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# Regulation of excitation and luminescence efficiencies of europium and terbium benzoates and 8-oxyquinolinates by modification of ligands

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## Abstract

The opportunities of optimisation of luminance of the lanthanide compounds by modification of ligands are discussed. Variations of the excitation and luminescence efficiencies at introduction of nitro- ($NO_2$), sulfo- ($SO_3^-$), hydroxy- (OH), amino- ($NH_2$), and phenylamino- ($NHC_6H_5$) groups in the aromatic ligands were studied. Investigation of luminescence and luminescence excitation spectra of europium and terbium compounds with 10 derivatives of benzoic acid, 2-furancarboxylic acid and their adducts with 1,10-phenanthroline and 2,2′-bipyridine was undertaken. Study of the spectra of lanthanide 8-oxyquinolinates was carried out also. Luminescence efficiencies were measured at 77 and 300 K. Paths of the energy transfer from the ligands to $Ln^{3+}$ ion were examined. Influence of radicals on the energies of the ligand triplet states and on the energies of the ligand–metal charge transfer states (LM CTS) of europium compounds was analysed. High luminescence efficiencies of europium and terbium benzoates, and terbium anthranylates and salicylates were obtained. Effect of increasing the luminescence efficiencies of europium salicylates and 8-oxyquinolinates at introduction of acceptor nitro-and sulfo-groups in the ligand was revealed. Channel of dissipation of the excitation energy through the ligand $\pi^*$–n transition of europium and terbium nitro- and dinitrobenzoates was found. Influence of relative positions of the lowest triplet levels of two non-equivalent ligands of compound on the energy transfer to $Eu^{3+}$ and $Tb^{3+}$ ions was considered.

*Keywords:* $Eu^{3+}$; $Tb^{3+}$; Benzoates; Anthranylates; Salicylates; 8-Oxyquinolinates; Luminescence excitation spectra; Luminescence efficiency; Ligand–metal charge transfer

## 1. Introduction

Lanthanide compounds with aromatic ligands can be used in organic light emitting diodes (OLEDs) as components forming the light-emitting layer of the device. The papers devoted to the fabrication of electroluminescent devices with terbium carboxylates are well known [1–3]. Besides, properties of thin films of the lanthanide (Er, Yb, and Nd) 8-oxyquinolinates as the organic infrared emitters were investigated [4–7]. Luminescent materials for OLEDs must have high luminescence intensity as a principal quality. They should have also high volatility or solubility, ability to form amorphous layers, significant mobility of the injected charge carriers, etc. Difficult problem of combination of such properties in one compound can be reduced by modification of ligands [8–10]. Effects of ligand radicals on luminescence, excitation and vibrational spectra of europium β-diketonates [11–14], europium and terbium acylpyrazolonates [15] as materials for applications have been discussed by us earlier. Moreover, one of us designs successfully the electroluminescent devices using the aluminium 8-oxyquinolinate, lanthanide β-diketonates and other luminescent compounds in the emitting layer [16].

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In this paper, luminescence and luminescence excitation spectra of europium and terbium carboxylates (benzoates, furoates, anthranylates and salicylates) and europium 8-oxyquinolinates will be presented. The luminescence efficiencies of these compounds are analysed in dependence on details of the structure. Spectra of some of these compounds were briefly discussed in [17]. We consider the luminescent properties of the lanthanide compounds at introduction of electron-withdrawing nitro- ($NO_2$) and sulfo- ($SO_3^-$) groups, and electron-donating amino- ($NH_2$), phenylamino- ($NHC_6H_5$), and hydroxy- (OH) groups in aromatic ligands. These groups influence the distribution of π-electronic density in the ligand. The effective charges on atoms coordinated by $Ln^{3+}$ ions can be changed in this way, and the interaction of the ligands with metal ion can be modified. As a consequence, the energies of the ligand–metal charge transfer states (LM CTS) and the positions of the triplet levels are changed. Investigations of processes of the excitation energy transfer and $Ln^{3+}$ luminescence efficiency in dependence on relative positions of the LM CTS, ligand singlet, triplet and lanthanide states were the subject of many publications, for example, [18–22].

