UDC 541.49:546.287:546.661:546.669:547.466 doi: 10.33609/2708-129X.86.6.2020.74-86

O.S. Berezhnytska[1,2*], N.B. Ivakha[1, 2], O.O. Rohovtsov [1], O.K.Trunova[1]

SYNTHESIS AND RESEARCH OF LANTHANIDE-CONTAINING HYBRID MATERIALS BASED ON POLYHEDRAL OLIGOMERIC SILSESQUIOXANES

[1] *V.I.Vernadsky Institute of General and Inorganic Chemistry of NAS of Ukraine*
Akad. Palladin Avenue, 32/34, Kyiv, Ukraine, 03142.
[2] *National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», 37, Prosp. Peremohy, Kyiv, Ukraine, 03056.*
** e-mail: berezhnytska@gmail.com*

New hybrid materials were synthesized based on meteacroacetophenate neodymium (III) and erbium (III) and polyhedral oligomeric sissesquioxane POSS formula $C_{24}H_{72}Cl_8N_8O_{12}Si_8$. A warehouse has been put in place for a new synthesis. The position of the bands in the IR spectra indicate the formation of a hybrid structure of the composition POSS-$[Ln(mphpd)_3]_4$. The shape, position, displacement and splitting of the spectral bands in the electronic spectra and diffuse reflectance spectra indicate the passage of the processes of complexation and the formation of complexes of non-cubic symmetry with coordination number 8. The shift of the bands of supersensitive indicates both additional coordination of nitrogen atoms of the silsesquioxane molecule and some deformation of the coordination polyhedron, which is due to steric difficulties. The results of EDX analysis, the method of dynamic light scattering and microphotographs are consistent and indicate the nanodispersity of the obtained systems.

Keywords: complexes, hybrid structure, luminescence materials, emission, nanosystems.

INTRODUCTION High luminescent characteristics of lanthanide compounds have been of interest to researchers for many years in a row. [1-4]. Oxides, salts and complexes of lanthanides intercalated into polymer matrices, hybrid systems, homo- and copolymers based on monomeric metal complexes are used as precursors of luminescent materials. Each of these areas is relevant. However, the requirements for materials are growing every year: mechanical stability, chemical inertness, thermal stability, high emission characteristics, etc. None of the existing materials can fully meet the requirements. Therefore, there is a need for targeted synthesis of such compounds and the establishment of composition-property correlations. Previous studies [5, 6] have shown the possibility of targeted synthesis of compounds with high emission characteristics. Obtaining homopolymers on the basis of monomeric metal complexes allows not only to obtain chemically homogeneous materials, but also to increase the efficiency of luminescence tenfold. On the other hand, the possibility of obtaining copolymers based on industrial monomers, such as styrene, vinylcarbazole, methyl methacrylate allows to influence the properties and change them by adjusting the ratio of metal complex: monomer. It was found that the luminescence intensity, surface morphology and stability of the material depend on the structure of the industrial monomer. However, due to the volume of organic monomer molecules, they can shield the emitting centers while reducing the emission intensity. In addition, polymers are prone to agglomeration with the formation of globular structures. Therefore, another approach to obtaining functional nanomaterials is of interest, namely the synthesis of hybrid structures based on metal complexes. The role of the matrix is to form a spatial structure, and the complex has special properties. Fixation of complexes on the matrix can occur in two ways. For example, due to the physical interaction of components by precipitation, spraying, sorption, microencapsulation, dispersion, etc. complex on the media. In this case, the functional component is usually linked to the matrix through physical interaction. In the formation of organo-inorganic materials with different morphology as an organic matrix often use mesh polymers, in which inorganic components act as fillers dispersed in polymers. To obtain such systems use sol-gel technologies [7], which allow to obtain materials with nanodispersed inorganic phase at the molecular level. The materials formed by this method are polydisperse in size and heterogeneous in chemical composition, which of course impairs their properties [8]. In another variant, the complex is fixed by covalent bonds. At the same time, a careful selection of both the ligand and the matrix comes to the fore. Functionalized polyhedral oligomeric silsesquioxanes (POSS) are proposed as a matrix. Hybrid materials based on POSS are quite easy to synthesize, they have high thermal and optical properties. One of the current directions in the creation of organo-inorganic is the selection of methods for obtaining nanostructuring agents that are able to be covalently attached to the matrix at the molecular level. This approach allows you to purposefully synthesize materials with different ratios of components and influence the properties of the final product [9-11]. Octahedral POSS of the general formula $R_8S_8O_{12}$ [12-14] seem to be especially promising compounds for the creation of hybrid organo-inorganic systems. Such molecules consist of a central inorganic nucleus of cubic shape with a size of ~ 1.5 nm and organic substituents R with various reactive groups, which allows for further modification of these compounds. For example, the inserting into such systems of compounds with luminescent properties can increase the emission characteristics. In [15] it was shown that the inserting of nanoparticles into the POSS promotes the growth of electroluminescence in the blue region of the spectrum, despite the fact that the obtained material is not a chemical interaction but the intercalation of nanoparticles in the POSS matrix. The use of hybrid structures as materials allows to increase the thermal stability of materials [16-18] due to the formation of chain or mesh structures, reduce emission quenching processes and sensitize luminescence due to additional covalent bonds that act as additional linkers.

