CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 7, No. 4, 2013 Chemistry

Irina Savchenko[1], Aleksandra Berezhnytska[2], Yaroslav Fedorov[2], Nataliya Rusakova[3], Vladimir Syromyatnikov[1] and Sergey Smola[3]

STRUCTURAL ORGANIZATION OF POLYMER METAL COMPLEXES WITH WATER OR PHENANTHROLINE AND THEIR INFLUENCE ON LUMINESCENCE PROPERTIES

[1] Taras Shevchenko National University of Kyiv,
60, Volodymyrska str., 01601 Kyiv, Ukraine; iras@univ.kiev.ua
[2] V.I.Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine,
32/34, Palladina Ave., 03680 Kyiv, Ukraine
[3] A.V. Bogatsky Physico-Chemical institute, National Academy of Sciences of Ukraine,
86, Lustdorfskaya doroga, 65080 Odessa, Ukraine

Received: March 05, 2013 / Revised: March 28, 2013 / Accepted: June 12, 2013

© Savchenko I., Berezhnytska A., Fedorov Y., Rusakova N., Syromyatnikov V., Smola S., 2013

Abstract. A monomer – 2-methyl-5-phenylpentene-1-dione-3,5, its solvent metal complex Eu(III)-water, hybrid metal complex Eu(III)-phenanthroline, new metallopolymers based on them are obtained. The results of above studies have shown that the configuration of the chelate unit is unchanged during polymerization. Using the electron microscopy the homogeneity of metal distribution in the polymer matrix of synthesized metallopolymer was confirmed. The similarity of monomers electronic absorption spectra with polymers spectra confirms the identical coordinative environment of lanthanide ions in both cases. The solubilization of europium *β*-diketonate complexes with phenanthroline was shown to change luminescence intensity in such complexes.

Keywords: metal-polymer complexes, spectra, solution, structure, luminescence.

1. Introduction

Modern technologies tend to lead to miniaturization of microelectronic devices, which pose a task for chemists to design and synthesize functional materials. Both inorganic and organic molecular materials exhibiting optical, magnetic, and electron-conducting properties are known [1]. The chemistry of molecular materials is extensively developed, and one of the most promising lines of this development is the design of materials based on organic metal complexes. A combination of metal ions and organic ligands in a molecule and the possibility of control over the composition and structure of the coordination compounds open the way to obtaining molecular materials on their basis with a wide range of functional properties. During last decade, an intensive search has been performed for novel thin-film electroluminescent materials based on organic metal complexes [2–4]. Coordination compounds of the rare earth elements 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 [5]. Almost all lanthanides may have luminescence provided by the correct ligand choice. Coordination compounds of the rare earth elements with *b*-diketones are perspective in terms of optical materials development, since they possess the high thermal stability, monochrome emission and high quantum efficiency and allow varying the properties through the introduction of an additional ligand. From this point of view, they can be used as emissive layers in organic electro-luminescent devices [6-10].

Complexes of europium(III) with organic ligands on the basis of *b*-diketones possess well-pronounced luminescent properties due to the effective energy transfer from the triplet states of the ligands to the lowest exited level of the trivalent europium, $^5D_0$, which, in turn, gives rise to radiation transitions. Recently, many reports have focused on lanthanide complexes containing polymeric luminescent materials, which are prepared by blending organic low-molecular weight lanthanide complexes into a polymer matrix [11]. However, sometimes it is difficult to disperse the organic low-molecular-weight lanthanide complexes uniformly in a polymer matrix. Compared to guest-host systems, the polymers with covalently bonded lanthanide chromophores can be used in pure forms without doping into other matrixes because of their own film-forming ability, enhanced solubility in solvents, better homogeneity and higher stability [12, 13].

The luminescence wavelengths set of europium exists regardless of the ligand used. On the other hand, the choice of the ligand is very important because it influences the stability and solubility of the complex as well as luminescence efficiency. 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 the low coordination level which results in composition heterogeneity. All these shortcomings influence the physical characteristics of obtained compounds.

