Optics and Spectroscopy, 2022, Vol. 130, No. 1

02

Role of LMCT states in luminescence excitation processes in europium indolecarboxylates

© V.I. Tsaryuk, K.P. Zhuravlev

Fryazino Branch, Kotel'nikov Institute of Radio Engineering and Electronics, Russian Academy of Sciences,
Fryazino, Moscow oblast, Russia

e-mail: kpz225@mail.ru

Received June 30, 2021
Revised June 30, 2021
Accepted July 14, 2021

The luminescence excitation energy transfer in europium and terbium indole-3-carboxylates, indole-3-acetates and indole-3-propionates as well as ternary indolecarboxylates containing 1,10-phenanthroline and 2,2'-bipyridine molecules have been studied. The luminescence excitation spectra, the lifetimes of the $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states, and the luminescence intensity are analyzed. The decisive role of ligand-metal charge transfer (LMCT) states in the quenching of the luminescence of europium aromatic carboxylates containing a π-excessive pyrrole or indole fragment is demonstrated. Most europium compounds are characterized by quenching due to the depopulation of the $^5D_0$ state of the Eu^{3+} ion through the low-energy LMCT state. But in some ternary compounds, the LMCT state being of higher energy participates in the nonradiative depopulation of the excited electronic states of the ligand.

Keywords: luminescence, Eu^{3+}, Tb^{3+}, LMCT, indolecarboxylate, π-excessive heterocycle.

DOI: 10.21883/EOS.2022.01.52996.26-21

Introduction

In coordination compounds of easily reducible lanthanide ions (Eu^{3+}, Yb^{3+}, Sm^{3+}, Tm^{3+}), the electron density of the highest filled orbital of „soft" donor ligand can shift towards the Ln^{3+} ion forming low-energy states of „ligand−metal" charge transfer (LMCT), which are often responsible for luminescence quenching [1–3]. With the help of theoretical modeling of the processes of lanthanide complexes quenching at different relative energies of the electronic states of the ligand, the LMCT state, and the $4f$-states of the Ln^{3+} ion two dominant quenching channels were determined: „$Ln^{3+} \rightarrow$ LMCT-state" and „ligand → LMCT-state" [4,5]. Nonradiative processes are most efficient when the LMCT state is located near the lowest ligand triplet [4]. The effect of the luminescence quenching of europium coordination compounds with the participation of LMCT states formed the basis of the thermal sensors proposed in the papers [6,7].

Charge transfer states $2p$(O)-Eu^{3+} have been identified in a number of aromatic europium carboxylates; their influence on the energy transfer to the Eu^{3+} ion is also considered [8–10]. When introducing electron-donor substituents -OCH_3, -OH, -NH_2 in ortho- or para-position of the aromatic ring of europium benzoate the shift of the electron density to the Eu^{3+} ion leads to the formation of low-energy states LMCT [8]. The incorporation of methylene groups -CH_2- into the carboxylate, which weaken the conjugation between the carboxyl group and the aromatic fragment, can also significantly decrease the energy of the LMCT state [9]. The appearance of an excess of electron density capable of shifting to the Eu^{3+} ion is possible in pyrrole-containing carboxylates, where parallel oriented orbitals of the lone pair of electrons of the nitrogen atom and π-electrons of the aromatic system of the ligand are conjugated. The participation of the LMCT state in the luminescence quenching of europium pyrrole-2-carboxylate $Eu(PCA)_3 \cdot 3H_2O$ ($[\{Eu(PCA)_3 \cdot (H_2O)_2\} \cdot H_2O]_n$) has recently been studied [10]. A similar effect should be expected in europium indolecarboxylates with the same mutual orientation of the ligand orbitals, but with an extended π-conjugated aromatic system. Efficient fluorescence quenching of indole solutions by Eu^{3+} and Yb^{3+} ions as compared to other Ln^{3+} ions relates to same nature phenomena [11].

In the present work, we consider the features of luminescence excitation of europium and terbium indole-3-carboxylates, indole-3-acetates and indole-3-propionates, including those with additional ligands: 1,10-phenanthroline and 2,2′-bipyridine. It is shown that in europium compounds the decisive role in the excitation energy transfer to the Eu^{3+} ion and luminescence quenching belongs to the low-energy LMCT state. A comparison is made with europium and terbium pyrrole-2-carboxylates and pyridinecarboxylates. The effect of methylene bridges on the structure of compounds and on the excitation energy transfer to the Ln^{3+} ion is discussed.

Only a few spectroscopic and X-ray diffraction studies of lanthanides pyrrole- and indolecarboxylates are known [12–15]. At the same time, a significant number of papers relates to the study of pyrrole-containing carboxylates of other metals and carboxylic acids with a pyrrole fragment [16–21]. Interest in these compounds is due to the fact that many biologically important compounds, such as hemoglobin, chlorophyll, vitamin B12, and a number of hormones, include fragments of pyrrole or indole. Indole derivatives, indolecarboxylic acids and corresponding metal complexes, including lanthanide complexes [13,15], exhibit anti-inflammatory, antibacterial, antiviral, and antioxidant activities [22,23].

Experimental part

Indole-3-carboxylates $Ln(ICA)_3 \cdot 3.5H_2O$ (**1**, **1a**), indole-3-acetates $Ln(IAA)_3 \cdot 1.5H_2O$ (**2**, **2a**) and indole-3-propionates $Ln(IPA)_3 \cdot H_2O$ (**3**, **3a**) (Ln = Eu, Tb), as well as ternary compounds with 1,10-phenanthroline (Phen) and 2,2′-bipyridine (Bpy): $Eu(ICA)_3 \cdot Bpy$ (**4**), $Tb(ICA)_3 \cdot Bpy$ (**5**), $Tb(ICA)_3 \cdot Phen \cdot H_2O$ (**6**), $Eu(IAA)_3 \cdot Phen$ (**7**), $Tb(IAA)_3 \cdot Phen$ (**8**), $Eu(IPA)_3 \cdot Bpy$ (**9**) were studied. Compounds in the form of powders were synthesized according to standard procedures [10]. The listed compounds are summarized in the Table. Figure 1 shows the formulas of the ligands containing the pyrrole fragment. Comparison of the spectroscopic characteristics of isostructural compounds of the easily reduced Eu^{3+} ion and the easily oxidized Tb^{3+} ion (in particular, **1** and **1a**, **2** and **2a**, **3**, and **3a**) facilitate the identification of LMCT states and the analysis of luminescence excitation energy transfer in europium compounds. The luminescence and luminescence excitation spectra of europium and terbium compounds, the lifetimes of the electronic states $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) and integral luminescence intensity, phosphorescence spectra of gadolinium compounds, and vibrational IR spectra were reviewed.