Since the molecules of the compounds that attach to the surface of the matrix set the properties of the materials, it is paramount to study the properties of such compounds and compare them with the properties of hybrid systems based on them. Previously, complexes of a number of lanthanides with methacroylacetophenone have been synthesized and described [19, 20]. Their structure and spectral-luminescent properties have been studied. The use of these compounds as precursors of hybrid systems is relevant. Therefore, this study is based on the synthesis, establishment of the structure and properties of the system composition POSS-[Er(mphpd)$_3$]$_4$ and POSS-[Nd (mphpd)$_3$]$_4$.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Synthesis of Ln (III) complexes with methacroylacetophenone (mphpd) was performed by the interaction of metal salts and mphpd sodium salt at a molar ratio of 1: 3 and pH = 8-8.5 in aqueous solutions, a detailed method of synthesis presented in paper [21].

POSS with the formula $C_{24}H_{72}Cl_8N_8O_{12}Si_8$ was purchased and used without further purification. Hybrid materials were obtained by direct synthesis by the interaction of POSS and β-diketonate complexes of neodymium (III) and erbium (III) in a mixture of $CHCl_3$-C_2H_5OH in a ratio of 1: 4, respectively. The synthesized compounds were investigated by elemental analysis, FTIR, electron and fluorescence spectroscopy, thermal analysis, dynamic light scattering and electron microscopy (SEM).

The hydrate composition of the complexes and their thermal characteristics were determined by the DTA method. Thermograms were recorded on a derivatograph Q – 1500 ° D of the system F. Paulik, J. Paulik, L. Erdey in the temperature range 20 - 500°C with a heating rate of 5°C/min. in a platinum crucible in the presence of a carrier (anhydrous Al_2O_3).

IR spectra were recorded on a Specord M80 spectrometer in the range of 400-4000 cm^{-1} in KBr pellet.

Diffuse reflection spectra in the range 300 - 1100 nm were recorded on a UV-VIS-IR Shimadzu UV-3600 spectrophotometer.

The excitation and luminescence spectra of solid complexes were recorded on a spectrofluorimeter Fluorolog FL 3-22, Horiba Jobin Yvon (Xe-lamp 450 W) with a light filter OS 11, with their subsequent adjustment taking into account the radiation distribution of the xenon lamp and the sensitivity of the photomultiplier tube. The InGaAs (DSS-IGA020L, Electro-Optical Systems, Inc, USA) photoresistance was used as a radiation receiver for the IR region when cooled to liquid nitrogen temperature.

The method of dynamic light scattering was used to determine the particle size of complexes dissolved in dimethylformamide at 25°C with Zeta Sizer Malvern.

Microphotographs were recorded on a scanning electron microscope (SEM) Tescan

Mira 3.

The results of EDX analysis indicate a uniform distribution of the metal in the hybrid material. The content of elements (ww,%) in the sample is: carbon 44.35, nitrogen 4.26, oxygen 37.37, sodium 0.42, silicon 11.93, neodymium 1.67.

In the IR spectra of the synthesized hybrid materials in the range of 400–650 cm^{-1} there are oscillation bands that correspond to the valence oscillations of the bonds (Ln-O) and (Ln-N) and the deformation oscillations of the chelate ring. The decrease in intensity compared to the spectra of $Ln(mphpd)_3$ complexes is due to the appearance of valence oscillations of the Ln-N bond and steric difficulties that arise when the complex coordinates to the sizable siloxane molecule. The presence of additional bands in this region indicates both the unevenness of the bonds in the metal cycle and the appearance of additional oscillations corresponding to the oscillations of the deformation of the Si-O bond (500 cm^{-1}, 660 cm^{-1}). An additional intense broad band appears in the IR spectra, which is characterized by fluctuations in the valence of the Si-O-Si siloxane bond with a maximum of 1050 cm^{-1}. The presence of a wide absorption band in the range of 1500–1700 cm^{-1}, characterized by valence oscillations of ν (CO) and ν (CC), confirms the bidentate-cyclic coordination of β-diketonates [22]. The wide band with the highest frequency (~1540-1660 cm^{-1}) includes the superposition of lines consisting of symmetric valence oscillation ($C\overset{\cdots}{=}O$), valence oscillation C=C bond, ν_{ph}, asymmetric valence oscillation ($C\overset{\cdots}{=}C$) and deformation oscillations of the amino group.

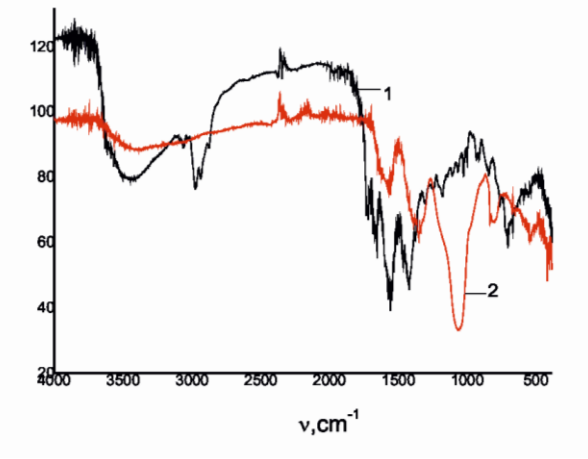

Fig.1 IR-spectra $Nd(mphpd)_3$ (1), $POSS\text{-}[Nd(mphpd)_3]_4$ (2)

Thus, the shape and position of the bands in the IR spectra indicate the formation of a hybrid structure of the composition POSS- $[Ln(mphpd)_3]_4$.

The absence of bands corresponding to the valence vibrations of water molecules suggests that the coordination of complexes to amino groups occurs due to the substitution of water molecules in the complexes.

The results of thermal analysis indicate the absence of water molecules in the obtained materials and high stability of hybrid structures. The stability of hybrid systems is proportional to the stability of metal polymers, which indicates the chemical rather than intermolecular interaction of siloxane molecules with β-diketonate complexes.