In this regard there is a necessity of macromolecular compounds synthesis where all functional groups are associated with metal ions. This may be achieved by homo-polymerization of the metal complexes. The complexity of this scheme is a reduction of reaction capability of monomer metal complexes during polymerization. The radical polymerization of monomer metal-complex with unsaturated substituents in chelate rings allows to obtain chemically homogeneous composition of the metal polymers [14, 15]. The presence of water molecules in the nearest coordination environment of the europium ion causes the luminescence extinguishing. Synthesis of adducts with phenanthroline can allow to obtain coordinatively saturated compounds with much higher luminescence efficiency.

Therefore, the main aim of this study is synthesis of europium complexes with 2-methyl-5-phenylpentene-1-dione-3,5 and phenanthroline as well as metallopolymers based on them and study of structure and some physico-chemical properties, specifically, the influence of water and phenanthroline configured-in the complex coordination sphere on the luminescence properties.

2. Experimental

Synthesis of 2-methyl-5-phenylpentene-1-dione-3,5 (mphpd) and metal complex was carried out according to the method described in [16].

In the three neck reactor equipped with a stirrer, reflux condenser and dropping funnel, with 0.5 mol metallic sodium (11.5 g) in 300 cm^3 dry diethyl ether the mixture of 0.5 M acetophenone and 0.5 mol of ethyl methacrylate were added drop by drop. The reactor was cooled with a mixture of salt and ice.

This reaction leads to yellow colored precipitate. The precipitate was stirred and left for 12 h at 293 K after adding the last portion. The precipitate was filtered then washed with a diethyl ether and dried in a desiccator over P_2O_5. The yield was 76 g (72 %).

Sodium salt of unsaturated β-diketone $C_{12}H_{11}O_2Na$ obtained by the above described method is a crystalline yellow substance with m_p 489 K. NMR: ^1H (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 complex was obtained by an exchange reaction between equimolar amounts of europium 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 ligand.

The polymerization was carried out at 353 K in the thermostat in a dimethylformamide solution with a monomer concentration of 0.03 mol/l and initiator 2,2'-azobisisobutyronitrile of 0.003 mol/l concentration. 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 (ESA and SDR), thermal and chemical analysis as well as dynamic light scattering method and electron microscopy. The elemental analysis for metal ions was carried out with ICPE Shimadzu 9000 atomic emission spectrometer. The infrared spectra were recorded in KBr tablets within the range of 4000–400 cm^{-1} with Spectrum BX II FT-IR manufactured by Perkin Elmer. The electronic absorption spectra were recorded using the 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 particle size studying was performed at 298 K using the equipment from “Zeta Sizer Nano by Malvern” Photomicrographs and electron diffraction were obtained by a transmission electron microscope “Hitachi H-800” (TEM). The excitation and luminescence spectra of solid samples and solutions (10^{-3} M, $CHCl_3$) 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.

3. Results and Discussion

The elemental analysis was carried out to establish the composition of the complex: Eu(mphpd)$_3$·2H$_2$O – 20.18 % Eu, (theor. (20.29) ; Eu(mphpd)$_3$·Phen – 16.91 % Eu, (theor. (17.02).

The IR spectra of synthesized compounds were recorded to establish the kind of coordination of the europium ion with the 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 comparison with *b*-diketone sodium salt to the long-wave region indicates a weakening of the metal–ligand bond, due to the increase of covalent bond. The low intensity band at 1660 cm^{-1} corresponds to the valent vibration of the double bond ν(C=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 indicate the formation of metal complexes.

Calculated covalence parameters (Table 2) from the electron spectra confirm the above assumption of increasing covalency of the metal-ligand in the range of Eu(acat)$_2$ < Eu(mphpd)$_3$ < [Eu(mphpd)$_3$] (acat-acetylacetonate).

