nm (${}^5D_0 \rightarrow {}^7F_2$). The splitting of each maximum in several portions is caused by the influence of Stark's electric field of the OCC $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$ molecule.

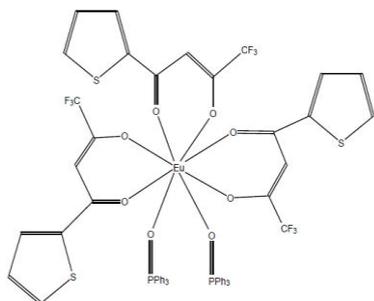


Fig. 1. Molecular structure of $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$.

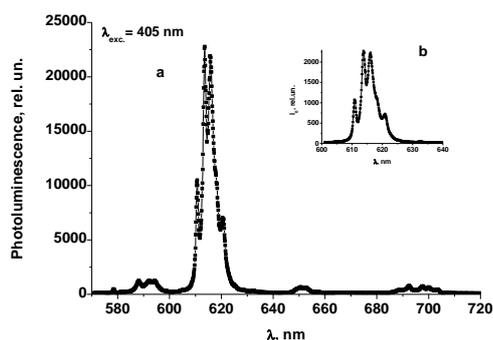


Fig. 2. The photoluminescence spectra of $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$ powder.

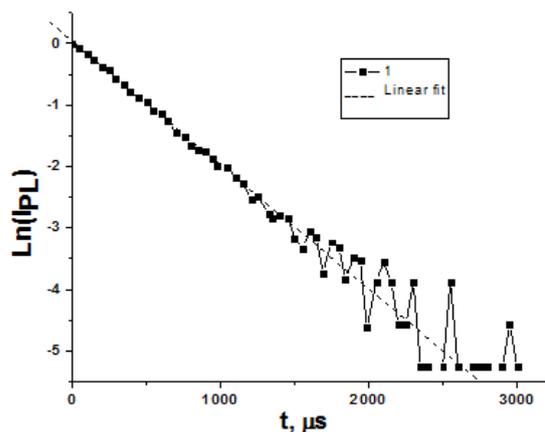


Fig. 3. Kinetics of photoluminescence decay of $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$ powder.

Using the Judd's theory from the photoluminescence were calculated the parameters: the transition probabilities.

Fig. 3 illustrates the dependence of the photoluminescence intensity kinetic decay built in $\ln(I_{\text{PL}}) - t$ coordinates. The linear dependence corresponds to the exponential decay of the photoluminescence after the equation $I = I_0 \exp(-t/\tau)$, where τ is the characteristics of the lifetime spontaneous photoluminescence of OCC $\text{Eu}(\text{TTA})_3(\text{Ph}_3\text{PO})_2$ ($\tau = 0.496$ ms).

The description of photoluminescence intensity and transitions is made in with Judd-Ofelt's theory [11, 12]. Using the Judd's theory were calculated the parameters of the transition probabilities and efficiency of PL.

The photoluminescence intensity is described by the formula:

$$I_{0 \rightarrow j} = h\nu_{0 \rightarrow j} A_{0 \rightarrow j} N_0 \quad (1)$$

where $h\nu_{0 \rightarrow j}$ is the energy maximum of the transition, N_0 is the concentration of the emitting level of Eu^{3+} ions and $A_{0 \rightarrow j}$ is the Einstein coefficients of spontaneous emission.

The coefficients of spontaneous emission $A_{0 \rightarrow j}$ are obtained from equation:

$$A_{0 \rightarrow j} = \frac{h\nu_{0 \rightarrow 1} \times S_{0 \rightarrow j}}{h\nu_{0 \rightarrow j} \times S_{0 \rightarrow 1}} \times A_{0 \rightarrow 1} \quad (2)$$

where $S_{0 \rightarrow j}$ corresponds to the area under the intensity curve related to the transition ${}^5D_0 \rightarrow {}^7F_j$ and $h\nu_{0 \rightarrow j}$ is the energy center of the transition.

For the experimental determination of the emission coefficients $A_{0 \rightarrow j}$ from the emission spectra the magnetic dipole used allowed ${}^5D_0 \rightarrow {}^7F_1$ transition, which is formally insensitive to the chemical environment around the Eu^{3+} compound and, consequently, can be used as a reference $A({}^5D_0 \rightarrow {}^7F_1) = 50 \text{ s}^{-1}$ [12].

