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SPECTRAL-LUMINESCENT CHARACTERISTICS OF COORDINATION COMPOUNDS AND METAL POLYMERS OF Yb(III)

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New mono- and heteroligand (with phenanthroline or dipyriddy) metal complexes of ytterbium (III) with 2-methyl-5-biphenylpentene-1-3,5-dione were synthesized in this work. Homo- and copolymers of ytterbium complex with methyl methacrylate or styrene were obtained by the method of radical polymerization. Coordination compounds were investigated by IR spectroscopy, diffuse reflectance spectroscopy, thermal and luminescence analyses. It was determined that the β -diketone molecules are bidentate-cyclically coordinated to the central atom, and the coordination sphere of the monoligand complex is supplemented by two water molecules, which in the case of heteroligand complexes (HLC) are replaced by phenanthroline or dipyriddy molecules. An increase in thermal stability of heteroligand complexes and metallopolymers was observed compared to the metallocomplex. The spectral properties of the synthesized compounds were studied and it was established that the structure of the coordination node of the elementary link of polymer macromolecules does not change during the polymerization process. It was shown that all the studied samples exhibited 4f-luminescence in the near-infrared region of the spectrum, while the lowest relative luminescence intensity was characteristic of ytterbium(III) homopolymer and copolymers, and the highest values were shown by heteroligand complexes with phenanthroline, which allows us to propose them as precursors of luminescent materials.

Keywords: ytterbium, β -diketone, complex, polymer, heteroligand compound, luminescence.

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Introduction

The field of production of polymer materials occupies a prominent place in modern industry due to a number of their valuable operational properties. However, industrial polymers (such as PVC, PE, PS, PMMA, etc.) cannot meet all the requirements of modern technology. Therefore, there is a constant search for ways of their modification and synthesis of fundamentally new materials. From this point of view, one of the interesting useful characteristics is the ability to luminescence. The development and synthesis of compounds that can demonstrate effective emission properties in different regions of the spectrum (both in the visible and in the infrared) do not stop [1–3]. Promising precursors of such

materials are first of all coordination compounds of lanthanides, in which intense luminescence can be manifested due to the selection of the optimal ligand and implementation of the «antenna» effect. It is obvious that in order to obtain a polymer material based on such complexes, it is necessary that the ligand has an unsaturated group capable of polymerization. Studies show [4] that in this case it is advisable to use unsaturated β -diketones as ligands, since they can form compounds with a whole range of lanthanides and exhibit effective emission properties.

It is known that due to the production of metal polymers by polymerization or copolymerization of metal chelate monomers, it is possible not only to

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Spectral-luminescent characteristics of coordination compounds and metal polymers of Yb(III)

uniformly distribute the emitting centers over the structure of the polymer chain, but also to eliminate one of the factors that negatively affects the luminescent characteristics of the final material, namely concentration quenching. The latter, in turn, is associated with a large number of radiating centers and is due to the transfer of excited state energy between luminescent points up to its complete deactivation. The phenomenon of concentration quenching is most typical for ions emitting in the IR region of the spectrum. Concentration quenching for lanthanide complexes is observed less frequently than for inorganic substances due to the coordination of lanthanide ions with voluminous organic ligands, which leads to a sufficient separation of emitting centers from each other. However, such a phenomenon can be observed for complexes with unbranched β -diketones. Therefore, the selection of substituents in the α -position of the β -diketonate ligand and structure-property correlations come to the fore.

The aim of this work was the synthesis of β -diketonate ytterbium complex with 2-methyl-5-biphenylpentene-1-3,5-dione (mbphpd) and its heteroligand (with 2,2'-dipyridyl (dipy) and 1,10-phenanthroline (phen)) derivatives to be used as monomers to obtain polymer compounds, as well as to study the emission properties of metal polymers and copolymers.

Experimental

As a ligand, we used 2-methyl-5-biphenylpentene-1-3,5-dione (mbphpd) – β -diketone, which contains biphenyl and unsaturated substituents in the α -position (Fig. 1), synthesized by Claisen condensation.

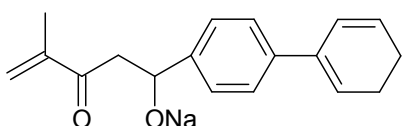
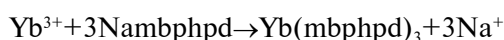


Fig. 1. 2-methyl-5-biphenylpentene-1-3,5-dione (mbphpd)

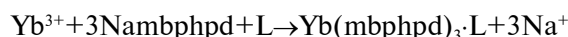
The synthesis of the Yb(III) complex with mbphpd was carried out by the interaction of an aqueous solution of ytterbium chloride ($\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, analytical grade) with an aqueous-alcoholic solution of the sodium salt of the ligand at a molar ratio of reagents of 1:3.5 (pH 8–8.5) at room temperature according to the following scheme:



The precipitate was centrifuged, washed with water 5 times and dried in a desiccator over anhydrous

CaCl_2 . Yb(III) β -diketonate powder has a yellow color due to the color of the ligand.

