

# Novel polymer metal complexes as precursors for electroluminescent materials

*I.Savchenko, A.Bereznitskaya<sup>\*</sup>, S.Smola<sup>\*\*</sup>, Ya.Fedorov<sup>\*</sup>, N.Ivaha<sup>\*</sup>*

Kyiv National T.Shevchenko University,  
60 Volodymyrska Str., 01033 Kyiv, Ukraine

<sup>\*</sup>V.Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, 32/34 Ac. Palladina Ave., 03142 Kyiv, Ukraine

<sup>\*\*</sup>A.Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, 86 Lustdorfskaya doroga, 65080 Odessa, Ukraine

*Received February 22, 2012*

The monomer — 2 methyl-5-phenylpentene-1-dione-3,5, their complexes with Nd(III), Eu(III), Er(III), new metallopolymers based of them are obtained. Structure of the monomer, the metal complexes and the metallopolymers confirmed by the data of NMR-, electronic, diffusion and infrared spectroscopies, elemental and termogravimetric analysis. The luminescent spectra of the obtained metallocomplexes and polycomplexes in solutions, films and solid state have been investigated and analyzed. The luminescence quantum yield of polycomplex based Eu(III) is maximal. The obtained polymetallocomplexes can be used as potential materials for organic light-emitting devices.

Получены мономер — 2-метил-5-фенилпентен-1-дион-3,5, его комплексы с Nd(III), Eu(III), Er(III), новые металлополимеры на их основе. Строение мономера, металлокомплексов, металлополимеров доказано с помощью данных, электронной, инфракрасной, диффузного отражения спектроскопии, элементного и термогравиметрического анализа. Изучены и проанализированы спектры люминесценции мономерных и полимерных металлокомплексов в растворах, пленках и твердом состоянии. Самый высокий квантовый выход люминесценции обнаружен для поликомплекса Eu(III). Полученные полиметаллокомплексы могут быть предложены как потенциальные материалы для электролюминесцентных устройств.

## 1. Introduction

Over the Nd(III), Eu(III) and Er(III)  $\beta$ -diketonate complexes with aromatic amines luminesce in the visible range and are very efficient luminophores [6, 7]. Their ability to convert UV into visible light offers promise for using them as fillers in various-purpose light-emitting materials. But these complexes are not technological.

Coordination compounds of the rare earth elements (REE) have several interesting functional properties (magnetic, optical), so they are perspective for use in the form of thin films in a variety of devices having a planar structure. Almost all lan-

thanides may have luminescence provided by the correct ligand choice. By the type of luminescence they can be divided into two groups: luminescent in the visible and near-IR range. The luminescent wavelength set of each rare earth element ion persists regardless of the ligand. On the other hand, the choice of the ligand is very important, because it affects stability, solubility of the complex and luminescence efficiency. The use of the exact metal-organic compounds is based on the fact that combination of metal ions and organic ligands in one molecule provides the possibility of their composition variety and structure, and in such a way their properties. Energy must not only be

transmitted from the central atom to the ligand, but also it should be transferred back. Coordination compounds of rare earth elements with  $\beta$ -diketones are perspective in terms of optical materials development, since it possess high thermal stability, monochrome emission and high quantum efficiency and allow varying the properties by an introduction of the additional ligand. From this point of view, it can be used as emissive layers in organic electro-luminescent devices [8]. It is known that the ions of ytterbium, neodymium, erbium and praseodymium absorb in the near IR range of communication frequencies. Unfortunately, use of complexes of these metals for OLED creation is somewhat limited due to the low intensity of luminescence caused by the undesirable crystallization or aggregation in the substrate films [9–11]. Because of that there is a necessity for the synthesis of macromolecular complexes on the basis of REE. The aim of this work is the synthesis and study of the complexes of neodymium, erbium and europium with 2-methyl-5-phenylpentene-1-dione-3,5 (mphpd), and metallopolymers on their basis.