Similarity of ESA and SDR shows a similar structure of the complexes in the solution and polycrystalline state. A slight shift of the maximum which is observed in the absorption spectra of the complex Eu(mphpd)$_3$·Phen indicates a replacement of water molecules in the nearest coordination environment without significant changes in the coordination polyhedron geometry. Unfortunately the electron spectrum of the europium complexes is not informative in terms of establishing symmetry. Thus most conclusions made about the lanthanides structure using the spectral studies are based on a number of assumptions but the totality of all research methods and the results of comparison with the literature data allow in some cases to establish the type of coordination and structure of the coordination polyhedron. An absence of significant shifts for metal polymers allows to suggest a similar structure for the coordination polyhedron of monomer and polymer complexes. Increasing of *b*-diketonate ligand donor ability and therefore rising of a bond strength metal–oxygen reduce the efficiency of the ligand-metal energy transfer and consequently reduce the luminescence efficiency. Basing on the covalency parameters we can observe the weakening of metal-ligand bond, which allows us to assume increasing of luminescence efficiency in the series: Eu(acetate)$_2$ < Eu(mphpd)$_3$ < Eu(mphpd)$_3$·Phen < [Eu(mphpd)$_3$]$_n$ ≤ [Eu(mphpd)$_3$·Phen]$_n$.

Photoluminescence studies have practically to confirm our assumption. The emission transitions assignment for all compounds is shown in Table 3.

The luminescence spectra of europium *β*-diketonates complexes in all samples are similar to each other and approve 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 Table 3).

The quantum yield of all samples was calculated in terms of recorded luminescence spectra (Fig.1). Quantum yields (φ) of sample solutions: 0.031, 0.038, 0.034 and 0.024, respectively for Eu(mphpd)$_3$, [Eu(mphpd)$_3$]$_n$, Eu(mphpd)$_3$(Phen), [Eu(mphpd)$_3$(Phen)]$_n$.

Decreasing of φ for [Eu(mphpd)$_3$(Phen)]$_n$ takes place probably due to the fact that the phenantroline in the polymer matrix rather shields emission centers of europium ions and then reduces the number of non-emission losses and displaces the solvent molecules from the metal coordination sphere.

On the basis of calculated values of parameter *b*, covalency parameter $b^{1/2}$ and parameter Sinha *d* (Table 2) in the observable complexes is essential cova-

Table 1

Some distinctive absorption bands for metallic complexes and metallopolymers

Complex	$^7F_0\to{}^5H_6$	Δ$_1$*	$^7F_0\to{}^5L_6$	Δ$_2$*	$^7F_0\to{}^5D_2$	Δ$_3$*	$^7F_0\to{}^5D_1$	Δ$_4$*
Eu(mphpd)$_3$·2H$_2$O	31420	30	25180	70	21280	220	18550	150
[Eu(mphpd)$_3$]$_n$	31400	50	25160	90	21260	240	18600	100
Eu(mphpd)$_3$·Phen	31400	50	25190	60	21270	230	18580	120
[Eu(mphpd)$_3$·Phen]$_n$	31420	30	25200	50	21320	180	18620	80