The synthesis of heteroligand compounds with 2,2'-dipyridyl (dipy) and 1,10-phenanthroline (phen) was carried out in water-ethanol solutions at the ratio $\text{Yb:Nambphpd:L}=1:3.5:1$ ($\text{L}=\text{dipy/phen}$) according to the following scheme:



After 3–5 hours, the process of complex formation was completed, the sediments were filtered and washed with ethanol.

Homopolymerization of the synthesized β -diketonates of Yb(III) complexes was carried out according to the method described elsewhere [5] by a radical mechanism that corresponds to the mechanism of polymerization of vinyl monomers. Polymerization conditions was performed at a temperature of 80°C , and 2,2'-azobisisobutyronitrile (AIBN) was used as an initiator. The kinetics of polymerization was studied by the dilatometric method. The kinetic parameters of the radical polymerization of complex (the rate of polymerization, the reduced rate of polymerization, and the total rate constant) of $\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$ were calculated.

Based on the data shown in Table 1, it can be argued that the nature of the metal ion, the nature of the ligand and its environment affects the reactivity of the monomeric complexes of different composition in the reactions of polymerization. The kinetic parameters of polymerization depend on electronic and steric properties of β -diketonates. In this case, the kinetic parameters of radical polymerization demonstrate very good agreement with literature data, and the rate constant is somewhat overstated compared to similar compounds [6]. Probably, the growth rate constant is due to the high resistance of this polymeric lanthanide complex.

Table 1

Kinetic parameters of the radical polymerization of complexes

Monomer	$V_p \cdot 10^5$, mol/(l·s)	$V_{\text{redpol}} \cdot 10^4$, s ⁻¹	$K_\Sigma \cdot 10^3$, l ^{1/2} /(mol ^{1/2} ·s)
$\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$	3.648	2.831	2.256

The synthesis of the copolymer of ytterbium (III) biphenylpentenedionate with methyl methacrylate (MMA) and styrene was carried out in a DMF solution at 80°C with a ratio of complex:comonomer=5–95 (wt.%) with the initiator AIBN (concentration of 1 w/w%) according to the standard method [7].

The synthesized complexes were investigated by the methods of IR spectroscopy, DRS, thermogravimetry and luminescence analysis.

IR spectra were recorded on a Specord M80 spectrometer in the region of 400–4000 cm^{-1} in KBr tablets. Diffuse reflection spectra were obtained on a Shimadzu UV-3600 UV-VIS-IR spectrophotometer in the range 300–1100 nm. Thermograms were recorded on the Q-1500 D derivatograph of the Paulik, Paulik and Erdey system in the temperature range of 20–500°C with the heating rate of 5°C/min. in a platinum crucible in the presence of a carrier (anhydrous Al_2O_3).

Excitation and luminescence spectra of solid complexes were recorded on a spectrofluorimeter Fluorolog FL 3-22, Horiba Jobin Yvon (X-lamp 450 W) using an OS 11 light filter with their subsequent adjustment taking into account the distribution of xenon lamp luminescent and the sensitivity of the photoelectric amplifier. An InGaAs photoresistor (DSS-IGA020L, Electro-Optical Systems, Inc, USA, cooled to liquid nitrogen temperature) was used as a luminescent receiver for the IR region.

Results and discussion

IR spectra of ytterbium(III) complexes with mbphpd were recorded to confirm the formation of coordination compounds and determine the mode of coordination of β -diketone to the metal. The assignment of the main bands in the spectrum was made based on the literature data [8,9] and shown in Table 2.

According to the presented results of the IR spectroscopic study, the following conclusions can be drawn:

– mbphpd in all mono- and polymeric compounds is coordinated to the central ion in a bidentate-cyclic manner ($\nu_{\text{as}}(\text{C}=\text{C})$ and $\nu_{\text{s}}(\text{C}=\text{O})$ vibration bands is in the region of 1550–1600 cm^{-1}), which is typical of β -diketonates lanthanides;

– the presence of vibration bands (Yb–O) in the low-frequency region of the spectrum indicates

the formation of metal complexes;

– monomeric compounds are characterized by the presence of an intense vibration band $\nu(\text{C}=\text{C})$ at $\sim 1650 \text{ cm}^{-1}$, which disappears almost completely in the case of metal polymers, appearing only in the form of a shoulder. This is explained by the fact that an insignificant part of the final unsaturated groups does not participate in the polymerization process;