The lifetime of the excited state (τ), the probabilities of radiative (A_r) and nonradiative processes (A_{nr}) are related by equation:

$$\frac{1}{\tau} = Ar + Anr \quad (3)$$

The emission quantum efficiency (η) of the 5D_0 excited state is determined according to the following expression:

$$\eta = \frac{Ar}{Ar + Anr} \quad (4)$$

where the probability Ar is obtained by summing of all probabilities $A_{0 \rightarrow j}$ describing the transitions ${}^5D_0 \rightarrow {}^7F_j$

Table 1. Experimental parameters of photoluminescence intensity $Eu(TTA)_3(Ph_3PO)_2$

| Ar, s^{-1} | Anr, s^{-1} | $Atot, s^{-1}$ | $\tau, \mu s$ | $\eta, \%$ |
|--------------|---------------|----------------|---------------|------------|
| 624. 99 | 1391. 1 | 2016. 1 | 496 | 31 |

SUMMARY

The luminescence of OCC compounds exhibit an impressive brightness and independent spectral stability. The possible applications of Eu^{3+} based organic OCC are as the new luminescent material for down conversion of light energy from UV to red, their application in PV structures with extended to UV spectral response and enhanced light harvesting efficiency.

There was found the effective transfer of energy from ligands with subsequent transfer of one to Eu^{3+} .

The $Eu(TTA)_3(Ph_3PO)_2$ coordinating compound have an abundant luminescence in the red domain of light and are perspectives for forming different optical elements with high luminescence efficiency and it can be used for elaboration of amplifiers, lasers, light emitting diodes, etc. Also it should be mentioned for the implementing the energy transfer from the UV to red light found in investigated OCC.

ACKNOWLEDGEMENTS.

This work was supported by the Supreme Council for Science and Technological Development of the Academy of Sciences of Moldova (Project no. 11. 817. 05. 03A and no. 11. 836. 05. 04A) and Science and Technology Center in Ukraine no 6117.

REFERENCES

- [1] Handbook on the Physics and Chemistry of Rare Earths, Vol. 44, Amsterdam: The Netherlands, 2014, pp. 169-281.]
- [2] L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini, E. Tondello, Design of luminescent lanthanide complexes: From molecules to highly efficient photo-emitting materials. , Coordination Chemistry Reviews 2010, 254, 487-505.
- [3] S. V. Eliseeva, J. -C. G. Bünzli, Lanthanide luminescence for functional materials and bio-sciences. Chemical Society Reviews 2010, 39, 189-227.
- [4] G. De Sa, O. Malta, C. de Mello Donegá, A. Simas, R. Longo, P. Santa-Cruz, E. Da Silva, Spectroscopic properties and design of highly luminescent lanthanide coordination complexes. Coordination Chemistry Reviews 2000, 196, 165-195.
- [5] M. Reddy, S. Sivakumar, Lanthanide benzoates: a versatile building block for the construction of efficient light emitting materials . Dalton Transactions 2013, 42, 2663-2678.
- [6] O. Pietraszkiewicz, S. Mal, M. Pietraszkiewicz, M. Maciejczyk, I. Czernski, T. Borowiak, G. Dutkiewicz, O. Drobchak, L. Pen ninck, J. Beeckman, Highly Photoluminescent Eu (III) Complexes of the New 1-Triphenylen-2-yl-3- Trifluoroacetylacetone. Journal of Photochemistry and Photobiology A: Chemistry 2012, 250, 85-91.
- [7] J. -C. G. Bünzli, On the design of highly luminescent lanthanide complexes Coordination Chemistry Reviews 2015, 293, 19-47.
- [8] G. Fomina, Z. V. Dobrokhotova, V. O. Kazak, G. G. Aleksandrov, K. A. Lysenko, L. N. Puntus, V. I. Gerasimova, A. S. Bogomyakov, V. M. Novotortsev, I. L. Eremenko, European Journal of Inorganic Chemistry Synthesis, structure, thermal stability, and magnetic and luminescence properties of dinuclear lanthanide(III) pivalates with chelating N-donor ligands. 2012, 2012, 3595-3610.
- [9] K. Binnemans, Lanthanide-based luminescent hybrid materials Chem. Rev. 2009, 109, 4283-4374.
- [10] O. T. Bordian, V. I. Verlan, M. S. Iovu, I. P. Culeac, V. E. Zubarev, D. E. Bojin, and M. Enachescu. Synthesis and optical characterization of $Eu(TTA)_3(Ph_3PO)_2$ Moldavian Journal of the Physical Sciences, Vol. 14, N3-4, 2015.
- [11] Judd B. R. Optical absorption intensities of rare-earth ions // Phys. Rev. APS, 127 (1962) 03, 750-761.
- [12] Ofelt G. S. Intensities of crystal spectra of rare earth ions // J. Chem. Phys. AIP Publishing, 37 (1962) 03, 511-520.