Photoluminescente properties of *Eu(o-MBA)₃Phen* organic compound embedded in PEPC polymer matrix

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We report preparation and characterization of new nanocomposite material based on oligomers poly-N-propyl carbazole (*PEPC*) and the organic compound *Eu(o-MBA)₃Phen*, where *o-MBA* – ortho-methylbenzoic acid, *Phen* – phenanthroline. Nanocrystals *Eu(o-MBA)₃Phen* with dimensions 20-50 nm have been incorporated into the polymer matrix PEPC with concentrations 5.78%, 2.73%, and 1.30%. Optical absorption thresholds are located in the range 3.34 - 3.40 eV in dependence on the concentration of *Eu(o-MBA)₃Phen* compound. The photoluminescence spectra show a number of strong emmission bands, which are associated with the transitions $^4D_0 \rightarrow {}^7F_i$ (i = 0,1,2,3,4) in the *4f* shell of the *Eu³⁺* ion. Examination of the photoluminescence spectra of luminophore organic compound *Eu(o-MBA)₃Phen* and nanocomposite *PEPC/Eu(o-MBA)₃Phen* demonstrates the enhancement of the photoluminescence emission in *PEPC/Eu(o-MBA)₃Phen* compared with *Eu(o-MBA)₃Phen*

1. Introduction

Over the last decade major efforts have been made in both research and application of rare earth (RE) organic materials and specifically of polymer nanocomposite (NC) materials with coordination compounds of RE ions [1-4]. One of the main advantages of lanthanide compounds is determined by their high luminescence in visible domain. Europium organic compounds present interest for application in laser sources, planar waveguide amplifiers, light emitting diodes, etc. [3-6]. They are also used as luminescent labels in biological systems [2].

Specific properties of lanthanides are determined by their optically active *4f* electrons which form a compressed electronic shell, shielded by the outer two completed shells *5s* and *5p*, that usually prevent any strong interaction of *4f* electrons with the environment [7]. For this reason intra-configurational *4f* optical transitions are characterized by atomic-like narrow absorption and emission bands. Consequently, *4f* optical transitions are not affected by nonradiative transitions caused by molecular thermal vibrations. On the other hand, the structure and spherical symmetry of the rare earth ion forbids direct optical transitions to *4f* levels. For this reason a free lanthanide ion does not exhibit any luminescence or absorption.

The formation of organic compounds based on the *Eu³⁺* ions leads to a larger distortion of spherical symmetry because of interaction of *Eu³⁺* ions with ligands. In this case, unlike the common fluorescence and phosphorescence in compounds, the complexes with rare-earths exhibit high luminescence efficiency and sharp emission bands [8-13]. Application of the complex compounds of lanthanide ions with various organic ligands allows increasing of the luminescence of central RE ion.

Another important advantage of the lanthanides is related to their property to coordinate with a large number of homo- and hetero- ligands to form organic coordination compounds. Various anionic and cationic ligands allow obtaining compounds, which are soluble in polar or nonpolar solvents. The synergistic complexation of the second ligand can not only lead to the formation of efficiently emitting *Eu(III)* complexes, but also to improving the plasticity and electron-transporting ability of the complex [14-15]. This offers the possibility to apply different technologies for deposition of thin films and to select the appropriate and compatible polymer as a matrix for coordination lanthanide compounds.

