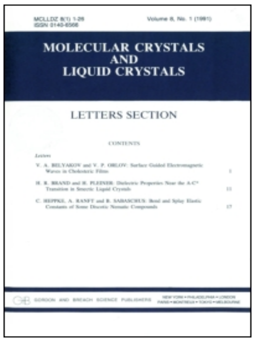

MOLECULAR CRYSTALS AND LIQUID CRYSTALS

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Poly complexes based unsaturated *β*-diketones and rare earth elements for optoelectronics

Irina Savchenko[a], Aleksandra Berezhnytska[b], Elena Trunova[b], N. Rusakova[c], Ya. Fedorov[b], and G. Grozduyk[d]

[a]National Taras Shevchenko University of Kyiv, Kyiv, Ukraine; [b]V. I. Vernadsky Institute of General and Inorganic Chemistry NASU, Kyiv, Ukraine; [c]A. V. Bogatsky Physico-Chemical Institute NASU, Odessa, Ukraine; [d]L. V. Pisarzhevskii Institute of the Physical Chemistry NASU, Kiev, Ukraine

ABSTRACT

The complexes of samarium(III) with 2-methyl-5-phenylpenten-1-3,5-dione (mphpd) $Sm(mphpd)_3\cdot 2H_2O$ and 2,6-dymethyl-heptene-1-3,5-dione (hdmhpd), $Sm(hdmhpd)_m$ were synthesized. The polycomplexes on their basis $[Sm(mphpd)_3]_n$, $[Sm(hdmhpd)_m]_n$ and copolymers with styrene $Sm(mphpd)_3$-co-styrene in ratio 5:95 were obtained by free-radical polymerization and the kinetics of polymerization was studied by dilatometric method at the first time. The method of dynamic light scattering and the results of electronic microscopy showed that the obtained polymer systems are nanoscale. The luminescent spectra of obtained metal complexes in solid state are investigated and analyzed. The electroluminescent spectra of organic planar heterostructure ITO/PEDOT:PSS/$\{[Sm(mphpd)_3]_n[Styrene]_m\}$/Al are examined.

KEYWORDS

complexes; copolymer; spectra; structure; luminescence

1. Introduction

In recent years, solutions to suppress global warming caused by greenhouse gases are a significant subject. For instance, the spread of fuel-efficient vehicles, replacement of old-model electrical appliances with new low-power consumption models, and the developments of green energies are on going. Also in the field of lighting, environmental issue is quite an important subject to challenge. The trend of replacing conventional inefficient lamps by highly efficient lamps such as compact fluorescent lamp or solid-state lighting is occurring in every sector or application. A light-emitting diode (LED) is well known as a high-efficiency SSL source, and LED equipment has gradually been replacing the conve ntional lighting sources such as those based on incandescent bulbs. An LED lamp is also partially used as a substitute of fluorescent lamp for indoor lighting and halogen lamp or high-intensity discharge lamp for automobile. An organic LED (OLED) is another candidate of an solid-state lighting device for next-generation lighting because it is superior to the conventional light sources thanks to its gentle surface emission, high design flexibility, compactness, light weight, and high response. Therefore, an OLED is expected as a novel-designed lighting application with multifunction, for example, color-tunable, transparent, ultra-thin, flexible, and wearable. OLEDs are among the most promising technologies for both the large OLED displays and the solid-state lighting panels [1–5]. The market share of organic light-emitting diodes has continued to increase in

CONTACT Irina Savchenko ✉ iras@univ.kiev.ua

high-end display applications such as smartphones and TVs as well as in relatively low-end applications such as digital signs.

Today, organic light emitting diodes are used commercially in displays and various lighting applications providing high external quantum efficiency (up to 19%) and low power consumption.

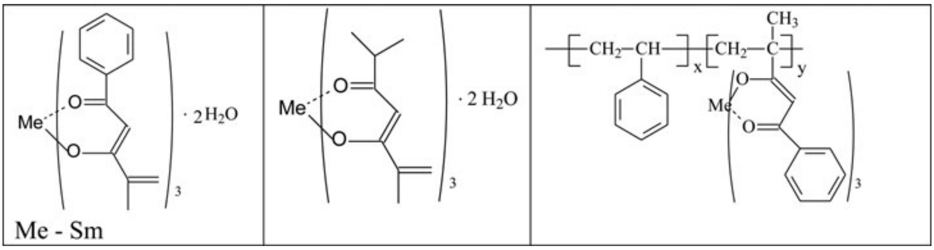
Organic conjugated polymers, like poly(para-phenylene vinylene) (PPV) doped by various chromophores, are now used in OLEDs as they lend the possibility to create charge carrier recombination and formation of excitons with high efficiency of light emission. Typical OLEDs are fabricated by spin-coating, inkjet printing or by vacuum deposition of organic materials on an indium-tin-oxide (ITO)-coated glass and with a multilayer structure of the device including NPB (N,N'-Bis(naphthalene-1-yl)-N,N'-bis(phenyl)-benzidine) and Alq_3 as the hole transport layer (HTL) and electron transport layer (ETL), respectively. These materials are presented here as typical examples. In between there is a doped emission layer (EML). Usually some additional layers which protect the ETL from reactions with the cathode material, or reduce the injection barrier and electron-hole quenching, are incorporated into the device architecture.