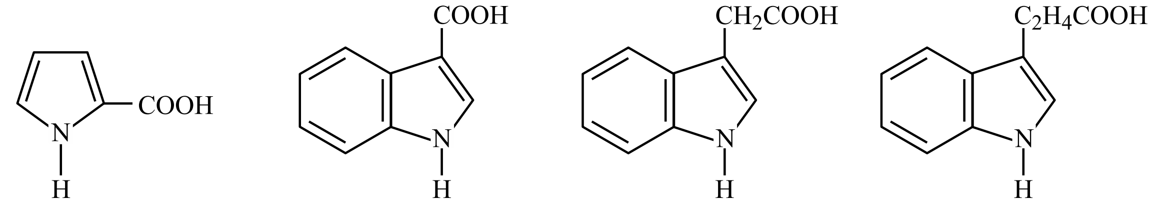
The luminescence and excitation spectra of europium and terbium compounds were obtained using LOMO ISP-51 spectrometers with a photoelectronic cassette FEK-2/3648 and SLM Aminco SPF 500 at 77 and 295 K. The excitation spectra were registered while monitoring the region of the most intense lines of transition $^5D_0{-}^7F_2$ (Eu^{3+}) and $^5D_4{-}^7F_5$ (Tb^{3+}). Phosphorescence spectra of gadolinium compounds and lifetimes of excited electronic states $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) were measured using setup based on LOMO UM-2 monochromator with a highly sensitive photomultiplier Hamamatsu H6780-20. The sources of luminescence excitation were a high-pressure mercury lamp DRSH-250 and LED Nichia High-Power LED NCSU033B. Luminescence was excited at a wavelength of 365 nm of UV radiation. Energy values of the lowest triplet state T_1 of ICA, IAA and IPA ligands, equal to ~ 23400, ~ 21800 and $\sim 21000\,cm^{-1}$ respectively, were determined by the short-wavelength edge of phosphorescence bands of binary compounds of gadolinium, registered at 77 K with a time delay. Approximate energy values of the lower excited singlet state S_1 of indolecarboxylate, equal to $32000{-}32800\,cm^{-1}$ in binary compounds and $25500{-}27000\,cm^{-1}$ in ternary compounds, were obtained from the long-wavelength edge of the ligand band in the excitation spectra of terbium or europium compounds at 77 K. These energy values refer to zero-phonon 0−0-transitions in wide bands of ligands $T_1{-}S_0$ and $S_0{-}S_1$ due to strong electron-vibrational interaction. To analyze decay processes of the states $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) mono- and biexponential fitting of the decay kinetics was applied using Origin 8.0 program. For most compounds, the experimental lifetimes were in better agreement with the biexponential decay law than with the monoexponential one. In these cases, the average lifetime was determined [24]. Deviations from the monoexponential nature of the luminescence are usually associated with the influence of uncontrolled impurities and/or with complex processes of excitation energy transfer to the Ln^{3+} ion. When estimating the integral intensities by the luminescence spectra, the samples of the compounds were under strictly identical conditions. Vibrational IR spectra of compound emulsions in Nujol and fluorinated oil were registered by Nicolet Magna 750 FTIR spectrophotometer at 295 K.

Results and discussion

Structure of lanthanide indolecarboxylates and luminescence features

In accordance with the experimental data, the structures of the compounds are formed from molecules consisting of Ln atom, three indolecarboxylate anions coordinated by the metal through oxygen atoms, and water molecules. In ternary compounds instead of water molecules there is a heterocyclic diimine molecule coordinated through two nitrogen atoms. According to the vibrational IR spectra, the binary compounds of europium and terbium with each of the three indolecarboxylic acids (**1** and **1a**, **2** and **2a**, **3** and **3a**) are isostructural, as pyrrole-2-carboxylates [10]. During the syntheses of extended series of ternary compounds, a tendency was revealed for the IAA and IPA ligands to form isostructural pairs of Eu and Tb complexes, while such a tendency was not observed for the ICA ligand. All ternary indolecarboxylates studied in this paper have different structures.

The interpretation of the IR spectra shown in Fig. 2 was carried out taking into account the results of study of indolecarboxylic acids and the corresponding complexes with metals [17–20,25]. Intense bands in the region of $1400{-}1600\,cm^{-1}$ refer to symmetric $\nu_s(COO^-)$ and antisymmetric $\nu_{as}(COO^-)$ stretching vibrations of the coordinated carboxyl group and complex stretching vibrations of aromatic rings. A small splitting $\nu(COO^-)$, amounting to $\sim 100\,cm^{-1}$ in most compounds, indicates the equivalence of the effective charges on the oxygen atoms and bidentate-cyclic and/or bridging bidentate coordination of carboxyl groups. The splitting increasing to $\sim 170\,cm^{-1}$ with a large number of components $\nu_s(COO^-)$ and $\nu_{as}(COO^-)$ in ternary compounds **7**, **8**, and **9** with IAA and IPA ligands is presumably related to several types of coordination



Pyrrole-2-carboxylic (PCA) Indole-3-carboxylic (ICA) Indole-3-acetic (IAA) Indole-3-propionic (IPA)

Figure 1. Structural formulas of pyrrole- and indolecarboxylic acids.