Rare-earth organic compounds are important for two more reasons. First, they exhibit good compatibility with polymers. Second, the intermolecular energy transfer in rare-earth NCs can enhance the luminescence efficiency of corresponding rare-earth ions [16-18]. Among perspective materials as matrix for coordination lanthanide compounds a special role belongs to polymers, which are sensitive to light, for example, polymers containing carbazole groups, such as polymer poly-(N-vinyl)carbazole (*PVC*) or oligomer poly-(N-epoxypropyl)carbazole (*PEPC*). They exhibit a p-type conductivity and possess good optical transparency. They are characterized by film forming ability, flexibility, thermoplasticity, and consequently, provide the manufacturing sector with low cost technology. The oligomer *PEPC* has wide application in optoelectronics for registration of information and for fabrication of electroluminescent devices [5,6]. This material also attracts interest as a polymer matrix because of its low optical absorption in visible range, simple technology, low cost, and refractive index depending on molecular mass. These characteristics of *PEPC* make it

very promising as a host matrix for RE organic compounds and organic dyes. Incorporation of organic nanoparticles into a polymer matrix proved to be an effective method for improving the performances of polymer NC materials and for obtaining novel structures with advanced physical properties. Compounds based on Eu^{3+} ion exhibit a strong emission at 613-620 nm, which coincides with the region of low optical loss in *PEPC* based composites, and has a large energy gap between the absorption and emissive state [1].

Consequently, one of the goals when preparing lanthanide-based compounds is to increase the main ligand hydrophobicity by direct synthesis in order to avoid coordinative attachment of H_2O molecules or other ligands with *O-H* group that can attenuate luminescence. In order to achieve this, it is necessary to introduce such ligands in the molecule with RE, that will make the RE ion more distant from influence of the outer environment.

In the present work we report the technology and characterization of organic coordination compound of the Eu^{3+} ion, surrounded by ligands of *o-MBA* and of phenanthroline in the matrix of *PEPC*. The final goal was to investigate the luminescence mechanism and excitation energy transfer to Eu^{3+} ion.

2. Experimental procedures

2.1. Preparation method and experimental set-up

The nanocomposite *PEPC/Eu(o-MBA)₃Phen* is composed of an organic compound luminophore *Eu(o-MBA)₃Phen* and a polymer matrix, represented by the oligomer *PEPC*. The chemical structures of the constituent components are illustrated in Fig. 1. All reagents had analytical grade and were used without further purification. 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.

PEPC and *Eu(o-MBA)₃Phen* were dissolved in toluene (ρ(*PEPC*) = 161.9 mg/ml and ρ(*Eu(o-MBA)₃Phen*) = 9.3 mg/ml) by the ultrasonic dispersing at room temperature. The *Eu(o-MBA)₃Phen* complex was incorporated into the polymer matrix in order to obtain compositions with different concentrations (5.74%, 2.87%, 1.43%). Substrates of quartz glass were used for deposition of thin films. Prior the deposition the quartz substrates were subjected to chemical and thermal treatment for cleaning. Thin film layers (1 μm) of nanocomposites were deposited on prepared substrates by spin-coating method and dried at the temperature 80–90 °C for 2 hours. The samples

obtained in this way have a homogeneous surface morphology. The *PEPC/Eu(o-MBA)₃Phen* compositions under UV excitation exhibit a strong sharp red band at ~ 612 nm both in solution and in solid state.
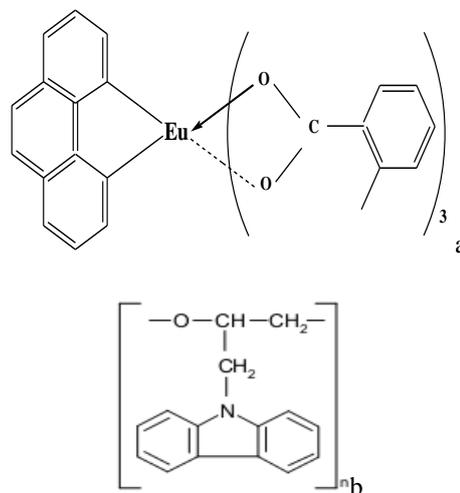
Fig. 1. The chemical structure formula: a) Eu(o-MBA)₃Phen; b) PEPC