Recently, rare earth complexes have attracted considerable attention for organic electroluminescent devices as well as for optical microcavity emitters owing to their inherent extremely sharp emission bands and potentially high internal quantum efficiency. However, there is a major problem using rare earth complexes because it is often impossible to form vacuum-vapor deposited films dueto their nonvolatile nature. Therefore, rare earth complexes often need additional solid support to provide enough process ability and stability for functional devices. For this purpose, the composites of macromolecules and organic lanthanide complexes were prepared either through traditional melt-extrusion and solution casting or through polymerization of lanthanide–monomer complexes [6–9].

It is well known that lanthanide b-diketonates have been intensively studied with respect to high fluorescent intensity and fluorescent efficiency due to high-energy transfer from β-diketonates to Ln^{3+} ions [10–12]. These OLEDs are thin, flexible, stable, and energy conserving devices; they have prompt response times (μs), high color purity and are suitable for large screen displays and even for illuminating wallpapers in the near future [13–18].

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.

The aim of this work were synthesis of Sm(III) complexes with 2-methyl-5-phenylpentene-1-dione-3,5 and 2,6-dymethyl-heptene-1-3,5-dione as well as (co)polymers based on them and investigations of properties of metal-containing polymeric systems.



Structure of monomers, (co)polymers and metal complexes confirmed by data of NMR-, electronic, diffusion and infrared spectroscopes, termogravimetric analysis.

2. Experimental

2.1. Synthesis

Synthesis of 2-methyl-5-phenylpentene-1-dione-3,5 (mphpd) and 2,6-dymethyl-heptene-1-3,5-dione was carried out under method [15].

2-methyl-5-phenylpentene-1-3,5-dione NMR: ^{1}N (D_2O) δ (ppm): 3.27 (singlet, 3N, 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).

2,6-dymethyl-heptene-1-3,5-dione NMR: ^{1}N (D_2O) δ (ppm): 1,08–1,14 (doublet, 6N, C-CH_3); 1,90 (singlet, 1H, CH_3); 3,11–3,17 (singlet, 2H, C-CH_2); 3,79 (triplet, 3N, CN) 5,05-5,78 (doublet, 2N, = CH-); 6,10–6,33 (doublet,2N -CN-CH_3), 16,73 (singlet, 4N, OH)

Complexes obtained by an exchange reaction between equimolar amounts of lantanide acetate and sodium 2-methyl-5-phenylpentene-1-3,5-dione salt or 2,6-dymethyl-heptene-1-3,5-dione in a water-alcohol solution at pH 8–10 with a slight excess of the ligand. The resulting precipitate was filtered off, washed with water several times and dried over anhydrous $CaCl_2$.

(Co)polymers were synthesized by free-radical polymerization in DMF. The polymerization was carried out in 10 wt.% DMF solution of monomers with AIBN as free radical initiator (1 wt.% with respect of monomers mass) at 80 °C for more than 8 hours in thermostat. The polymerization mixture was poured into methanol. The solid precipitate was filtered, dissolved in DMF, and reprecipitated into methanol and then dried at 20°C overnight. Yield: 85–95%.

2.2. Characterization methods

The synthesized compounds have been studied by NMR, IR-, electronic absorption, diffuse reflectance spectroscopy and thermal analysis. 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, Nicolet Nexus 670 FTIR spectrometer. Thermograms were recorded on a TA instruments Q -1500 D apparatus by system of Setsys evolution-1750 at a heating rate of 5 °C/min from room temperature up to 500°C in platinum capsule in presence carrier Al_2O_3 (anhydrous).

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 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. The particle size studying was performed at 25°C using the equipment from «Zeta Sizer Nano by Malvern». Photomicrographs were obtained by a scanning electron microscope «Hitachi H-800” (SEM).

