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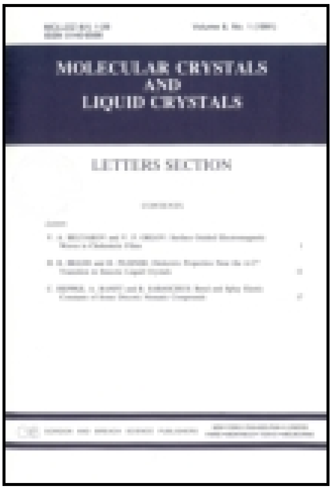

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Copolymers of Rare Earth Elements Complexes with Unsaturated β-diketones and N-vinylcarbazole for OLEDs

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Copolymers of Rare Earth Elements Complexes with Unsaturated β-diketones and N-vinylcarbazole for OLEDs

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With the aim of a simplification of the incorporation of layers in an electroluminescent cell, the emission layer (rare earth elements complex), hole conduction layer (such as N-vinylcarbazole), and electron conduction layer (1,10–phenanthroline) can be superposed in one macromolecule.

Copolymers 2-methyl-5-phenylpentene-1-dione-3,5 with N-vinylcarbazole in a ratio of 5:95, which contain Pr, Nd, Er, and Eu with 1,10-phenanthroline, were synthesized for the first time. The luminescence spectra of the obtained metallocomplexes and copolymers in solutions, films, and solid state are investigated and analyzed. These polymetallocomplexes can be used as promising materials for organic light-emitting devices.

Keywords complexes; copolymer; spectra; structure; luminescence

1. Introduction

Lanthanide(III) complexes have attracted great interest of coordination chemists owing to an inherently long emission lifetime and a narrow spectral bandwidth of the emission of the central Ln(III) ion. Strong luminescence in the visible red region, from Eu(III) ions in particular, is widely exploited in applications such as analytical sensors, imaging techniques, displays, and organic light-emitting diodes [1–5]. It is well known that the use of organic chromophores as light-harvesting groups can overcome the poor absorbance of light by Eu(III) ions. As usual, however, the excitation of a ligand-centered transition in the UV region is required, which is harmful in some practical applications, especially biological ones. Accordingly, extensive research efforts have been directed at minimizing the excitation photon energy. Organic light emitting diodes (OLEDs) have many advantages such as the low voltage operation, self-radiation, light weight, thin thickness, wide view angle, and fast response time to overcome the shortcomings of available liquid crystal displays. Therefore, a lot of attention is paid to them as the promising display devices, which have already developed and used in manufactured goods [6–7]. In addition, OLEDs are regarded as the most feasible candidates for flexible displays.

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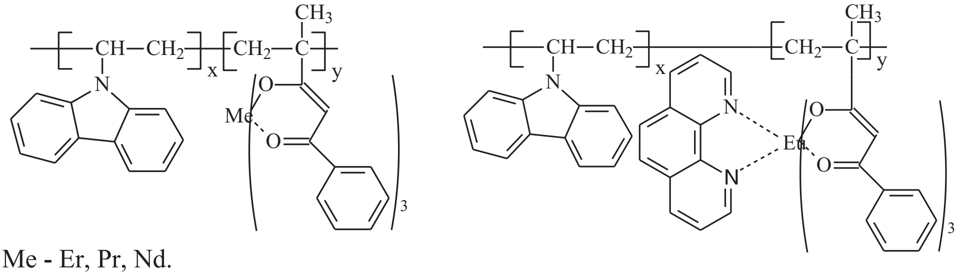

Scheme 1. Molecular structures of studied copolymer complexes.

The OLEDs, generally, consist of a hole injection layer, a hole transporting layer, an emissive layer, and an electron transporting layer. When the voltage is applied to the OLED cell, the positive and negative charges injected from the electrodes recombine in the emissive organic layer, resulting in electroluminescent light. Several organic electroluminescent materials have been developed, with a main focus on fluorescent molecules and polymers [8,9]. This kind of material, however, exhibits the emission spectra with a typical width of 100–200 nm, which is not well suitable for display applications, since pure red, green, and blue emissions are required. In this context, rare-earth (RE)-based complexes are interesting candidates to be used for this purpose [10–12]. Due to the intra f–f transitions of rare-earth ions and their unique ligand-mediated energy transfer mechanism, these ions present emission bands extremely sharp, when electronic transitions occur, which results in almost monochromatic and long-lifetime emission [13,14]. Furthermore, once both singlet and triplet excitons are involved in the emission process, and the efficient ligand-to metal intramolecular singlet–triplet-rare earth ion energy transfer is operative, rare-earth ions can theoretically reach the 100-% quantum efficiency, which is four times higher than that of similar devices based on fluorescent materials.