Microscopic investigations of the morphology of films surface were carried out with transmission electron microscope (TEM) Philips EM 410 and optical microscope МИК-4. Photoluminescence spectra were excited by a N_2-laser (λ = 337 nm) or a diode laser (λ = 405 nm) and have been registered using a set-up with a MDR-23 monochromator with cooled Hamamatsu photon counting module H9319-12 connected to a PC. Optical fibers were used for excitation and collection of the PL light. For optical transmission measurements a Specord UV/Vis (300-800 nm) CARL ZEISS Jena unit was used. All measurements were performed at room temperature. IR spectra of NCs were measured on Perkin Elmer spectrophotometer. The *Eu(o-MBA)₃Phen* particles size determined from TEM images was found to be between 20-50 nm (Fig. 2).
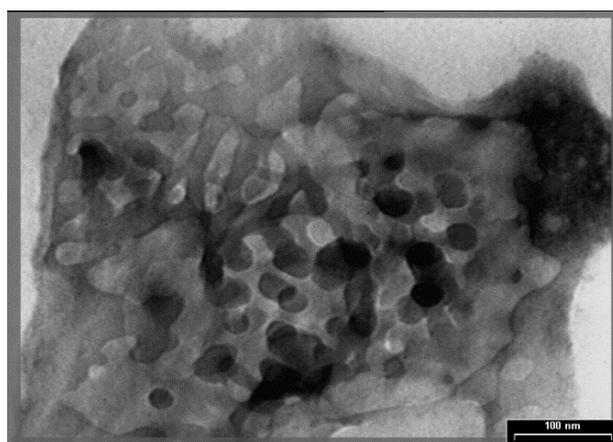
Fig. 2. The TEM image of PEPC/Eu(o-MBA)₃Phen

2.2. Optical absorption of NCs thin films

Fig. 3 illustrates the absorption spectra of NC thin films with different concentrations of *Eu(o-MBA)₃Phen* (5.7%, 2.7%, 1.3%). The absorption edges are estimated at 3.34–3.40 eV. While increasing the concentration of *Eu(o-MBA)₃Phen* in NC the absorption within these bands increases and the threshold shifts to infrared.

IR spectra of NCs (Fig. 4) show the characteristic absorption bands at the following oscillation frequencies (cm⁻¹): 658.1, 665.1, 704.4, 723.7, 740.2, 758.5, 776.9, 791, 837.8, 858.5, 849, 1047.6, 10101.8, 1141.2, 1155, 1209.8, 1284.9, 1449.9, 1347.9, 1390.3, 1449.9, 1494.9, 1518.3, 1529.9, 1570.1, 1589.1, 1611.4, 1691, 2923.5, 2962.1, 3014.4, 3049.3. Reducing the concentration of *o-MBA* in the nanocomposite leads to disappearing of the characteristic absorption band *v(C=O)* at 1691 cm⁻¹, while two absorption bands associated with the carboxyl group

$v_{as}(COO)$ at 1611.4 cm⁻¹ and 1449.9 cm⁻¹ appear, confirming that the carboxylic group was coordinated to the Eu^{3+} ion. In addition, the absorption band of *v(C=N)* at 1560 cm⁻¹ in phenanthroline shifts to 1518.3 cm⁻¹ in the spectra of the complex, which is related to coordination of the two Nitrogen atoms with Eu^{3+} ion [19-22].