## 2. Experimental procedure

2-Methyl-5-phenylpentene-1-dione-3,5 and metal complexes were synthesized in accordance with the procedure described in [12]. The polymerization of monomeric metal complexes was carried out at 80°C in dimethylformamide (DMF) solution at a concentration of monomer 0.3 mol/l and the concentration of the initiator 2,2'-azo-bis(isobutyronitrile) — 0.003 mol/l in thermostat during 20 h. The obtained metal polymers were precipitated from the solution by propanol-2 and reprecipitated from DMF into ethanol.

The synthesized complexes were studied by IR-, UV-spectroscopy and diffuse reflectance spectroscopy, thermal and elemental analysis.

Metal elemental analysis was carried out using atomic-emissive spectrometer Shimadzu ICPE-9000.

Thermograms were recorded by TA instruments Q-1500 D apparatus of system of F.Paulik, J.Paulik, L.Erdey at a heating rate of 5°C/min from room temperature up to 500°C in platinum capsule in presence carrier Al<sub>2</sub>O<sub>3</sub> (anhydrous).

Infrared spectra were recorded using Perkin-Elmer Spectrum BX II FT — IR spectrophotometer over the range of 4000–400 cm<sup>-1</sup> with KBr pellets.

Electronic absorption spectra and diffuse reflectance spectra were recorded applying Shimadzu spectrophotometer in the region 30000–12000 cm<sup>-1</sup>.

Excitation spectra and luminescence spectra of solid samples and solutions (10<sup>-3</sup> M, CHCl<sub>3</sub>) were recorded on spectrofluorimeter "Fluorolog FL 3-22", "Horiba Jobin Yvon" (Xe-lamp 450 W) using OC 11 filter. As a radiation detector for IR region a photoreceptor InGaAs (DSS-IGA020L, Electro-Optical Systems, Inc, USA) was used. It was cooled to the liquid nitrogen temperature. The excitation spectra and luminescence spectra were corrected in accordance with the distribution of the radiation sensitivity of xenon lamp and a photomultiplier.

## 3. Results and discussion

With the aim to determine the way of ligand functional groups coordination to metal ions the IR spectra of synthesized compounds were studied.

In the IR spectra of the synthesized complexes and metallopolymers in 1500–1600 cm<sup>-1</sup> there are bands corresponding to stretching vibrations of the  $\nu$  (C–O) and  $\nu$  (C–C), which confirms the bidentate cyclic coordination of the ligand to the metal ions (Table 1). At the same time a higher frequency band should be attributed to the stretching vibrations  $\nu$  (CC) and a lower frequency to the stretching vibrations of the  $\nu$  (CO). The region 1640–1680 cm<sup>-1</sup> contains stretching vibrations  $\nu$  (C=C) [14]. In the case of metallopolymer this band disappears or significantly reduces in intensity indicating the presence of only the terminal unsaturated groups. Fairly broad band of coordinated water molecules is observed in the region 3300–3700 cm<sup>-1</sup>.

In IR spectra of the metallopolymers [Nd(mphpd)<sub>3</sub>]<sub>n</sub>, [Eu(mphpd)<sub>3</sub>]<sub>n</sub>, [Er(mphpd)<sub>3</sub>]<sub>n</sub> comparatively with monomeric metal complexes the location of main absorption bands are shifted in short-wave spectrum region, their intensity is lower significantly. The intensity decreases especially which corresponds to vibration of the double bond. Presented results confirm the polymer complex formation.

