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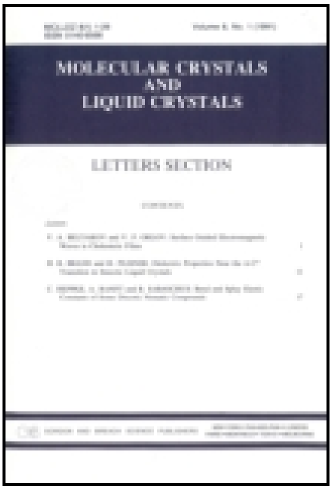

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The New Nanosized Systems on the Basis Eu(III) Complexes as Precursors for Organic Electroluminescent Diodes

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The New Nanosized Systems on the Basis Eu(III) Complexes as Precursors for Organic Electroluminescent Diodes

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Novel Eu(III) complex with 2-methyl-5-phenylpentene-1-dione-3,5, metallopolymer based on and copolymer with N-vinylcarbazole were obtained. The kinetics of polymerization was studed by dilatometric method. The complex and metallopolymer were investigated and characterized by a number of physicochemical methods. The obtained results allowed to determine the composition, structure and symmetry of synthesized compounds. On the basis of metallopolymers was constructed the electroluminescent diode.

Keywords Europium complex; metallopolymer; thin film; luminescence; nanomaterial; electroluminescent diodes

1. Introduction

Over the last decade, light emitting diodes based on organic materials have become the new competitive devices due to ease of fabrication and high performance [1–3].

Many reports have focused on the discovery of new and improved electroluminescent (EL) materials for the construction of reliable organic luminescent emitting diodes (OLED) [4–6]. There are many different factors influence on the performance of OLEDs, such as the quantum efficiency, thermal stability, and charge carrier mobility. On the other side, manufacturability is also an important factor. To date, the most widely used electron-transporting and host emitting material in OLEDs is still the complexes of aluminum, because they are thermally stable, easily synthesized and purified, highly fluorescence and has excellent electron-transporting mobility. However, the degradation in organic EL

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*Corresponding author, O. Berezhnytska. E-mail: olekberez@gmail.com devices is unavoidable. The mechanism is not yet clear fully, but some researchers believe that degradation primarily caused by the organic material's morphological changes.

As known, β-diketonate europium complexes exhibit the luminescence in the visible spectrum, and are efficient phosphors, and can be used as a source of white light for TV screens and mobile phones [7–10]. The use of multifunctional materials in modern organic electroluminescent devices will reduce the amount of organic layers, through the use of polymeric material for film depositing from solution.

As we know, low molecular weight of complexes were not practically feasible, because at the film often crystallize or aggregation substance. To resolve this problem, we obtain polymeric metal complexes with desired properties.

As known, some polymers have electron conductivity. One of them is vinylcarbazole which using as conducting layer in OLED. Therefore, is reasonable synthesis of copolymer based on metallocomplexes and vinylcarbazole.

The object of the study was selected europium complex with 2-methyl-5-phenylpentene-1-dione-3,5 (mphpd), metallopolymer and copolymer based on.

Besides, in the investigated films obtained by deposition from solution metallopolymer of europium $[Eu(mphpd)_3]_n$, and vinylcarbazole copolymer based on it $[Eu(mphpd)_3]_nVC$.

2. Experimental

2.1 *Materials*

The sodium salt of 2-methyl-5-phenylpentene-1-dione-3,5 was prepared by means of Claisen condensation of acetophenone with ethyl methacrylate. The methods of preparation and purification of Na(mphpd) are described in [11]. The acetate of europium and vinylcarbazole was purified prior to use unless otherwise indicated.

As a substrate thickness of 1 mm glass coated with ITO layer was produced by Merck (surface resistance 8–12 Ohm/m) was used.

2.2 *Methods*

The synthesized complexes were studied by IR-, UV-spectroscopies and diffuse reflectance spectroscopy, elemental analysis, electronic microscopy, dynamic light scattering and luminescence spectroscopy.