A spectacular increase of luminescence efficiencies of europium 5-sulfo-8-oxyquinolinate and, especially, 3,5-dinitrosalicylate under UV excitation was obtained. However, presence of nitro-groups in the benzoate ligand may form a channel of degradation of the excitation energy through $\pi^*$–n transition of $NO_2$-group. In compounds with two non-equivalent ligands the luminance can be adjusted by shifts of the triplet levels of both ligands. Luminescence spectra of europium aromatic carboxylates can be tuned by the change of the size and donor–acceptor ability of ligand radicals, in analogy to europium β-diketonates [12]. Spectroscopic studies presented here open a way for application of some of compounds with aromatic ligands as electroluminescent emitters having high luminance and better chemical stability than β-diketonates utilized in OLEDs.

## 2. Compounds investigated and experimental details

Europium and terbium compounds with benzoic (Benz), 4-nitrobenzoic (NBenz), 3,5-dinitrobenzoic (DNBenz), 4-hydroxybenzoic (OHBenz), 2-furancarboxylic (Fura), anthranylic (2-aminobenzoic) (Anthr), phenylanthranylic (2-(phenylamino)benzoic) (PhAnthr), salicylic (2-hydroxybenzoic) (Sal), 3-methylsalicylic (MSal), 5-sulfosalicylic (SSal), 3,5-dinitrosalicylic (DNSal) acids, as well as compounds of 8-hydroxyquinoline (Oxin), 5-nitro-8-hydroxyquinoline (NOxin), 5-sulfo-8-hydroxyquinoline (SOxin) were synthesized (Table 1). Adducts of the salts of aromatic carboxylic acids with 1,10-phenanthroline (Phen) and 2,2′-bipyridine (Bpy) molecules were investigated also. The salts were synthesised by the exchange of cations in mixture of water or ethanol solutions of lanthanide chloride and sodium salt of aromatic acid. The adducts were obtained by mixing of ethanol solution of heterocyclic diimine with solution of the lanthanide salt of aromatic acid. Composition of compounds synthesised and the details of their structures were controlled by the elemental analysis, vibrational spectroscopy, and by comparison of the europium and terbium luminescence spectra, in analogy to [23].

Table 1
Chemical formulae of lanthanide compounds with aromatic ligands

| Compound | Chemical formulae |
|---|---|
| LnBenz | $Ln(Benz)_3{\cdot}2.5H_2O$ |
| LnNBenz | $Ln(4\text{-}NO_2Benz)_3{\cdot}3H_2O$ |
| LnDNBenz | $Ln(3,5\text{-}NO_2Benz)_3{\cdot}3H_2O$ |
| LnFura | $Ln(2\text{-}Fura)_3{\cdot}3H_2O$ |
| LnAnthr | $Ln(2\text{-}NH_2Benz)_3{\cdot}H_2O$ |
| LnPhAnthr | $Ln[2\text{-}(C_6H_5NH)Benz]_3{\cdot}nH_2O$ |
| EuSal | $Eu(Sal)_3{\cdot}1.5H_2O$ |
| TbSal | $Tb(Sal)_3{\cdot}nH_2O$ |
| LnMSal | $Ln(3\text{-}CH_3Sal)_3{\cdot}3H_2O$ |
| LnSSal{1} | $Ln(5\text{-}SO_3Sal){\cdot}3H_2O$ |
| EuSSal{2} | $Eu_2(5\text{-}SO_3Sal)_3{\cdot}10H_2O$ |
| LnDNSal | $Na_3Ln(3,5\text{-}NO_2Sal)_3{\cdot}2H_2O$ |
| LnOxin | $Ln(Oxin)_3$ |
| LnNOxin | $Ln(5\text{-}NO_2Oxin)_3$ |
| LnSOxin | $Ln_2(5\text{-}SO_3Oxin)_3{\cdot}8H_2O$ |
| LnLigPhen, LnLigBpy | $LnLig_3Phen$, $LnLig_3Bpy$ (Lig = Benz, NBenz, DNBenz, Fura, 4-OHBenz, Anthr, PhAnthr);<br>$LnLig_3Phen_{1.5}$ (Lig = Sal, MSal);<br>$Ln_2Lig_3Phen$ (Lig = SSal) |