Electronic spectra of Nd(III) complexes and metallopolymer based on it correspond to the ion of Nd<sup>3+</sup> and have a set of transitions from <sup>4</sup>I<sub>9/2</sub> main (quantum) state. The absorption bands of the metallopolymer are slightly shifted to the longer wavelengths compared to the monomer metal complex

Table 1. Some distinctive absorption band of metallic complexes and metallopolymers

Complex	$\nu(\text{M-O})$	$\nu_{as}(\text{C-O})$	$\nu_{as}(\text{C-C})$	$\nu_s(\text{C-O})$	$\nu_s(\text{C=C})$
Nd(mphpd) <sub>3</sub> ·2H <sub>2</sub> O	420	1466	1559	1580	1671
[Nd(mphpd) <sub>3</sub> ] <sub>n</sub>	430	1465	1557	1557	1654sl.
Er(mphpd) <sub>3</sub> ·2H <sub>2</sub> O	420	1465	1557	1594	1676
[Er(mphpd) <sub>3</sub> ] <sub>n</sub>	425	1470	1575	1575	–
Eu(mphpd) <sub>3</sub> ·2H <sub>2</sub> O	420sl.	1467	1554	1594	1666
[Eu(mphpd) <sub>3</sub> ] <sub>n</sub>	430sl.	1470	1560	1560	1667sl.

that indicates a weakening of the metal — ligand bond (Table 2). The shift of the main absorption bands as in the case of monomeric complex and for metallopolymers in the long wavelength region, compared to the spectra of aqua-ions, and increase in intensity indicate the formation of metal complexes, as well as indirectly confirm increasing in the covalency of the metal — ligand bond.

In the case of erbium complexes a band pattern of Er<sup>3+</sup> ion transition with <sup>4</sup>I<sub>15/2</sub> main (quantum) state is observed (Table 3).

For europium complex in the visible (Table 4) spectrum it is set of bands at corresponding to the transition <sup>7</sup>F<sub>0</sub> main (quantum) state. Absorption bands for complexes of erbium and europium are shifted in the long wavelength region, compared to the spectra of corresponding metal salts on account of the complexation.

Electronic absorption spectra (EAS) of metallopolymers are analogous to EAS of monomeric complexes. But, main absorption bands of polycomplexes undergo the long-wavelength shift 10–110 cm<sup>-1</sup> that indicates decay of the metal bond with ligand in the polymer. A decrease of the intensity of all absorption bands for metallopolymers and their bathochromic shift in comparison with monomeric spectra testifies to polymer structure formation. The similarity of monomers EAS with polymers spectra confirms the identical coordinative environment of lanthanide ions in the both cases.

Diffuse reflection spectra and electronic absorption spectra of all samples do not differ much, suggesting a similar structure in solution and polycrystalline state.

Differential thermal analysis (DTA) of the obtained compounds for an identification of the complexes hydrated composition and their temperature behavior has been performed.

Based on the results of thermal analysis, the dehydration of unsaturated complexes

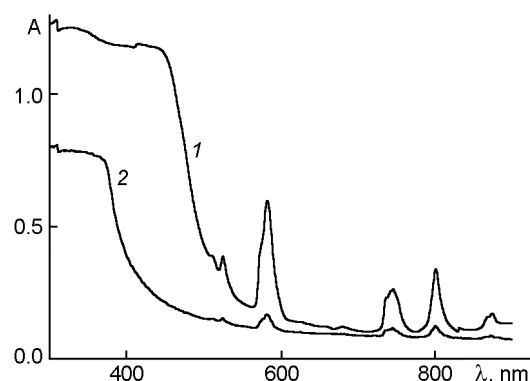


Fig. 1. Electronic absorption spectra of Nd(mphpd)<sub>3</sub>·2H<sub>2</sub>O (1) and [Nd(mphpd)<sub>3</sub>]<sub>n</sub> (2).

occurs at higher temperatures 120–150°C [15] than in the case of acetylacetonates. Neodymium complex dehydration occurs at the temperature 130°C and it is attended by the small endoeffect with the mass loss 7 % ( $\Delta m_{theor.} = 7.13$  %), which corresponds to the decoupling of three coordinative water molecules. The small endoeffect at the temperature 210°C probably is conditioned of the complex melting temperature, the mass loss is insignificant (2 %). The further temperature increase is attended by the small exoeffect at 225°C, which corresponds to the beginning of the complex polymerization. The significant exoeffect and the mass loss 25.5 % ( $\Delta m_{theor.} = 25$  %) at 285°C corresponds to the removal of one ligand molecule. The following heating is attended by exoeffects at temperatures 340, 360, 385, 425, 457°C and results in the total complex decomposition  $\Delta m = 18$  %. The total weight loss is 76 % in the investigated temperature interval.