In the electronic absorption spectra of the studied systems, there are bands π→π* of ligand transitions and bands f-f transitions of lanthanide ion, which are part of the complexes. If in the absorption spectra of the solutions there is a small shift in the maxima of the absorption bands, it indicates the

Table 1
Assignment of lines in diffuse reflectance spectra of neodymium compounds

Transition	Nd_{aq}^{3+}	$Nd(mphpd)_3$	POSS-NdL_3
$^4I_{9/2}\rightarrow{}^2P_{1/2}$	23064	23255	20920 weak
$^4I_{9/2}\rightarrow{}^4G_{9/2}$	19560	19520	19531
$^4I_{9/2}\rightarrow{}^4G_{7/2}$	19157	19050	19065
$^4I_{9/2}\rightarrow{}^4G_{5/2},\ {}^2G_{7/2}$	17360	17168	17240
$^4I_{9/2}\rightarrow{}^4F_{9/2}$	14720	14700	14727
$^4I_{9/2}\rightarrow{}^4F_{7/2}$	13513	13400	13420
$^4I_{9/2}\rightarrow{}^4H_{9/2}$	12594	12470	12480
$^4I_{9/2}\rightarrow{}^4F_{3/2}$	11560	11430	11470

Table 2
Assignment of lines in diffuse reflectance spectra of erbium compounds

Transition	Er^{3+}	$Er(mphpd)_3$	POSS-ErL_3
$^4I_{15/2}\rightarrow{}^4G_{11/2}$	26585	26309	26525
$^4I_{15/2}\rightarrow({}^2G,\ {}^4F)_{9/2}$	24744	24520	24600
$^4I_{15/2}\rightarrow{}^4F_{5/2}$	22378	22270	22173
$^4I_{15/2}\rightarrow{}^4F_{7/2}$	20709	20538	20530
$^4I_{15/2}\rightarrow{}^4H_{11/2}$	19334	19190	19250
$^4I_{15/2}\rightarrow{}^4S_{3/2}$	18570	18450	18426
$^4I_{15/2}\rightarrow{}^4F_{9/2}$	15452	15324	15320
$^4I_{15/2}\rightarrow{}^4I_{9/2}$	12567	12488	12485

substitution of water molecules in the immediate coordination environment without a significant change in the geometry of the coordination polyhedron [23].

In the spectra of hybrid systems, a stronger splitting of the spectral lines corresponding to supersensitive transitions is observed in comparison with similar bands in the electronic spectra of complexes (Fig.2).

Thus, the absorption band corresponding to the transition $^4I_{9/4} \rightarrow {}^2S_{3/2},\ {}^4F_{7/2}$ is split into 3 components, the absorption band corresponding to the transition $^4I_{9/4}\rightarrow{}^4F_{3/2}$ is split into 4 components, which indicates the non-cubic symmetry of the ligand field and slight deformation of the coordination polyhedron of hybrid structures, compared with metal complexes (Table 1). In the [POSS-$[Nd(mphpd)_3]_4$ spectra, the absorption band corresponding to the $^4I_{9/2}\rightarrow{}^2P_{1/2}$ transition is difficult to differentiate due to the shift of the charge transfer band due to the replacement of water molecules by the sizable POSS molecule.

The half-width of the supersensitive transition $^4I_{9/4}\rightarrow{}^4G_{5/2},\ {}^2G_{7/2}$ is (-310 cm^{-1}) and (+270 cm^{-1}), the band contains a split shoulder, which probably indicates a high symmetry of the ligand field, but a significant deformation of the coordination polyhedron. The shape and position of the bands in the electronic spectra and diffuse reflectance spectra of POSS- $[Nd\ (mphpd)_3]_4$ corresponds to the coordination number 8 [24]. The ratio of the intensities of the absorption bands in the region of supersensitive transitions in the spectra of the crystalline sample at 12480 cm^{-1} ($^4I_{9/2}\rightarrow{}^4H_{9/2}+{}^4F_{5/2}$) and 17240$см^{-1}$ ($^4I_{9/2}\rightarrow{}^2G_{7/2}+{}^4G_{5/2}$) for POSS-$[Nd(mphpd)_3]_4$ is 0.83, while for $Nd(mphpd)_3$ - 0.57, and for the aquacomplex - 1.12, which suggests a decrease in symmetry in the case of a hybrid system compared to the original metal complex and an increase compared to the aqua ion.