Some of compounds with heterocyclic diimines $LnLig_3$ Phen and $LnLig_3Bpy$ (Lig = Benz, OHBenz, Fura,) seem to have content and structure like dimeric europium carboxylates with the metal coordination number equal to 9, such as $Eu(CH_3COO)_3$ Phen [24], $Eu(Fura)_3Phen$ [25] and several europium benzoates, in particular, 2,3-dimethylbenzoate with 2,2′-bipyridine [26]. Lanthanide salicylates and methylsalicylates with Phen under consideration have content $LnLig_3Phen_{1.5}$. The content of lanthanide sulfosalicylates with Phen is $Ln_2Lig_3Phen$. Two europium sulfosalicylate salts $Eu(5\text{-}SO_3Sal){\cdot}3H_2O\{1\}$ and $Eu_2(5\text{-}SO_3Sal)_3{\cdot}10H_2O\{2\}$ were investigated.

The luminescence and luminescence excitation spectra were measured with LOMO DFS-12 spectrometer (high resolution), LOMO UM-2 monochromator (low resolution) and SLM Aminco SPF spectrofluorimeter at 300 and 77 K. Both LOMO instruments were controlled by computer and the spectra were registered in digital form. The luminescence spectra were recorded in the regions of $^5D_0$–$^7F_0$–$^5D_0$–$^7F_4$ ($Eu^{3+}$) and $^5D_4$–$^7F_6$–$^5D_4$–$^7F_0$ ($Tb^{3+}$) transitions. The registration of excitation spectra was realized in the regions of $^5D_0$–$^7F_2$ ($Eu^{3+}$) and $^5D_4$–$^7F_5$ ($Tb^{3+}$) transitions. The luminescence efficiency was estimated as the integral intensity of all $Ln^{3+}$ electronic transitions of compounds placed in the same conditions (Table 2). In this case, a region 300–380 nm of the spectrum of DRSh-250 mercury high-pressure lamp including the intense Hg 365 nm line was isolated by UV filters and used for luminescence excitation. Such an excitation was not optimal for all compounds investigated. The lumi-

Table 2
Luminescence efficiency of europium and terbium compounds with aromatic ligands at 77 K (relative units)

| | |
|---|---|
| Eu compounds | |
| EuBenz | 10 |
| EuFura | 60 |
| EuLigPhen (Lig = Benz, Fura) | 300–200 |
| EuLigBpy (Lig = Benz, Fura) | 150–50 |
| EuLig (Lig = NBenz, DNBenz) | 2–0.35 |
| EuLigPhen(Bpy) (Lig = NBenz, DNBenz) | 50–5 |
| EuLig (Lig = PhAnthr, Anthr, Sal, MSal, SSal) | 0–3 |
| EuDNSal | 500 |
| EuLigPhen(Bpy) (Lig = PhAnthr, Anthr) | 5–15 |
| EuLigPhen (Lig = Sal, MSal, SSal) | 70–35 |
| EuOxin | 0.5 |
| EuNOxin | 7 |
| EuSOxin | 55 |
| Tb compounds | |
| TbLig (Lig = Benz, Fura) | 20–35 |
| TbLigPhen (Lig = Benz, Fura) | 260–150 |
| TbBenzBpy | 140 |
| TbLig (Lig = NBenz, DNBenz) | 0.5–0 |
| TbLigPhen(Bpy) (Lig = NBenz, DNBenz) | 10–1 |
| TbPhAnthr | 50 |
| TbLig (Lig = Sal, Anthr, MSal) | 100–150 |
| TbSSal | 300 |
| TbDNSal | 0 |
| TbLigPhen(Bpy) (Lig = PhAnthr, Anthr) | 170–200 |
| TbLigPhen (Lig = MSal, SSal) | 250–400 |
| TbOxin | 0 |
| TbNOxin | 0 |
| TbSOxin | 0 |

nescence efficiency of $Eu(Benz)_3 \cdot 2.5H_2O$ salt equal to 10 at 77 and 300 K was taken as a standard.