The mass loss is 5.3 % ( $\Delta m_{theor.} = 4.7$  %) for erbium complex at 125°C, which corresponds to the decoupling of two coordinative water molecules accordingly. The small

Table 2. Energy transition in Nd electronic absorption spectrum

Transition	Nd <sup>3+</sup> , cm <sup>-1</sup>	Nd(mphpd) <sub>3</sub> , cm <sup>-1</sup>	Δ, cm <sup>-1</sup>
4I <sub>9/2</sub> → 2P <sub>1/2</sub>	23064	23255 <sub>arm</sub>	200
4I <sub>9/2</sub> → 4G <sub>9/2</sub>	19560	19520	40
4I <sub>9/2</sub> → 4G <sub>7/2</sub>	19160	19050	90
4I <sub>9/2</sub> → 4G <sub>5/2</sub>	17360	17152	200
4I <sub>9/2</sub> → 4F <sub>9/2</sub>	14720	14700	20
4I <sub>9/2</sub> → 4F <sub>7/2</sub>	13480	13400	80
4I <sub>9/2</sub> → 4H <sub>9/2</sub>	12560	12470	90
4I <sub>9/2</sub> → 4F <sub>3/2</sub>	11560	11430	130

Table 3. Energy transition in Er electronic absorption spectrum

Transition	Er <sup>3+</sup> , cm <sup>-1</sup>	Er(mphpd) <sub>3</sub> , cm <sup>-1</sup>	Δ, cm <sup>-1</sup>
4I <sub>15/2</sub> → 4F <sub>7/2</sub>	20480	20523	43
4I <sub>15/2</sub> → 4H <sub>11/2</sub>	19160	19120	40
4I <sub>15/2</sub> → 4S <sub>3/2</sub>	18400	18382	20
4I <sub>15/2</sub> → 4F <sub>9/2</sub>	15320	15270	50
4I <sub>15/2</sub> → 4I <sub>9/2</sub>	12480	12450	30

exoeffect in the region 190°C can be conditioned by both the polymerization process and the complex melting. The process of the complex decomposition begins with the removal of one ligand molecule, which corresponds of the exoeffect at 248°C and the mass loss 28 % ( $\Delta m_{theor.} = 24.5$ ). The following heating is attended by exoeffects at temperatures 337, 384, 419, 460°C, 484°C and results in the total complex decomposition  $\Delta m = 15$  %. The total weight loss is 66 % for erbium complex. The europium complex thermogram is analogous to the erbium complex thermogram.

The presented results allow to assume that the complexes composition corresponds to the formula, Nd(mphpd)<sub>3</sub>·3H<sub>2</sub>O, Er(mphpd)<sub>3</sub>·2H<sub>2</sub>O, Eu(mphpd)<sub>3</sub>·2H<sub>2</sub>O, and metallopolymers formula following:

Luminescence spectra of the synthesized compounds were recorded in the solid state and in a solution. The excitation spectrum of Nd(mphpd)<sub>3</sub> in the solid state consists of a single band with maximum at 363 nm. In the excitation spectrum of the solution the long-wavelength shift of the band ( $\Delta\lambda = 15$  nm) is observed.