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, $CHCl_3$) 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

3.1. Spectral properties

The monomeric complexes of $Sm(mphpd)_3 \cdot 2H_2O$ and $Sm(hdmhpd)_3 \cdot 2H_2O$ were prepared in an aqueous alcohol solution at pH 8–10.

$$Sm(NO_3)_3 + Na\left(mphpd\right) \rightarrow Sm\left(mphpd\right)_3 + 3NaNO_3$$

The identification of compounds was performed by elemental analysis, the samarium percentage in $Sm(mphpd)_3 \cdot 2H_2O$ (%): 20.08 (calculated), 20.12 (found).

The monomeric and polymeric complexes of Sm with 2-methyl-5-phenylpenten-1-3,5-dione (mphpd), $Sm(mphpd)_3 \cdot 2H_2O$, 2,6-dymethyl-heptene-1-3,5-dione (hdmhpd) $Sm(hdmhpd)_3 \cdot 2H_2O$ were synthesized at the first time. The metallopolymers on their basis $[Sm(mphpd)_3]_n$ and copolymers $Sm(mphd)_3$-co-styrene were obtained by free-radical polymerization with the initiator AIBN and the kinetics of polymerization was studied by dilatometric method.

Note that in the synthesis of 2,6-dymethyl-heptene-1-3,5-dione held its partial oligomerization confirming NMR spectra. In this regard, complexes that were obtained on the basis of the ligand is already oligomeric compounds and subsequent polymerization of not needed. This unexpected effect has allowed us to compare the properties of metallopolymer obtained in two ways: by homopolymerization of monomeric complex (mphpd) and by reaction between metal salt and polymeric ligand (hdmhpd).

Kinetic parameters of radical polymerization of complex $Sm(mphpd)_3$ were calculated: the rate of polymerization is $1{,}34 \cdot 10^{-4}$ mol/L·s, the reduced rate of polymerization is $6{,}38 \cdot 10^{-}s^{-1}$, the total rate constant is $8{,}16 \cdot 10^{-3}$ $dm^{1.5}/\ (mol^{0.5} \cdot s)^1$ respectively.

The differential thermal analysis (DTA) of obtained compounds for the identification of the complexes hydrated composition and their temperature behavior was performed. The presented results allow to assume that the complex composition corresponds to the formula $Sm(mphpd)_3 \cdot 2H_2O$. As for the complex $Sm(dmhpd)_m$, set its exact composition is not possible, due to the compound is oligomer but the results of thermal analysis can assume that water affiliate to lanthanide ion coordination environment.

With the aim of the identification of ligand functional groups coordination method to metal ions were studied the IR spectra of synthesized compounds (Fig 1, Table 1).

In the IR spectra of the synthesized complexes and metallopolymers in 1500–1600 cm^{-1}, there are bands corresponding to stretching vibrations of the ν (C-O) and ν (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 ν (CC) and a lower frequency to the stretching vibrations of the ν (CO). The region of 1640–1680 cm^{-1} contains stretching vibrations ν (C = C) for $Sm(mphpd)_3 \cdot 2H_2O$. In IR spectrum $Sm(dmhpd)_m$ the band of stretching vibrations ν (C = C) almost is absent owing to its oligomerization. Proof of this fact is the shift of stretching vibrations bands in the low-frequency region.

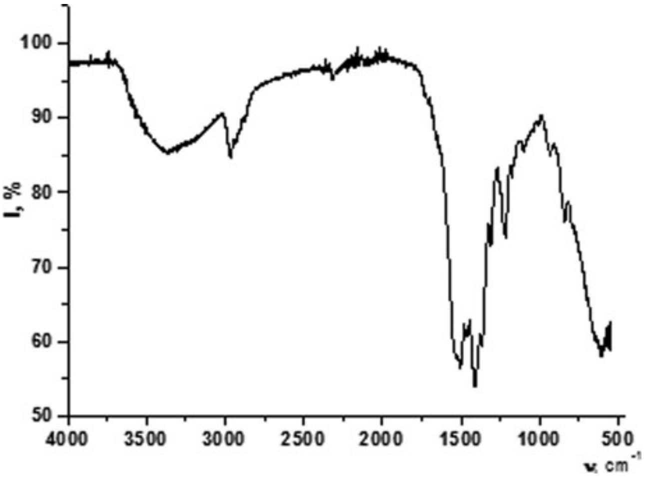


Figure 1. IR-spectrum of Sm(dmphpd)$_m$.

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 diketonate ligands with delocalized system of π-bonds in the chelate ring.

In IR spectra of the polycomplexes comparatively with monomeric complexes the location of main absorption bands are shifted in short-wave spectrum region, their intensity is lower significantly, the intensity is decreased especially which corresponds to vibration of the double bond. In the case of polycomplexes the band ν (C = C) disappears or is significantly reduced in intensity, indicating the presence of only the terminal unsaturated groups. Presented results are confirmed of the polymer complex formation.