– in the region of 3300–3600 cm^{-1} for the hydrated Yb complex, the presence of a wide range of stretching vibrations $\nu(\text{O}=\text{H})$ of water molecules, in the case of a heteroligand complex, such a band is absent, which indicates the displacement of H_2O molecules from the complex and the coordination of phen and dipy molecules with an ytterbium (III) ion. In the case of polymer complexes, a band of low intensity is observed in this range, which is due to the presence of a small amount of water in the frame of metal polymers;

– a number of bands in the IR spectra of HLC at $\sim 2900 \text{ cm}^{-1}$ corresponds to the sum of the frequencies $\nu(\text{C}=\text{H})$ α, α' -dipy and phen, and the bands in the range of 1000–1300 cm^{-1} are related to planar deformation vibrations of C–H and stretching vibration of aromatic rings of both the donor atoms α, α' -dipy and phen and the biphenyl substituent.

In general, the IR spectra of the studied compounds have a rather complex structure. In certain ranges, it is rather difficult to clearly assign all the vibration bands due to their overlap. However, we can confidently speak about the complex formation process and the method of coordination of β -diketone to the central atom (bidentate-chelate), which does not change even during the formation of heteroligand and polymer systems.

From the point of view of preparing new materials capable of exhibiting luminescent properties, an important stage is the study of their thermal stability. The thermal analysis of the synthesized compounds carried out under atmospheric conditions made it possible to establish that the coordination sphere of the ytterbium (III)

Table 2

Assignment of vibration bands in the IR spectra of Yb(III) β -diketonates

Complex	$\nu(\text{Yb}-\text{O})+\delta_{\text{hel. ring}}$	$\nu(\text{Yb}-\text{N})$	$\nu_{\text{as}}(\text{CC})$	$\nu_{\text{s}}(\text{CO})$	$\nu_{\text{s}}(\text{C}=\text{C})$
$\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$	411, 429, 450	–	1560	1576	1653
$\text{Yb}(\text{mbphpd})_3 \cdot \text{dipy}$	407, 430, 449	469	1560	1575, 1597	1652
$\text{Yb}(\text{mbphpd})_3 \cdot \text{phen}$	410, 428, 451	474	1558	1576, 1607	1653
$[\text{Yb}(\text{mbphpd})_3]_n$	406, 427, 455	–	1559	1581, 1599	1652sh
$[\text{Yb}(\text{mbphpd})_3 \cdot \text{dipy}]_n$	412, 432, 458	482	1559	1578, 1603	1652sh
$[\text{Yb}(\text{mbphpd})_3 \cdot \text{phen}]_n$	409, 432, 461	481	1561	1580, 1607	1651sh
$[\text{Yb}(\text{mbphpd})_3]_n[\text{MMA}]_m$	450, 490	–	1560, 1540	1588, 1605	–
$[\text{Yb}(\text{mbphpd})_3]_n[\text{Styrene}]_m$	445, 470	–	1559, 1542	1582, 1604	1670sh

complex with mbphpd is supplemented by two water molecules (Δm in the temperature range of 125–145°C is 3.7%).

In the case of heteroligand complexes, water molecules are completely replaced by donor atoms of phenatrolin and dipyrityl, and thermal stability increases by ~50°C (removal of phen and dipy molecules occurs at 175–205°C). Correlations of weight loss with specific constituents of polymeric compounds were not made, since it is impossible to determine their molecular weights directly in this case. Therefore, for metal polymers, only the thermal-oxidative resistance was estimated, which increases by ~60°C compared to monomeric precursors, which may be due to a decrease in the mobility of polymer chains. Based on this, it can be said that the synthesized metal polymers have a sufficiently high thermal stability, which is a positive factor for further possible use as luminescent materials.

Based on the results of IR and thermal analysis, it can be concluded that the composition of β -diketonate corresponds to the formula $\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$, and $\text{Yb}(\text{mbphpd})_3 \cdot \text{phen}$ or $\text{Yb}(\text{mbphpd})_3 \cdot \text{dipy}$ in the case of heteroligand systems. For polymers, the composition of the complexes does not change, so we can write down their formulae as follows: $[\text{Yb}(\text{mbphpd})_3 \cdot \text{L}]_n$ (L=phen, dipy).

The diffuse reflection spectra of all synthesized samples were recorded in this work. Usually, the electronic spectra of lanthanide coordination compounds consist of a series of narrow linear transition bands, which are due to the rather weak interaction of 4f orbitals with the electron shells of the ligands. At the same time, the 4f-electrons in the ytterbium ion are the least shielded among other lanthanide ions, which leads to a stronger interaction of electrons with the coordination environment of the metal. This leads to the appearance of broader bands in the electronic spectra of ytterbium coordination compounds compared to other Ln^{3+} ions.

