

# Synthesis and luminescent properties of ligand-Europium(III) Coordination Compounds

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**Abstract.** We propose a new technology for preparation of luminescent coordination organic compounds (COC) with  $Eu^{3+}$  ions with down-conversion of light and extended absorption spectral response to UV. The optimal ionic and neutral ligands for coordination of rare-earth ions were selected for each specific organic compound  $Eu(TTA)_3H_2O$ ,  $Eu(TTA)_3Phen$ ,  $Eu(TTA)_3(Ph_3PO)_2NO_3$ ,  $Eu(TTA)_3(Ph_3PO)_2$ ,  $Eu(DBM)_3Phen$  and  $Eu(o-MBA)_3Phen$ . Selection of different COC was aimed at obtaining the compatibility with polymer and improving the efficiency of the luminescence through energy transfer. Characterization of  $Eu$  coordinating compounds was carried out by UV-Vis absorption and PL spectroscopy. The mechanism of energy transfer to rare-earth ions has been discussed.

**Keywords:** Europium coordination compound, photoluminescence, energy transfer

## 1 Introduction

Europium(III) complex compounds with organic ligands are widely used in bio-medical diagnostics as well as in photonic devices and solar energy conversion [1-3].

The main purpose of this work was to study the optical properties of the ligands applied for obtaining coordination compounds with  $Eu^{3+}$  ion with the important electronic transitions of level  $^5D_0 \rightarrow ^7F_j$  in the  $4f$  shield.

## 2 Optical properties of ligands

Physical properties of coordination compounds with rare-earth ions (absorption, luminescence, etc.), their compatibility with various solvents and polymers, depend in a great extent on the underlying ligands compounds. We have analyzed available literature data in order to choose the optimal ligands applicable for the accomplishment. From different types of ligands we have investigated optical properties and solubility of the following materials: *1,3-diphenylpropane-1,3-dione (DBM)*, *triphenylphosphineoxide (TPPO)*, *4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA)*, *1,10-phenanthroline (Phen)*, *2-methylbenzoic acid (o-MBA)*.

(a)

(b)

(d)

(e)

(c)

Fig. 1. Illustration of chemical structure of the ligands used in preparation of organic rare-earth coordination compounds: (a) *Phen*; (b) *TPPO*; (c) *o-MBA*; (d) *TTA*; (e) *DBM*.

Optical transmission measurements were carried out in the range 300-800 nm on the spectrometer *Specord UV VIS (Carl Zeiss, Jena)*. Optical transmission spectra of the ligands in methanol saturated solutions were registered by use of standard UV fused quartz cuvettes with two polished sides with 10 mm path length. All the measurements of PL spectra were carried out in the same conditions of excitation with a nitrogen laser 337 nm at room temperature.

The chemical structures of investigated ligands are illustrated in Fig. 1. Fig. 2 shows the plot of the absorption spectrum of ligands and methanol (the solvent using for dissolving of the ligands was methanol). The absorption threshold of the ligands was determined from the Tauc plot [6]  $(\alpha h\nu)^{1/n} = f(h\nu)$ , where the value of the exponent  $n$  is determined by the nature of the transition of amorphous – crystalline

material: for allowed direct transitions  $n = 1/2$ . Consequently, the absorption threshold was estimated from experimental data, plotted according to the Tauc equation in the coordinates  $(ah\nu)^{1/n}$  vs.  $h\nu$ . From linear interpolation of the experimental plot we obtained the energy values for the absorption threshold,  $E_g = LOMO - HOMO$ . In this way, from experimental data we estimated for each ligand the energy values  $E_g$ : *TTA* – 3.06; *DBM* – 3.11; *Phen* – 3.56; *TPPO* – 3.72; *o-MBA* – 4.15;  $H_2O$  – 4.25 eV.

For optical measurements the ligands were divided into two groups: a) ligands with valence anionic–cationic bonds - *TTA*, *DBM* and *o-MBA*; and b) ligands with coordinating bonds to  $Eu^{3+}$  ion - *Phen*, *TPPO* and  $H_2O$ . These ligands are used for obtaining the organic coordination compounds of rare-earths. They are responsible for the energy transition to the central lanthanide ion ( $E_g$  is comparable to the energy of transitions  ${}^5D_0 \rightarrow {}^7F_j$  for the ion  $Eu^{3+}$  within the  $4f$  shell) and for compatibility with a particular group of solvents.