In the electronic absorption spectra of complexes for "hypersensitive" transitions Sm (III) ($^6H_{5/2}\rightarrow{}^6P_{3/2}$) only one undissociated (unsplit) band are observed, indicating the existence of a solution of one type of compound. In the absorption spectra of both Sm(III) complexes halfwidth band $^6H_{5/2}\rightarrow{}^6P_{3/2}$ is 220–270 cm^{-1}, which is characteristic compounds of low symmetry. To consider the influence on the environment ligand field Ln^{3+} ions were chosen "hypersensitive" bands that corresponds to transition $^6H_{5/2}\rightarrow{}^6P_{3/2}$. The choice of these bands in the spectra of compounds Ln (III) due to the fact that these transitions in the absence of a magnetic field is degenerate and, consequently, only one absorption band are observed. In complexes these bands shift under the influence of crystal field ligands, and its value determinates the deviation from the ionicity of the band lanthanide-ligand. In the electronic absorption spectra of metallopolymeric complexes Sm(III) (table 2) a slight shift of the bands "hypersensitive" transitions in low frequencies are observed compared to the spectra of monomeric complexes are evidence of weakening connection of metal with donor atoms β-diketones in the polymer, as well as the near coordination environment of central ion both in

Table 1. Some distinctive absorption band of Sm(III) complexes and metallo(co)polymers with styrene.

Complex	ν(M-O) $+\delta_{\text{chelate ring}}$	ν_{as} (C $\overset{\cdots}{\cdots}$ C)	ν_s (C $\overset{\cdots}{\cdots}$ O)	ν_s (C = C)	ν_{as} (C $\overset{\cdots}{\cdots}$ O)
Sm(mphpd)$_3$·2H$_2$O	418; 438; 458; 576;	1560	1592	1659$_{\text{split.}}$	1427
[Sm(mphpd)$_3$]$_n$	413;425; 557; 598;	1554	1598$_{\text{split}}$	1671$_{\text{sl.}}$	1429; 1456
Sm(dmhpd)$_m$	489; 546,	1540	1545	—	1459
[Sm(mphpd)$_3$]$_n$[Styrene]$_m$	450, 540	1600		—	1460

Table 2. Energy transition (cm^{-1}) in Sm(III) electronic absorbtion spectra.

Transition	$Sm(mphpd)_3$	$[Sm(mphpd)_3]_n$	$Sm(dmhpd)_x$
$^6H_{5/2}\rightarrow{}^4N_{7/2}$	28115	28230	28110
$^6H_{5/2}\rightarrow{}^4D_{3/2}$	27592	27650	27680
$^6H_{5/2}\rightarrow{}^6P_{7/2}$	26740	26670	26680
$^6H_{5/2}\rightarrow{}^4L_{15/2}$	25550	25600	25190
$^6H_{5/2}\rightarrow{}^6P_{3/2}$	24740	24940	24720
$^6H_{5/2}\rightarrow{}^2L_{15/2}$	24340	24360	24275
$^6H_{5/2}\rightarrow{}^4M_{19/2}$	23819	23800	23766
$^6H_{5/2}\rightarrow{}^4G_{9/2}$	22570	22680	22720
$^6H_{5/2}\rightarrow{}^4F_{5/2}$	22080	22120	22110

monomeric and polymeric complexes. Unfortunately, in electronic absorption spectra of synthesized copolymers absorption bands which are characteristic of f-f transitions of lanthanide ions, are either absent or low-intensity and extended, but there are π-π transitions of ligand ($\sim$ 35000 cm^{-1}) which imposed on π-π transitions of styrene. In the electronic absorption spectrum of complex $[Sm(mphpd)_3]_n[Styrene]_m$ band at 24903 cm^{-1} weaks, which corresponds to the transition $^6H_{5/2}\rightarrow{}^6P_{3/2}$ of Sm $^{3+}$.

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

Obviously, the polymerization does not lead to significant changes in the geometry of coordination polyhedra, and in metallopolymers a slight weakening of the metal-oxygen band are occured due to additional lanthanide ion interaction with neighboring ligands.

With the shift of the bands of supersensitive transitions in the low-frequency region compared with the corresponding bands in the metal complexes can be judged on the formation of copolymers. Note, that in copolymers the bathochromic shift of absorption bands is slightly larger than in metallopolymers ($\Delta\nu \sim 40$ cm^{-1}), due to the complicated structure of copolymers, but coordinating unit of lanthanide ion is remained. The results of the above study showed that the configuration of the chelate unit is unchanged during the polymerization.