The diffuse reflection spectra of mono-, heteroligand, and polymeric samples of

ytterbium(III) contain one diffuse band of the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition (Table 3), which is typical of $\text{Yb}(\text{III})$ coordination compounds ($\lambda_{\text{max}}=972\text{--}976\text{ nm}$).

Since, as can be seen from Table 3, there are no significant shifts of the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition band upon passing from the hydrated complex to heteroligand compounds and metal polymers, it can be argued that the structure of the coordination site does not undergo significant changes. However, during the formation of HLC or polymer complexes, the M–O distance may slightly increase compared to $\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$ due to partial neutralization of the charge of the central atom and the appearance of steric hindrances in the coordination of voluminous ligands. Based on the presented results and data [10], we can assume that the coordination polyhedron of the synthesized complexes is a square antiprism.

In order to search for compounds capable of exhibiting efficient luminescence in the IR spectral region, we studied the emission properties of $\text{Yb}(\text{III})$ complexes with mbphpd in this work. The expediency of studying HLC is due to the fact that their production makes it possible to level the negative quenching effect of O–H groups of water molecules [11,12]. Metal polymers, as is known, also exhibit a number of advantages (higher chemical and thermal stability and the ability to form film materials). This made it possible to choose them as objects of study of luminescent characteristics.

To determine the potential possibility of intramolecular energy transfer from the ligand to the metal, using the fluorescence and phosphorescence spectra at 77 K of the complex of gadolinium with biphenylpentenedione (synthesized according to the same scheme and procedure as the $\text{Yb}(\text{III})$ complex under study), 19960 cm^{-1} was calculated. This value of E_{T} (mbphpd) is much higher than the emitting level of the ytterbium (III) ion (10300 cm^{-1}). That is, such complexes can exhibit 4f luminescence.

The luminescent properties of all synthesized mono- and polycomplexes of ytterbium in the solid state at room temperature were investigated. A comparative analysis of emission properties was carried out. It was also appropriate to compare the

Table 3

The position of the characteristic transition band of the ytterbium (III) ion in coordination compounds

Compound	λ_{max} , nm	Compound	λ_{max} , nm
$\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$	974.1	$[\text{Yb}(\text{mbphpd})_3]_n$	972.2
$\text{Yb}(\text{mbphpd})_3 \cdot \text{dipy}$	975.2	$[\text{Yb}(\text{mbphpd})_3 \cdot \text{dipy}]_n$	972.7
$\text{Yb}(\text{mbphpd})_3 \cdot \text{phen}$	975.8	$[\text{Yb}(\text{mbphpd})_3 \cdot \text{phen}]_n$	973.5
$[\text{Yb}(\text{mbphpd})_3]_n[\text{MMA}]_m$	972.5	$[\text{Yb}(\text{mbphpd})_3]_n[\text{Styrene}]_m$	973.0

luminescence characteristics of the synthesized coordination compounds with the previously studied analogous complexes with an aromatic substituent, namely, with methacroylacetoophenoate compounds [6].

The emission excitation spectrum of powders (Fig. 2) of the complex of ytterbium (III) with biphenylpentenedione consists of one band split into two components with maxima $\lambda_{1\max}=323$ nm and $\lambda_{2\max}=367$ nm, respectively. At the same time, the excitation spectrum of $\text{Yb}(\text{mphpd})_3$ consists of a broad diffuse band with a maximum at 340 nm. Therefore, the emission spectra of complexes with different ligands were recorded at different excitation wavelengths.

Figure 3 shows the emission spectra of mono- and heteroligand complexes of ytterbium with mbphpd. Upon excitation to the maxima of these

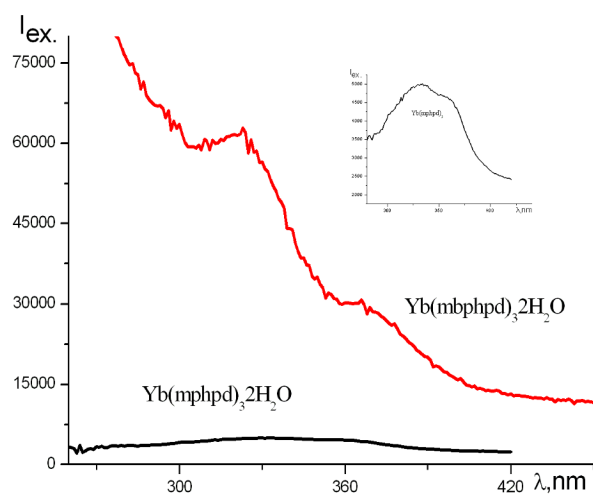


Fig. 2. Excitation spectra of coordination compounds of ytterbium (III)