The polymerization was carried out at 80°C in dimethylformamide solution at a concentration of monomer, 0.05 mol/l and the concentration of the initiator 2,2 '-azo-bis (isobutyronitrile) – 0.0005 mol/l per 20 hours. The kinetic of polymerization was studied by dilatometric method per 3 hours. Obtained metallopolymers was separated from propanol-2 solution. The elemental analysis for metal ions was carried out on ICP AES Shimadzu 9000 atomic emission spectrometer. Infrared spectra were recorded on a Fourier-spectrophotometer over the range 4000–400 cm^{-1} in a tablets with KBr. The electronic absorption spectra were recorded on a Shimadzu spectrophotometer and diffuse reflectance spectra on a Specord M-40 spectrophotometer in the region 30000–12000 cm^{-1}. The excitation spectra and luminescence spectra of solid samples and solutions ($10–^{3}$ M, $CHCl_3$) were recorded on a spectrofluorimeter «Fluorolog FL 3–22», «Horiba Jobin Yvon» (Xe-lamp 450 W) using OC 11 filter. As a radiation detector for the IR region was used photoresistor InGaAs (DSS-IGA020L, Electro-Optical Systems, Inc., USA) cooled to liquid nitrogen temperature. The excitation spectra and luminescence spectra were corrected in accordance with the distribution of the radiation sensitivity of the xenon lamp and a photomultiplier.

The particle size studying was performed at 25°C using the equipment from «Zeta Sizer Nano by Malvern».

Photomicrographs were filmed on electron microscopes: «Hitachi H-800» (TEM) and Tescan Mira3 (SEM).

2.3 Synthesis

The complex was obtained by an exchange reaction between equimolar amounts of europium acetate and sodium salt of methacroylacetophenone in a 1:3 water-alcohol solution at pH 9–9.5 with a slight excess of the ligand:

$$\mathrm{Eu(CH_3COO)_3 + 3Na(mphpd) \rightarrow Eu(mphpd)_3{+}3CH_3COONa}$$

Polymerization scheme is shown in Fig. 1.

The copolymerization with vinylcarbazole was carried out at 80°C in dimethylformamide solution at a ratio of complex: vinylcarbazole 5:95 (mass%). The molecular structure of copolymer shown in Scheme 1.

For obtaining of metallopolymer films dissolved in chloroform, the concentration of the initial solution was 10^{-3} M. Selection of solvent was carried out by studying colloidal solutions of polymers by dynamic light scattering. The emitter solution was applied to a substrate with ITO by spin-coating.

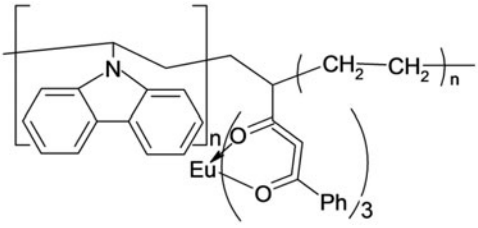
A solution (1 ml) was dropped in the center of the substrate fixed on the holder rotating with the initial speed of 200 rpm, and further acceleration of up to 2000 rpm.

3. Results and Discussion

The sodium salt of unsaturated β-diketone $C_{12}H_{11}O_2Na$ obtained by the described [11] method is a crystalline yellow substance with melting point = 216°C. **NMR: ^{1}H** (D_2O) δ (ppm): 3.27 (singlet, 3H, CH_3); 3.47(singlet, 1H, =CH−); 5.27 (singlet, 1H, $=CH^2$); 5.58 (singlet, 1H, $=CH_2$); 7.15–7.60(multiplet, 5H, Ph).

The europium percentage in complex $Eu(mphpd)_3 \cdot 2H_2O$ (%): 20.29 (calculated), Eu - 20,18 (found).

The kinetic parameters of radical polymerization $V_r = 2{,}72 \cdot 10^{-5}$ mol / (L · s) $V_{pr.} = 5{,}43 \cdot 10^{-4}\ s^{-1}$, $K = 77{,}7 \cdot 10^{-4}$, $L^{1/2}$ / ($mol^{1/2}$ · s) have very good agreement with literature data [12], however, the rate constant is somewhat overstated. Since no literature data for lanthanide complexes polymerization, the obtained results were compared with similar complexes for 3d metals. Probably, the growth rate constant due to the high resistance of



Scheme 1. Molecular structure of studied copolymer.

