

Synthesis and characterization of copolymers of lanthanide complexes with styrene

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With aim of the simplification of the layers incorporation in the electroluminescent cell can be superposed the emission layer (unsaturated rare earth elements complex), electronic conduction layer (1,10 – phenanthroline) in one macromolecule.

Copolymers of 2-methyl-5-phenylpentene-1-dione-3,5 with styrene in ratio 5:95, which containing Eu, Yb and Eu, Yb with 1,10-phenanthroline were synthesized at the first time. The luminescence spectra of obtained metal complexes and copolymers in solutions, films and solid state are investigated and analyzed. The solubilization of β -diketonate complexes with phenanthroline was shown to change luminescence intensity in such complexes. Obtained copolymers can be used as potential materials for organic light-emitting devices.

Introduction

Over the last decade, organic light-emitting devices have attracted great interest for their manifold applications in different areas, varying from white lighting, such as light bulbs replacement, to multicolor displays for televisions and cell phones [1-3]. There has been a large research activity on coordination compounds of the lanthanide ions with organic ligands including β -diketones, which can act as excellent light conversion molecular device, light-emitting diodes, polymer sol-gel derived glasses, electroluminescent devices [4-7].

On the basis of the unique photophysical properties of lanthanide cations (long luminescence lifetime and very sharp emission

band), rare earth metal complexes, especially europium(III) complexes, as luminescent materials have received increasing attention for application such as analytical sensors, imaging techniques, displays and organic light-emitting diodes [8-13].

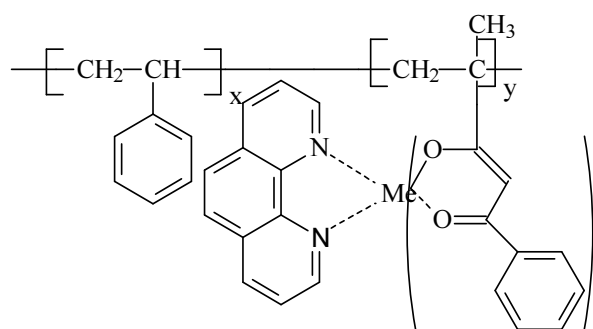
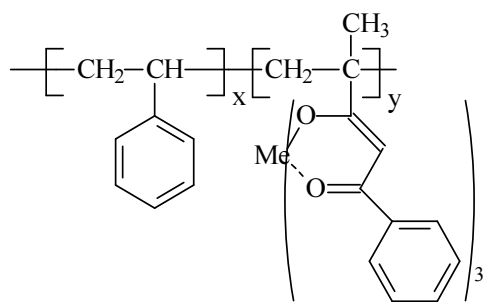
Recently, europium complexes have attracted more interest in organic light-emitting diodes (OLED) for their saturated red-emission [14-18]. Also several europium complexes have been applied as red emitters in electroluminescent devices [19-23].

Using the monomer complex has a number of disadvantages connected with aggregation or crystallization of the film.

Therefore, there is a necessity of the polymeric materials synthesis. It is well known that metal polymers are mainly produced by intercalation of metals in the polymer ligand matrix. This method has a lot of disadvantages such as partial degradation of the polymer chain and low yield of the synthesized polymers as well as low coordination level which results in composition heterogeneity. All these shortcomings have an influence upon physical characteristics of obtained compounds.

The aim of this work were synthesis of Eu, Yb complexes with 2-methyl-5-phenylpentene-1-dione-3,5 and phenanthroline as well as copolymers based on them with styrene and investigations of optical properties of metal-containing polymeric systems depending on influence of phenanthroline configured-in the complex coordination sphere on the luminescence properties and concentration of rare earth elements complexes in polymeric materials.

Copolymers of 2-methyl-5-phenylpentene-1-dione-3,5 with styrene in ratio 5:95, which containing Eu, Yb and Eu, Yb with 1,10-phenanthroline were synthesized at the first time.