Luminescent lanthanide complexes characteristics depend on the choice of the ligand. The resonance energy of lanthanide ion must be higher than the triplet energy level of the ligand and the difference between the energy levels of the ligand triplet and singlet levels of lanthanide ions must be in the range of 2000–3500 cm^{-1}. The calculated value of energy triplet levels of ligand are higher emitting levels of lanthanide ions Sm (III) ($^4G_{5/2}$, 17850 cm^{-1}) and the difference in energies S_1 and T_1 is 2050 cm^{-1}, indicating the possibility of intramolecular energy transfer excitation from lower triplet levels of β-diketones on emissive levels of lanthanide ions. The polymerization leads to increase of triplet energy level ($\Delta E = 700$ cm $^{-1}$), due to the delocalization of the electron density in the ligand molecule. The calculated value of triplet energy ligand levels in the polymers are above emitting levels of ions $\Delta E =$ Sm (III) (2750 cm^{-1}), which indicates the possibility of intramolecular energy transfer excitation. The increase of difference in energies for polymer complexes compared to monomeric may promoute to the increase of the luminescence efficiency.

The luminescence spectra of the synthesized compounds were recorded in the solid state and in a solution.

In the excitation spectrum of $Sm(mphpd)_3$ the broad diffuse band in the 300–370 nm (line halfwidth of $\sim$ 120 nm) are observed (fig. 2).

The Sm^{3+} ion with $4f^5$ configuration has complicated energy levels and different conceivable transitions inter f levels. It can be seen that the red light of Sm^{3+} ion consists of three emission peaks in the visible region at 562, 599, and 645 nm, which are ascribed to the

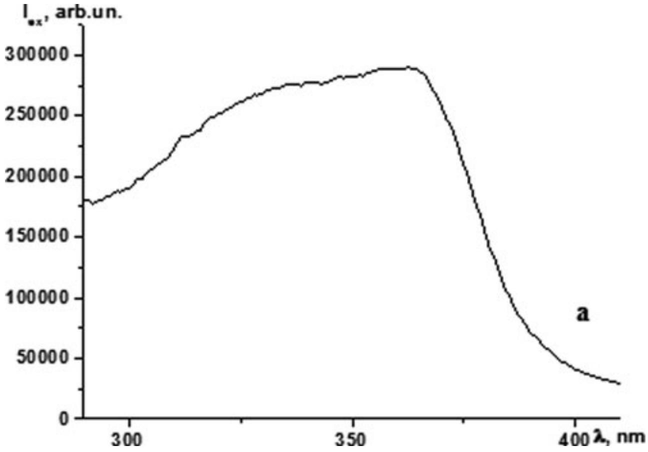


Figure 2. Excitation spectrum ($\lambda_{em} = 645$ nm) of $Sm(mphpd)_3{\cdot}2H_2O$ (1) in solid state ($\lambda_{ex} = 357$ nm, 298K).

intra-4f-shell transition from the excited level $^4G^{5/2}$ to the ground levels $^6H^{5/2}$, $^6H^{7/2}$, and $^6H^{9/2}$, respectively (Figs. 3, 4).

For all synthesized compounds the orange 4f-luminescence is observed, and maximum intensity is characteristic for the supersensitive magnetic dipole transition $^4G_{5/2}{\rightarrow}^6H_{9/2}$„ which corresponds to the band with a maximum at 644–647 nm. In photoluminescence spectrum of solution the locations of emissive maximums not change concerning their locations in luminescence spectrum of solid complex, indicating that the same coordination environment of samarium ions in solution and solid state. (fig. 5)

The calculation of the quantum yield of 4f-luminescence ions Sm (III) is conducted on the basis of an integrated luminescence intensity of all transitions except the transition $^4G_{5/2}{\rightarrow}^6H_{7/2}$, whose contribution is less than 1%. It was established, that for the complex $Sm(mphpd)_3$ in solution $\varphi_{4f} = 0{,}00021$ at $\lambda_{ex} = 371$ nm and 0.00033 at $\lambda_{ex} = 420$ nm, for solid sample $\varphi_{4f} = 0{,}0055$.

The form, intensity and splitting of spectral lines for complexes Sm $(mphpd)_3$ and Sm $(dmhpd)_m$ virtually identical, indicating that the same structure of coordination polyhedra for both complexes.