Note: peak shift as compared with aqua-ion, cm^{-1}

Table 2

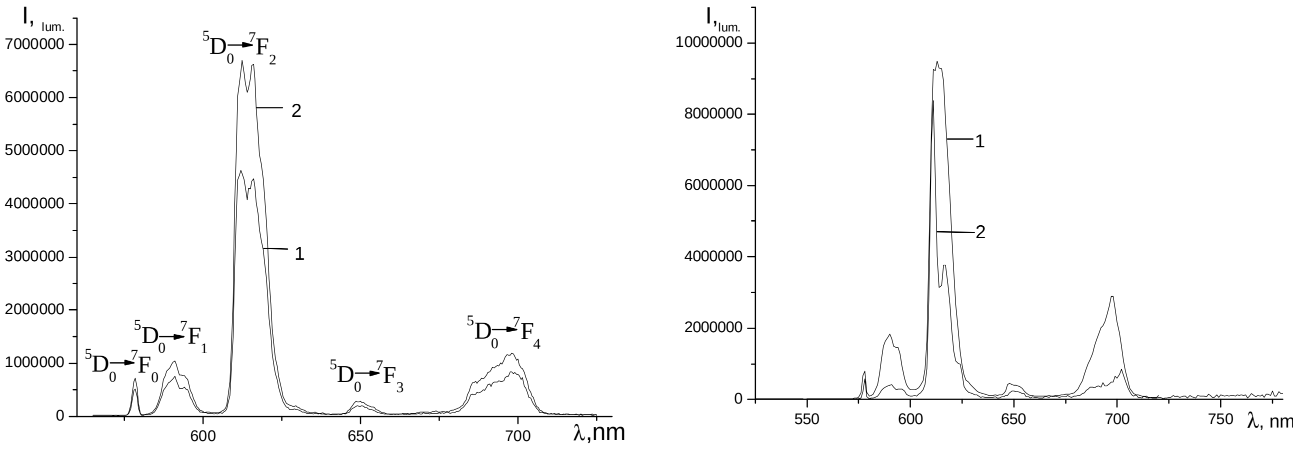
Covalence parametrs of obtained compounds

Complex	*b*	*b*$^{1/2}$	*d*
$Eu(mphpd)_3 \cdot 2H_2O$	0.9897	0.0717	1.04
$[Eu(mphpd)_3]_n$	0.9888	0.0748	1.13
$Eu(mphpd)_3 \cdot Phen$	0.9893	0.073	1.08
$[Eu(mphpd)_3 \cdot Phen]_n$	0.9916	0.0648	0.847

Table 3

Energy transition in Eu luminescence spectrum

Transition	$Eu(mphpd)_{3,}$ cm^{-1}	$[Eu(mphpd)_3]_{n,}$ cm^{-1}	$Eu(mphpd)_3(Phen)]$, cm^{-1}	$[Eu(mphpd)_3(Phen)]_{n,}$ cm^{-1}
$^5D_0 \rightarrow {}^7F_0$	17331	17301	17331	17331
$^5D_0 \rightarrow {}^7F_1$	16978 16849	16920 -	16977 16921	16949 16844
$^5D_0 \rightarrow {}^7F_2$	16287 16234	16340 -	16340 16233	16313 -
$^5D_0 \rightarrow {}^7F_3$	15408	15385	15384	15385
$^5D_0 \rightarrow {}^7F_4$	14468 14347	14535 14327	14490 14347	14556 14327



a) b)

Fig. 1. Luminescence spectra: a) $[Eu(mphpd)_3]_n$, (1) and $[Eu(mphpd)_3 \cdot Phen]_n$ (2) in $CHCl_3$ solution, T = 77 K ; l = 362 nm; b) $Eu(mphpd)_3$ (1) and $Eu(mphpd)_3 \cdot Phen$ (2) in a solid state, T = 298 K, l = 362 nm

lency contribution in the bond of metal-ligand. Metallopolymer has a maximal covalency contribution that points to the maximal luminescence efficiency and is coordinated with results of luminescence investigations. Maximal luminescence efficiency is observed for monomer and polymer complexes with phenanthroline. Phenanthroline substitutes two water molecules in complexes and generates adducts as formula $Eu(mphpd)_3 \cdot Phen$ and $[Eu(mphpd)_3 \cdot Phen]_n$. In the solutions the phenanthroline molecule will screen the emissive centers and occupy the distant location.It is well known [17] that the near surroundings slightly affect the lanthanide ions $4f^n$-electron level configuration but these levels split under the influence of crystal field surrounding due to coulomb and spin-orbit interaction. Based on the splitting analysis one can determine the luminescence center environment symmetry. The symmetry type of the europium complexes [18] can be qualitatively assessed without determining the crystal field parameters from experimental data on the quantities Stark splitting, but only comparing quantity of experimental splitting level component with the value of the angular momentum J and with their theoretically possible number.