In particular, lanthanide(III) complexes with beta-diketonate ligands show intense photoluminescence [15–17] and electroluminescence [18,19]. This is a consequence of the high absorption of the beta-diketonate species and its efficient energy transfer [20–22].

In the past decades, various electrophosphorescent organic small molecules, including iridium (Ir), platinum (Pt), ruthenium (Ru), europium (Eu), and osmium (Os) complexes doped into a wide band-gap small molecule-host have been used to make high-efficiency electrophosphorescent devices. Meanwhile, the use of a conjugated polymer as the host material is attractive, since it allows LEDs to be made at room temperature via spin-coating, screen printing, or inkjet printing technique [23–29].

In this paper, we report our findings on the synthesis and photophysical properties of N-vinylcarbazole copolymers with Pr, Nd, Er, and Eu with 1,10-phenanthroline complexes.

With the aim of a simplification of the incorporation of layers in a electroluminescent cell, the emission layer (rare earth elements complex), hole conduction layer (such as N-vinylcarbazole), and electronic conduction layer (1,10–phenanthroline) can be superposed in one macromolecule.

Copolymers 2-methyl-5-phenylpentene-1-dione-3,5 with N-vinylcarbazole in a ratio of 5:95, which contain Pr, Nd, Er, and Eu with 1,10-phenanthroline, were synthesized for the first time.

Structure of monomers, copolymers, and metal complexes confirmed by data of NMR-, electronic, diffusion, and infrared spectroscopes, and thermogravimetric analysis.

2. Experimental

2.1. Synthesis

Synthesis of 2-methyl-5-phenylpentene-1-dione-3,5 (mphpd) and metal complex was carried out by the method developed in [30].

2-methyl-5-phenylpentene-1-dione-3,5 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 complexes were obtained with the exchange reaction between equimolar amounts of metal 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.

Copolymers were synthesized by the free-radical polymerization in DMF. The polymerization was carried out in a 10 wt.% DMF solution of monomers with AIBN (azobisisobutyronitrile) as a free radical initiator (1 wt.% with respect to the mass of monomers) at 80°C for more than 8 h in a thermostat. The polymerization mixture was poured into methanol. The solid precipitate was filtered, dissolved in DMF, reprecipitated into methanol and then dried at 20°C overnight. Yield: 88–98%.

2.2. Characterization Methods

The synthesized compounds have been studied by NMR, IR-, electronic absorption and diffuse reflectance spectroscopy (ESA and SDR), thermal analysis, and the dynamic light scattering method. The infrared spectra were recorded in KBr tablets at the range 4000-400 cm^{-1} with a Spectrum BX II FT - IR device manufactured by Perkin Elmer. The electronic absorption spectra were recorded using a spectrophotometer Shimadzu "UV-VIS-NIR Shimadzu UV-3600", and the diffuse reflectance spectra were obtained, by using a Specord M-40 spectrophotometer in the range 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 a filter OS11. An InGaAs photoresistor (DSS-IGA020L, Electro-Optical Systems, Inc., USA) cooled to the temperature of liquid nitrogen was used as a radiation detector in the infrared region. The excitation and luminescence spectra were adjusted to the distribution of a xenon lamp reflection and the photomultiplier sensitivity.

3. Results and Discussion

3.1. Spectral Properties

With the aim of the identification of the coordination of ligand functional groups 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^{-1}, there are the bands corresponding to the stretching vibrations of ν (C—O) and ν (C—C), which confirms the bidentate cyclic coordination of the ligand to metal ions (Table 1). At the same time, a higher frequency band should be attributed to the stretching vibrations of ν (C—C), and a lower frequency to the stretching vibrations of ν (C—O). The region of 1640–1680 cm^{-1} contains the stretching vibrations ν (C=C). There is also a broad absorption band of coordinated water molecules at 3400–3200 cm^{-1}. Thus, the obtained results indicate a cyclic bidentate coordination of mphpd molecules in the complexes.