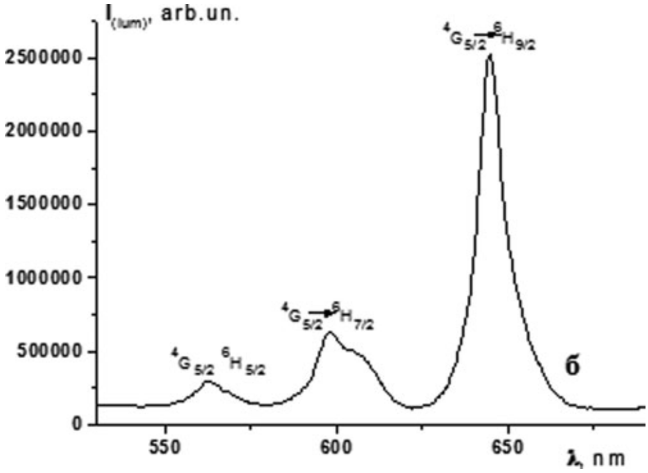


Figure 3. 4f-luminescence spectrum of $Sm(mphpd)_3{\cdot}2H_2O$ (1) in solid state ($\lambda_{ex} = 357$ nm, 298K).

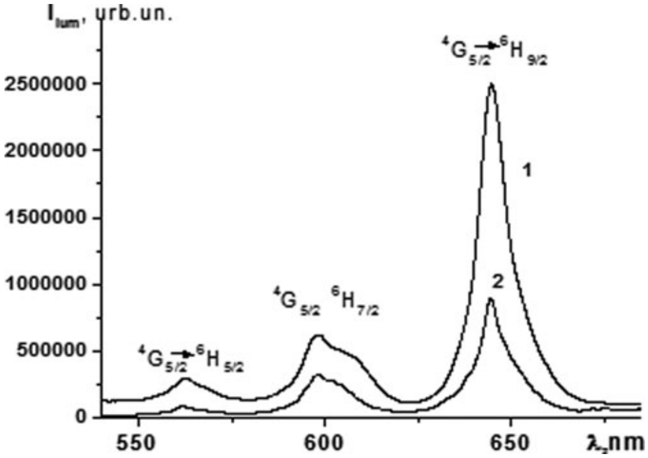


Figure 4. 4f-luminescence spectra of Sm(mphpd)$_3$·2H$_2$O (1) and Sm(dmhpd)$_m$ (2) in solid state ($\lambda_{ex} = 357$ nm, 298K).

Low luminescence intensity Sm (dmhpd)$_m$ due to both chemical heterogeneity of oligomer and the screening of samarium emitting centers by neighboring ligand molecules Analysis of monomer and polymer micrographs (Fig. 6) showed the ordering structure of metal polymer as compared with monomer.

Light-emitting organic planar hetero structures - multilayer semiconductor structures with their thick several orders smaller than their linear dimensions were fabricated on the basis of the synthesized samarium metal polymers.

This device consists two organic layers situated between a low work function metal cathode such as calcium and a higher work function anode, often transparent indium-tin oxide (ITO). The emission layer – polycomplex $\{[Sm(mphpd)_3]_n[Styrene]_m\}$, hole conduction layer – the mixture PEDOT:PSS were used. PEDOT:PSS - poly(3,4-ethylenedioxythiophene):polystyrene sulfonate is a polymer mixture of two ionomers.

Emission layer was applied to the surface (PEDOT:PSS) by spin-coating in nitrogen filled sealed box from chloroform solutions (with concentration 10^{-2} – 10^{-3}M). Cathode (Al) was applied by magnetron metal spraying. All devices have the structure with two organic

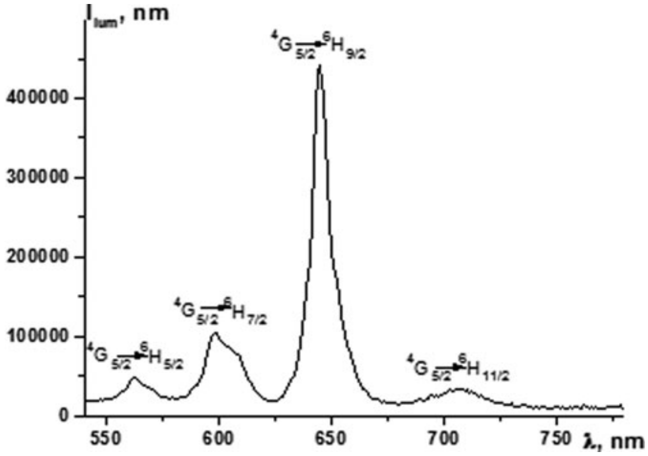


Figure 5. 4f-luminescence spectrum of Sm(mphpd)$_3$·2H$_2$O (1) in solution CHCl$_3$ ($\lambda_{ex} = 376$ nm, 273K).