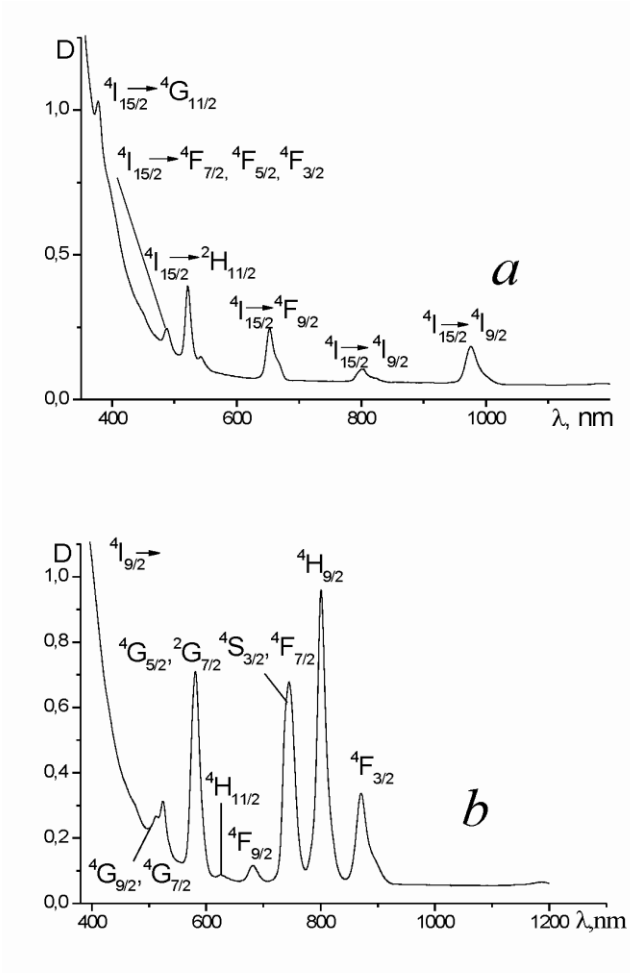

Fig.2 – Diffuse reflectance spectra POSS-Er(mphpd)$_3$ (*a*)and POSS-Nd(mphpd)$_3$ (*b*)

The shape and position of the bands in electronic spectra and diffuse reflectance spectra practically do not differ, which indicates a similar structure of compounds in solution and in the solid state. In the electronic spectra and diffuse reflectance spectra of Er(III) complexes, a set of bands corresponding to erbium ion transitions from the $^4I_{15/2}$ ground state is observed. The bands $^4I_{15/2} \rightarrow {}^2H_{11/2}$ (520 нм) and $^4I_{15/2} \rightarrow {}^4G_{11/2}$ (377 nm) are the most sensitive to changes in the ligand field (Table 2). As can be seen from the table, the bands are shifted compared to metal complexes in the short-wavelength region, which indicates the deformation of the coordination polyhedron due to the coordination of the volume molecule of the polyhedral oligomeric silsesquioxane. It should be noted that compared to the bands of the aquaion there is a slight long-wavelength displacement. Thus, hybrid systems occupy an intermediate position in symmetry between aqua and metal complexes.

The shape, position, displacement and splitting of the spectral bands in the electronic spectra and diffuse reflectance spectra indicate the passage of the processes of complexation and the formation of complexes of non-cubic symmetry with co-ordination number 8. Thus, the presence of insignificant displacements of the absorption bands indicates the invariance of the coordination environment and the geometry of the coordination polyhedron for metal complexes and hydride systems based on them. The shift of the bands of supersensitive transitions in comparison with the spectra of metal complexes indicates both additional coordination of nitrogen atoms of the silsesquioxane molecule and some deformation of the coordination polyhedron, which is due to steric difficulties. According to the set of data from thermal and spectroscopic studies, the structure of the obtained hybrid material can be represented as follows (Fig. 3)

The method of dynamic light scattering shows that the studied systems are polydisperse with a uniform distribution of the dispersed phase in the dispersion medium.

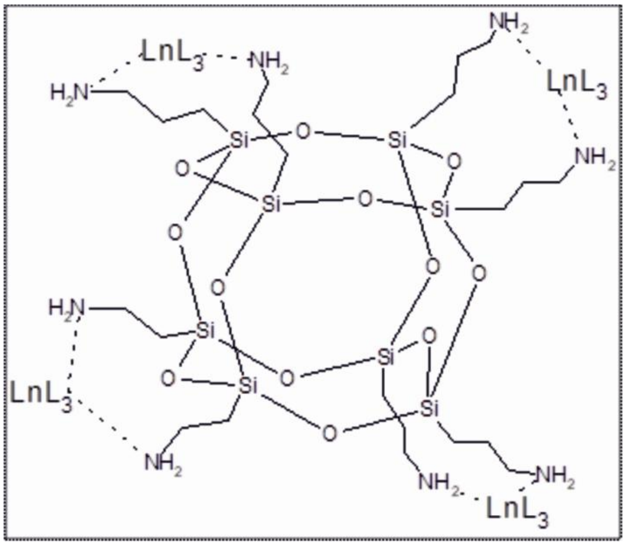

Fig.3 – Approximate structure of the hybrid based on POSS-MPOSS[Ln(mphpd)$_3$]$_4$

The predominant particle radius is 20 nm, such particles in the system 97%. In the case of monocomplexes, the particle size was in the range of 30-50 nm. Obviously, the formation of hybrid systems reduces the dispersion of particles, which may be due to the high dispersion of silsesquioxanes, which in turn contributed to changes in surface morphology, shape and size of nanoparticles.

The analysis of microphotographs confirms the conclusions made on the basis of the method of dynamic light scattering and testifies to the nanodispersity of the obtained systems. Microphotographs of hybrids (Fig. 4) differ significantly from previously studied monomeric, metalpolymeric and copolymeric compounds. In microphotographs of metal-polymer and copolymer powders, spherical particles were clearly distinguished, and depending on the structure of the industrial monomer (styrene, vinylcarbazole) their size differed significantly, for compounds based on