Table 1. Some distinctive absorption band of metallic complexes and metallocopolymers with N-vinylcarbazole (VC)

Complex	ν(M—O)	ν_{as}(C—O)	ν_{as}(C—C)	ν_{s}(C—O)	ν_{s}(C=C)
Nd(mphpd)$_3$·2H$_2$O	420	1466	1559	1580	1671
Er(mphpd)$_3$·2H$_2$O	420	1425	1540	1595	1676
Eu(mphpd)$_3$·(phen)	410	1467	1553	1593	1660
Pr(mphpd)$_3$·2H$_2$O	420	1418	1554	1592	1679
Er(mphd)$_3$-co-VC	420	1454	1557	1595	—
Eu(mphpd)$_3$(phen)-co-VC	420	1452	1560	1598	—
Nd(mphpd)$_3$-co-VC	420	1420	1552	1594	—
Pr(mphd)$_3$-co-VC	420	1418	1554	1596	—

In the IR spectra of copolymers comparatively with those of monomeric metallocomplexes, the location of main absorption bands are shifted into the short-wave spectrum region, their intensity is lower significantly, and the intensity is essentially decreased, which corresponds to vibrations of the double bond (C=C).

The electronic spectra of Nd (III) complexes corresponding to an ion Nd $^{3+}$ have a set of transitions from the $^{4}/_{9/2}$ main (quantum) state. The shift of the main absorption bands in the case of monomeric complex into the long wavelength region as compared with the spectra of aqua-ions and the increase in the intensity indicate the formation of metal complexes and indirectly confirm the increase in the covalency of the metal - ligand bond (Table 2).

In the case of erbium complexes, a band pattern of the Er^{3+} ion transition with the ^{4}I$_{15/2}$ main (quantum) state is observed (Table 3).

For the europium complex in the visible spectrum, we observe the set of bands corresponding to the transition ^{7}F$_0$ main (quantum) state. The absorption bands for complexes of erbium and europium are shifted into the long wavelength region, as compared with the spectra of corresponding metal salts with regard for the complexation (Table 4).

The electronic spectra of Pr (III) complexes correspond to an ion Pr^{3+} and are composed of 4 absorption bands, which are found in the visible spectrum. The absorption bands of the monomer metal complex (^{3}H$_4$→^{3}P$_0$) are shifted to the longer wavelengths as compared with

Table 2. Energy transition in Nd electronic absorbtion spectrum

Transition	Nd^{3+}, cm^{-1}	Nd(mphpd)$_3$, cm^{-1}	Δ, cm^{-1}
^{4}I$_{9/2}$→^{2}P$_{1/2}$	23064	23255 $_{\text{arm}}$	200
^{4}I$_{9/2}$→^{4}G$_{9/2}$	19560	19520	40
^{4}I$_{9/2}$→^{4}G$_{7/2}$	19160	19050	90
^{4}I$_{9/2}$→^{4}G$_{5/2}$	17360	17152	200
^{4}I$_{9/2}$→^{4}F$_{9/2}$	14720	14700	20
^{4}I$_{9/2}$→^{4}F$_{7/2}$	13480	13400	80
^{4}I$_{9/2}$→^{4}H$_{9/2}$	12560	12470	90
^{4}I$_{9/2}$→^{4}F$_{3/2}$	11560	11430	130

Table 3. Energy transition in Er electronic absorbtion spectrum

Transition	Er^{3+}, cm^{-1}	$Er(mphpd)_3$, cm^{-1}	Δ, cm^{-1}
$^4I_{15/2} \rightarrow {}^4F_{7/2}$	20480	20523	43
$^4I_{15/2} \rightarrow {}^4H_{11/2}$	19160	19120	40
$^4I_{15/2} \rightarrow {}^4S_{3/2}$	18400	18382	20
$^4I_{15/2} \rightarrow {}^4F_{9/2}$	15320	15270	50
$^4I_{15/2} \rightarrow {}^4I_{9/2}$	12480	12450	30

those of aqua-ions, which indicates the formation of compounds with a greater coordination number than that of Pr inorganic salt [31].

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

The differential thermal analysis (DTA) of the obtained compounds to identify the composition of hydrated complexes and their temperature behavior was performed.

Based on the results of thermal analysis, the dehydration of complexes with unsaturated bonds occurs at higher temperatures 120–150°C [32] than that in the case of acetylacetonates. The neodymium complex dehydration occurs at a temperature of 130°C and is attended by the small endoeffect with a mass loss of 7% ($\Delta m_{\text{Teop.}} = 7.13\%$), which corresponds to the decoupling of three coordinative water molecules. The small endoeffect at a temperature of 210°C is probably caused by the complex melting; in this case, 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 a mass loss of 25.5% ($\Delta m_{\text{Teop.}} = 25\%$) at 285°C correspond to the removal of one ligand molecule. The following heating is attended by exoeffects at temperatures of 340, 360, 385, 425, and 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% ($\Delta m_{\text{Teop.}} = 4.7\%$) for the erbium complex at 125°C, which corresponds to the decoupling of two coordinative water molecules. The small exoeffect in the region near 190°C can be induced by the polymerization process, rather than by the complex melting. The process of complex decomposition begins with the removal of one ligand molecule, which corresponds of the exoeffect at 248°C and a mass loss of 28% ($\Delta m_{\text{Teop.}} = 24.5$). The subsequent heating is attended by exoeffects at temperatures of 337, 384, 419, 460C, and 484°C and results in the total complex decomposition with $\Delta m =$ 15%. The total weight loss is 66% for the erbium complex. The Pr complex thermogram is analogous to that of the erbium complex.