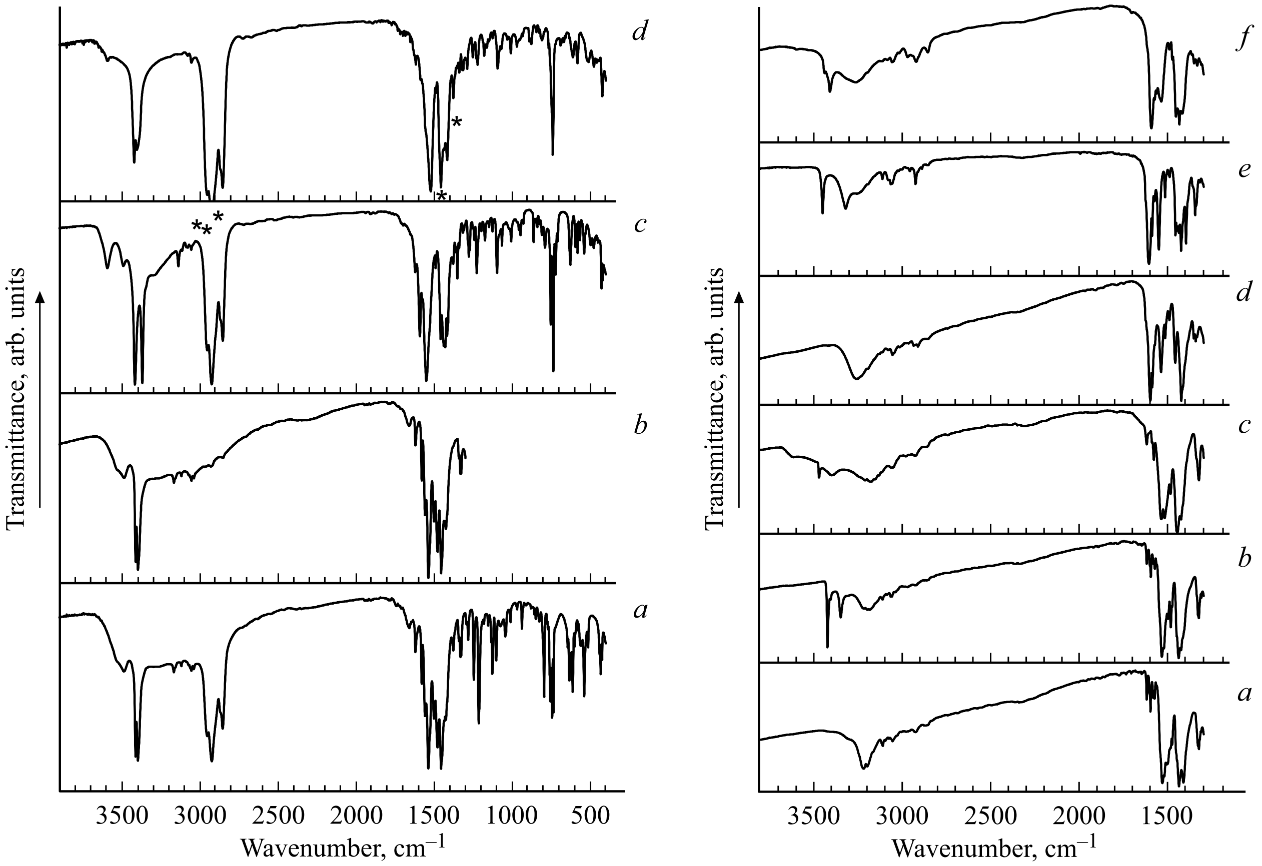


Figure 2. Vibrational IR spectra at 295 K: (left) $Eu(ICA)_3 \cdot 3.5H_2O$ (**1**) (*a, b*), $Eu(IAA)_3 \cdot 1.5H_2O$ (**2**) (*c*), $Eu(IPA)_3 \cdot H_2O$ (**3**) (*d*); (right) $Eu(ICA)_3 \cdot Bpy$ (**4**) (*a*), $Tb(ICA)_3 \cdot Bpy$ (**5**) (*b*), $Tb(ICA)_3 \cdot Phen \cdot H_2O$ (**6**) (*c*), $Eu(IAA)_3 \cdot Phen$ (**7**) (*d*), $Tb(IAA)_3 \cdot Phen$ (**8**) (*e*), $Eu(IPA)_3 \cdot Bpy$ (**9**) (*f*). Spectra *a, c* and *d* in the left panel are layers in Nujol (asterisks mark bands of Nujol), other spectra are layers in fluorinated oil.

of COO^--groups, including the tridentate bridging cyclic coordination.

Bands in the region of 2800–3700 cm^{-1} refer to symmetric and antisymmetric stretching vibrations of coordinated and outer-sphere water molecules $\nu(H_2O)$, stretching vibrations ν(N–H) and ν(C–H). Two strong lines at 3400 cm^{-1} in the spectra of binary compounds indicate that N–H-group is free and does not participate in the formation of hydrogen bonds. The appearance of two ν(N–H) components is due to the non-equivalence of the ligands. The wide band in the region of 2600–3650 cm^{-1} of the spectra of binary compounds is related to the network of hydrogen bonds formed by water molecules. The intensity of this band is consistent with the number of water molecules in the compounds.

The appearance of widened band at 3200 cm^{-1} in ternary compounds and the weakening or disappearance of narrow lines of N–H-group indicates the formation of hydrogen bonds with oxygen atoms of carboxyl groups N–H$\cdots$O. The compounds contain both bound and un-

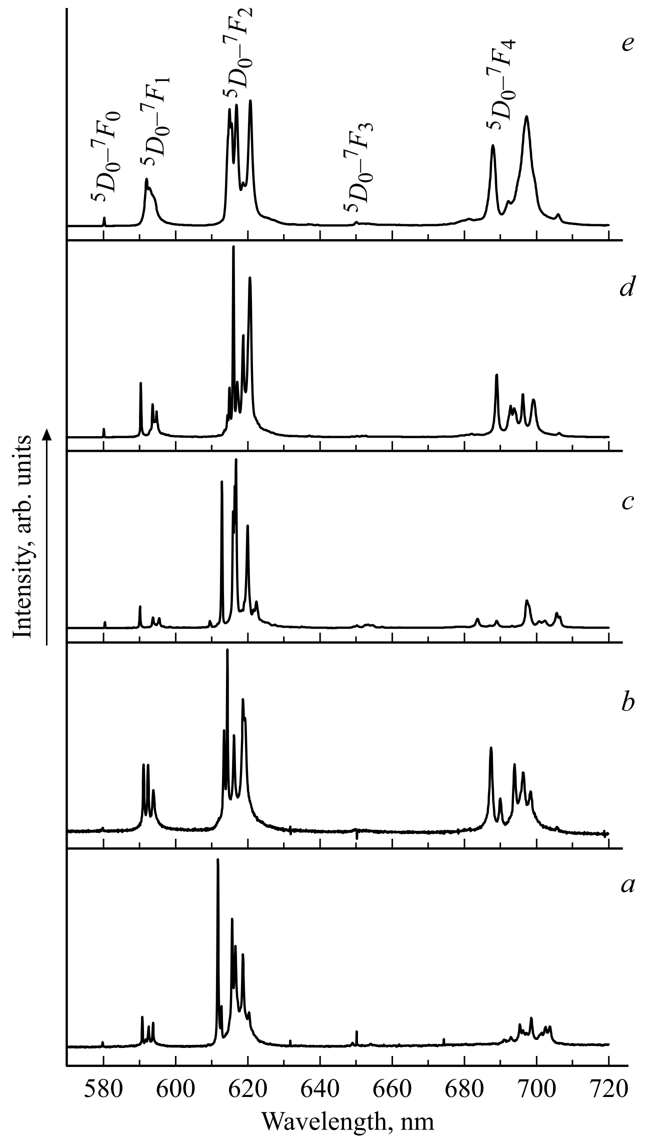


Figure 3. Luminescence spectra $Eu(ICA)_3 \cdot 3.5H_2O$ (**1**) (*a*), $Eu(IAA)_3 \cdot 1.5H_2O$ (**2**) (*b*), $Eu(ICA)_3 \cdot Bpy$ (**4**) (*c*), $Eu(IAA)_3 \cdot Phen$ (**7**) (*d*), $Eu(IPA)_3 \cdot Bpy$ (**9**) (*e*) at 77 K.