2.3. Photoluminescence of nanocomposites

Fig. 5 illustrates the photoluminescence spectra of the NC *PEPC/Eu(o-MBA)₃Phen* registered in the range 570-700 nm under excitation of laser beam 405 nm. In Fig. 6 one clearly observes well developed emission lines centered at 579, 590, 617, 650 and 987 nm. When increasing the concentration of the Europium complex in the NC the PL intensity increases significantly. The intensity of the main maximum is about 16 times higher than others PL bands.
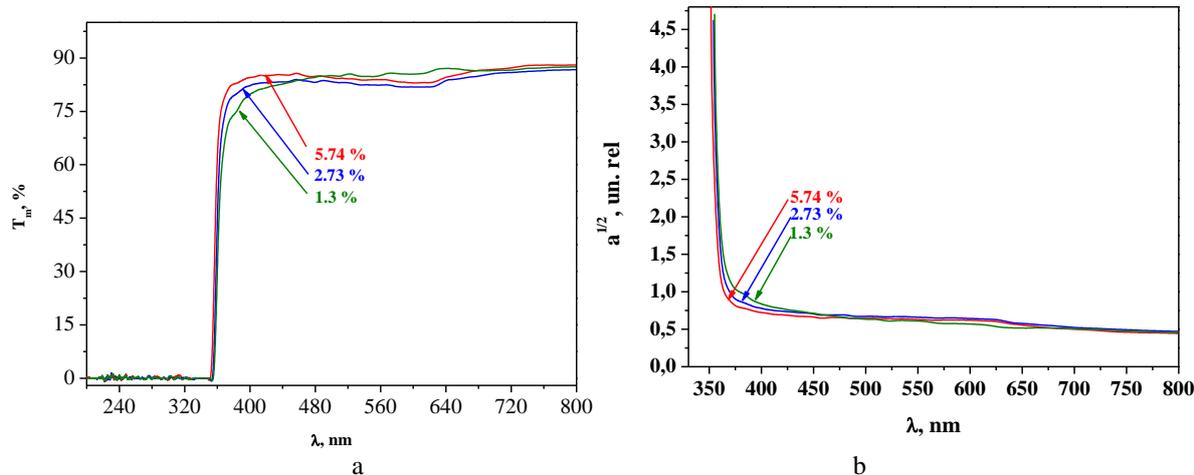
Fig. 3. Transmission spectra (a) and optical absorption (b) of nanocomposites PEPC/Eu(o-MBA)₃Phen
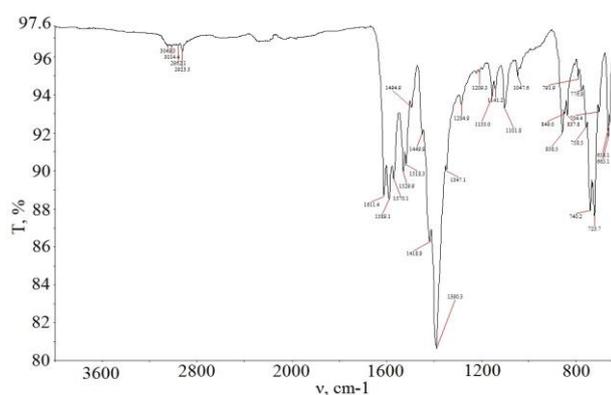
Fig. 4. IR spectra of PEPC/Eu(o-MBA)₃Phen deposited on (KBr)
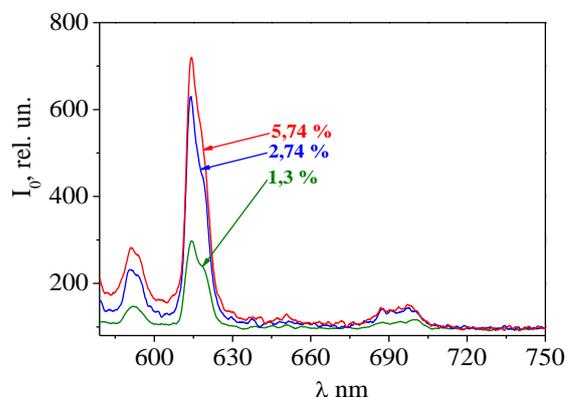
Fig. 5. PL spectra of composite PEPC/Eu(o-MBA)₃Phen at different concentrations of Eu(o-MBA)₃Phen

The FWHM (full width at half maximum) is ~ 15 nm.