## 3. Results and discussion

### 3.1. Benzoates and furancarboxylates

To facilitate the examination of spectra, luminescence efficiencies and processes of the excitation energy transfer all the compounds under investigation were arranged in three groups.

The luminescence excitation spectra of europium and terbium benzoates and furancarboxylates related to the first group are presented in Figs. 1–4. The excitation spectra of EuBenz and TbBenz salts resemble one another. These spectra consist of the strong $\pi$–$\pi^*$ band with the long-wavelength edge at ∼300 nm and a weak intraligand charge transfer (ILCT) band with the edge at ∼370 nm. The ligand bands in the excitation spectra of terbium benzoate and furoate salts are more intense than ones in the excitation spectra of europium salts, as multi-phonon quenching of $Tb^{3+}$ luminescence is less effective than quenching of $Eu^{3+}$.

The excitation spectra of LnLigPhen and LnLigBpy compounds include, as a rule, strong bands due to n–$\pi^*$ and $\pi$–$\pi^*$ transitions of heterocyclic diimine molecules. The long-wavelength edges of wide band of Phen and Bpy ligands are at ∼350 and ∼325 nm, respectively. The TbLigPhen (Lig = Benz, NBenz, DNBenz) excitation spectra, presented in Fig. 3, resemble well enough the excitation spectra of europium compounds EuLigPhen with the same benzoate derivatives (Fig. 1). There are no ligand bands in the LnNBenz and LnDNBenz (Ln = Eu, Tb) excitation spectra (Figs. 1c, e and 3c). Moreover, the intensity of all $Ln^{3+}$ transitions situated higher than 390 nm is extremely weak in all europium and terbium nitro- and dinitrobenzoates including compounds with the heterocyclic diimines. In the excitation spectrum of EuNBenz salt $^7F_0$–$^5L_6$ transition is also quenched. The cause of such behaviour of nitro- and dinitrobenzoate spectra consists in the dissipaton of the excitation energy through the excited state of $NO_2$-group. This state is located higher than 390 nm in majority of compounds except LnNBenz salts, where it is situated somewhere lower than 390 nm.

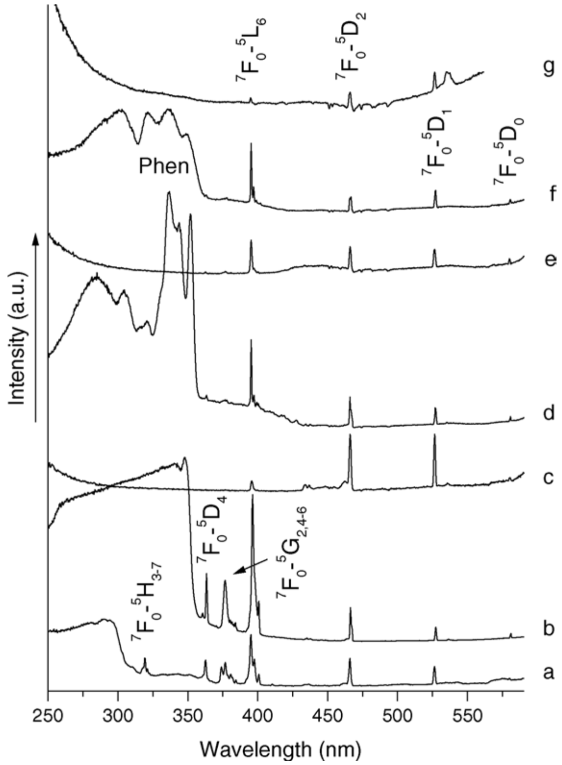

Fig. 1. Luminescence excitation spectra of EuBenz (a), EuBenzPhen (b), EuNBenz (c), EuNBenzPhen (d), EuDNBenz (e), EuDNBenzPhen (f, g) at 77 (a–f) and 300 K (g).