bound N−H-groups with the exception of indolecarboxylate $Eu(ICA)_3 \cdot Bpy$ (**4**) and indoleacetate $Eu(IAA)_3 \cdot Phen$ (**7**), where all N−H-groups are involved in hydrogen bonds. The water molecules of the complex $Tb(ICA)_3 \cdot Phen \cdot H_2O$ (**6**) also form hydrogen bonds.

The maximum possible number of Stark components of electronic transitions in the luminescence spectra of europium indolecarboxylates and the different nature of the splitting (Fig. 3) indicate a low symmetry of the nearest environment of the Ln^{3+} ion with different types of distortions. In the investigated indole-3-acetates and indole-3-propionates the methylene bridges -CH_2- „move" the bulky aromatic fragment away from the Ln^{3+} ion, this reduces its steric effect on the nearest environment of Ln^{3+} and leads to crystal field distortions decreasing similarly to lanthanide phenyl- and naphthylcarboxylates [9,26]. This is indicated by decreasing of the integral intensity of the hypersensitive electric dipole transition $^5D_0-^7F_2$ with respect to the intensity of the magnetic dipole transition $^5D_0-^7F_1$. The rate of natural radiative processes also decreases, which leads to increased lifetimes of the states $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) to 1.27−1.74 ms in **7**, **8**, and **9** ternary compounds with IAA and IPA ligands as compared with lifetimes equal to 0.67−0.90 ms in **4**, **5**, and **6** compounds with the ICA ligand (Table).

Another manifestation of the methylene bridges effect on the characteristics of indolecarboxylates relates to Eu^{3+} luminescence quenching through the LMCT states. „Decoupling" of $\pi-\pi$-system of an aromatic carboxylate by $-CH_2-$ groups can lead to the electron density shift of the carboxyl group to the Eu^{3+} ion to form low-energy LMCT states, as observed in europium phenyl- and naphthylcarboxylates [9,26]. If in europium indole-3-carboxylates the electron density shifts free from π-excessive indole fragment to the Eu^{3+} ion, then in indole-3-acetates and indole-3-propionates such shift is blocked by methylene bridges. But at the same time, blocking causes the shift to Eu^{3+} of the electron density present on the carboxyl group.

The low intensity of the luminescence of lanthanide binary compounds is explained by the low probability of intercombination conversion and, accordingly, the weak population of the triplet due to the large energy range S_1-T_1, which increases from ~ 8600 to ~ 10200 and $\sim 11800\,cm^{-1}$ in compounds with ICA, IAA and IPA ligands, by high rate of multiphonon nonradiative relaxation due to the water molecules presence, and also, as will be shown below for europium compounds, by the quenching effect of low-energy LMCT states. The higher by one−two orders of magnitude of luminescence intensity of ternary lanthanide compounds at 77 K is due to the presence of wide absorption band of ligands in the region of used excitation 365 nm, smaller intervals S_1-T_1 in both ligands and, accordingly, a higher probability of intercombination conversion, the absence of quenching water molecules, and, according to the low-temperature excitation spectra, by the absence of quenching involving LMCT in europium compounds.

Lifetimes of $^5D_0$ *(*Eu^{3+}*)- and* $^5D_4$ *(*Tb^{3+}*)-states*

The lifetime of the lower excited emitting state Ln^{3+} in lanthanide coordination compounds can be represented as $\tau = 1/(k_r + k_{vibr} + k_{LMCT} + k_{BT} + k_{Ln-Ln})$, where k_r is rate of natural radiative process, and the remaining contributions to τ are the rates of nonradiative processes [27]. k_{vibr} refers to multiphonon relaxation involving high-frequency stretching vibrations of ligands, k_{LMCT} describes the depletion of the level Ln^{3+} through the low-energy LMCT state, k_{BT} is back energy transfer from the level Ln^{3+} to the lowest ligand triplet, k_{Ln-Ln} is concentration quenching. As a rule, the concentration quenching of Ln−Ln in carboxylates, where the distance Ln−Ln exceeds 4 Å, is negligibly small [10,28]. The rates k_r and k_{vibr} do not depend significantly on temperature in the used temperature range [1]

Studied europium and terbium indolecarboxylates, lifetimes τ (ms) of $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states and the change in the luminescence intensity with temperature increasing from 77 to 295 K. $\lambda_{exc} = 365$ nm

№	Compound	$\tau_{77\,K}$ (Eu^{3+})	$\tau_{295\,K}$ (Eu^{3+})	$\tau_{77\,K}$ (Tb^{3+})	$\tau_{295\,K}$ (Tb^{3+})	$I_{295\,K}/I_{77\,K}$ (Eu^{3+})	$I_{295\,K}/I_{77\,K}$ (Tb^{3+})
1, 1a	$Ln(ICA)_3 \cdot 3.5H_2O$ (Ln = Eu, Tb)	0.51	0.22	0.71	0.70	0.24	1
2, 2a	$Ln(IAA)_3 \cdot 1.5H_2O$ (Ln = Eu, Tb)	0.73	~ 0.21	1.09	1.06	0.06	0.5
3, 3a	$Ln(IPA)_3 \cdot H_2O$ (Ln = Eu, Tb)	0.90	~ 0.16	1.21	1.13	0.01	0.3
4	$Eu(ICA)_3 \cdot Bpy$	0.67	0.63			0.05	
5	$Tb(ICA)_3 \cdot Bpy$			0.79	0.83		2
6	$Tb(ICA)_3 \cdot Phen \cdot H_2O$			0.90	0.51		0.1
7	$Eu(IAA)_3 \cdot Phen$	1.27	0.40			0.01	
8	$Tb(IAA)_3 \cdot Phen$			1.74	~ 0.05		0.01
9	$Eu(IPA)_3 \cdot Bpy$	1.56	1.19			0.04	

in contrast to k_{LMCT} and k_{BT}. k_{BT} contribution is relevant only for some terbium compounds under study, where the energies of the triplet state of the ligand and states $^5D_4$ are sufficiently close. Therefore, the processes involving LMCT, described by k_{LMCT}, are responsible for the lifetime reduction of $^5D_0$ state and, accordingly, the luminescence intensity decreasing of the europium compounds presented in the Table, with temperature increasing. The effect of the LMCT state on luminescence is determined both by the position of the minimum of the potential curve of this state and by the shape of the curve. If the LMCT energy is sufficiently high, then this state may be involved in the depletion of the electronic levels of the ligand, which will lead to decreasing of the luminescence quantum yield, but will not affect the lifetime of $^5D_0$-state [5,26,29,30].