The registered PL bands, which correspond to radiative transitions involving internal energy levels of Eu^{3+} ion, are observed in the range 570–700 nm. It is interesting that all emission bands of the PL spectrum have a specific shape, consisting of three maxima (Fig. 6). For

example, for the main band–centered at 617 nm one can clearly distinguish the maxima at 612, 617 and 620 nm.
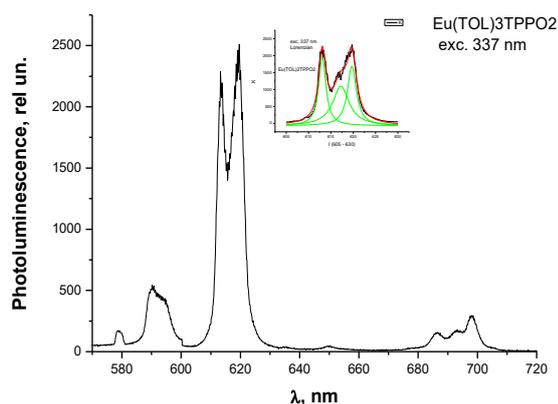
Fig. 6. The detailed photoluminescence of the nanocomposite PEPC/Eu(o-MBA)₃Phen

3. Discussion of results

The threshold of optical absorption was determined from the Tauç's plot $(\alpha h\nu)^{1/2}$ vs. $h\nu$. It was found that the optical absorption threshold at different concentrations of *Eu(o-MBA)₃Phen* in PEPC is approximately the same (3.34–3.40 eV). This probably is caused by the absorption of the coordinating ligand o-MBA, incorporated in the organic compound. This correlates with the difference of the energy levels LUMO and HOMO of the coordinative bonds in the Eu(o-MBA)₃Phen compound. The energy difference LUMO - HOMO for the ligand itself and for the PEPC oligomer corresponds to the UV domain. In the case of PEPC this difference is greater compared to that of the ligands.

Photoluminescence properties of the nanocomposites are determined by the internal transitions of Eu^{3+} ion $^5D_0 \rightarrow {}^7F_i$ (i = 0,1,2,3 and 4). There is a rather weak band at 579 nm associated with the $^5D_0 \rightarrow {}^7F_0$ transition which is independent on the symmetry of surrounding ligands. Based on selection rules [1], the band at 590 nm is attributed to the $^5D_0 \rightarrow {}^7F_1$ parity-allowed magnetic dipole transition, which is independent of the surrounding symmetry. The $^5D_0 \rightarrow {}^7F_2$ transitions represent allowed electrical-dipole transitions. The most intensive band around 617 nm belongs to the $^5D_0 \rightarrow {}^7F_2$ transition that is hyper-sensitive to the symmetry of the crystal field, surrounding the Eu^{3+} ion, and it will be relatively strong if the symmetry is low. In this respect, the red-to-orange emission intensities ratio $R = I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_i)$ is an asymmetry parameter for the Eu^{3+} sites and a measure of the extent of Eu^{3+} interaction with surrounding ligands, and in our case it indicates also on a significant asymmetry around the rare-earth ions.

Splitting of each line of the transition $^5D_0 \rightarrow {}^7F_i$ (i = 0 - 4) into three components indicates on the influence of the inner coordination sphere of the central ion Eu^{3+}. The fine structure of the PL spectrum probably depends on the symmetry of the ligands molecules *o-MBA* that determines

the effectiveness of the energy transfer to the Eu^{3+} ion (Fig. 5, 6).