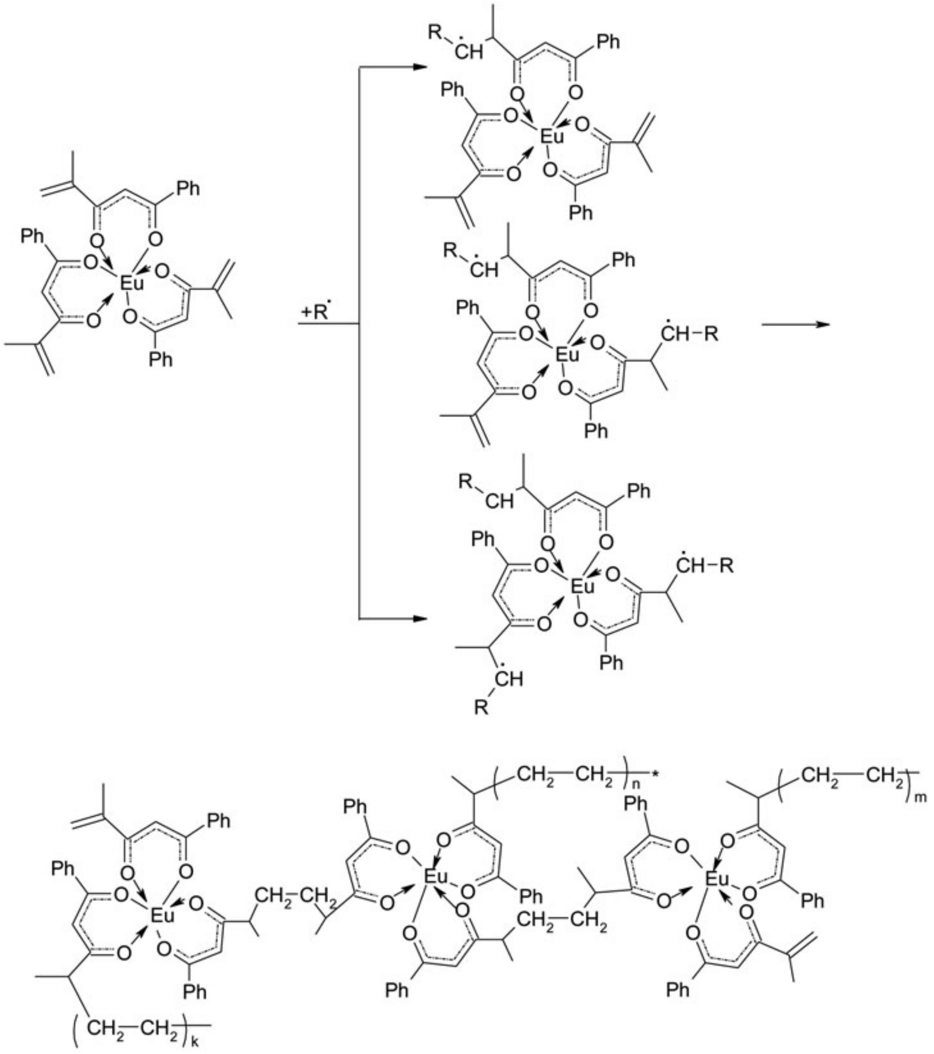
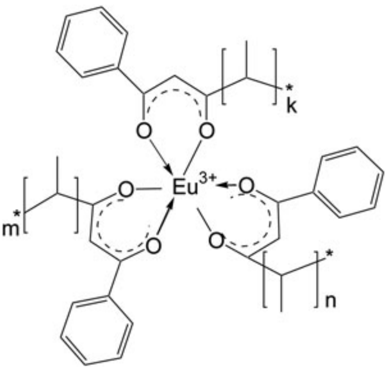


Figure 1. Scheme of Eu(mphpd)$_3$ radical polymerization.

polymeric lanthanide compared to metallopolymers of 3d metals. The molecular structure of metalopolymer of europium (III) shown in Scheme 2.

In the IR spectra of the synthesized complexes and metallopolymers in region 1500–1600 cm^{-1}, there are bands corresponding to stretching vibrations of the (CO) and (CC), which confirm the bidentate cyclic coordination of the ligand to the metal ions. The low intensity band at 1660 cm^{-1} corresponds to the (C=C). Also there is a broad absorption band of coordinated water molecules at 3400–3200 cm^{-1} [13,14].

Electronic spectra of the monomer as well as metal polymeric complexes have a set of bands corresponding to the europium ion. Shift of the main absorption bands ($^7F_0 \rightarrow {}^5D_2$, $^7F_0 \rightarrow {}^5D_1$) in the long wavelength region in comparison with the spectra of aqua-ions, and their increase of intensity indicates the formation of metal complexes, may be evidence of the formation of compounds with coordination number greater than inorganic



Scheme 2. Molecular structure of Eu^{3+} metallopolymer.

salts of europium [15]. An absence of significant shifts for metallopolymers allows to suggest a similar structure for the coordination polyhedron of monomer and polymer complexes.