In europium binary compounds **1**, **2**, **3** and terbium compounds **1a**, **2a**, **3a** at 77 K the lifetime τ increases successively in the series of ICA, IAA, IPA ligands (Table), which is largely due to decreasing of the number of water molecules and, accordingly, decreasing of multiphonon relaxation rate. In compounds with the highest water content: $Ln(ICA)_3 \cdot 3.5H_2O$ (**1**, **1a**), except for the significant contribution of k_{vibr} to τ, the increased contribution to τ will also given by k_r due to distortions introduced by steric hindrance. According to the excitation spectra (Fig. 4), in europium binary compounds at 77 K the contribution of quenching involving charge transfer states k_{LMCT} is also active. The longer lifetime in terbium compounds is explained by the absence of this quenching channel in addition to the larger energy interval between ^5D_J- and ^7F_J-multiplets, which causes a smaller value of multiphonon relaxation.

Lifetime of $^5D_4$-state in terbium compounds, except for $Tb(ICA)_3 \cdot Phen \cdot H_2O$ (**6**) and $Tb(IAA)_3 \cdot Phen$ (**8**), does not change with temperature increasing or changes slightly. In **6** and **8** compounds the lifetime decreases upon heating, respectively from 0.90 to 0.51 ms and from 1.74 to ~ 0.05 ms, and the luminescence intensity also decreases. In **6** this is due to the back transfer of excitation energy from $^5D_4$-level (~ 20500 cm^{-1}) to phenanthroline triplet (~ 21500 cm^{-1} [28], $\Delta =\sim 1000$ cm^{-1}), while ICA triplet (~ 23400 cm^{-1}) is located too high to participate in the back transfer. In compound **8**, the back transfer on triplets of both ligands is possible: Phen and IAA (~ 21800 cm^{-1}). In compound $Tb(ICA)_3 \cdot Bpy$ (**5**) the triplet of additional ligand Bpy (~ 22500 cm^{-1}), as well as ICA, is located significantly above the level $^5D_4$, so there is no back transfer of excitation energy.

Successive decrease in the lifetime of $^5D_0$-state at 295 K in relation to its value at 77 K in the series of europium binary compounds **1**, **2**, **3** indicates the $^5D_0$−LMCT activation energy decreasing. A sharper drop in the luminescence intensity of europium compounds upon heating as compared to terbium compounds also indicates the involvement of the LMCT states in the quenching of the former. In compound **1** the electron density of the ligand due to its excess on the indole fragment shifts to the Eu^{3+} ion resulting in the formation of the low-energy LMCT state. In compounds **2** and **3** this shift is modified with methylene bridges, as described above.

In the europium ternary compound $Eu(ICA)_3 \cdot Bpy$ (**4**) the lifetime of $^5D_0$-state upon temperature increasing changes slightly, while the luminescence intensity drops sharply. This indicates the transfer of the excitation energy from the electronic states of the ligand to the LMCT state with its further nonradiative relaxation. In the case of compounds $Eu(IAA)_3 \cdot Phen$ (**7**) and $Eu(IPA)_3 \cdot Bpy$ (**9**) both the lifetime of the state $^5D_0$, and the luminescence intensity decrease, this is associated with the $^5D_0$ level depletion upon the LMCT state participation.

Luminescence excitation spectra

The conclusions about the LMCT state effect on the processes of luminescence quenching of europium indolecarboxylates obtained from the data analysis of the Table are confirmed by the luminescence excitation spectra. The spectra presented in Fig. 4 indicate the difference in the processes of energy transfer in europium and terbium indole-3-carboxylates, as in case of pyrolle-2-carboxylates [10]. The efficiency of excitation of the Tb^{3+} ion in both of them through the wide band of the