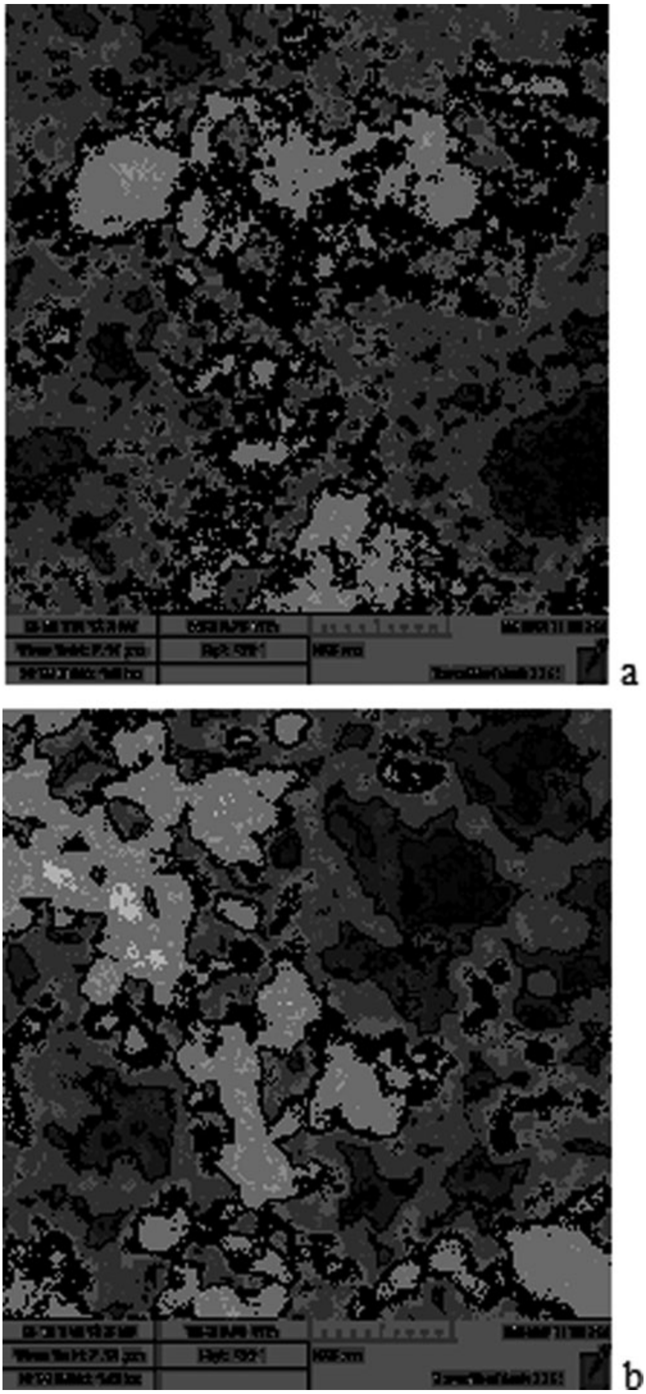


Figure 6. SEM micrographs of powders Sm(mphpd)$_3$ (a), [Sm(mphpd)$_3$]$_n$ (б).

layers ITO/ PEDOT:PSS/metal complexes/Al. The current-voltage characteristics of samples are exponential dependences which characterized for p-n transition.

Intense electroluminescence ITO/PEDOT:PSS/ {[Sm(mphpd)$_3$]$_n$[Styrene]$_m$}/Al (Fig.) for this device was observed in the red region at $\lambda = 533$ nm and $\lambda = 562$ nm, corresponding to emission copolymer layer. In addition, in the range of 420–470 nm ($\lambda = 429$ and

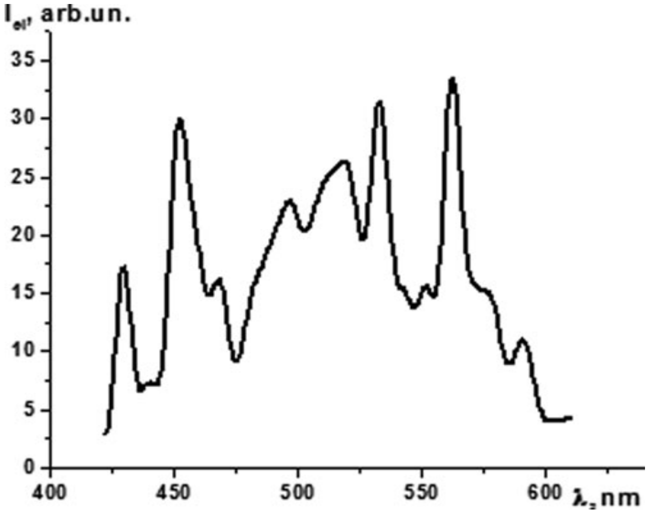


Figure 7. Electroluminescence spectrum of ITO/PEDOT:PSS/{$[Sm(mphpd)_3]_n[Styrene]_m$}/Al, 10,2 B-7 mA: Rotational speed 1000 r/m.