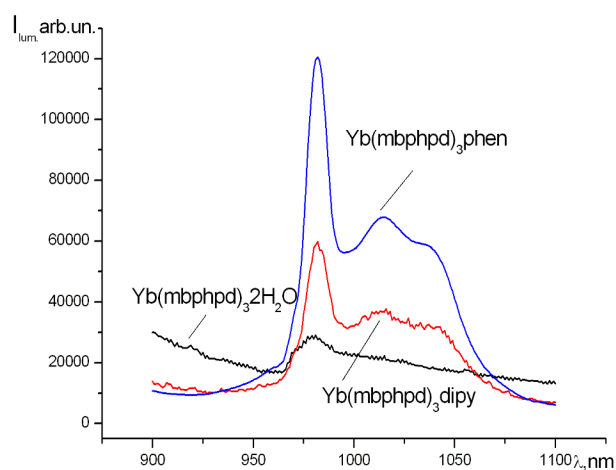


Fig. 3. Luminescence spectra of mono- and heteroligand ytterbium complexes

bands, 4f-luminescence is observed in the near-IR range. The presented spectra contain a broadened band that corresponds to the transition from the excited ${}^2F_{5/2}$ level of the Yb (III) ion.

The band ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ is degenerate; λ_{\max} is 979–981 nm with a shoulder at ~1020–1040 nm, which is due to the influence of the crystal field of the ligand. The presence of emission for ytterbium complexes indicates intramolecular energy transfer from coordinated ligands to the ${}^2F_{5/2}$ Yb(III) level. As can be seen from the figure, for $\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$, the half-width of the line is slightly higher than for HLC, which is due to exchange interactions between neighboring complex molecules and slight concentration quenching by the nearby ytterbium ion. In general, Yb(III) compounds are characterized by a broadened band, but its narrowing in the case of HLC may indicate a decrease in nonradiative transitions. The position of the maxima of the emission bands for the presented monomer complexes also confirms the invariance of the coordination number of the central atom during the formation of heteroligand compounds compared to their hydrated analogue.

A comparison of the relative luminescence intensity of the presented complexes showed that the addition of the donor molecule dipyrindyl and phenantroline leads to a 2-fold and 4-fold increase in emission intensity, respectively, and the position of the band shifts by 4 nm to the long-wavelength region. This is due to the steric effect and the possibility of stacking interaction of the aromatic systems (phenanthroline/dipyrindyl) and the biphenyl substituent in the ligand molecule. In general, such differences in the emission intensity of mono- and heteroligand complexes are due to the absence of water in the nearest coordination environment of the central ion, weaker exchange interactions of the ytterbium ion with the neighboring emitting centers, and, presumably, the deformation of the coordination polyhedron.

Figure 4 shows the luminescence spectra of hydrated and phenanthroline complexes of ytterbium with methacroylacetoophenone and biphenylpentenedione. The shape and position of the bands in the spectra of ytterbium complexes based on mphpd and mbphpd are the same, which is due to the same nature of the ligands.

The displacement of the transition band ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ in all cases does not exceed 3 nm, which indicates the invariance of the coordination node in the studied samples. As can be seen from Fig. 4, compounds based on mbphpd have higher relative emission intensity. The highest absolute values are