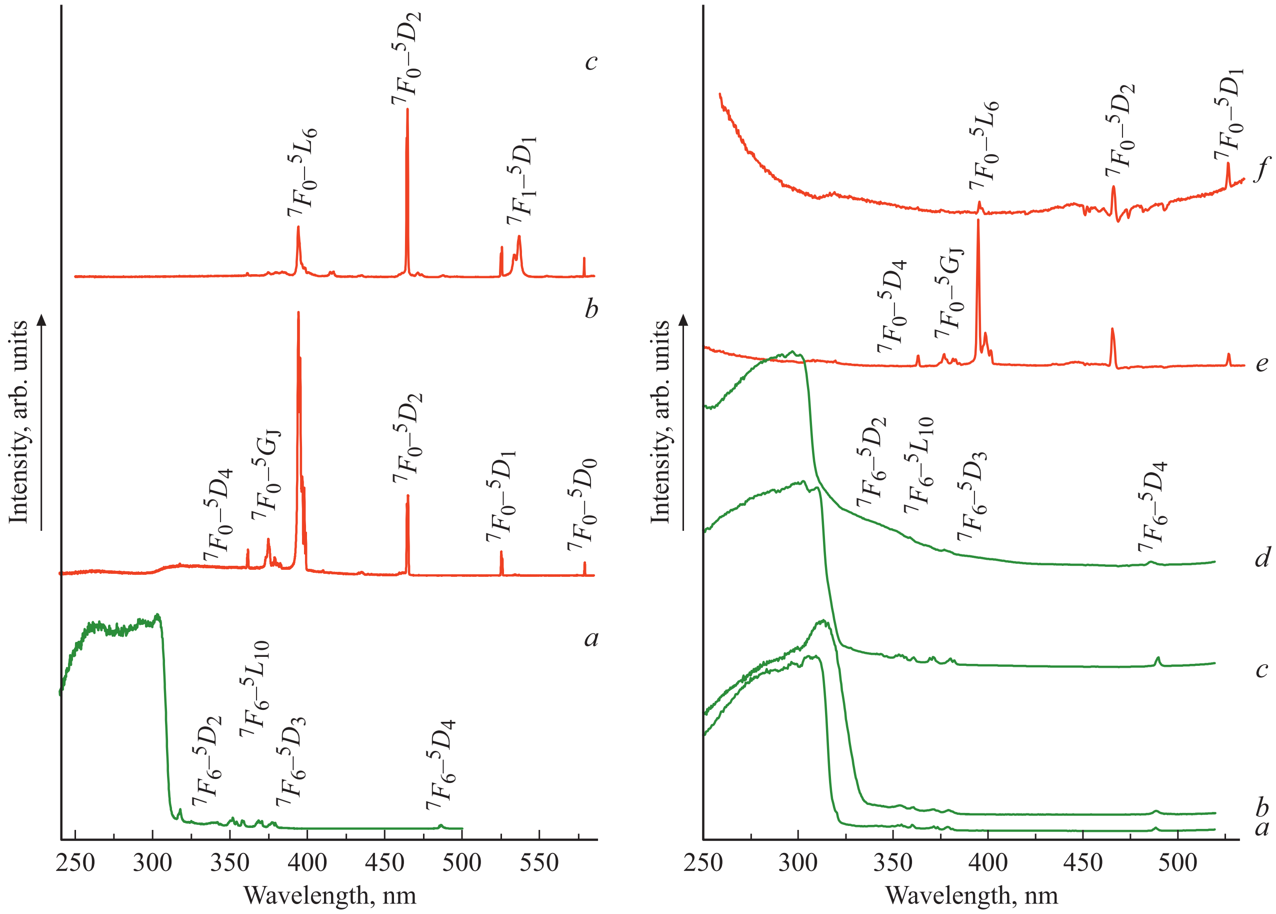


Figure 4. Luminescence excitation spectra: (left) pyrrolecarboxylates $Tb(PCA)_3 \cdot 3H_2O$ at 77 K (*a*) and $Eu(PCA)_3 \cdot 3H_2O$ at 77 (*b*) and 295 K (*c*); (right) binary indolecarboxylates $Tb(ICA)_3 \cdot 3.5H_2O$ (**1a**) at 77 (*a*) and 295 K (*b*), $Tb(IAA)_3 \cdot 1.5H_2O$ (**2a**) (*c*), $Tb(IPA)_3 \cdot H_2O$ (**3a**) (*d*), $Eu(ICA)_3 \cdot 3.5H_2O$ (**1**) (*e*) and $Eu(IAA)_3 \cdot 1.5H_2O$ (**2**) (*f*) at 77 K.

ligand in the UV range is high as compared to the efficiency of excitation of the Eu^{3+} ion. The short-wavelength part of this band belongs to transitions S_0–S_1 (π–π^*). The long-wavelength part of the band can be attributed to intraligand charge transfer (ILCT), associated with the electron density shift of π-electrons of the aromatic system, which includes the lone pair of electrons of the nitrogen atom, to COO^--group [31]. The excitation band of terbium indolecarboxylate $Tb(ICA)_3 \cdot 3.5H_2O$ (**1a**) has a longer wavelength edge than that of terbium pyrrolecarboxylate $Tb(PCA)_3 \cdot 3H_2O$ due to longer π–π-conjugated system. The hypsochromic shift of the band in terbium indolepropionate $Tb(IPA)_3 \cdot H_2O$ (**3a**) as compared to **1a** is associated with weakening of the conjugation system of π-electrons by methylene bridges $-(CH_2)_2-$.

Very low intensity of the ligand bands and narrow lines of the Eu^{3+} ion in the region shorter than 390 nm in the excitation spectra of $Eu(ICA)_3 \cdot 3.5H_2O$ (**1**) and $Eu(IAA)_3 \cdot 1.5H_2O$ (**2**) (Fig. 4) as in spectra of europium pyrrole-2-carboxylate $Eu(PCA)_3 \cdot 3H_2O$ refers to luminescence quenching involving the LMCT state. In pyrrolecarboxylate the intensity decreasing of the lines of transition $^7F_0$–$^5L_6$ of the Eu^{3+} ion at room temperature is observed, while the excitation spectra of indolecarboxylates **1** and **2** at 295 K were not registered due to extremely weak luminescence. Taking into account the temperature behavior of the lifetime of $^5D_0$-states and luminescence intensity of binary europium indolecarboxylates (Table), which differs from the behavior of these characteristics for terbium isostructural compounds, it can be assumed that in the former the minimum of the potential LMCT curve is below $^5D_0$-state, which contributes to the depletion of the latter. According to the spectroscopic data, the LMCT energy, as well as the activation energy (equal to ~ 3900 cm^{-1} for pyrrole-2-carboxylate [10]) should not differ much in indole-3-carboxylate **1** and pyrrole-2-carboxylate, while in indole-3-acetate **2** and indole-3-propionate **3** the activation energy should be lower.

In most lanthanide ternary compounds and, in particular, in europium and terbium indolecarboxylates with 2,2′-bipyridine (Fig. 5), the excitation band extends to the long-wavelength range up to ~ 400 nm. Since the long-wavelength edge of the band of Phen and Bpy in the excitation spectra usually lies near ~ 350 and ~ 325 nm,