Table 4. Energy transition in Eu electronic absorbtion spectrum

Transition	Eu^{3+}, cm^{-1}	$Eu(mphpd)_{3,}$ cm^{-1}	Δ, 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

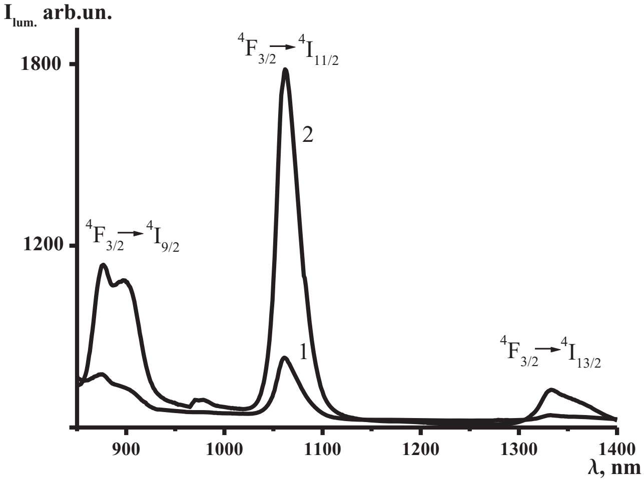

Figure 1. Luminescence spectra of Nd(mphpd)$_3$·2H$_2$O (1) and [Nd(mphpd)$_3$]$_n$ (2) in solid state (λ_{ex} = 362 nm, 298 K).

The presented results allow us to assume that the compositions of complexes correspond to the formulas Nd(mphpd)$_3$·3H$_2$O, Er(mphpd)$_3$·2H$_2$O, and Pr(mphpd)$_3$·2H$_2$O.

The luminescence spectra of the synthesized compounds were recorded in the solid state and in a solution. The excitation spectrum of Nd(mphpd)$_3$ in the solid state consists of a single band with maximum at 363 nm. In the excitation spectrum of the solution, a long-wavelength shift of the band ($\Delta\lambda$ = 15 nm) is observed.

In the excitation at the maximum of this band, the 4f-luminescence of samples is observed in the solid state and in the solution. The luminescence spectrum consists of three bands corresponding to the transitions from the excited level of ions Nd(III) $^4F_{3/2}$ into the multiplets of the main (quantum) level ^4I_j, j = 9/2 (I, 875 and 888 nm), 11/2 (II, 1061 nm), and 13/2 (III, 1332 nm) (Fig. 1).

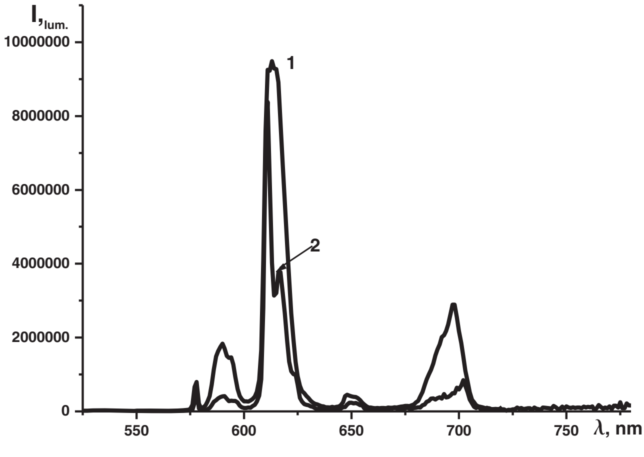

Figure 2. Luminescence spectra of 1-Eu(mphpd)$_3$, 2-Eu(mphpd)$_3$·Phen in solid state, T = 298K, λ = 362 nm.

