

## LUMINESCENCE OF NANOCOMPOSITES WITH DIFFERENT COORDINATION OF $\text{Eu}^{3+}$ IONS AND POLYMERS

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**Abstract.** *Thin films (1-3  $\mu\text{m}$  thickness) of nanocomposites (NCs) based on organic compounds with  $\text{Eu}^{3+}$  ions ( $\text{Eu}(\text{TTA})_3\text{H}_2\text{O}$ ,  $\text{Eu}(\text{TTA})_3\text{Phen}$ ,  $\text{Eu}(\text{DBM})_3\text{Phen}$  and  $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$ ) and polymer polyvinylpyrrolidone (PVP) or copolymer styrene-butylmethacrylate in ratio of 1:1 (SBMA) were obtained by chemical methods and with different molar ratios into organic polymer matrix. NCs have been characterized by measurements of optical transmission and photoluminescence (PL). The PL of nanocomposites in all type of compounds with  $\text{Eu}^{3+}$  ions were detected the same spectra as specific for internal transitions  $4f \rightarrow 4f$  of the  $\text{Eu}^{3+}$  ion  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_i$  ( $i = 0, 1, 2, 3$  and  $4$ ) centered at 537, 578, 615, 632, 649, 690 and 705 nm, respectively at  $T=300$  K. The dominant PL is in the position to 612 - 615 nm and the halfwidth is less than 10 nm and it is attributed to the transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ . In nanocomposites, the effect of energy transfer from polymer matrix to coordinated molecule with subsequent transfer of them to  $\text{Eu}^{3+}$  ions have been identified. It was proposed some applications of given nanocomposites in optoelectronics and medicine.*

**Key words:** *nanocomposites, rare earth, photoluminescence, polymer, energy transfer, laser emission.*

### I. Introduction

Nanocomposites based on polymers and coordinate compounds (CC) of rare earth metals are excellent materials for a new generation of light emitting devices with high efficiency due to strong luminescence, easy colour tunable, temperature insensitivity, and high stability. Luminous properties of the complex coordinated compounds and nanocomposites on their basis can be a subject of different applications in medicine, solar cells devices on the flexible substrates, optical signal amplification, etc. Improving of their luminescence properties depends on the type of ligands using for surrounding of the rare earth ions. Photoactive complexes of organic compounds of lanthanides may be used, as an example, like the trivalent ion of Europium ( $\text{Eu}^{3+}$ ) chelated with  $\beta$ -diketonates when the coordination number of  $\text{Eu}^{3+}$  varies in range from 6 to 9. Such surrounding of  $\text{Eu}^{3+}$  ion is necessary in order to improve luminescence efficiency, and to obtain a final stable compound for various practical applications.

The fundamental studies of the spectroscopy photophysic of rare earth metals and applications of the technology connected with effective luminescence with the halfwidth of the luminescence bands less than 10 nm in the visible and near-infrared regions of spectrum at different excitations are of special interest.

Advantage of application of CC of rare earth ions with  $\beta$ -diketonates and ligands in nanocomposites is based on the so-called "antenna" effect, or the transfer of excitation energy from outside of the system of  $\text{Eu}^{3+}$  ion towards their energy levels. The population of upper energy levels with subsequent transition to ground states is increased in this case. The intermolecular energy transfer to the  $\text{Eu}^{3+}$  ion takes place via the levels of ligands and their surroundings.

In previous paper we report the investigations of the NCs in polymer matrix  $Eu(TTA)_3H_2O$ ,  $Eu(TTA)_3Phen$  were introduced [1-4]. In present work are investigated NCs with a wide range of ligands and different coordination number for  $Eu^{3+}$  ions to determine the effective method of energy transfer from the polymer matrix and ligands to  $Eu^{3+}$  ion. For this purpose, it are analyzed together the properties of optical and of photoluminescence of the polymeric NCs with the compounds  $Eu(TTA)_3H_2O$ ,  $Eu(TTA)_3Phen$ ,  $Eu(DBM)_3Phen$  and  $Eu(TTA)_2(Ph_3PO)_2NO_3$ , which were obtained in similar conditions of technology.