Europium luminescence spectra (Fig. 1) at 77 K allow to establish the short-range coordination environment symmetry. The transition band $^5D_0$ **à** $^7F_0$ 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 the electric dipole transition $^{5}D_{0}$ **à** $^{7}F_{2}$ compared with relatively low intensity magnetic dipole transition $^{5}D_{0}$ **à** $^{7}F_{1}$ suggests not center-symmetric nature of the environment for all investigated compounds. Considering the comparison of theoretical and experimentally obtained values of Stark splitting (Table 4) one can assume C_{3v} symmetry of the nearest coordination environment with polyhedron two head-trigonal prism (1 line $^{5}D_{0}$ **à** $^{7}F_{0}$ and 2 lines $^{5}D_{0}$ **à** $^{7}F_{2}$) for mono ligand complex and metallopolymer.

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.

All compounds were studied by dynamic light scattering in order to determine particle size, as well as for solvent selection for the homogeneous thin films modelling. Investigations were carried out in chloroform and dimethylformamide. The size of monomer and polymer particles is virtually identical that is based on particle size distribution diagram (Fig. 2).

Monomer units are joined into long chains in the polymer. They do not have freedom of an independent translational motion so these polymer systems are characterized by the low entropy. Polymers are capable for self-organization because of low entropy due to system ordering. The particle size is about 100 nm when the polymer is in the form of coil and about 10 nm if it is rolled into the globule. Thus the polymers have a globular structure in our case.

Polymeric films based on $[Eu(mphpd)_{3}]n$, $[Eu(mphpd)_{3}(Phen)]_{n}$ were obtained. Films were precipitated by centrifugation from the chloroform solution.

Table 4

The number of Stark structure ion levels components Ln (III) in the crystalline field of certain symmetry

Theoretical splitting					
symmetry	J				
	0	1	2	3	4
cubic	1	1	2	3	4
Hexagonal and trigonal	1	2	3	5	6
tetragonal	1	2	4	5	7
Rhombic	1	3	5	7	9
Experimental splitting					
$Eu(mphpd)_{3,}$	1	2	2	2	3
$[Eu(mphpd)_{3}]_{n}$	1	2	2	3	4
$Eu(mphpd)_{3}(Phen)$	1	2	3	3	5
$[Eu(mphpd)_{3}(Phen)]_{n}$	1	3	3	2	5

The system is homogeneous in terms of uniform distribution of metal throughout the polymer matrix as seen from the micrographs of powdered samples and films (Fig. 3).

The present electron diffraction (Fig. 3d) confirms the absence of a short-range and long-range order so the metal polymer is X-ray amorphous.

4. Conclusions

The results of the above study showed that the configuration of the chelate unit is unchanged during polymerization. The results of the chemical analysis correspond to the calculated composition, all the functional groups of the macroligand are bound to the metal ion. It was shown that all synthesised compounds are nano systems. Using electron microscopy confirmed the homogeneity of metal distribution in the polymer matrix of the synthesized metallopolymer.

The similarity of monomers electronic absorption spectra with polymers spectra confirms the identical coordinative environment of lantanide ions in both cases. The solubilization of europium β-diketonate complexes with phenanthroline, was shown to change luminescence intensity in such complexes.