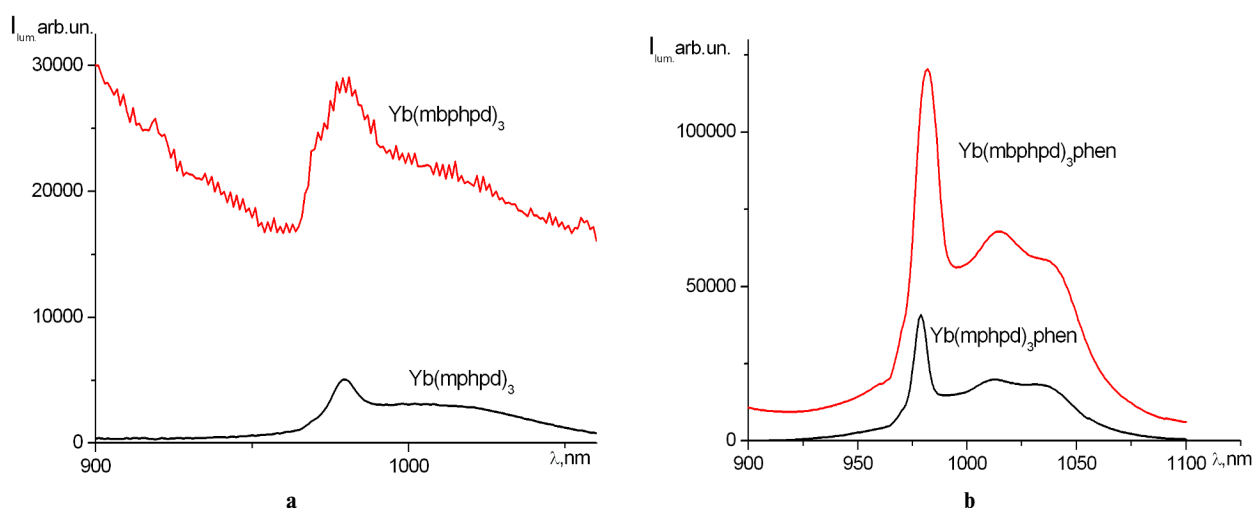


Fig. 4. Comparative emission spectra of the investigated complexes (a) and methacroyacetophenone compounds (b)

achieved in the case of phenanthroline HLC with mbphpd, which is almost three times higher than the luminescent intensity of the phenanthroline complex with methacroyacetophenone (Fig. 4,b). It is obvious that this is due to the additional antenna effect of the biphenyl substituent.

A similar dependence is observed for hydrated complexes (Fig. 4,a), I_{lum} $\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$, is 5 times higher than I_{lum} for $\text{Yb}(\text{mphpd})_3 \cdot 2\text{H}_2\text{O}$. Adding phenanthroline to the composition of the complex, which replaces water molecules in the closest coordination environment of the ytterbium (III) ion, neutralizes the quenching effect of water molecules and, as expected, leads to an increase in the emission characteristics of the studied systems. The addition of a biphenyl substituent and heterocyclic molecules to the composition of the complex probably contributes to the formation of a more «rigid» structure around the central ion, leading to an increase in the luminescent intensity.

The relatively low values of the luminescence intensities of monoligand complexes with aromatic substituents (mphpd and mbphpd) compared to the previously studied similar aliphatic β -diketonate compounds [13] are due to the steric factor, in particular the shielding of the emitting centers by voluminous molecules, as well as the large energy difference between the triplet level of the ligand and the emitting level of the lanthanide ion. Somewhat higher emission intensity for mbphpd may be due to an additional antenna effect or stacking–stacking interaction between adjacent biphenyl substituents. The presence of additional interactions is also evidenced by the blurring of the lines in the luminescence spectrum of $\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$.

Presumably, the presence of one more aromatic ring in the structure of biphenylpentenedione weakens the bond between the Yb(III) ion and the ligand due to the redistribution of electron density and, as a result, promotes more efficient energy transfer from the ligand to the metal. Despite the rather large difference ($\sim 10500 \text{ cm}^{-1}$) between the energy of the triplet level T_1 of the ligand and the resonance level $^2F_{5/2}$ of the Yb^{3+} ion, the energy transfer in the case of heteroligand ytterbium complexes still turned out to be effective. Probably, due to the shielding of the central atom by voluminous aromatic ligands, it was possible to avoid the nonradiative photon deactivation of the excited states.

Figure 5 shows the luminescence spectra of ytterbium metallopolymers. The relative intensity of the presented samples increases in the same sequence as for monomeric compounds: $\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$, $\text{Yb}(\text{mbphpd})_3\text{-dipy}$, and $\text{Yb}(\text{mbphpd})_3\text{-phen}$. Thus,

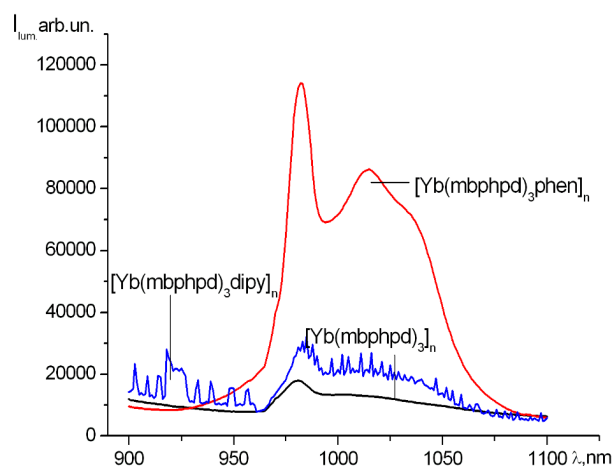


Fig. 5. Luminescence spectra of ytterbium metallopolymers

the value of I_{lum} for the dipyriddy complex is 2 times higher than that of the phenanthroline complex and 6.5 times higher than the relative emission intensity of the polymer $[Yb(mbphpd)_3]_n$. At the same time, the structure of the spectrum of the metallopolymer based on HLC with dipy indicates the presence of significant exchange interactions in this sample.