## II. Methodology

The synthesis of coordinated compounds tris(2-thenoyltrifluoroacetate)Europium(III) monoqua ( $Eu(TTA)_3H_2O$ ), tris(dibenzoilmetane)(monophenanthroline)Europium(III) ( $Eu(DBM)_3Phen$ ), bis(thenoyltrifluoroacetato)bis(triphenylphosphine oxide)(mononitrate)Europium(III) ( $Eu(TTA)_2(Ph_3PO)_2NO_3$ ), tris(2-thenoyltrifluoroacetato)(monophenanthroline)Europium(III)  $Eu(TTA)_3Phen$  were performed in Institute of Chemistry of the Academy of Sciences of Moldova by coauthors Prof. C.I. Turta and Dr. V.E. Zubarev and were described in detail [1-4]. The formulas of the structure of coordinated compounds with rare earth are shown on Fig.1(a,b,c,d).

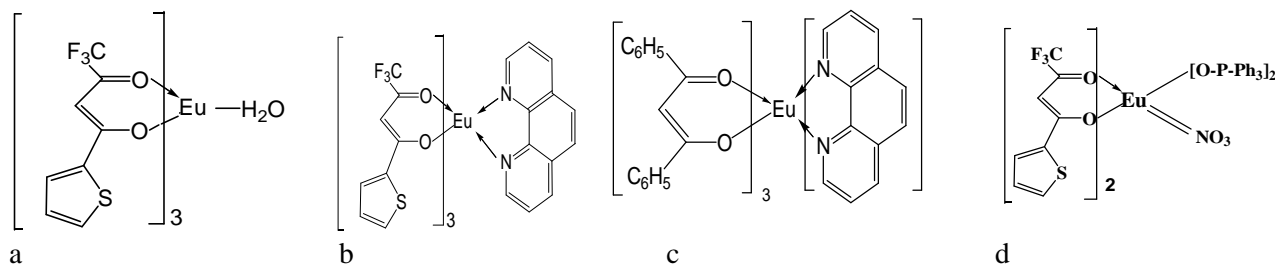


Fig.1. Formula of the structure of  $Eu(TTA)_3H_2O$  (a),  $Eu(TTA)_3Phen$  (b),  $Eu(DBM)_3Phen$  (c),  $Eu(TTA)_2(Ph_3PO)_2NO_3$  (d).

Polymeric nanocomposites CC with rare earth were prepared from chemical solutions of separate components and the method were described separately in [7]. Polyvinylpyrrolidone ( $(C_6H_9NO)_n$ ) was used as the polymer with an average molecular weight  $1300000 \text{ g}\cdot\text{mol}^{-1}$ , white to light yellow, hygroscopic, amorphous powder and copolymer styrene-butylmethacrylate (in ratio 1:1) (purchased from Aldrich Chemical Company). The different Europium complexes were successfully incorporated with different molar ratios into organic polymer matrix via sol-gel process. Drop- and spin-coated thin films on optical glass and quartz substrates were obtained. The dried layers with thickness around 1-3  $\mu\text{m}$  turn out to be transparent in visible range of spectrum.

The microscopic investigations of the morphology of the NC surface on a microscope MII-4 show that the dimensions of coordinated compounds particles, incorporated in the polymer matrix are invisible and hence are less than 100 nm. Photoluminescence spectra have been measured using a set-up based on MDR-23 monochromator connected to PC. NC excited with  $N_2$ -laser ( $\lambda = 0.337 \mu\text{m}$ ) or Deuterium lamp have generated some sharp emission bands in the spectral range of 300 – 800 nm. For optical transmission investigations a Specord UV/VIS (300÷800 nm) CARL ZEISS Jena unit was used. Absorption and luminescence properties of powder of Europium complex and NC were measured on each step of technology.

## III. Experimental results

All NCs under the action of ultraviolet light have strong red photoluminescence. Fig.2(a,b) shows as example the surface images of the NC films at 6 % and 10 % concentration of  $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$  in the matrix of PVP under visible (Fig. 2a) and UV illumination (Fig. 2b). The photos also reveal that coordinate complexes are dispersed in PVP homogeneously without any phase separation.