452 nm) is a sufficiently intense emission bands due to exciton luminescence PEDOT:PSS. However, the electroluminescence does not cover the basic maximum intensity of transition Sm^{3+} ($^4G_{5/2} \to {}^6H_{9/2}$, $\lambda \sim 645$ nm), which requires the reproduction of the results in order to expand the range (fig. 7).

Thus, the obtained results suggest that the correct selection of ligand, conductive layer, solvent and film thickness, this metal polymers can be used as precursors in organic electroluminescence diodes.

4. Conclusions

In conclusion, a nowel structures - complexes of Sm with 2-methyl-5-phenylpenten-1-3,5-dione and 2,6-dymethyl-heptene-1-3,5-dione, polycomplexes on their basis and copolymer with styrene in ratio 5:95 has been proposed.

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.

The similarity of monomers electronic absorption spectra with (co)polymers spectra confirms of identical coordinative environment of lanthanide ions in both cases.

The results of the above study showed that the configuration of the chelate unit is unchanged during the polymerization.

The present investigation suggests that obtained polycomplexes are potentional candidates as materials for organic light-emitting devices and other optical applications.

References

[1] Chen, B., Wen, G., Wu, J., & Feng, J. (2015). *Macromol. Rapid Commun.*, *36*, 1836.
[2] Eliseeva, S. V., & Bunzli, J. -C. G. (2010). *Chem. Soc. Rev.*, *39*, 189.
[3] Feng, J., & Zhang, H. (2013). *Chem. Soc. Rev.*, *42*, 387.
[4] Yan, B. (2012). *RSC Adv.*, *2*, 9304.
[5] Mishchenko, A., Berezhnytska, O., & Savchenko, I. (2014). *Mol. Cryst. Liq. Cryst.*, *590*, 49.

[6] Savchenko, I. O., Berezhnytska, A. S., & Fedorov Ya. V. (2014). *Mol. Cryst. Liq. Cryst.*, *590*, 66.

[7] Ding, Y., Wang, Y., Li, H., Duan, Z., Zhang, H., & Zheng, Y. (2011). *J. Mater. Chem.*, *21*, 14755.

[8] Wen, T., Zhang, W., Hu, X., He, L., & Li, H. (2013). *Chem. Plus. Chem.*, *78*, 438.

[9] Graffion, J., Catton, X., Man, M. W. C., Fernandes, V. R., Andr, P. S., Ferreira, R. A. S., & Carlos, L. D. (2011). *Chem. Mater.*, *23*, 4773.

[10] Yan, B., & Shao, Y.-F. (2013). *Dalton Trans.*, *42*, 9565.

[11] Wang, D., Wang, H., & Li, H. (2013). *ACS Appl. Mater. Interfaces*, *5*, 6268.

[12] Peng, Z.X., & Qing, Z.G. (2014). *Sci. China Chem.*, *57*, No. 2, 243.

[13] Savchenko, I., Berezhnytska, O., & Denysova, Z (2014). *Mol. Cryst. Liq. Cryst.*, *590*, 58.

[14] Guang, L.Y., Ping, G.Z., Bing, G.H., Jing, Z.S., Lin, L.K., Ying, W., Ran, D.H., Li, Z., & Jun, Z.F. (2015). *Optoelectronics Letters*, *11*, 0041.

[15] Savchenko, I., Bereznitskaya, A., & Fedorov, Ya. (2013). *Chem. & Chem. Technolog.*, *7*, N 4, 423.

[16] Savchenko, I., Berezhnytska, A., & Ivakha, N. (2015). In: *Nanocomposites, Nanophotonics, Nanobiotechnology and Applications*, Springer Proc. in Phys. 156, Chapter 6, Springer International Publishing: Switzerland, 85.

[17] Sun, Y., Yang, B., Guo, G., Liu, Y., & Zhao, G. J. (2011). *Inorg. Organomet. Polym.*, *21*, 395.

[18] Savchenko, I., Berezhnytska, A., & Mishchenko, A. (2015). In: *Nanoplasmonics, Nano-Optics, Nanocomposites, and Surface Stadies*, Springer Proc. in Phys., 167, Chapter 30, Springer International Publishing: Switzerland, 433.