To check this assumption let us demonstrate n–$\pi^*$ band of $NO_2$-group in the luminescence excitation spectrum of europium nitropropionate $Eu(NO_2C_2H_4COO)_3 \cdot 3H_2O$ (Fig. 5). The spectrum of propionate $Eu(C_2H_5COO)_3 \cdot 3H_2O$ consists only of narrow lines of $Eu^{3+}$ transitions. In the spectrum of nitropropionate a wide band of $NO_2$-n–$\pi^*$ transition with weak lines of $Eu^{3+}$ transitions on its ridge appears. At excitation in this region weak $Eu^{3+}$ luminescence and ligand fluorescence are observed. The $(CH_2)_2$-spacer in nitropropionate radically lowers the interaction of two parts of ligand.

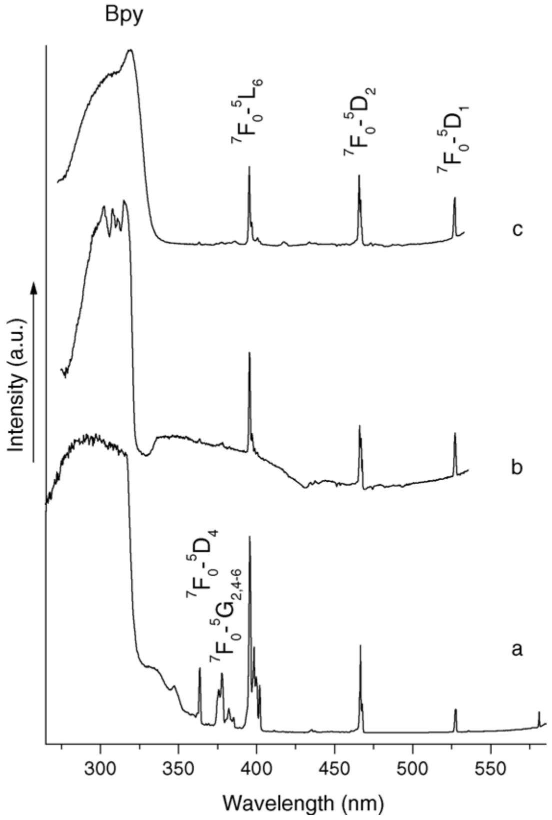

Fig. 2. Luminescence excitation spectra of EuBenzBpy (a), EuNBenzBpy (b), EuDNBenzBpy (c) at 77 K.

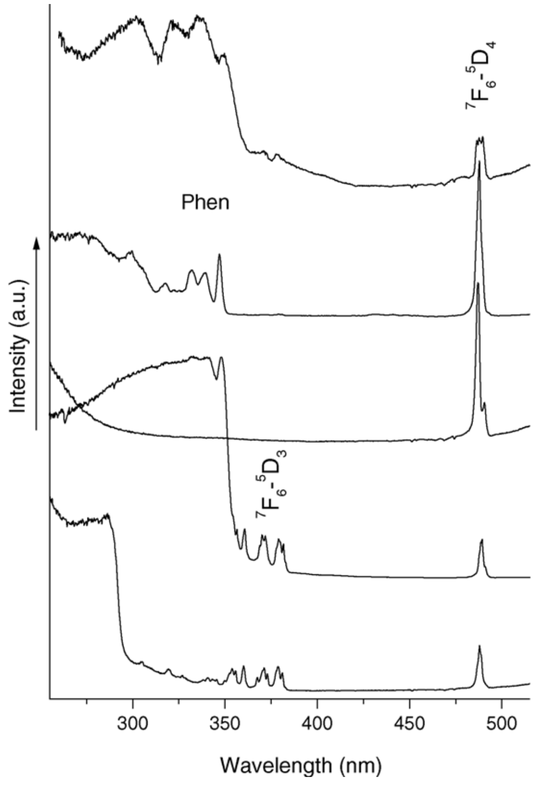

Fig. 3. Luminescence excitation spectra of TbBenz (a), TbBenzPhen (b), TbNBenz (c), TbNBenzPhen (d), TbDNBenzPhen (e) at 77 K.