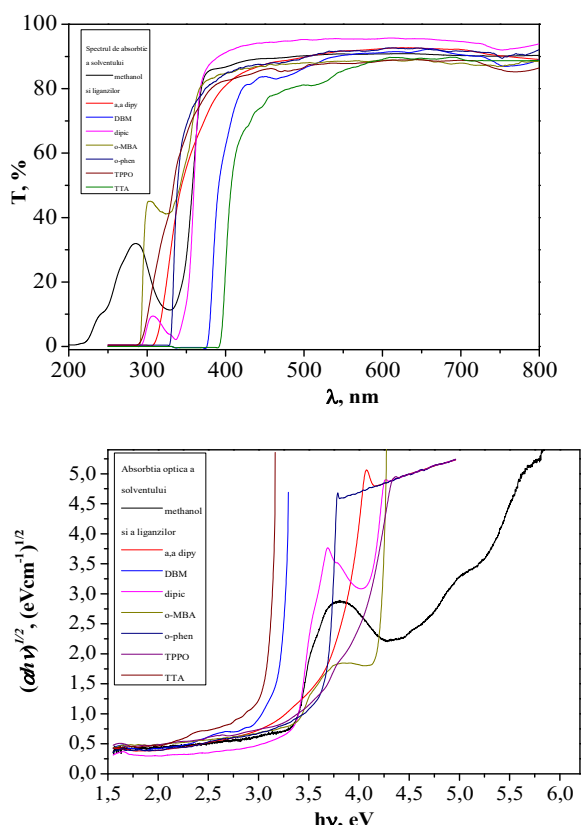


Fig. 2. Optical transmission spectra of the solvent and solutions of ligands in methanol (a) and their corresponding absorption spectra plotted in Tauc coordinates (b).

### 3 Synthesis of Europium(III) coordination compounds

All reagents used for preparation of the Europium(III) coordination compounds were of analytical grade and were used without further purification.

***Eu(TTA)<sub>3</sub>H<sub>2</sub>O***. The compound *tris(2-thenyltrifluoroacetate) (aqua) Europium(III)* was prepared using the method described in [3,7] with some modifications and in the presence of sodium hydroxide. The purification was carried out by dissolution in benzene with the subsequent precipitation in hexane.

***Eu(TTA)<sub>3</sub>Phen***. *Tris(2-thenyltrifluoroacetato)(monophenanthroline) Europium(III)* was obtained similar to [3,7] with some modifications. In 10 ml of hot ethanol 3 mmol of *thenyltrifluoroacetone* and 1 mmol of *o-phenanthroline* were dissolved and 3 mmol of 1N *sodium hydroxide* was added. The mixture was stirred while 1 mmol of *Europium nitrate hexahydrate* in 5 ml of water was added dropwise. A dense white microcrystalline precipitate separated immediately. After cooling the mixture, the solid was collected and purified by dissolution in benzene (30 ml) and precipitation in hexane. Anal. calcd. for  $C_{36}H_{20}EuF_9N_2S_3O_6$ : C – 43.42; H – 2.02; N – 2.81. Found: C – 43.19; H – 2.44, N – 2.63.

***Eu(DBM)<sub>3</sub>Phen***. *Tridibenzoyl methane o-phenanthroline Europium(III)*: 0.67 g of *DBM* was dissolved in 10 ml of *ethanol*. To this solution add 0.2 g of *phenanthroline* - light yellow transparent solution. 3 ml of 1N *NaOH* solution was added to the received solution. Instant color becomes intense yellow. 0.26 g of *EuCl<sub>3</sub>* salt were added 5 ml of *ethanol*. Incomplete dissolution was observed and turbidity remains. And upon addition of 1 ml  $H_2O$  the material was completely dissolved but the turbidity remained. To the fertile solution add a few drops of *EuCl<sub>3</sub>* solution, and it immediately precipitates. The yellow viscous compound was formed, which was subsequently dissolved, filtered and washed with ethanol and chloroform. As a result, after filtration and drying, 0.55 g of the material was dissolved in acetone. Anal. calcd. for  $C_{57}H_{41}EuN_2O_6$ , %: C - 6.33; H - 4.13; N - 2.80. Found: C - 68.43; H - 4.28; N - 2.29.

***Eu(o-MBA)<sub>3</sub>Phen***. A warmed *ethanol* solution (96%) containing 0.4 g (3 mmol) of *o-methylbenzoic acid* and 0.2 g (1 mmol) of *1,10-phenanthroline* was adjusted to pH 6.0–7.0 with 1M *NaOH* solution. Further, *Europium chloride* (1 mmol) dissolved in 5 ml of water was added dropwise to the organic mixture and stirred. A light pink

precipitate was formed immediately. The precipitate was filtered, washed with small portions of ethanol, dried thoroughly in air. The synthesis yield was 0.56 g (37.6%). For  $C_{36}H_{29}O_6N_2$  it was calculated, %: *Eu* - 20.61; *C* - 58.63; *H* - 3.97; *N* - 3.80; Found, %: *Eu* - 20.88; *C* - 59.23; *H* - 4.17; *N* - 3.75.