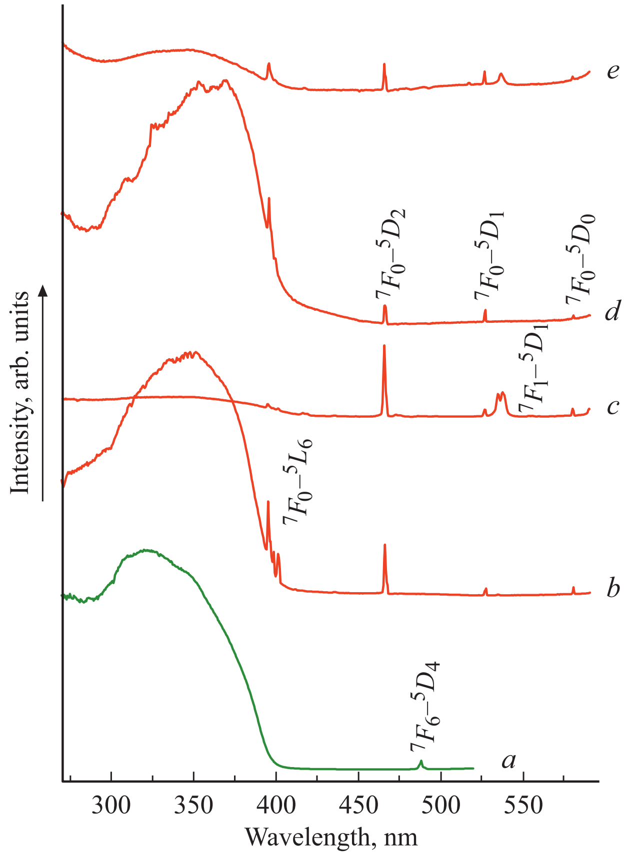


Figure 5. Luminescence excitation spectra of ternary indolecarboxylates: $Tb(ICA)_3 \cdot Bpy$ (**5**) at 77 (*a*), $Eu(ICA)_3 \cdot Bpy$ (**4**) at 77 (*b*) and 295 K (*c*), $Eu(IPA)_3 \cdot Bpy$ (**9**) at 77 (*d*) and 295 K (*e*).

respectively, this widening is due to the strength change of the binding of the indolecarboxylate ligand in the crystal lattice during the ternary compounds formation. The band shift can be associated with both the donor ability increasing of the ligand aromatic system and by the acceptor ability increasing of the COO^--group. A similar extension of the fluorescence excitation band is also observed in zinc indole-3-propionate with 1,10-phenanthroline [21].

In contrast to compound $Tb(ICA)_3 \cdot Bpy$ (**5**), which has a wide excitation band at both 77 and 295 K, in europium compounds $Eu(ICA)_3 \cdot Bpy$ (**4**) and $Eu(IPA)_3 \cdot Bpy$ (**9**) at 295 K the intensity decreasing of the ligands band and lines of high-frequency transitions of the Eu^{3+} ion is observed. The quenching LMCT states participate in the excitation energy transfer process. As noted above, when the temperature changed from 77 to 295 K, the luminescence intensity decreased in both europium compounds, but the lifetime decreased only in **9**. This indicates a higher position of the LMCT level in compound **4** and a back transfer of the excitation energy, presumably from the ICA ligand triplet to LMCT, with its further degradation into the crystal lattice, in contrast to quenching of $^5D_0$-state in **9**. In these compounds, upon excitation into the Bpy absorption band the energy can be transferred from the Bpy singlet state ($\sim 30500\,\text{cm}^{-1}$) to the indolecarboxylate singlet ($\sim 25500-27000\,\text{cm}^{-1}$) followed by quenching by two different mechanisms. The higher LMCT energy and higher activation energy in europium ternary compounds as compared to binary ones are evidenced by the presence of the ligands band in the former at 77 K and its absence in the latter.

In contrast to the previously studied lanthanide pyridinecarboxylates [32], in which the lone pair of electrons of the nitrogen atom does not interact with the π-electron system of the pyridine ring because of orthogonal orientation of orbitals [31], in indolecarboxylates, as well as in pyrrolecarboxylates, *p*-orbital of the nitrogen atom is included in conjugation with π-electron system of the heterocycle due to the parallel orientation of the orbitals. The electrons dektet distributed over nine atoms of the system of two cycles of indole-3-carboxylate, and the electrons sextet distributed over five atoms of the cycle of pyrrole-2-carboxylate provide an excess of electron density in the aromatic system, due to which low-energy LMCT states appear in europium compounds. In europium pyridinecarboxylates there is no excess electron density in the ligand in comparison with these systems, therefore the LMCT state, which is high-energy, has not been identified [32]. The luminescence excitation spectra of europium and terbium pyridinecarboxylates are identical in the region of the electronic bands of the ligand and has low dependence on temperature.

Conclusions

Luminescence excitation processes in indole-3-carboxylates $Ln(ICA)_3 \cdot 3.5H_2O$, indole-3-acetates $Ln(IAA)_3 \cdot 1.5H_2O$ and indole-3-propionates $Ln(IPA)_3 \cdot H_2O$ ($Ln = Eu$, Tb) were studied, as well as in the series of europium and terbium ternary indolecarboxylates with 1,10-phenanthroline and 2,2′-bipyridine. The luminescence excitation spectra, the lifetimes of the states $^5D_0$ (Eu^{3+}) and $^5D_4$ $(Tb)^{3+}$) and luminescence intensity were analyzed. Vibrational IR spectra indicate the same structure of europium and terbium binary compounds with each of the three indolecarboxylic acids. In all binary compounds N–H-group is free. Ternary compounds are characterized by a different structure with a network of hydrogen bonds formed by N–H-groups.

The primary role of the LMCT states in the excitation energy transfer to the Eu^{3+} ion and in the luminescence quenching of aromatic europium carboxylates containing pyrrole or indole fragment is demonstrated. The conjugation of parallel oriented orbitals of the lone pair of electrons of the nitrogen atom and the π-electrons system of the aromatic fragment of the ligand creates an excess of electron density, which in indole-3-carboxylates, as in pyrrole-2-carboxylates, can shift towards the Eu^{3+} ion with the formation of low-energy LMCT states. In indole-3-acetates and indole-3-propionates the formation of

LMCT states is modified by methylene bridges. In the studied europium compounds with π-excessive ligands two channels of luminescence quenching with the participation of LMCT are active. Most europium compounds are characterized by quenching determined by the nonradiative deactivation of $^5D_0$-state of the Eu^{3+} ion through a low-energy state of „ligand−metal“charge transfer. But in some ternary compounds, the charge transfer state, being high energy state, is involved in emptying the excited electronic states of the ligand.

Acknowledgments

The authors would like to thank Cand. Sc. Chemistry V.A. Kudryashova for synthesizing the compounds studied in this paper. The authors are also grateful to Prof. Janina Legendziewicz (University of Wrocław, Poland) for the opportunity to measure the luminescence excitation spectra in her laboratory.