Fig.3 shows the optical absorbance spectra ( $D(h\nu)$ ) of samples of thin layers of NC on glass substrates for different concentration of  $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$  in PVP at room temperature ( $T=293$  K). The transmissions spectra ( $T(\lambda)$ ) of all investigated NCs are similar. Thin layers of NCs on quartz substrates in ultraviolet region (UV) show clearly 4 absorption bands with maximums at 3.0 - 3.15, 3.8, 4.5 and 4.8 eV, and with increasing of the CC concentration in NC they grow until complete darkening in UV range.

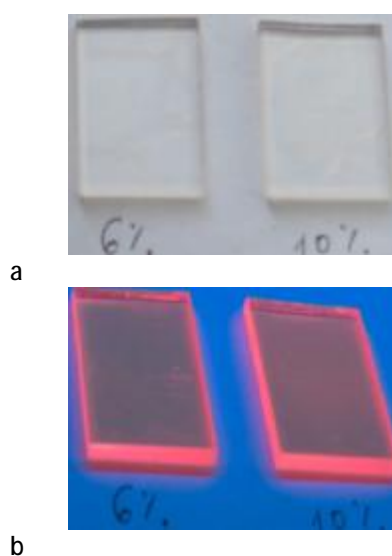


Fig.2. Samples of thin layers of NC illuminated with visible (a) and UV light (b).

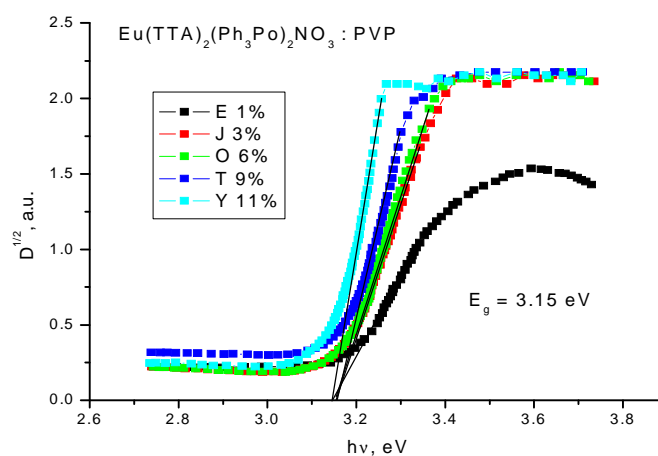


Fig.3. The optical absorbance spectra of samples of thin layers of NC on glass substrates for different concentration of  $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$  in PVP at room temperature ( $T=293$  K).

The sharp absorption threshold is presented for all concentrations of CC in NCs in the range of 370 - 380 nm of spectrum. The absorption spectra ( $\alpha(\lambda)$ ) are calculated from the transmission spectra  $T(\lambda)$  by the formula  $\alpha(\lambda) = -\ln T/d$  (where  $d$  is the thickness of NC,  $\alpha$  – absorption coefficient). The energies of forbidden bands of NC ( $\Delta E_{HL} = \text{LUMO} - \text{HOMO}$ , where  $\text{HOMO}$  is energy of high CC upied molecular orbital and  $\text{LUMO}$  – low unCC upied molecular orbital) were obtained from extrapolations of straight lines of absorbance vs energy in coordinates ( $D^{1/2}(h\nu)$ ) and also by the second method from 80 % of absorption threshold of  $T(\lambda)$ . The values of  $\Delta E_{HL}$  are in the range 2.9 eV for NC  $\text{SBMA}/\text{Eu}(\text{TTA})_3\text{H}_2\text{O}$  and  $\text{SBMA}/\text{Eu}(\text{DBM})_3\text{Phen}$  and 3.2 eV for NC  $\text{SBMA-PVP-Eu}(\text{TTA})_3\text{Phen}$  and  $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$ .

On Fig.5a,b the spectra of photoluminescence of NC  $\text{PVP-Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$  films are presented. The detected fluorescence bands correspond to the radiative transitions between the energy levels of the Europium ions centred at 537, 580, 615, 650 and 702 nm, and can be attributed to the spin forbidden  $4f - 4f$  transitions  ${}^5D_0 \rightarrow {}^7F_i$  ( $i = 0,1,2,3$  and 4), respectively. The most effective luminescence has the maximum at 615 nm at temperature 293 K which is about 20 times higher than others, and its halfwidth is less than 10 nm.