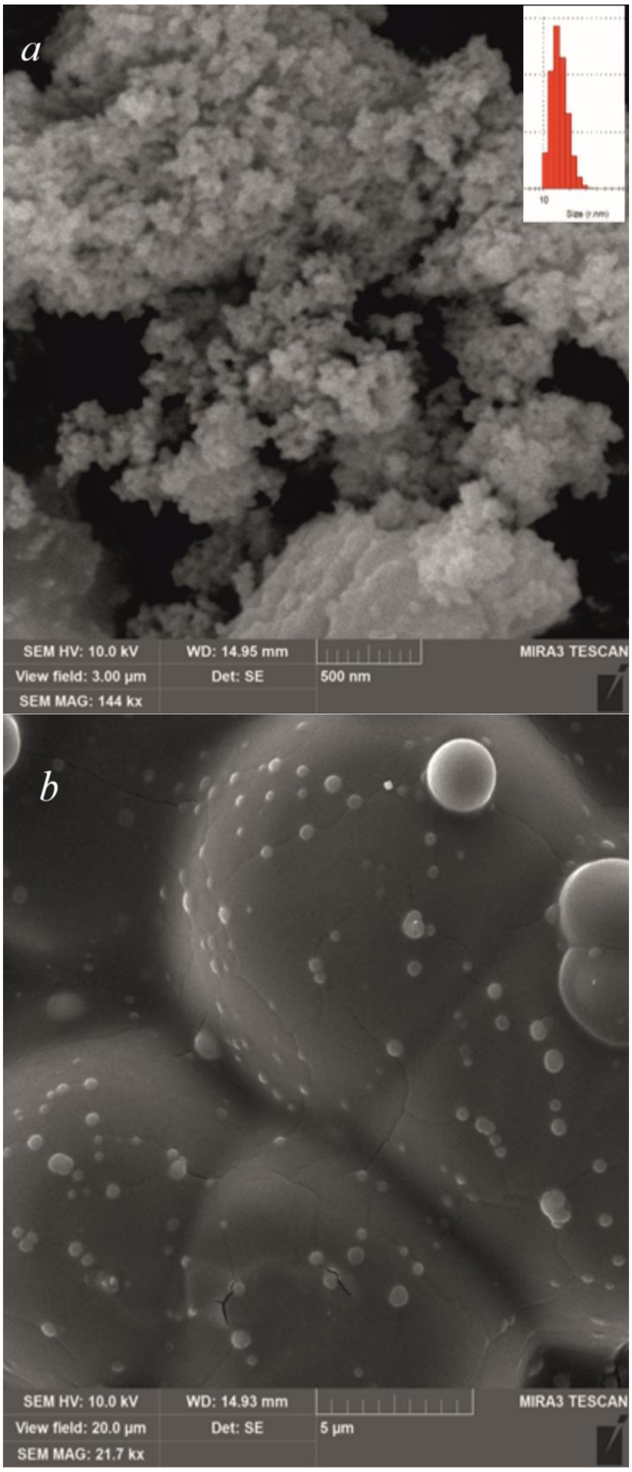

Fig.4 – SEM- Microphotographs of hybrid structures powder (*a*) and film (*b*) [POSS-Nd(mphpd)$_3$]$_n$

methyl methacrylate was characterized by the formation of a spongy structure [5, 18]. In the case of hybrid systems, we observe significant differences from the previously studied monomeric, metal-polymer and copolymer compounds. Surface morphology also corresponds to amorphous systems, however, this is the only similarity. Loose, spongy, layered homogeneous structure is an intermediate between monomer complexes and metal polymers based on methyl methacrylate. Microphotographs of the film indicate the absence of aggregation. It is known that POSS molecules can be chemically integrated into the structure of the polymer matrix due to the interaction of reactive POSS groups with functional groups of monomers, oligomers and polymers that form the polymer matrix [25]. The same happens in the case of coordination of POSS molecules thr functional groups to metal complexes (Fig. 4). The difference between microphotographs of films and powders is due to the different morphology of the surface. Films were obtained by precipitation of solutions with a concentration of $5{\cdot}10^{-4}$M.

If in the case of powders there is a slight agglomeration, then this process is absent in the films, due to both the degree of dilution of the solutions and the stabilizing effect of the bulk molecules of polyhedral oligomeric silsesquioxanes.

Thus, the results of EDX analysis, the method of dynamic light scattering and microphotographs are consistent and indicate the nanodispersity of the obtained systems. The main idea of the study was to obtain materials with high luminescent properties, so the study of luminescent characteristics was of considerable interest. For effective luminescence, the energy difference between the triplet level of the ligand and the singlet level of the lanthanide ion should be in the range of 2500-3500 cm^{-1}. Therefore, for the experimental determination of the energy of singlet and triplet levels in the studied β-diketonate complexes, the fluorescence and phosphorescence spectra of gadolinium-containing compounds were studied, which allowed to calculate the energies of triplet levels [26].

Studies have shown that for the Er(III) ion the energy of the singlet level is 18600 cm^{-1}, so the difference between the singlet and triplet level is low, is in the range of 1100-2000 cm^{-1}, which explains the low luminescence efficiency Er(mphpd)$_3$. It is known that functionalized POSS molecules are able not only to show luminescence, but also to enhance luminescence in the blue region. However, studies have shown that the luminescence intensity of POSS-[Er(mphpd)$_3$]$_4$, as well as the metal complex, is low, which indicates that the main contribution to the emission is the coordination fragment (Fig. 5). The expected sensitization effect was not observed, which is due to both energy dependence and shielding of the radiating center by the bulky POSS molecule.