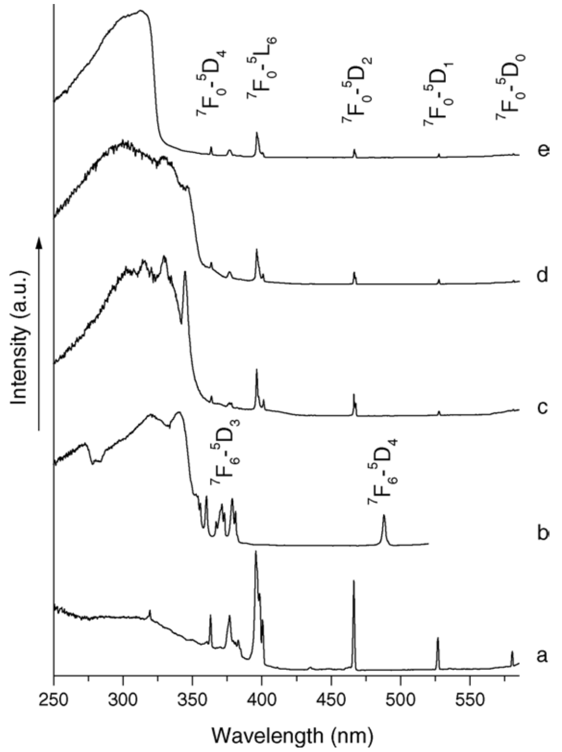

Fig. 4. Luminescence excitation spectra of EuFura (a), TbFura (b), EuOHBenzPhen (c), EuFuraPhen (d), EuFuraBpy (e) at 77 K.

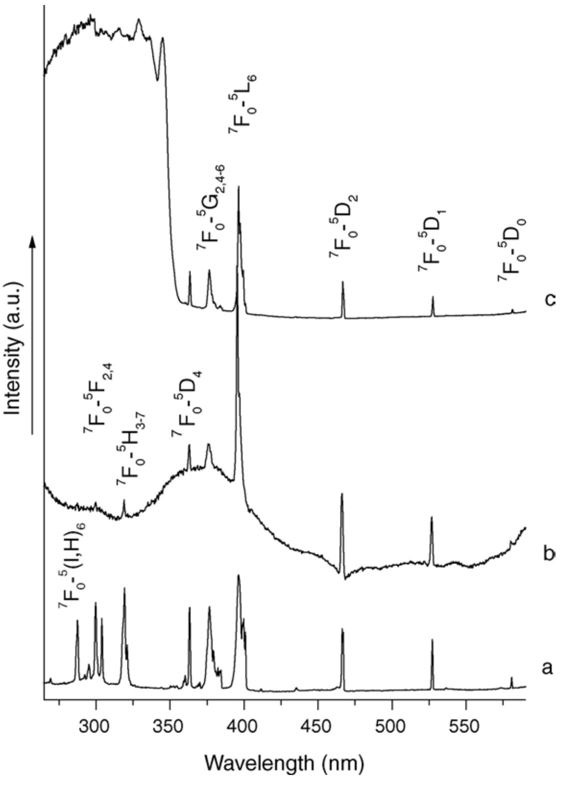

Fig. 5. Luminescence excitation spectra of $Eu(C_2H_5COO)_3 \cdot 3H_2O$ (a), $Eu(NO_2C_2H_4COO)_3 \cdot 3H_2O$ (b), $Eu(NO_2C_2H_4COO)_3$ Phen (c) at 77 K.

So, a lot of the excitation energy of nitrogroups is dissipated by phonons of the crystal lattice.

The $NO_2$-n–π* transition, with participation of ILCT, in the lanthanide 4-nitrobenzoates shifts to long-wavelengths in comparison with its location in the lanthanide 3,5-dinitrobenzoates because of stronger charge transfer in the former compounds. Position of the $NO_2$-substituents in aromatic acid influences also the interaction of the $CO_2^-$ group with metal cation, which is minimum in compounds with *para*-$NO_2$-group [27]. The strength of the “metal–ligand” bonds is one of factors regulating the energy transfer from ligand to $Ln^{3+}$ ion [13].