The optimal concentrations of  $\text{Eu}(\text{TTA})_2(\text{Ph}_3\text{PO})_2\text{NO}_3$  in nanocomposite were found in the range of 6 – 12 % (Fig.6). This is roughly true for all the NC. There is an almost monotonous increase of intensity of photoluminescence up to some 10% of the CC concentration in NC, and this

feature is characteristic for all thin film samples at room temperature. The main feature of these characteristics is a quite low signal of photoluminescence in liquid solution samples, while thin film samples exhibits a significant increase of the intensity of photoluminescence. The effective excitation of PL of the organic coordinated compound with  $Eu^{3+}$  ion in NC thin films was attained.

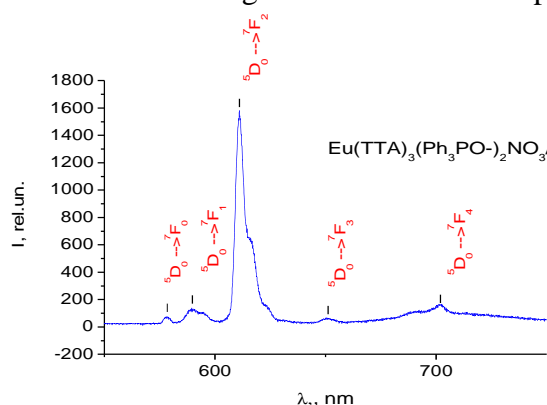


Fig.4. The photoluminescence spectra of thin layer of NC PVP-Eu(TTA)<sub>2</sub>(Ph<sub>3</sub>PO)<sub>2</sub>NO<sub>3</sub> at 6 wt.% of concentration of complex CC in NC at room temperature (T=293 K).

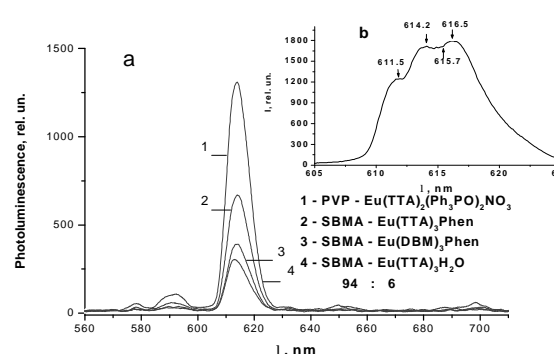


Fig.5. The photoluminescence spectra of thin layer of NC of different coordinate complex in NC (a) and detailed of the maxima at 612 – 615 nm at room temperature (T=293 K).

#### IV. Discussion

The measuring of PL spectra determine the effective transfer of energy from polymer matrix *PVP* to LUMO energy levels of chelates of the complex  $Eu(TTA)_2(Ph_3PO)_2NO_3$  and subsequent energy transfer to the energetic levels of  $Eu^{3+}$  ion. HOMO and LUMO of complex  $Eu(TTA)_2(Ph_3PO)_2NO_3$  are found to be situated between levels *S* and *T* of polymer, and this case is similar to the doping case of semiconductor into its forbidden band with particularities of they dimensions.

Rare-earth of NCs show high photoluminescence efficiency with sharp emission bands involving electrons associated with inner *4f* orbitals of the central rare-earth metal ions. We consider that the enchancing of PL in NCs is determined by the effective transfer of energy from polymer matrix to chelates of the CC complex and subsequent energy transfer to the energetic levels of  $Eu^{3+}$  ion. HOMO and LUMO energy levels of complexes are found to be situated between singlet *S* and triplet *T* levels of polymer, and this case is similar to the doping case of semiconductor into its forbidden band with particularities of they dimensions. The enchancing of PL can be explained by the coordination ability of the organic counterpart of the host structure of polymer, which is strong enough to stabilise the position of chelates in *Eu-CC* neighbourhood after the incorporation process. Nanocomposites display a bright and narrow  $Eu^{3+}$  ion emission, which is due to the so-called “antenna” effect, defined as a light conversion process via an absorption energy transfer-emission sequence involving distinct absorption by a polymer and ligand and their energy transfer to  $Eu^{3+}$  ions and later their emission.