***Eu(TTA)<sub>2</sub>(Ph<sub>3</sub>PO)<sub>2</sub>NO<sub>3</sub>***. The synthesis of organic coordinated compound of *bis(thenoyltrifluoroacetato) bis(triphenyl-phosphine oxide)(mononitrate) Europium (III)* was carried out after the scheme described in for analogue compounds with some modifications. An amount of 4 mmoles (0.44 g) of  $\beta$ -diketone and 2 mmoles (0.56 g) of neutral ligand were dissolved in 10 ml. of hot 96% ethanol, and 2 ml. of 1N sodium hydroxide were added. The mixture was stirred, while 1 mmole of *Europium nitrate* in 5 ml of water was added dropwise. A type of light cream precipitate formed immediately. The precipitate was filtered off, washed with ethanol, dried thoroughly in air, and the solid complex was obtained. Yield was (0.85 g). For  $C_{52}H_{38}F_6EuNO_9P_2S_2$  anal. calcd, %: *C* = 51.49; *H* = 3.16; *N* = 1.15; *S* = 5.28. Found, %: *C* = 51.49; *H* = 3.48; *N* = 0.95; *S* = 5.14.

***Eu(TTA)<sub>3</sub>Ph<sub>3</sub>PO***<sub>2</sub>. The synthesis of *bis(thenoyltrifluoroacetato) bis(triphenylphosphine oxide)(mononitrate) Europium(III)*. 0.66 g (3 mmole) of *thenoyltrifluoroacetone (TTA)* and 0.56 g (2 mmole) of *triphenylphosphine oxide (TPPO)* were dissolved in 10 ml of warm 96% ethanol and 3 ml of a 1 N sodium hydroxide solution was added. The mixture was stirred, while 1 mmole of *Europium chloride* in 5 ml of water was added dropwise. A light pink precipitate was immediately formed. 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. The yield was 0.68 g. For  $C_{60}H_{42}F_9EuO_8P_2S_3$  calcd, %: *C* = 52.53; *H* = 3.09. Found, %: *C* = 52.37; 52.28; *H* = 3.18; 2.98.

Fig. 3 illustrates the chemical structure formulas synthesized as described above. The photoluminescence spectra of all coordinating compounds with the  $Eu^{3+}$  ions are of the same shape and with the same emission peaks. The only difference between them is the maximum magnitude of the PL intensity that determines the efficacy. Radiative transitions can be observed in PL spectra of *Europium* ions centered at 580, 590, 612-615, 651, and 700 nm (Fig. 4). These transitions are attributed to internal 4*f* electron transitions of  $Eu^{3+}$  ion  $^3D_0 \rightarrow ^7F_i$  (*i* = 0,1,2,3 and 4), respectively, with a strong emission band in 612-615 nm domain ( $^3D_0 \rightarrow ^7F_2$ ). From comparison of the photoluminescence spectra of investigated organic compounds one can observe a

larger enhancement of the luminescence intensity in the case of  $Eu(TTA)_3Ph_3PO)_2$  compound.