Weak band assigned to $NO_2$-group n–π* transition with admixture of ILCT is seen in the 350–425 nm region of the excitation spectra of EuNBenzPhen (Fig. 1d) and EuNBenzBpy (Fig. 2b). At excitation in transitions of aromatic anion and in the short-wavelength $Ln^{3+}$ transitions the absorbed energy is transferred to the excited states of $NO_2$-group. The direct excitation of $NO_2$-group through n–π* transition occurs too. Then, the excitation energy can be dissipated in the lattice, transferred to the lowest excited ligand singlet and triplet levels, generating ligand fluorescence and $Ln^{3+}$ luminescence. The excitation energy transfer from Phen to the $NO_2$-group can also occur. Contribution of this process increases in case of proximity of Phen excited states to $Ln^{3+}$ states located higher than 390 nm, in particular, to $^5D_3$ states of $Tb^{3+}$ (compare Figs. 1d and 3d), in case of the short-wavelength shift of n–π* transition of $NO_2$-group (Figs. 1f and 3e), and at heating of compounds from 77 to 300 K, for example, the EuDNBenzPhen (Fig. 1g). The effect of this process is low in compounds with Bpy. Besides of the closeness of excited states of Phen, $Ln^{3+}$ and $NO_2$-group, an important condition of Phen quenching consists in a proper spatial location of two different aromatic ligands of compound. The quenching effects are not observed in the excitation spectrum of europium nitropropionate with Phen (Fig. 5c), where the $NO_2$-radical of aliphatic ligand is isolated.

High enough luminescence efficiencies of europium and terbium salts LnBenz, LnFura (10–60) and high efficiencies of their adducts with Phen (150–300) and Bpy (50–150) were observed (Table 2). Lower luminescence intensity of compounds with Bpy can be caused by lower rigidity of molecular skeleton and by higher triplet energy of Bpy (∼23000 $cm^{-1}$ [28,22]) in comparison with Phen (∼22100 $cm^{-1}$ [29,22]). The decrease of the luminescence intensity of europium benzoate salts in the row of Benz (10)–NBenz (2)–DNBenz (0.35) and very weak luminescence of TbNBenz and TbDNBenz salts (0.5–0) can be explained by participation of $NO_2$-group in the quenching processes discussed above and, first of all, by low energy of the triplet states of nitrobenzoate anions in relation to the energy of $^5D_0$ ($Eu^{3+}$) and $^5D_4$ ($Tb^{3+}$) levels. The luminescence intensities of these compounds under UV excitation used do not vary much in the temperature interval from 77 to 300 K.

The intensities of the luminescence of europium and terbium benzoates point to the fact that the triplet levels of NBenz and DNBenz are significantly lower than the triplet of Benz (∼25000 $cm^{-1}$ [30,21]), the $^5D_4$ level of $Tb^{3+}$, and, probably, even lower than the $^5D_0$ level of $Eu^{3+}$ ion. The participation of triplets of both non-equivalent ligands of compound in the excitation of lanthanide benzoates and furancarboxylates with Phen and Bpy gives rise to the increase of the luminescence efficiency. However, the luminescence intensity of terbium nitrobenzoates with heterocyclic diimines (1–10) is noticeably weaker, than intensity of corresponding europium compounds (5–50). Decrease of the luminescence efficiency by a factor of $10^2$ in the rows of benzoates LnLigPhen and LnLigBpy (Lig = Benz, NBenz, DNBenz) means that the excitation energy transfer to the lowest triplet of compound occurs. Here it is the triplet of Phen (Bpy), NBenz and DNBenz, respectively. Higher efficiency of $Eu^{3+}$ and $Tb^{3+}$ luminescence can be obtained at more optimal excitation through Phen and Bpy absorption bands. The highest efficiency of the excitation through Phen and Bpy bands can be reached in europium 2-furancarboxylates and 4-hydroxybenzoates (Fig. 4c–e).