In contrast to erbium complexes, for neodymium compounds the luminescence intensity is quite high (Fig. 6). The luminescence spectrum of POSS-[Nd(mphpd)$_3$]$_4$ consists of three bands corresponding to the transitions from the excited level of the Nd(III) $^4F_{3/2}$ ion to the base level multiples $^4I_{9/2}$ (878 and 898 nm),

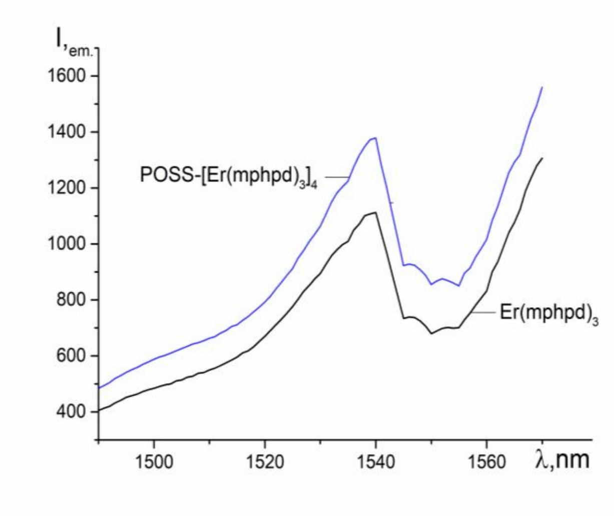

Fig. 5. Luminescence spectra of Er(III) compounds

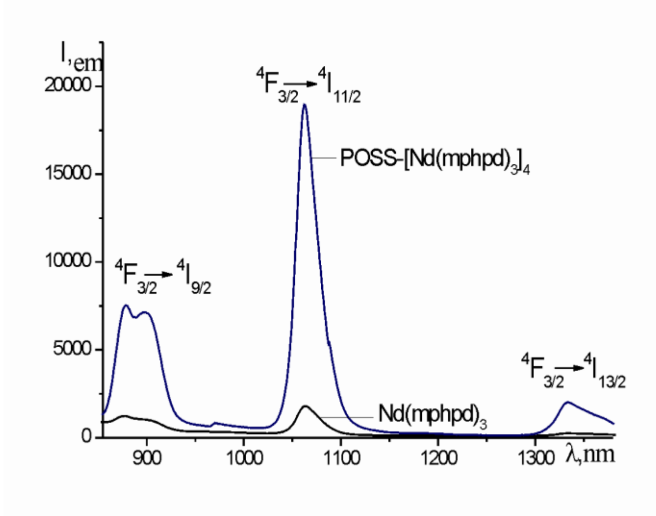

Fig. 6. Luminescence spectra of Nd(III) compounds

$^4I_{11/2}$ (1062 nm) and $^4I_{13/2}$ (1333 nm). The absence of band splitting, which corresponds to the transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$, indicates a fairly high symmetry of the complex and the presence of a single coordination center. The transition band $^4F_{3/2} \rightarrow {}^4I_{9/2}$ is split into two components, which indicates non-cubic symmetry of the ligand field. As can be seen, the maxima of the transitions are slightly shifted to the long-wavelength region, but the band of the most intense transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ is practically not shifted, which indicates the same coordination environment of the central ion in both compounds. As can be seen from the figure, the luminescence intensity of POSS-[Nd(mphpd)$_3$]$_4$ is 10 times higher than for neodymium methacrylacetophenoate (III).

Thus, obtaining hybrid systems based on coordination compounds of lanthanides (Nd(III), Er(III)) allows to obtain materials with high luminescent characteristics.

CONCLUSIONS. In this work synthesizes new hybrid systems based on the β-diketonate complexes of lanthanides and polyhedral oligomeric silsesquioxanes, which allows to increase the thermal and chemical resistance of materials. The composition and structure of the synthesized compounds are established. It is shown that the replacement of water molecules in the coordination environment of lanthanide complexes by POSS functional groups allows to obtain hybrid materials for special purposes. It is established that the structure of the coordination polyhedron c.a. it does not change, but only slightly deforms. Analysis of microphotographs and the method of dynamic light scattering indicate the formation of nanosystems with particles of about 20 nm. Microphotographs of the films indicate the stabilizing effect of POSS molecules, which prevents agglomeration. It is shown that these complexes exhibit high luminescence intensity, which allows their use as precursors of luminescent materials. The presence of a large number of emitting centers allows to offer these compounds as markers for the protection of securities.

ACKNOWLEDGEMENT

The team of authors would like to express their gratitude to the colleagues of the A.V.Bohatsky Physico-Chemical Institute of NASU Smola S.S and Rusakova N.V.

The work is done within the theme № III-03-12 (310E) «New inorganic compounds and highly efficient functional materials (physico-chemical basis of design? Heterogeneous-heterophase synthesis, structure, properties)»

СИНТЕЗ ТА ДОСЛІДЖЕННЯ ЛАНТАНІДВМІСНИХ ГІБРИДНИХ МАТЕРІАЛІВ НА ОСНОВІ ПОЛІЕДРАЛЬНИХ ОЛІГОМЕРНИХ СИЛСЕСКВІОКСАНІВ

О.С. Бережницька[1,2*], Н.Б. Іваха[1, 2], О.О. Роговцов[1], О.К.Трунова[1]

[1]Інститут загальної та неорганічної хімії ім.В.І.Вернадського НАН України, просп. Академіка Палладіна, 32/34, Київ, 03142, Україна
[2]Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського», просп. Перемоги, 37, Київ, 03056, Україна
[*]e-mail: olekberez@gmail.com