In the excitation at the maximum of this band a 4f-luminescence of the samples is observed in the solid state and in the solu-

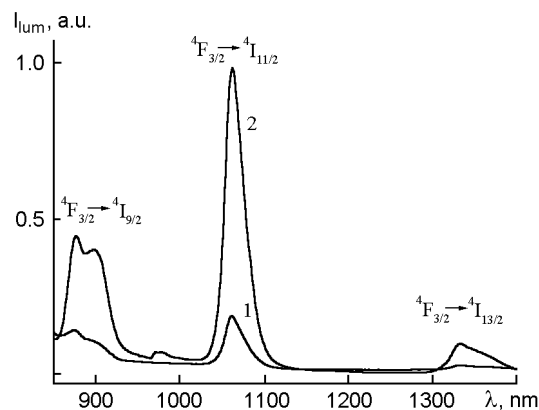


Fig. 2. Luminescence spectra of Nd(mphpd)<sub>3</sub>·2H<sub>2</sub>O (1) and [Nd(mphpd)<sub>3</sub>]<sub>n</sub> (2) in solid state ( $\lambda_{ex} = 362$  nm, 298 K).

tion. The luminescence spectrum consists of three bands corresponding to the transitions from the excited level of ion Nd(III) 4F<sub>3/2</sub> into the multiplets of the main (quantum) level 4I<sub>j</sub>,  $j = 9/2$  (I, 875 and 888 nm), 11/2 (II, 1061 nm) and 13/2 (III, 1332 nm) (Fig. 2).

The excitation spectrum of the sample Nd(mphpd)<sub>n</sub> is similar to the above spectra. In the excitation at 362 nm for the solid samples a 4f-luminescence of Nd(III) is observed with almost the same intensity compared to the solid sample Nd(mphpd)<sub>3</sub>.

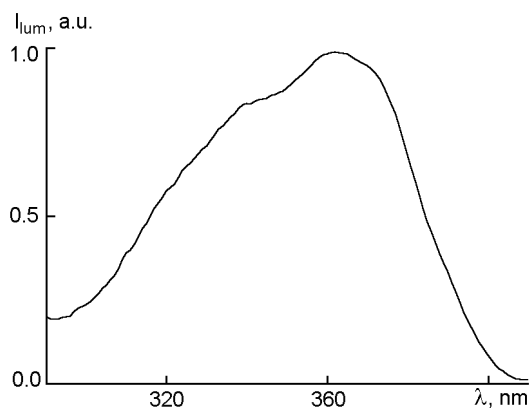


Fig. 3. Excitation spectrum of  $[\text{Er}(\text{mphpd})_3]_n$  ( $\lambda_{lum} = 1540 \text{ nm}$ ,  $298 \text{ K}$ ).

The bands maxima corresponding to the transitions  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ , and  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$  undergo a long-wavelength shift of 2 nm in comparison with the spectra of the solid state monomers.

The luminescence spectra of erbium complex and metalopolymer are analogous, the band, which corresponds to  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition, is observed. The luminescence intensity of the present samples not differs practically that testifies to the low polymerization degree of the obtained metalopolymer (Fig. 3).

The intensive red luminescence is observed for europium complex and metalopolymer. The most intensive band corresponds to transition  ${}^5D_0 \rightarrow {}^7F_2$  in region 610–630 nm. The bands with considerably less intensity are in spectrum region 575–580, 585–600, 650–670 and 680–705 nm which correspond to transitions  ${}^5D_0 \rightarrow {}^7F_j$ ,  $j = 0, 1, 3$  and 4 accordingly. The band corresponding to transition  ${}^5D_0 \rightarrow {}^7F_0$  shows in the image of the symmetric single line (Fig. 4) that allow to assume of the one luminescence centre.