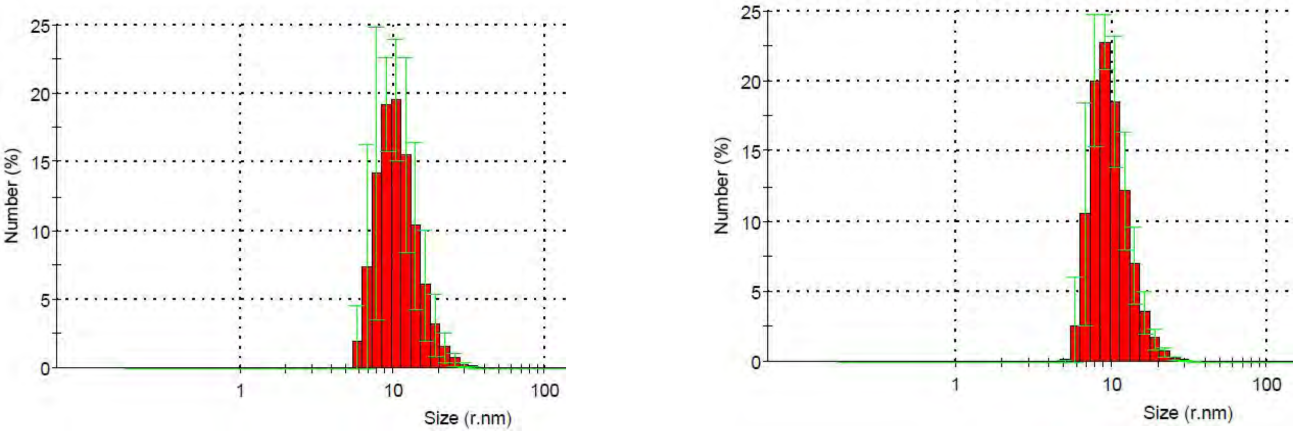


Fig. 2. The polydisperse assignment of particles in system $[Eu(mphpd)_{3}]$ and $[Eu(mphpd)_{3}]_{n}$

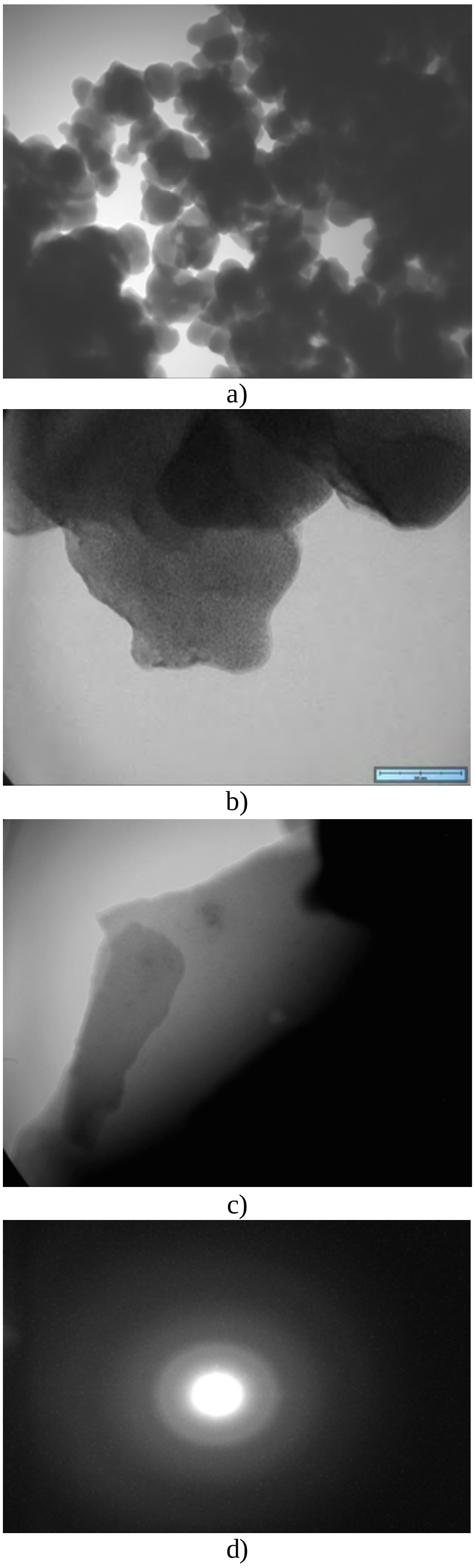


Fig. 3. TEM microphotos of metallopolymer $[Eu(mphpd)_3]_n$: powder (a, b), film (c) and electron diffraction (d); U=150 кV, cursor – 50 nm

The luminescence intensity of metallopolymer with Eu is less in the solution than in the frozen solution or solid state because of the water molecules in the solvent as OH-oscillator quenchers.