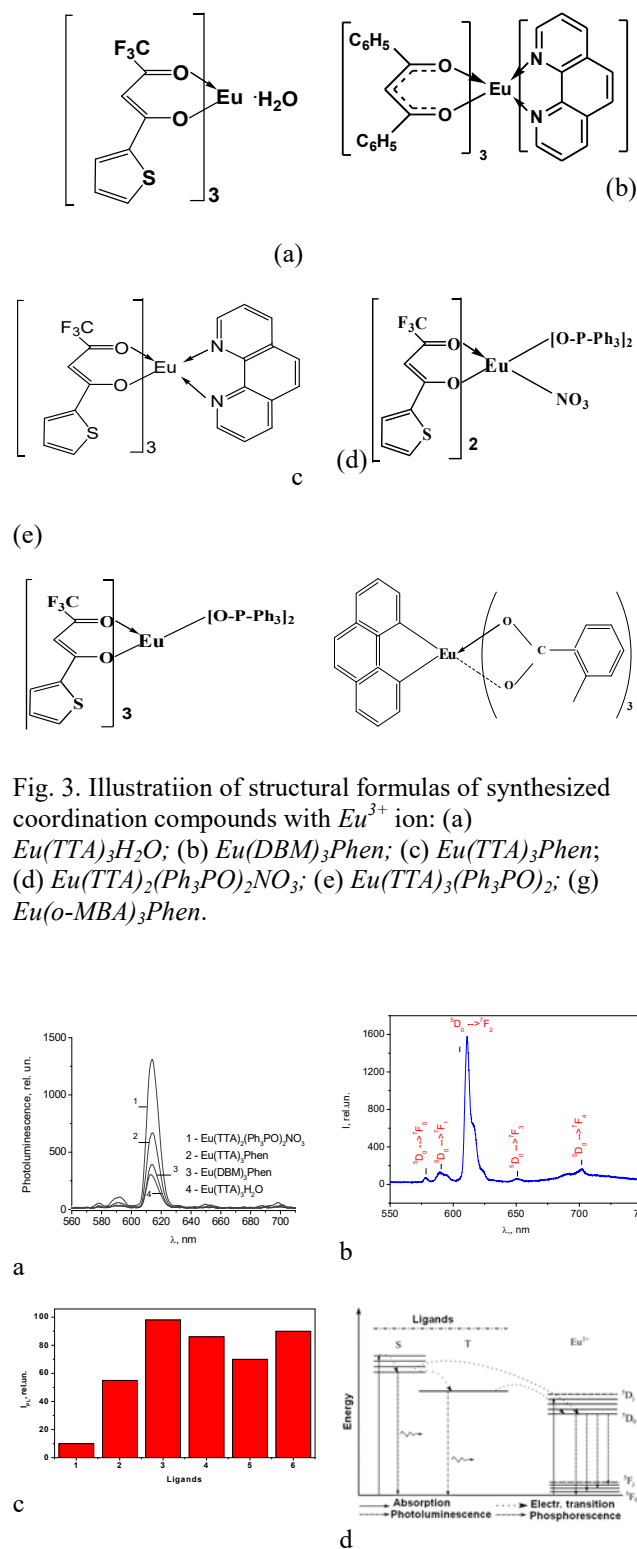


Fig. 4. Illustration of PL spectra: (a) PL spectra of the COC powders; (b) PL spectrum of  $Eu(TTA)_2(Ph_3PO)_2NO_3$  powder at 6 wt. % of concentration COC in solution; Fig. 7(c) shows the maximum values of PL intensity in  $Eu(III)$  COC with different ligands: 1 –  $Eu(TTA)_3H_2O$ ; 2 -  $Eu(TTA)_3Phen$ ; 3 -  $Eu(TTA)_3(Ph_3PO)_2$ ; 4 -  $Eu(TTA)_3(Ph_3PO)_2NO_3$ ; 5 -  $Eu(DBM)_3Phen$ ; 6 -  $Eu(o-MBA)_3Phen$ . Fig. 7(e) illustrates the diagram of possible Dexter and Foerster transfer of excitation energy to  $Eu^{3+}$  ion (antenna effect).

PL high efficiency in coordinating compounds with  $Eu^{3+}$  ions can be explained by the mechanism of energy transfer through the excited electrons from the *S* and *T* levels of the ligands to the  $Eu^{3+}$  central ion (Fig. 4). The observed photoluminescent emission bands are associated with the radiative transitions  ${}^5D_0 \rightarrow {}^7F_i$  from the excited state in the  $Eu^{3+}$  4*f* shell. Experimental results indicate that among our investigated compounds  $Eu(TTA)_3(Ph_3PO)_2$  exhibits the most efficient transfer of energy from ligands to  $Eu^{3+}$  (Fig. 4a).

From analysis of experimental results on photoluminescence and absorption spectra we can identify the cascade of the energy transfer from LUMO energy levels of ligands to the energetic levels of the 4*f* electronic shell of the  $Eu^{3+}$  ion (Fig. 4d). It should be noted that the energy of singlet (*S*) and triplet (*T*) levels of ligands in COC are higher than the energies of corresponding PL of  $Eu^{3+}$  ion  ${}^5D_0 \rightarrow {}^7F_i$ .

#### 4 Conclusions

A series of new photoluminescent coordination organic compounds based on the  $Eu^{3+}$  ion were synthesized and their optical properties were investigated by UV-Vis and PL spectroscopy. It was established that the energy of the absorption threshold  $E_g$  for all investigated ligands is greater than the energy required for excitation of the transitions  ${}^7F_0 \rightarrow {}^5D_0$  within the  $Eu^{3+}$  ion shell 4*f*. The PL emission spectra of investigated coordinating compounds are associated with the internal transitions of  $Eu^{3+}$  ion,  ${}^5D_0 \rightarrow {}^7F_i$  ( $i = 0,1,2,3$  and 4), which peak positions are centered at 537, 580, 612-615, 650 and 702 nm. The half-width of the PL band at 612-615 nm is less than 10 nm, which indicates that COC exhibits an atom-like fluorescence emission with high intensity and color purity. The mechanism of energy transfer in COC to rare-earth ions has been discussed.

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