The near-term environment influences weakly on the level position of  $4f^n$ -electronic coordination of lanthanide ions. However, these levels split under the influence of crystal field that allow to determine the environment symmetry of the luminescence centre under the splitting values analyzing. Symmetry type can be estimated qualitatively in concordance with the shtarks splitting of europium ion transition in luminescence spectra. The qualitative appearance of transition shtarks splitting for presented compounds indicates about appreciable hexagonal deformation inside of the crystal field, that corresponds to presence of two

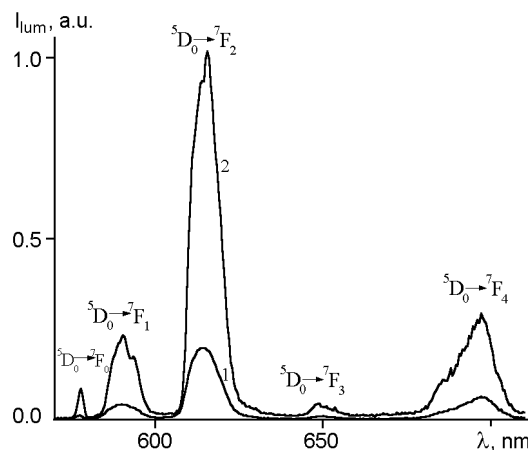


Fig. 4. Luminescence spectra of  $[\text{Eu}(\text{mphpd})_3]_n$  in solution ( $\text{CHCl}_3$ ,  $\lambda_{ex} = 362 \text{ nm}$ ,  $C_{\text{Eu}} = 10^{-3} \text{ M}$ ), at  $298 \text{ K}$  (1) and  $77 \text{ K}$  (2).

Table 4. Energy transition in Eu electronic absorption spectrum

Transition	$\text{Eu}^{3+}$ , $\text{cm}^{-1}$	$\text{Eu}(\text{mphpd})_3$ , $\text{cm}^{-1}$	$\Delta$ , $\text{cm}^{-1}$
${}^7F_0 \rightarrow L$	31480	31450	30
${}^7F_0 \rightarrow E$	25380	25320	60
${}^7F_0 \rightarrow {}^5D_2$	21480	21280	200
${}^7F_0 \rightarrow {}^5D_1$	18870	18730	150

components  ${}^5D_0 \rightarrow {}^7F_1$ -transition and two components  ${}^5D_0 \rightarrow {}^7F_2$  — transition in the spectrum. The symmetry type without measurement of polarized characteristics no established definitely.

Luminescence quantum yield of the monomeric and polymeric metalocomplexes were calculated (Table 5) without erbium. The  $4f$ -luminescence of erbium is weak relatively and it is detected in the range of 1450–1560 nm that corresponds to the bandwidth (the maximum half-height) for  $\text{Er}(\text{mphpd})_3 \cdot 2\text{H}_2\text{O}$  — 18 FWHM, and  $\text{Er}(\text{mphpd})_n$  — 19 FWHM, therefore the luminescence quantum yield of its complexes no established definitely. The luminescence quantum yield of polycomplex based on  $\text{Eu}(\text{III})$  is maximum (Table 5), which outnumber the values for known low-molecular Eu complexes on several exponents.

Investigations of a particle size were performed at  $25^\circ\text{C}$  on Zeta Sizer Malvern instrument. The results show that the systems obtained are polydispersed with a predominance of particles 12–45 nm for the metal