Comparing heteroligand metal-polymer compounds with their prototypes, it can be seen that in the case of monoligand and dipyriddy complexes, the relative luminescent intensity decreased by almost 2 times. $[Yb(mbphpd)_3 \cdot phen]_n$ shows almost identical I_{lum} values compared to its monomeric counterpart. Such results can be explained by the steric factor, which comes to the fore during polymerization. Voluminous substituents prevent the formation of high molecular weight polymers, which is desirable for exhibiting high emission properties. However, despite the fact that the expected increase in the emission efficiency in the case of metal polymers of ytterbium (III) did not occur, nevertheless $[Yb(mbphpd)_3 \cdot phen]_n$ exhibits a rather high I_{lum} values, commensurate in magnitude with the indices for monomeric β -diketonate complexes of Yb(III) with aliphatic substituents that have been studied earlier [13].

It is known that metallopolymers have a number of advantages, in particular, high thermal and chemical stability and the ability to form films of a given thickness. It is possible to adjust the thickness of the film by changing the physicochemical properties (concentration of metallopolymer, and the nature of a solvent), and physical parameters (speed of rotation of the base). In addition, the synthesized complexes can be precursors of copolymer materials based on methyl methacrylate and styrene. Obtaining copolymers will allow not only reducing the cost, but also increasing the stability of the synthesized materials. Copolymers, due to high adhesion together with moderate viscosity, are able to form uniform (homogeneous) films. Obtaining copolymers allows avoiding the effect of concentration quenching of the emission due to the low concentration of the metal complex in the macromolecular chain. The different molecular weight of copolymers obtained on different carriers (methyl methacrylate, styrene) allows us to establish the peculiarities of the influence of the polymer matrix on the properties of the synthesized materials of various industrial monomers. It will contribute to the production of the film and will allow regulating it purposefully. Since polymer samples are capable of forming film coatings, which is an absolute advantage from a technological point of view, this sample can be used as a precursor of

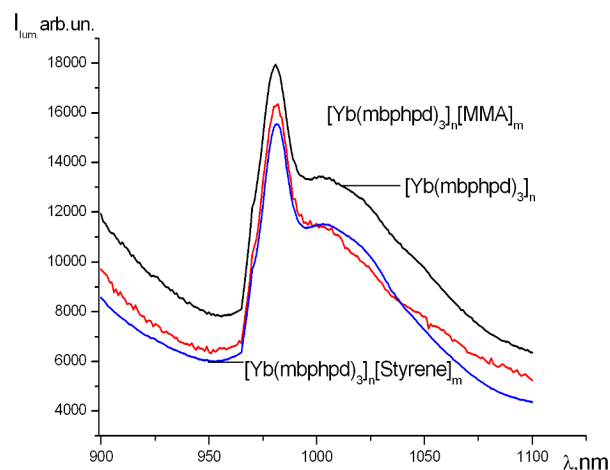


Fig. 6. Emission spectra of Yb(III) copolymer compounds

luminescent materials.

As already mentioned, the presence of an unsaturated substituent in the β -diketonate molecule allows it to be used as a monomer in polymerization and copolymerization reactions. Copolymers $[Yb(mbphpd)_3]_n[MMA]_m$ and $[Yb(mbphpd)_3]_n[Styrene]_m$ were prepared and their spectral-luminescence characteristics were investigated. Compared to the monomeric complex, the intensity decreased almost by half, but the position of the band did not change, in the copolymers, as in the metallopolymer, there is no additional splitting and broadening of the band. Comparative analysis of the luminescence spectra of copolymers and the metal-polymer complex shows a slight decrease in the relative emission intensity of 10–12% (Fig. 6). Moreover, as can be seen from Fig. 6, the lowest relative intensity is typical for $[Yb(mbphpd)_3]_n[Styrene]_m$, i.e. for a copolymer based on an aromatic monomer.

We can assume that this is due to both steric or conformation difficulties and the formation of cross-linked polymer structures caused by the additional stacking-stacking interactions of biphenyl substituents and the styrene fragment. The formation of cross-linked structures reduces the freedom of translational movement of molecules, increases the entropy of the system, causes shielding of the emission centers and, accordingly, a decrease in the emission intensity. However, despite the decrease in the relative emission intensity, these polymer systems are promising precursors of luminescent materials, both powders and films, due to their higher chemical and thermal stability, low cost, and high film-forming ability.

Conclusions

Monomeric, metallopolymer and copolymer complexes of ytterbium (III) based on unsaturated

β -diketone, 2-methyl-5-biphenylpentene-1-3,5-dione (mbphpd), were synthesized. It was determined that β -diketone is bidentately coordinated to the ytterbium ion, and the composition of the monomer complexes corresponds to the following formulae: $\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$ and $\text{Yb}(\text{mbphpd})_3 \cdot \text{phen}/\text{Yb}(\text{mbphpd})_3 \cdot \text{dipy}$. It was shown that the thermal stability increased in the following series: monocomplex – HLC – metallopolymers. The adjunction of additional ligands into the composition of the complex does not cause changes in the close coordination environment of the central ytterbium ion. A coordination polyhedron is a square antiprism.