The experimental data of photoluminescence can be explained from the viewpoint of the surrounding environment where the  $Eu^{3+}$  ion resides. Polymers and CC significantly affected the strength of the hypersensitive transitions ( ${}^5D_0 \rightarrow {}^7F_i$  ( $i = 0,1,2,3$  and  $4$ ) for  $Eu^{3+}$ ) of the complexes and the maximum of PL intensity at 612-615 nm.

For the Europium complex, the intensity of the transitions of  ${}^5D_0 \rightarrow {}^7F_i$  ( $i = 0,1,2,3$  and  $4$ ) increases in the nanocomposite with grows the concentration of CC in NC. When  $Eu(TTA)_2(Ph_3PO)_2NO_3$  complexes were incorporated into *PVP*, the complexes exhibited disorder.

Under the influence of the electric field of the surrounding ligands, the distortion of the symmetry around the lanthanide ion by the capping *PVP* due to the polarization of  $Eu^{3+}$ , which increases the probability for electric dipole allowed transitions. The influence of *PVP* on the coordinated environment of Europium ions changes the energy-transfer probabilities of electric-dipole transitions, accounting for the increase in luminescent intensity of 612 - 615 nm maxima of NC.

The difference of in intensity of PL of *Eu* complex in different nanocomposites can be interpreted as follows: when *Eu* complexes are introduced into the *PVP*, the molecular motion is restricted and the stretching and bond vibration are weakened by the polymer, both of which decrease the non-radiative transition. These results show that the nanocomposites could provide a relatively stable environment for lanthanide complexes and improve their luminescence properties.

We suppose that the interaction of macromolecular ligands at high concentrations of  $Eu^{3+}$  ion leads to partial formation of coordinated unsaturated complexes and ionic aggregates, leading to the quenching of luminescence. From these positions, the resulting polymer composites open the most promising way to neutralize the coordinated complexes and to obtain structurally homogeneous materials with desired properties. From the spectra of NC (Fig. 5a,b), we can also suppose a low local symmetry of ligand field of ion  $Eu^{3+}$  observed line transition  ${}^5D_0 \rightarrow {}^7F_0$ , which is interdicted under the high asymmetry of the luminescence centre. The intensity of the transition  ${}^5D_0 \rightarrow {}^7F_0$  is comparable with intensities of  ${}^5D_0 \rightarrow {}^7F_1$ , indicating also a significant asymmetry around of rare-earth ions. The presence of splitting of the transition line  ${}^5D_0 \rightarrow {}^7F_1$  on three components and of the transition line  ${}^5D_0 \rightarrow {}^7F_2$  on five components indicates the absence of spherical symmetry.

## V. Conclusion

From transmission spectra of NC measured in range 200 to 800 nm we have identified the absorption bands with maximums centred at 3.8, 4.5 and 4.8 eV in the UV, and the threshold of absorption forbidden band  $\Delta E_{HL} = 2.9 - 3.2$  eV for different NC was estimated. It is shifted slightly in the IR direction of the spectrum with increasing the percentage of *CC* concentration in NC.

The photoluminescence spectra of NC was attributed to the internal of transition of  $Eu^{3+}$  ion  ${}^5D_0 \rightarrow {}^7F_i$  ( $i = 0,1,2,3$  and 4) centred at 537, 580, 612 - 615, 650 and 702 nm. The halfwidth of PL band at 612 - 615 nm is less than 10 nm, which indicates that the nanocomposite exhibits high fluorescence intensity and colour purity.

The positive influence of *PVP* and *SBMA* polymers matrixes on the coordinative environment of  $Eu^{3+}$  ions was determined. A possible method of the fluorescence raising of NC are energy transfer from polymers *PVP* and *SBMA* levels and from levels of ligand to internal levels of  $Eu^{3+}$  ion. It was demonstrated the PL amplification in the NC compared with organic complex compound samples.

## VI. Acknowledgments

This work was supported by Project of Institute of Applied Physics of the Academy of Sciences of Moldova (nr. 11.817.05.03A) and Project of State Program of Moldova Republic (nr. 11.817.05.04A).

We are grateful Buzurniuc S. for her help.

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