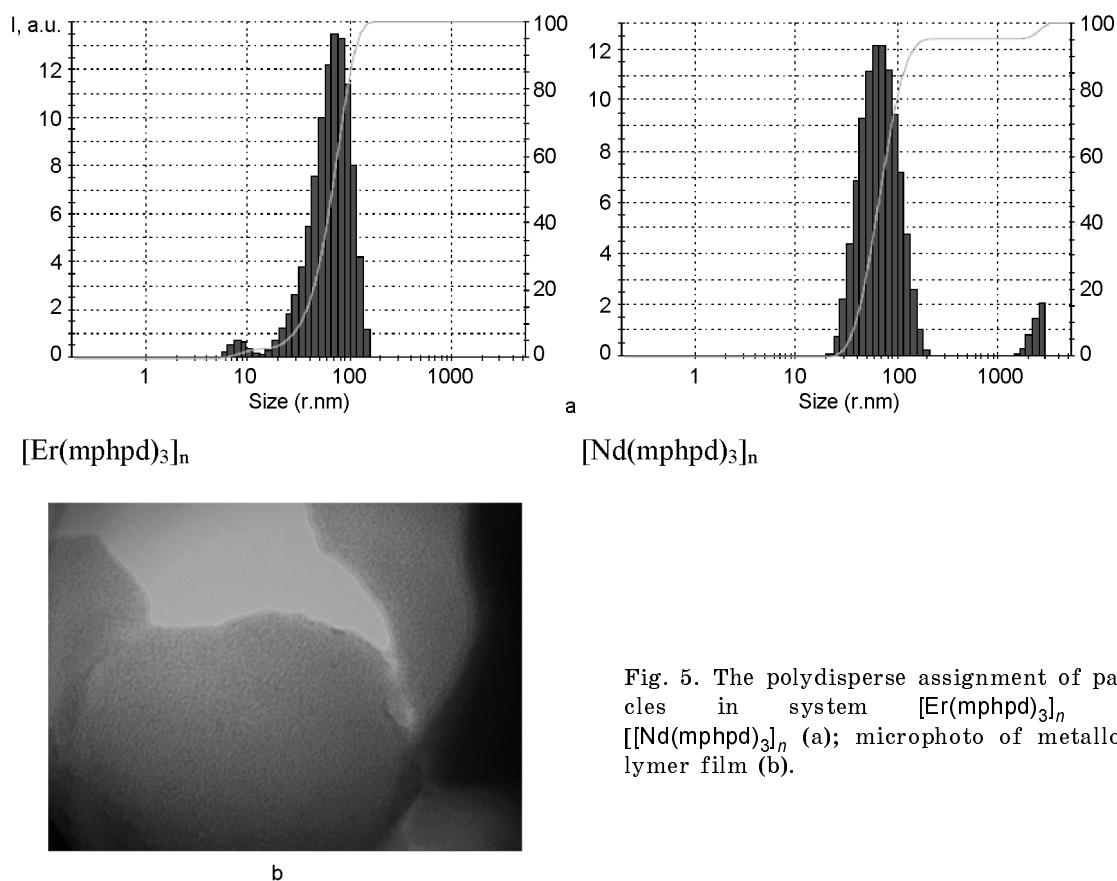


Fig. 5. The polydisperse assignment of particles in system  $[\text{Er}(\text{mphpd})_3]_n$  and  $[\text{Nd}(\text{mphpd})_3]_n$  (a); microphoto of metallopolymer film (b).

complexes and 92–115 nm for the metallopolymer.

This difference in size of nanoparticles is related to the complex molecular mass and geometrical molecular structure probably. In polymer the monomeric links connected in long chains. The chains have not a freedom of the independent translational motion therefore polymer systems have the low entropy. Owing to the low entropy and the system order polymers are inclined to the self-organization. Even low energy interactions of atomic groups result in the structure ordering. The nanoscale arises for

polymers kindly. If the polymer is like the ball it has size about 100 nm, if it coagulates into a globule — the size is about 10 nm. In this case the polymer is there in a ball state but not a globule that is caused by the steric factor — the volumetric chelate unit structure.

Obtained polymers spreads evenly by substrate, generates the homogeneous film (Fig. 5b), has high luminescent properties, that enable to confirm about the possibility of its application as organic layer in OLED equipments.

Table 5. The luminescence quantum yield of monomeric and polymeric metal complexes

Complex		The luminescence quantum yield, $\varphi \cdot 10^3$
$\text{Eu}(\text{mphpd})_3 \cdot \text{H}_2\text{O}$	Solution	320
$\text{Eu}(\text{mphpd})_n$	Solution	460
$\text{Nd}(\text{mphpd})_n$	Solid	1,72
	Solution	0.86
$\text{Nd}(\text{mphpd})_3 \cdot \text{H}_2\text{O}$	Solid	1.21 ( $\text{CHCl}_3-d_6$ )
		0.31
	Solution	0.12
		0.26 ( $\text{CHCl}_3-d_6$ )

#### 4. Conclusions

The results of the above study show that the configuration of the chelate unit is unchanged during the polymerization. The results of the chemical analysis correspond to the calculated composition: all the functional groups of macroligand are bound to the metal ion.