Photoluminescence excitation in NC structures occurs not only as a result of light absorption by the Eu^{3+} ion or ligands, but also as a result of light absorption by the organic moiety of organic coordinative complex and polymeric matrix (Fig. 7). When absorbing a photon the molecule of polymer or organic compound is excited from its ground state to the singlet state (S_1). From this excited state the molecule can be deactivated through radiative transition to the ground state S_0 (ligand or polymer luminescence), or it can nonradiatively relax to the triplet state T_1 with longer life time. The excited molecule can relax from the T_1 level to the ground state $T_1 \rightarrow S_0$, (molecular phosphorescence), and if the energy of the T_1 level of the ligand $E(T_1)$ is greater than or equal to the energy of lanthanide resonant level, then the excitation energy $E(T_1)$ can be transferred to Eu^{3+} resonant level. In this case the RE ion is promoted to an excited state with subsequent radiative transition and emission of a photon. Surrounding the Eu^{3+} ions by ligands leads, on the one hand, to reduction of non-radiative energy losses due to exclusion of the vibrational coupling. On the other hand, this leads to increasing the transfer of energy to the Eu^{3+} ions through the „antenna" effect. The organic ligands absorb the light energy and transfer it to the central ion of lanthanide, which results in a narrow emission band in the visible region [23].
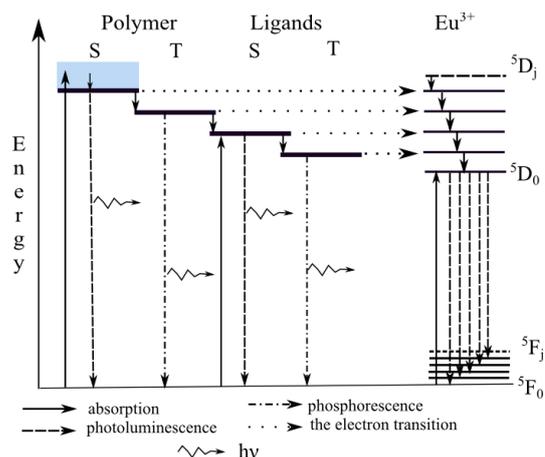
Fig. 7. Illustration of the posible transitions after excitation and photoluminescence in the nanocomposite PEPC/Eu(o-MBA)₃Phen

We can observe that the absorption energy of ligands and PEPC polymer is higher than emission energy of the Eu^{3+} resonance level as well as of the energy of triplet level of polymer and ligands (Fig. 7). This means that the probability of transition from S and T levels to $^5D_0$ level of Eu^{3+} ion is higher. Finally, the excitation energy received by Eu^{3+} ion from PEPC and ligands is determined by its absorption and by the rate of its nonradiative loss. Therefore it is necessary in future to design ligands that would have strong absorption at energy near to absorption edge of the Eu^{3+} ion. In order to decrease the deactivation energy of non-radiative processes of the ligands containing

O-H, *C-H*, and *N-H* groups it would be necessary to replace the hydrogen atom in these groups by deuterium or an halogen (F^-, Cl^-)[5].

As we can see, the organic ligands play a key role in the energy transfer processes. In addition to a negatively charged ligand, the Eu^{3+} ion also needs a zero-charged ligand, called synergetic ligand, for structure stability. The synergetic ligand can reduce, for example, the rate of non-radiative decays and strongly enhance the fluorescence intensity of the complexes.

4. Conclusion

Nanocomposite materials based on coordination compound *Eu(o-MBA)₃Phen* were synthesized and characterized by absorption and photoluminescence spectroscopy in UV-Vis range. From optical transmission spectra we have identified the basic absorption bands at 3.34–3.40 eV. It slightly shifts to IR with increasing of the concentration of *Eu(o-MBA)₃Phen* complex in NCs.

The photoluminescence spectra show a strong emission bands centered at 579, 590, 617, 650, 687 nm, which is associated with the transitions $^4D_0 \rightarrow {}^7F_i$ (i = 0,1,2,3,4) in the 4f shell of the Eu^{3+} ion. From comparing the photoluminescence spectra of the *Eu(o-MBA)₃Phen* compound and of the *PEPC/Eu(o-MBA)₃Phen* nanocomposite one can observe the enhancement of the photoluminescence emission in the nanocomposite, determined by the energy transfer from polymer matrix to the Eu^{3+} ion.

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