Results and discussion

The IR-spectra of synthesized compounds were registered to establish the type of coordination of the lanthanide ion with a mphpd functional groups. Analysis of IR spectra showed a presence of stretching vibrations of C-O and C-C bonds at 1500-1600 cm^{-1} , that confirms the cyclic bidentate coordination of ligand to metal ions. A slight shift of the main absorption band for the complex in a comparison with β -diketone sodium salt to the long-wave region indicates a weakening of the metal - ligand bond, due to increase of covalent bond. The low intensity band at 1660 cm^{-1} corresponds to the valent vibration of the double bond $\nu(\text{C}=\text{C})$. Also there is a broad absorption band of coordinated water molecules at 3400-3200 cm^{-1} . Thus, obtained results indicate a cyclic bidentate coordination of mphpd molecules in the complex.

Electronic spectra of the monomer as well as metal polymeric complexes have a set of bands corresponding to europium ion (table 1). Shift of the main absorption bands in the long wavelength region in comparison with the spectra of aqua-ions, and their increase in intensity indicates the formation of metal

complexes. Electronic spectra of the $\text{Yb}(\text{mphpd})_3 \cdot 2\text{H}_2\text{O}$ have a singular transition band ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ corresponding to ytterbium ion. A slight shift of the maximum which is observed in absorption spectra of the complex $\text{Yb}(\text{mphpd})_3 \cdot 2\text{H}_2\text{O}$ in comparison with the spectra of aqua-ions indicates the formation of metal complex and a weakening of the metal – ligand bond (fig.1).

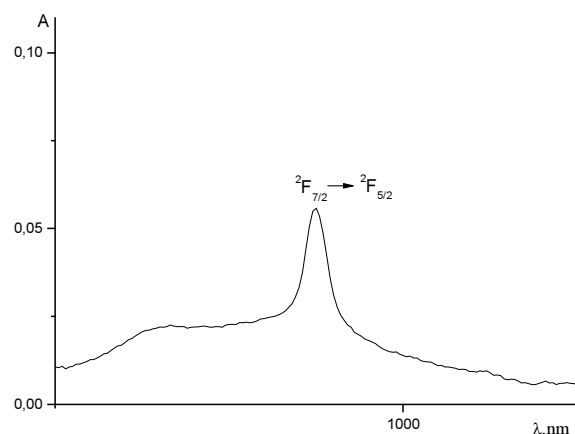


Fig.1. Electronic absorption spectrum of $\text{Yb}(\text{mphpd})_3 \cdot 2\text{H}_2\text{O}$.

Similarity of electronic absorption and diffuse reflectance spectroscopy (ESA and SDR) show a similar structure of the complexes in solution and polycrystalline state. A slight shift of the maximum which is observed in absorption spectra of the complex $\text{Eu}(\text{mphpd})_3 \cdot \text{Phen}$ indicates a replacement of water molecules in the nearest coordination environment without significant changes in the coordination polyhedron geometry.

The luminescence spectra of europium β -diketonates complexes in all samples are similar to each other and approving the structure similarity of coordination polyhedrons which are distorted antiprism. All the samples have an equal number of the magnetic and electric

dipole transitions as well as the forbidden transitions (see the table 2).

Europium luminescence spectra (fig. 2a) at 77K allow to establish the short-range coordination environment symmetry.