The investigations conducted in the present work allowed to determine the composition, structure and properties of the complexes and metallopolymers on their basis obtained for the first time. It was shown that all synthesized compounds are nano systems.

The luminescence quantum yield of polycomplex based on Eu(III) is maximal. The obtained polymetallocomplexes can be used as potential materials for organic light-emitting devices.

#### References

1. F.Xu, C.Wang, L.Yang et al., *Synth Met.*, **152**, 221 (2005).
2. H.Li, F.Zhang, Y.Wang, D.Zheng, *Mater. Sci. Eng. B*, **100**, 40 (2003).
3. J.Kido, Y.Okamoto, *Mater. Chem. Rev.*, **102**, 2357 (2002).
4. C.R.Silva, F.Li, C.Huang, Z.Zheng, *Thin Solid Films*, **517**, 957 (2008).
5. M.A.Guedes, T.B.Paolini, MCFC Felinto et al., *J. Luminescence*, **131**, 99 (2011).
6. S.B.Meshkova, Z.M.Topilova, V.F.Shul'gin, *Uchenye Zapiski Tavricheskogo National Univers., Seriya Biologoya, Khimiya*, **22**, 176 (2009).
7. V.V.Semenov, N.V.Zolotareva, L.G.Klapshina et al., *Zh. Obshchei Khimii*, **79**, 1802 (2009).
8. Katkova M.A., Vituhnovsky A.G., Bochkarev M.N., *Uspekhi Khimii*, 74(12), 1193-1215 (2005).
9. M.Hasegawa, A.Nakao, M.Masui et al., *Chem. Phys.*, **269**, 323 (2001).
10. Q.Ling, M.Yang, W.Zhang et al., *Thin Solid Films*, **417**, 127 (2002).
11. L.Zeng, M.Yang, P.Wu et al., *Synth. Met.*, **144**, 259 (2004).
12. A.I.Voloshin, N.M.Shavaleev, V.P.Kazakov, *J. Photochem. Photobiol. A:Chem.*, **134**, 111 (2004).
13. Uflyand I.E., Il'chenko I.A., Starikov A.G., Shejkner V.N., Pomogajlo A.D., *Izvestiya AN ser. khim.*, 451-453 (1990).
14. V.Ya.Zub, A.S.Berezhnitskaya, I.A.Savchenko et al., *Zh. Koordinats. Khimii*, **30**, 709 (2004).
15. Movchan T.I., Solov'yova T.I., Petrova L.A., et al., *Izvestiya RAN Ser. Khim.*, №1, 43-47 (1994).

## Нові полімерні металокомплекси як прекурсори для електролюмінесцентних матеріалів

I.Савченко, О.Бережницька, С.Смола, Я.Федоров, Н.Іваха

Одержано мономер — 2-метил-5-фенілпентен-1-діон-3,5, його комплекси з Nd(III), Eu(III), Er(III), нові металополімери на їх основі. Будову мономера, металокомплексів, металополімерів доведено за допомогою даних ЯМР-, електронної, інфрачервоної, дифузного відбиття спектроскопії, елементного і термогравіметричного аналізу. Вивчено і проаналізовано спектри люмінесценції мономерних і полімерних металокомплексів у розчинах, плівках, твердому стані. Найбільший квантовий вихід люмінесценції знайдено для полікомплексу Eu(III). Одержані поліметалокомплекси можуть бути запропоновані як потенційні матеріали для електролюмінесцентних пристроїв.