Нові гібридні матеріали були синтезовані на основі метакроїлацетофеноату неодиму(III) та ербію (III) та поліедрального олігомерного силсесквіоксану (POSS) загальної формули $C_{24}H_{72}Cl_8N_8O_{12}Si_8$. Встановлено склад та будову синтезованих сполук. В ІЧ-спектрах синтезованих гібридних матеріалів в діапазоні 400–650 см$^{-1}$ присутні смуги коливань, що відповідають валентним коливанням зв'язків (Ln-O) і (Ln-N) та деформаційним коливанням хелатного кільця. Зниження інтенсивності порівняно зі спектрами комплексів $Ln(mphpd)_3$ обумовлено появою валентних коливань зв'язку Ln-N та стеричними труднощами, які виникають, при координації молекули силоксану. В ІЧ-спектрах з'являється додаткова інтенсивна широка смуга, характерна для валентного коливання зв'язку Si-O-Si з максимумом 1050 см$^{-1}$. Наявність широкої смуги поглинання в діапазоні 1500–1700 см$^{-1}$, підтверджує бідентатно-циклічну координацію β-дикетонатів. Таким чином, форма та положення смуг в ІЧ-спектрах вказують на утворення гібридної структури POSS-$[Ln(mphpd)_3]_4$. Форма, положення, зміщення та розщеплення спектральних смуг в ЕСП та ЕСДВ свідчить про проходження процесів комплексоутворення та одержання комплексів некубічної симетрії з К.Ч. лантаніду 8. Наявність незначних за величиною (до 200см$^{-1}$) зміщень смуг поглинання свідчить про незмінність координаційного оточення та геометрії координаційного поліедру для комплексів металів та гібридних систем на їх основі. Зміщення смуг надчутливих переходів порівняно зі спектрами металокомплексів лише вказує на додаткову координацію атомів азоту молекули силсесквіоксану та деяку деформацію координаційного поліедру, що обумовлено стеричними труднощами. Результати EDX аналізу, методу динамічного розсіяння світла та мікрофотографій добре узгоджуються та свідчать про нанодисперсність отриманих систем.

Ключові слова: комплекси, гібридні структури, люмінесцентні матеріали, емісія, наносистеми

СИНТЕЗ И ИССЛЕДОВАНИЕ ЛАНТАНИДСОДЕРЖАЩИХ ГИБРИДНЫХ МАТЕРИАЛОВ НА ОСНОВЕ ПОЛИЭДРАЛЬНЫХ ОЛИГОМЕРНЫХ СИЛСЕСКВИОКСАНОВ

А.С. Бережницкая[1,2*], Н.Б. Иваха[1, 2], А.А. Роговцов[1], Е.К.Трунова[1]

[1]*Институт общей и неорганической химии им. В.И. Вернадского НАН Украины, просп. Академика Палладина, 32/34, Киев, 03142, Украина*
[2]*Национальный технический университет Украины «Киевский политехнический институт имени Игоря Сикорского», просп. Победы, 37, Киев, 03056, Украина*
[*]*e-mail:* olekberez@gmail.com

Новые гибридные материалы были синтезированы на основе метакроилацетофеноата неодима(III) и эрбия (III), а также полиэдрального олигомерного силсесквиоксана (POSS) общей формулы $C_{24}H_{72}Cl_8N_8O_{12}Si_8$. Установлено состав и строение синтезированных соединений. В ИК-спектрах синтезированных гибридных материалов в диапазоне 400–650 см$^{-1}$ присутствуют полосы колебаний, которые отвечают валентным колебаниям связей (Ln-O), (Ln-N) и деформационным колебаниям хелатного кольца. Снижение интенсивности по сравнению со спектрами комплексов Ln(mphpd)$_3$ обусловлено появлением валентных колебаний связи Ln-N и стерическими трудностями, которые возникают при координации силоксана. В ИК-спектрах гибридов проявляется дополнительная интенсивная широкая полоса, характерная для валентного колебания связи Si-O-Si, с максимумом 1050 см$^{-1}$. Наличие широкой полосы в диапазоне1500–1700 см$^{-1}$ подтверждает бидентатно-циклическую координацию β-дикетонатов. Таким образом, форма и положение полос в ИК-спекрах указывают на образование гибридной структуры POSS-[Ln(mphpd)$_3$]$_4$. Форма, положение, смещение и расщепление спектральных полос в ЭСП и ЭСДО свидетельствуют о прохождении процессов комплексообразования и получении комплексов некубической симметрии с К.Ч. лантанида 8. Наличие незначительных по величине (до 200см$^{-1}$) смещений полос поглощения свидетельствует о неизменности координационного окружения и геометрии координационного полиэдра для комплексов металлов и гибридных систем на их основе. Смещение полос сверхчувствительных переходов по сравнению со спектрами металлокомплексов указывает лишь на дополнительную координацию атомов нитрогена молекулы силсесквиоксана и некоторую деформацию координационного полиэдра, обусловленную стерическими трудностями. Результаты EDX анализа, метода динамического рассеивания света и микрофотографий хорошо согласуются и свидетельствуют о нанодисперсности полученных систем.

Ключевые слова: комплексы, гибридные структуры, люминесцентные материалы, эмиссия, наносистемы.

REFERENCES

1. Santos H.P., Gomes E.S., Santos M.V., D'Oliveira K.A., Cuin A., Martins J.S., Quirino W.G., Marques L.F. Synthesis, structures and spectroscopy of three new lanthanide β-diketonate complexes with 4,4'-dimethyl-2,2'-bipyridine. Near-infrared electroluminescence of ytterbium (III) complex in OLED. *Inorganica Chimica Acta* 2018. - doi: https://doi.org/10.1016/j.ica.2018.09.030
2. Bünzli J-C. G., Eliseeva S. V. Rare earths: jewels for functional materials of the future. *New J. Chem*. 2011. **35**: 1165-1176.
3. Ning Y., Zhu M., Zhang J.-L. Near-infrared (NIR) lanthanide molecular probes for bioimaging and biosensing. *Coordination Chemistry Reviews*. 2019. **399**: 213028.
4. Bünzli J-C. G. Review: Lanthanide coordination chemistry from old concept to coordination polymers. *J. of Coordination Chemistry*. 2014. http: //dx.doi.org/10.1080/00958972.2014.957201.