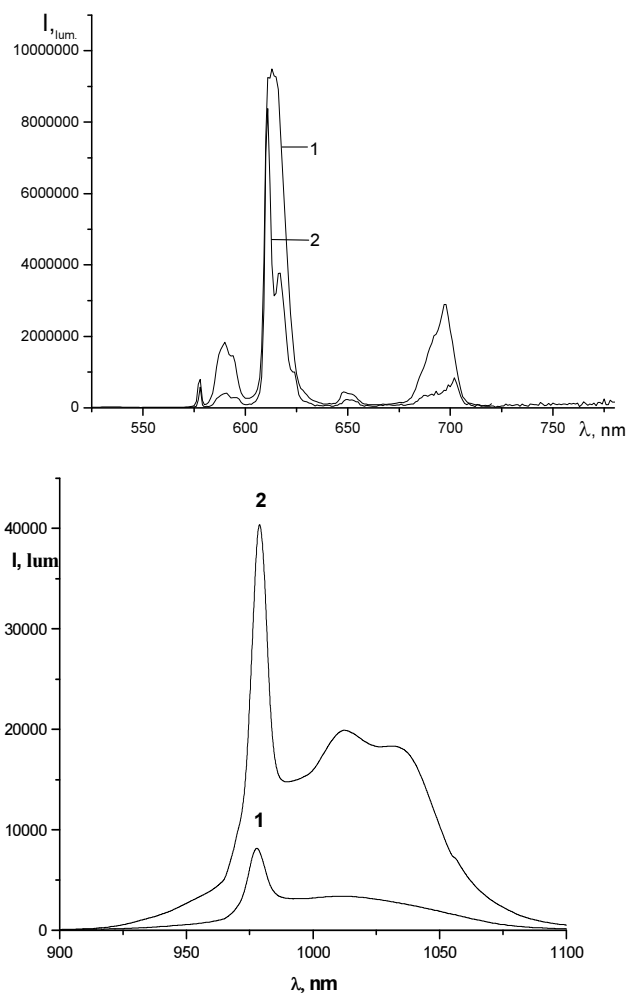


Fig. 2. Luminescence spectra of a) 1- $\text{Eu}(\text{mphpd})_3 \cdot \text{Phen}$; 2- $\text{Eu}(\text{mphpd})_3$, in solid state, $T=298 \text{ K}$, $\lambda=362 \text{ nm}$ b) 1 - $\text{Yb}(\text{mphpd})_3$, 2 - $\text{Yb}(\text{mphpd})_3 \cdot \text{Phen}$

The transition band ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ in luminescence spectra of all compounds appears as a symmetrical single line and indicates a presence of one luminescence center. High-intensity lines caused by electric dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ compared with relatively low intensity magnetic dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ suggests not center-symmetric nature

of the environment for all investigated compounds.

As for phenantroline complexes, obviously phenantroline is a part of the complex and forms an adduct but not a mixed-complex due to spaciousness of the diketonate fragment. Based on the number of the splitting components we can assume a significant rhombic distortion.

The luminescence intensity of complexes based on Eu(III) and Yb(III)-phenanthroline is greater in comparison with complex without additional ligand (fig.2). The phenanthroline displaces the coordinate water out of the coordinate sphere which is quenching agent.

The luminescence intensity of copolymer of styrene with Eu(III)-phenanthroline complex (fig.3) is identical practically with homopolymer of Eu(mphpd)₃·Phen [13].

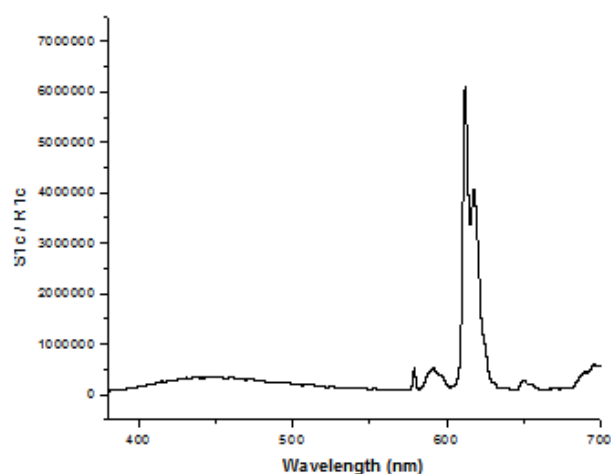


Fig. 3. Luminescence spectrum of Eu(mphpd)₃·Phen-co-styrene in solid state, T=298K, λ=358 nm