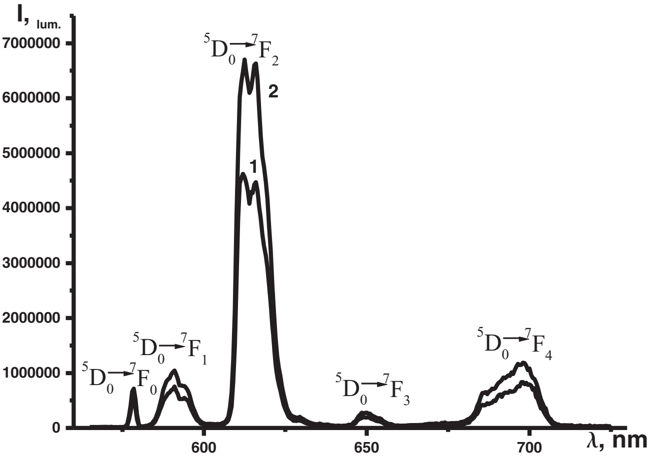

Figure 3. Luminescence spectra of 1-[Eu(mphpd)$_3$]$_n$, 2-[Eu(mphpd)$_3$·Phen]$_n$ in solution CHCl$_3$, T = 77K, λ = 362 nm.

The luminescence spectrum of the erbium complex is analogous with the band, which corresponds to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition.

The intensive red luminescence is observed for europium complexes and metallopolymers. The most intensive band corresponds to the transition $^5D_0 \rightarrow {}^7F_2$ in the region 610 630 nm. The bands with considerably less intensities are in spectral regions 575–580, 585–600, 650–670, and 680–705 nm and correspond to the transitions $^5D_0 \rightarrow {}^7F_j$, j = 0, 1, 3, and 4, respectively. The band corresponding to the transition $^5D_0 \rightarrow {}^7F_0$ contains the symmetric single line (Fig. 2), which allows us to assume the presence of the single luminescence center. Europium luminescence spectra (Fig. 3) at 77K allow us to establish

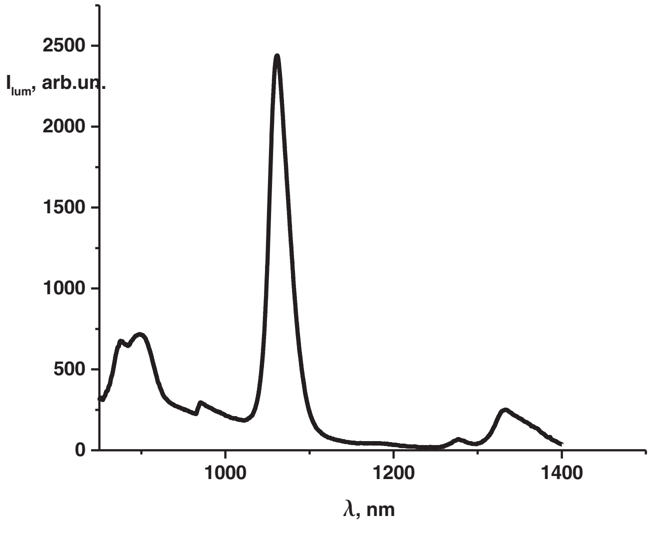

Figure 4. Luminescence spectrum of Nd(mphpd)$_3$·2H$_2$O-co-VK in solid state (λ_{ex} = 350 nm, 298 K).

the short-range coordination environment symmetry. The transition band $^5D_0 \rightarrow {}^7F_0$ in the luminescence spectra of all compounds appears as a symmetric single line and indicates the presence of one luminescence center. High-intensity lines caused by the electric dipole transition $^5D_0 \rightarrow {}^7F_2$, as compared with those of the relatively low-intensity magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$, suggest the not center-symmetric nature of the environment for all investigated compounds.

The luminescence spectra of europium β-diketonates complexes in all samples are similar to one another and approve the structure similarity of coordination polyhedra which are distorted antiprisms.

The luminescence intensity of copolymer VK with Nd(mphpd)$_3$ complex is greater in comparison with those of the respective monomeric and polymeric complexes (Fig. 4).

4. Conclusions

The investigations conducted in the present work allowed us to determine the composition, structure, and properties of the certain complexes and metallopolymers on their basis obtained for the first time.

The similarity of the electronic absorption spectra of monomers with those of copolymers confirms the identical coordinative environments of lanthanide ions in both cases. We have shown that the formation of the complexes of europium β-diketonate with phenanthroline changes the luminescence intensity.

Thus, the obtained copolymers which contain 5% emission components (lanthanide complex) in a polymer chain only, the hole conduction layer (such as N-vinylcarbazol), and electronic conduction layer (1,10–phenanthroline) in one macromolecule are comparable with suitable homopolymers [16] concerning the luminescence properties and can be used as potential materials for organic light-emitting devices.

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