Very high quantum yield of luminescence allows the possibility of using these compounds as organic layers in electroluminescence devices.

References

[1] Yersin H.: Highly Efficient OLEDs with Phosphorescent Materials, Wiley-VCH, Weinheim 2008.
[2] Katkova M., Vitukhnovsky A. and Bochkarev M.: Russ. Chem. Rev., 2005, **74**, 1089.
[3] Driesen K.and Binnemans K.: Liquid Crystals, 2004, **31**, 601.
[4] Xiang N., Leung L., So S. and Gong M.: Spectrochimica Acta A, 2006, **65**, 907.
[5] Silva C., Li F., Huang C. and Zheng Z.: Thin Solid Films, 2008, **517**, 957.
[6] Guedes M., Paolini T., Felinto M. *et al.*: J. Lumin., 2011, **131**, 99.
[7] Sun M., Xin H., Wang K. *et al.*: Chem. Commun., 2003, 702.
[8] Ling Q., Yang M., Zhang W. *et al.*: Thin Solid Films, 2002, **417**, 127.
[9] Terai T., Kikuchi K., Iwasawa S. *et al.*: J. Am. Chem. Soc., 2006, **128**, 6938.
[10] Sun J., Zhang X., Xia Z. and Du H.: J. Appl. Physics, 2012, **11**, 1.
[11] Brito H., Teotonio E., Fett G. *et al.*: J. Lumin., 2008, **128**, 190.
[12] Zeng L., Yang M., Wu P. *et al.*: Synth. Met., 2004, **144**, 259.
[13] Jiu H., Liu G., Zhang Z. *et al.*: J. Rare Earths, 2011, **29**, 741.
[14] Savchenko I., Bereznitskaya A., Smola S. *et al.*: Funct. Mater., 2012, **4**, 541.
[15] Bereznitskaya A., Savchenko I., Trunova E. *et al.*: Dopov. Nats. Akad. Nauk Ukrainy, 2012, **11**, 132.
[16] Voloshin A., Shavaleev N. and Kazakov V.: J. Photochem. Photobiol. A, 2000, **134**, lll.
[17] Tsaryuk V., Zolin V. and Legendziewicz J.: Spectrochimica Acta A, 1998, **54**, 2247.
[18] Tsaryuk V., Legendziewicz J., Puntus L. *et al.*: J. Alloys and Compounds, 2000, **300-301**, 464.

СТРУКТУРНА ОРГАНІЗАЦІЯ ПОЛІМЕРНИХ МЕТАЛОКОМПЛЕКСІВ З ВОДОЮ АБО ФЕНАНТРОЛІНОМ І ЇХ ВПЛИВ НА ЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ

Анотація. *Одержано мономер – 2-метил-5-феніл-пентен-1-діон-3,5, його сольватний металокомплекс з водою на основі європію, гібридний металокомплекс з фенантроліном та нові металополімери на їх основі. Проведені дослідження показали, що конфігурація хелатного вузла під час полімеризації не змінюється. З використанням електронного мікроскопу встановлено рівномірний розподіл металу в полімерній матриці синтезованих металополімерів. Порівняння електронних спектрів поглинання мономерів і полімерів показало ідентичне координаційне оточення йону лантаніду в обох випадках. Солюбілізація β-дикетонатних комплексів європію з фенантроліном призводить до зміни інтенсивності люмінесценції в таких комплексах.*

Ключові слова: *металополімерні комплекси, спектри, розчин, структура, люмінесценція.*