The luminescence excitation spectra of the polymer sample in the solid state and dissolved in chloroform and photoluminescence spectrum of a film based on it were written. Luminescence spectra of both samples are similar. For them, there is an intense red light luminescence, in which the greatest intensity spectrum are band with a maximum in 612–616 nm, corresponding electric - dipole transition $^5D_0 \rightarrow {}^7F_2$. In addition, the band has lower intensity correspond $^5D_0 \rightarrow {}^7F_0$ (577–578nm) transition, magnetic - dipole transition $^5D_0 \rightarrow {}^7F_1$ (589–593) and electric - dipole transitions $^5D_0 \rightarrow {}^7F_3$ (648–653 nm), $^5D_0 \rightarrow {}^7F_4$, (691–700 nm) (Fig. 2a, b). According to the spectral study of metallopolymers the luminescence quantum yield was calculated, which is 0.038.

On the basis of the splitting can determine the symmetry of environment for center of luminescence [16,17]. In the luminescence spectrum at 77 K (Fig. 2b) there is a small number of lines for the transitions $^5D_0 \rightarrow {}^7F_1$ (2 components), $^5D_0 \rightarrow {}^7F_2$ (2 components), $^5D_0 \rightarrow {}^7F_3$ (3 components), $^5D_0 \rightarrow {}^7F_4$ (3 components) (Fig. 2a). Comparison of experimental results with the literature [18, 19] suggests a trigonal environment luminescence centers C_{3v} symmetry, coordination polyhedron is a trigonal two-caped prism.

Considering that the aim of the study is the synthesis of new materials that can be used as layers in organic electroluminescent devices, a necessary condition is to obtain homogeneous films based on them. Therefore, by electron microscopy were analyzed film and powdered sample $[Eu(mphpd)_3]_n$. The micrographs analysis show (Fig. 3a, Fig. 3b) the nanoparticle system is obtained with a uniform distribution of the dispersed phase in the dispersion medium, confirming the homogeneity of the chemical metallopolymers composition.

To establish the dimension of monomer and polymer complexes were investigated by dynamic light scattering in chloroform solution. Based on the distribution diagram in chloroform solution of the polymer particle size is 10 nm, and the system is monodisperse. Perhaps, that metallopolymer $[Eu(mphpd)_3]_n$ has a globular structure. In DMF solution particle size is 30–200 nm, the system is polydisperse. Therefore, in order to obtain homogeneous films as solvent chloroform was chosen.

The films composition was examined with an electron microscope (EDAX), and it is relatively REM adequate composition solution from which the film was prepared. The films are transparent in the visible spectrum, have good adhesion to the substrate.