5. Berezhnytska O., Savchenko I., Ivakha N., Trunova O., Rusakova N., Smola S., Rogovtsov O. Synthesis, characterization and luminescent properties of polymer complexes of Nd(III) with *β*-dicarbonyl ligands. *Nanoscale Research Letters*. 2017. **12.** (338). 1-8.

6. Savchenko I.A., Berezhnytska A.S., Ivakha N.B., Trunova E.K. New nanosized systems based lantanide diketonate complexes for OLEDs In book Springer Proceedings in Physics *«Nanocomposites, Nanophotonics, Nanobiotechnology, and Applications»*. 2015. **15685:** 94.

7. Starovoitova I.A., Khozin V.G., Abdrakhmanova L.A., Ushakova G.G Hybrid organo-inorganic binders obtained by sol-gel technology, and their practical use in composite materials. *Proceeding Of KSUCE*. 2010. **2**. 14.

8. Babkina N.V., Martyniuk I.S., Alekseeva T.T. Features of the viscoelastic behavior of organo-inorganic Ti-containing copolymers and interpenetrating polymer networks based on them. *Polymer Journal*. 2013. **35**. 237-242.

9. Aguiar F. P., Costa I. F., Espínola J. G. P., Faustino W.M., Moura J. L., Brito H.F., Paolini T.B., Felinto M.C.F.C., Teotonio E.E.S. Luminescent hybrid materials functionalized with lanthanide ethylenodiaminotetraacetate complexes containing β-diketonateas antennaligands. *Journal of Luminescence*. 2016. **70**. 538–546.

10. Sui Y.-L., Yan B. Luminescent molecular hybrid system derived from 2-furancarboxylic acid and silylated monomer coordinated to rare earth ions. *Applied Surface Science*. 2006. **252**. 4306–4311.

11. Yan B. Lanthanide-Functionalized Metal–Organic Framework Hybrid Systems To Create Multiple Luminescent Centers for Chemical Sensing. *Acc. Chem. Res*. 2017. **50**. 2789-2798.

12. Pielichowski K., Njuguna J., Janowski B., Pielichowski J. Polyhedral oligomeric silsesquioxanes (POSS)-containing nanohybrid polymers. *Adv. Polym. Sci*. 2006, **201:**225-296. https://doi.org/10.1007/12_077

13. Zhang W., Muller A.H.E. Architecture, self-assembly and properties of well-defined hybrid polymers based on polyhedral oligomeric silsequioxane (POSS). *Progress in Polymer Science*. 2013. **38**. .8: 1121-1162. https://doi.org/10.1016/j.progpolymsci.2013.03.002

14. Zhou H., Ye Q., Xu J. Polyhedral oligomeric silsesquioxane-based hybrid materials and their applications. *Mater.Chem.Front*. 2017. **1**: 212-230. https://doi.org/10.1039/C6QM00062B.

15. Cho H., Hwang D., Lee J., Jung Y., Park J., Lee J., Lee S., Shim H. Electroluminescent polyhedral oligomeric silsesquioxane-based nanoparticle. *Chem. Mater*. 2006. **18**: 3780-3787. https://doi.org/10.1021/cm061011f.

16. Matejka L., Murias P., Plestil J. Effect of POSS on thermomechanical properties of epoxy–POSS nanocomposites *Eur.Polym.J*. 2012. **48**. 260–274. https:/ /doi.org/10.1016/ j.eurpolymj.2011.11.009.

17. Chi C., Li X. Near-Infrared Emissive Lanthanide Hybridized Nanofibrillated Cellulose Nanopaper as Ultraviolet Filter. *Carbohydrate Polymers*. 2018. **186**. 176-183, https://doi.org/10.1016/j.carbpol.2017.12.088.

18. Ma J., Yan B. Novel hybrid materials of lanthanide coordination polymers ion exchanged Mg-Al layered double hydroxide: Multi-color photoluminescence and white color thin film. *Dyes and Pigments*. 2018. **153**. 266-274.

19. Berezhnytska O. S., Ivakha N. B., Trunova O. K., Savchenko I. O., Rusakova N. V. The new NIR-emitting compounds based on β- dicarbonyl ligands. *Molecular Crystals and Liquid Crystals*. 2018. **670**. 1. 20–30.
20. . Ivakha N.B, Savchenko I.O., Berezhnytska O.S.,. Rusakova N.V,. Trunova O.K Ytterbium metal polymers as precursors of luminescent materials emitting in the near infrared region. *Applied Nanoscience. 2020.* https://doi.org/10.1007/s13204-020-01342-w.
21. Berezhnytska O.S., Savchenko I.O., Trunova O.K., Rohovtsov O.O., Ivakha N.B. New precursors for producing nanomaterials based on a neodymium complex. *Dopovidi NAS of Ukraine*. 2012. **11.** 132-138.
22. Nakamoto K. Infrared spectroscopy of inorganic and coordination compounds. – M.:Mir. -1991. – 536p.
23. Davydenko N.K., Yatsymirskyi K.B. Patterns of band shift in the spectra of lanthanide ions upon complexation in solutions. *TEC*. 1970. **6**. 5. 620–628.
24. Sinha S. D. Spectroscopic Investigation of Some Neodimium. *Spectrochim. Acta.* 1966. **22**. 57-62.
25. Humenna M.A., Shevchuk A.V., Boichuk V.V., Klymenko N.S., Shevhenko V.V. The influence of chemical nature of the end groups on the structure and properties of amino- and hydroxyl-containing oligomeric silsesquioxanes *Dopovidi NAS of Ukraine*. 2007. **10.**128-134.

Надійшла 12.06.20