Funding

The work was performed under the State Assignment of the Ministry of Science and Higher Education of the Russian Federation.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] G.F. de Sá, O.L. Malta, C. de Mello Donegá, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. da Silva Jr. Coord. Chem. Rev., **196** (1), 165 (2000). DOI: 10.1016/S0010-8545(99)00054-5

[2] G.K. Liu, M.P. Jensen, P.M. Almond. J. Phys. Chem. A., **110** (6), 2081 (2006). DOI: 10.1021/jp0558674

[3] S. Petoud, J.-C.G. Bünzli, T. Glanzman, C. Piguet, Q. Xiang, R.P. Thummel. J. Lumin., **82** (1), 69 (1999). DOI: 10.1016/S0022-2313(99)00015-0

[4] W.M. Faustino, O.L. Malta, G.F. de Sá. J. Chem. Phys., **122**, 054109 (2005). DOI: 10.1063/1.1830452

[5] W.M. Faustino, O.L. Malta, G.F. de Sá. Chem. Phys. Lett., **429** (4−6), 595 (2006). DOI: 10.1016/j.cplett.2006.08.059

[6] D.V. Lapaev, V.G. Nikiforov, V.S. Lobkov, A.A. Knyazev, Yu.G. Galyametdinov. Opt. Mater., **75**, 787 (2018). DOI: 10.1016/j.optmat.2017.11.042

[7] K. Yanagisawa, Y. Kitagawa, T. Nakanishi, T. Seki, K. Fushimi, H. Ito, Y. Hasegawa. Chem. Eur. J., **24** (8), 1956 (2018). DOI: 10.1002/chem.201705021

[8] V.I. Tsaryuk, K.P. Zhuravlev. J. Lumin., **237**, 118159 (2021). DOI: 10.1016/j.jlumin.2021.118159

[9] V. Tsaryuk, K. Zhuravlev, V. Kudryashova, V. Zolin, J. Legendziewicz, I. Pekareva, P. Gawryszewska. J. Photochem. Photobiol. A: Chem., **197** (2−3), 190 (2008). DOI: 10.1016/j.jphotochem.2007.12.022

[10] K.P. Zhuravlev, Ł. Michnik, P. Gawryszewska, V.I. Tsaryuk, V.A. Kudryashova. Inorg. Chim. Acta., **492**, 1 (2019). DOI: 10.1016/j.ica.2019.04.014

[11] A. Tine, P. Valat, J.J. Aaron. J. Lumin., **36** (2), 109 (1986). DOI: 10.1016/0022-2313(86)90059-1

[12] A.K. Solanki, A.M. Bhandari. J. Inorg. Nucl. Chem., **41** (9), 1311 (1979). DOI: 10.1016/0022-1902(79)80045-7

[13] F.-Y. He, L. Wang, Zh. Chen, J. Wu. Synth. React. Inorg. Met.-Org. Chem., **24** (4), 575 (1994). DOI: 10.1080/00945719408000134

[14] G.-L. Law, K.-L. Wong, K.-K. Lau, H.-L. Tam, K.-W. Cheah, W.-T. Wong. Eur. J. Inorg. Chem., **2007** (34), 5419 (2007). DOI: 10.1002/ejic.200700584

[15] Z.-N. Wang, X.-T. Xu, X. Lv, F.-Y. Bai, S.-Q. Liu, Y.-H. Xing. RSC Adv., **5** (126), 104263 (2015). DOI: 10.1039/C5RA19376A

[16] Y. Shimazaki, T. Yajima, M. Takani, O. Yamauchi. Coord. Chem. Rev., **253** (3−4), 479 (2009). DOI: 10.1016/j.ccr.2008.04.012

[17] V. Viossat, P. Lemoine, E. Dayan, N.-H. Dung, B. Viossat. J. Mol. Struct., **741** (1−3), 45 (2005). DOI: 10.1016/j.molstruc.2005.01.040

[18] B. Morzyk-Ociepa. Vibr. Spectrosc., **49** (1), 68 (2009). DOI: 10.1016/j.vibspec.2008.04.014

[19] K. Szmigiel-Bakalarz, A. Skoczyńska, M. Lewańska, D. Günther, O. Oeckler, M. Malik-Gajewska, D. Michalska, B. Morzyk-Ociepa. Polyhedron., **185**, 114582 (2020). DOI: 10.1016/j.poly.2020.114582

[20] M. Cinar, M. Karabacak, A.M. Asiri. Spectrochim. Acta A., **137**, 670 (2015). DOI: 10.1016/j.saa.2014.08.090

[21] X.-J. Deng, Q. Yu, H.-D. Bian, H.-D. Ju, B.-L. Wang. Trans. Met. Chem., **41**, 591 (2016). DOI: 10.1007/s11243-016-0057-0

[22] T.V. Sravanthi, S.L. Manju. Eur. J. Pharm. Sci., **91**, 1 (2016). DOI: 10.1016/j.ejps.2016.05.025

[23] A. Kumari, R.K. Singh. Bioorg. Chem., **89**, 103021 (2019). DOI: 10.1016/j.bioorg.2019.103021

[24] R.K. Bauer, P. de Mayo, W.R. Ware, K.C. Wu. J. Phys. Chem., **86** (19), 3781 (1982). DOI: 10.1021/j100216a016

[25] A. Tine, Ph. Guillaume, A. Massat, J.-J. Aaron. Spectrochim. Acta A., **54** (10), 1451 (1998). DOI: 10.1016/S1386-1425(98)00046-8

[26] K. Zhuravlev, V. Tsaryuk, V. Kudryashova, I. Pekareva, J. Sokolnicki, Yu. Yakovlev. J. Lumin., **130** (8), 1489 (2010). DOI: 10.1016/j.jlumin.2010.03.018

[27] M.H.V. Werts, R.T.F. Jukes, J.W. Verhoeven. Phys. Chem. Chem. Phys., **4** (9), 1542 (2002). DOI: 10.1039/B107770H

[28] V.I. Tsaryuk, K.P. Zhuravlev, A.V. Vologzhanina, V.A. Kudryashova, V.F. Zolin. J. Photochem. Photobiol. A: Chem., **211** (1), 7 (2010). DOI: 10.1016/j.jphotochem.2010.01.012

[29] F.R. Gonçalves e Silva, R. Longo, O.L. Malta, C. Piguet, J.-C.G. Bünzli. Phys. Chem. Chem. Phys., **2** (23), 5400 (2000). DOI: 10.1039/B005624N

[30] K.P. Zhuravlev, V.I. Tsaryuk, V.A. Kudryashova. J. Fluorine Chem., **212**, 137 (2018). DOI: 10.1016/j.jfluchem.2018.06.002

[31] Sverdlova O.V. *Elektronnye spektry v organicheskoy khimii.* (Leningrad „Khimiya“, Leningradskoe otd., 1985) (in Russian).

[32] V.F. Zolin, L.N. Puntus, V.I. Tsaryuk, V.A. Kudryashova, J. Legendziewicz, P. Gawryszewska, R. Szostak. J. Alloys Compd., **380** (1−2), 279 (2004). DOI: 10.1016/j.jallcom.2004.03.055