For all synthesized ytterbium compounds, 4f-luminescence is observed in the near-IR region of the spectrum. The large energy gap between the triplet level of the ligand and the resonant level of the lanthanide ion determines the low emission intensity of $\text{Yb}(\text{mbphpd})_3 \cdot 2\text{H}_2\text{O}$ and the presence of additional exchange interactions, which is reflected in the form of spectral lines (splitting, broadening, blurring of the band, absence of a clear maximum). Substitution of water molecules by dipy and phen donor molecules increases the emission intensity by 2–4 times, respectively, which is due to the absence of the quenching effect of water molecules and the additional antenna effect of phenanthroline and dipyrindyl molecules. Polymerization and copolymerization processes cause a decrease in the relative emission intensity, but contribute to an increase in the chemical and thermal stability of the complexes. During the polymerization of the heteroligand dipyrindyl complex, the emission intensity is reduced by half, and there is a broadening and splitting of the spectral lines, which may be a consequence of the decrease in the symmetry of the coordination polyhedron. The monomeric and polymeric HLC with phenatroline show maximum emission intensity.

Thus, the presented results indicate the possibility of using the synthesized coordination compounds of Yb(III), metal and copolymers as precursors of luminescent materials.

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**СПЕКТРАЛЬНО-ЛЮМІНЕСЦЕНТНІ
ХАРАКТЕРИСТИКИ КООРДИНАЦІЙНИХ СПОЛУК І
МЕТАЛОПОЛІМЕРІВ Yb(III)**

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Синтезовано нові моно- та змішанолігандні (з фенантроліном та дипіридилем) металокомплекс ітербію(III) з 2-метил-5-біфенілпентен-1-3,5-діоном. Методом радикальної полімеризації одержано гомо- та кополімери ітербієвого комплексу з метилметакрилатом та стиролом. Координаційні сполуки досліджено методами ІЧ-спектроскопії, СДВ, термічним і люмінесцентним аналізом. Встановлено, що молекули β-дикетону координуються до центрального атома бідентатно-циклічно, а координаційна сфера монолігандного комплексу доповнюється двома молекулами води, яка у випадку гетеролігандних сполук заміщується молекулами фенантроліну та дипіридилу. Відмічено підвищення термічної стійкості змішанолігандних комплексів та металополімерів порівняно з металокомплексом. Проведено вивчення їх спектральних властивостей і встановлено, що будова координаційного вузла елементарної ланки макромолекул полімерів не змінюється при проходженні процесу полімеризації. Показано, що всі досліджені зразки проявляють 4f-люмінесценцію в ближній інфрачервоній ділянці спектру, при цьому найнижча відносна інтенсивність люмінесценції характерна для гомополімеру та кополімерів ітербію (III), а найвищі її значення демонструють змішанолігандні комплекси з фенантроліном, що дозволяє запропонувати їх як прекурсори люмінесцентних матеріалів.

Ключові слова: ітербій, β-дикетон, комплекс, полімери, змішанолігандні сполуки, люмінесценція.

**SPECTRAL-LUMINESCENT CHARACTERISTICS OF
COORDINATION COMPOUNDS AND METAL
POLYMERS OF Yb(III)**

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New mono- and heteroligand (with phenanthroline or dipyriddy) metal complexes of ytterbium (III) with 2-methyl-5-biphenylpentene-1-3,5-dione were synthesized in this work. Homo- and copolymers of ytterbium complex with methyl methacrylate or styrene were obtained by the method of radical polymerization. Coordination compounds were investigated by IR spectroscopy, diffuse reflectance spectroscopy, thermal and luminescence analyses. It was determined that the β-diketone molecules are bidentate-cyclically coordinated to the central atom, and the coordination sphere of the monoligand complex is supplemented by two water molecules, which in the case of heteroligand complexes (HLC) are replaced by phenanthroline or dipyriddy molecules. An increase in thermal stability of heteroligand complexes and metallopolymers was observed compared to the metal complex. The spectral properties of the

synthesized compounds were studied and it was established that the structure of the coordination node of the elementary link of polymer macromolecules does not change during the polymerization process. It was shown that all the studied samples exhibited 4f-luminescence in the near-infrared region of the spectrum, while the lowest relative luminescence intensity was characteristic of ytterbium (III) homopolymer and copolymers, and the highest values were shown by heteroligand complexes with phenanthroline, which allows us to propose them as precursors of luminescent materials.

Keywords: ytterbium; β-diketone; complex; polymer; heteroligand compound; luminescence.

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