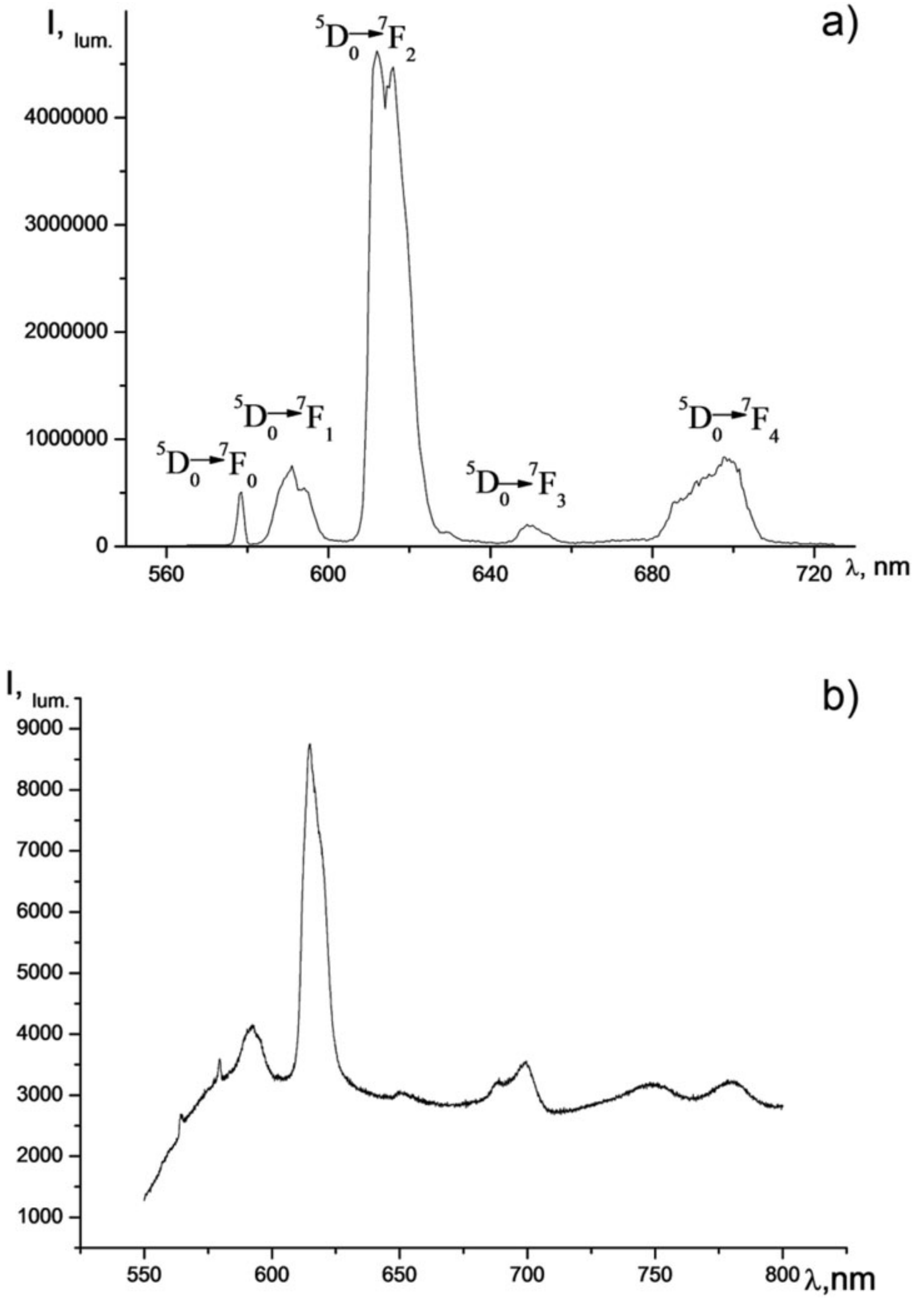


Figure 2. Luminescence spectra of $[Eu(mphpd)_3]_n$ (a) in solution ($CHCl_3$, $\lambda_{ex} = 362$ nm, $C_{Eu} = 10^{-3}$ M), and films based on (b) at 77 K.

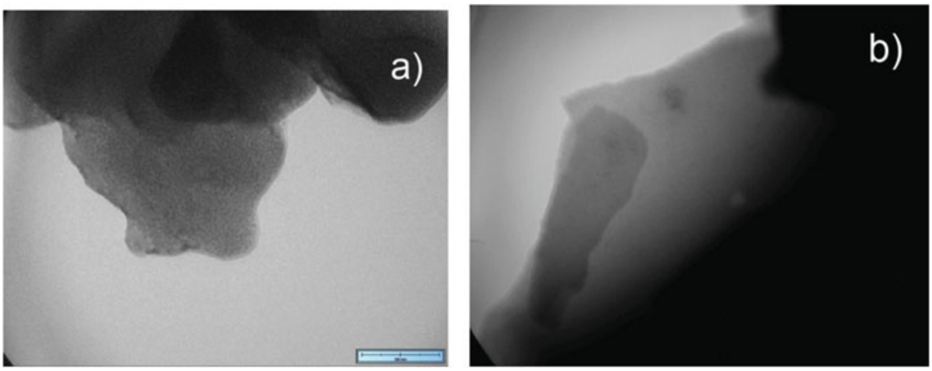


Figure 3. TEM microphoto of metallopolymer $[Eu(mphpd)_3]_n$ powder (a) and film (b) U = 150 кВ.

During the work we have produced organic light-emitting planar heterostructure with thickness, which is several orders smaller than their linear dimensions. As the emitting layers were used coordination compounds $[Eu(mphpd)_3]_n$ and $[Eu(mphpd)_3]_n$VC.

Unfortunately, a study was spotted low conductivity of films for obtained complexes, unbalanced hole and electron currents as well as the beginning of electroluminescence at relatively large values of the applied voltage. Therefore, this work requires further investigation.

4. Conclusions

The structure similarity of coordination polyhedra for complex and polymer based on which are distorted antiprism established. The luminescence spectra of polymer and films based on europium complexes are similar to each other. Very high quantum yield of luminescence allows possibility of using these compounds as organic layers in electroluminescent devices.

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