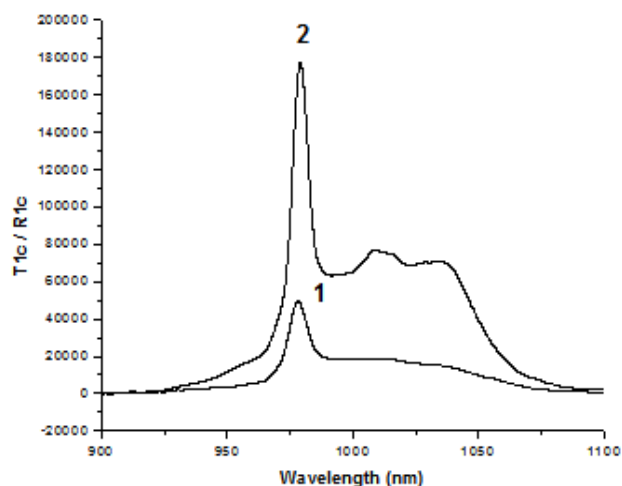


Fig. 4. Luminescence spectra of 1) Yb(mphpd)₃·3H₂O-co-styrene; 2) Yb(mphpd)₃·Phen-co-styrene in solid state, T=298K, λ=336 nm

The luminescence intensity of copolymer of styrene with Yb(III)-phenanthroline complex is greater in several times in comparison with copolymer with Yb(mphpd)₃·3H₂O (fig.4) and respective monomeric complexes (fig.2b).

Conclusions

The solubilization of Eu(III) and Yb(III) β-diketonate complexes with phenanthroline, was shown to change luminescence intensity in these complexes. The luminescence intensity of these complexes is greater in comparison with complex without additional ligand.

Thus, obtained copolymers which containing 5 % emission components (lanthanide complex) in polymer chain only are comparably with suitable homopolymers concerning luminescence properties and can be perspective for optical application.

Experimental part

NMR: ¹H (D₂O) δ (ppm): 3.27 (singlet, 3H, CH₃); 3.47(singlet, 1H, =CH-); 5.27

(singlet, 1H, =CH₂); 5.58 (singlet, 1H, =CH₂); 7.15-7.60 (multiplet, 5H, Ph).

Complexes obtained by an exchange reaction between equimolar amounts of lanthanide acetate and sodium 2-methyl-5-phenylpentene-1-dione-3,5 salt in a water-alcohol solution at pH 9-9.5 with a slight excess of the ligand.

The polymerization was carried out at 80° C in the thermostat in dimethylformamide solution with monomer concentration 0.03 mol/l and initiator 2,2'-azobisisobutyronitrile concentration 0.003 mol/l. Thus, obtained metal polymers precipitate out from propanol-2 solution.

The synthesized compounds have been studied by NMR, IR-, electronic absorption and diffuse reflectance spectroscopy. The infrared spectra were recorded in KBr tablets at a range of 4000-400 cm⁻¹ with Spectrum BX II FT - IR manufactured by Perkin Elmer. The electronic absorption spectra were recorded using spectrophotometer Shimadzu «UV-VIS-NIR Shimadzu UV-3600" and the diffuse reflectance spectra were obtained using the Specord M-40 spectrophotometer in the range of 30000-12000 cm⁻¹. The excitation and luminescence spectra of solid samples and solutions (10⁻³ M, CHCl₃) were recorded on a spectrofluorometer «Fluorolog FL 3-22», «Horiba Jobin Yvon» (Xe-lamp 450 W) with the filter OS11. The InGaAs photoresistor (DSS-IGA020L, Electro-Optical Systems, Inc, USA) cooled to the temperature of liquid nitrogen was used as a radiation detector for infrared region. The

excitation and luminescence spectra were adjusted to a distribution of a xenon lamp reflection and the photomultiplier sensitivity.

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