The luminescence spectra of some of compounds LnLigPhen, LnLigBpy for Lig = Fura, Benz, OHBenz recorded with high resolution are given in Fig. 6. These spectra as well as the vibrational IR spectra point to likeness of crystal structures of compounds investigated and the structure of $Eu(Fura)_3Phen$ [25], displaying, first of all, similarity of the

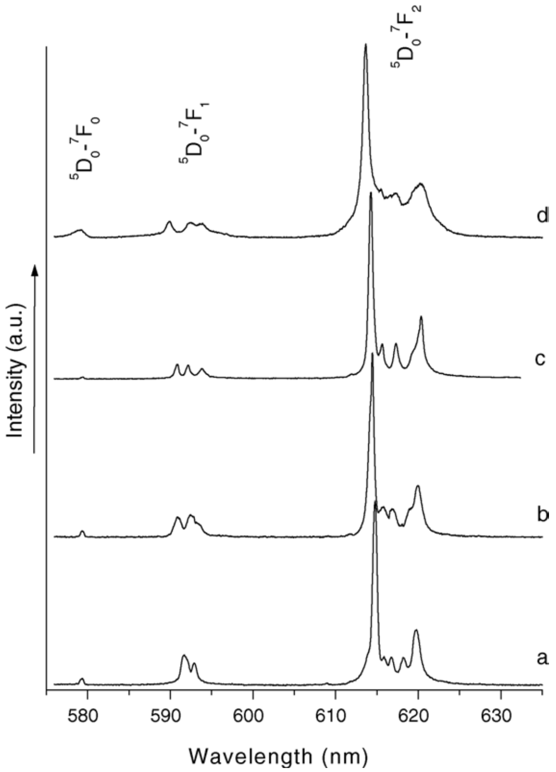

Fig. 6. Luminescence spectra of EuFuraBpy (a), EuFuraPhen (b), EuBenzPhen (c), EuOHBenzPhen (d) at 77 K (spectrometer DFS-12).

charge arrangement around $Eu^{3+}$ ion in the enumerated compounds. Decrease of Stark splitting of $^5D_0$–$^7F_{1,2}$ transitions and improvement of monochromaticity are observed in the spectra going from “d” to “a”. Weakening of the crystal field is conditioned by steric factor and by strengthening of the ligands acceptor ability.

Thus, spectroscopic studies of europium and terbium benzoates and furancarboxylates demonstrated identity of excitation spectra, luminescence efficiencies and processes of transfer and degradation of the excitation energy in compounds of both lanthanides. Characteristics of europium compounds discussed in the next item differ substantially from that of terbium compounds.

### 3.2. Anthranylates and salicylates

The second group of compounds includes europium and terbium anthranylates and salicylates. It is impossible to explain spectroscopic behaviour of europium and terbium salts with derivatives of anthranylic and salicylic acids (and their adducts with heterocyclic diimines) by position of the triplet levels alone. In comparison with low luminescence intensity of EuPhAnthr, EuAnthr, EuSal, EuMSal, EuSSal salts (0–3), strong luminescence of dinitrosalicylate EuDNSal (500 at 77, 100 at 300 K) was revealed. On the contrary, majority of terbium salts have high luminescence intensity: TbPhAnthr (50), TbAnthr, TbSal, TbMSal (100–150), TbSSal (300), but dinitrosalicylate TbDNSal do not luminesce.

Luminescence spectra of europium salicylates measured with low resolution but with high signal to noise ratio are given in Fig. 7. In comparison with lanthanide carboxylates with heterocyclic diimines, which often form similar structures (Fig. 6), the salts seldom have related structures. The spectra in Fig. 7 can serve as fingerprints of the different charge arrangements around $Eu^{3+}$ ion in salts presented.

High efficiency of $Eu^{3+}$ excitation through the ligand absorption bands is characteristic feature of EuDNSal (Fig. 8g). The excitation of $Eu^{3+}$ ions through the ligand bands is not observed in other europium salicylate salts (Fig. 8a–d) and in EuAnthr. The excitation spectrum of the latter salt was not recorded satisfactorily because of poor emission signal. In the excitation spectrum of EuDNSal the band with maximum at ∼360 nm is attributed to $\pi$–$\pi^*$ transition, the band at ∼450 nm is assigned to ILCT with contribution of $NO_2$-groups.

Ligand–metal charge transfer band (LM CTB) was found in absorption spectra of EuSal and EuAnthr in contrast to spectra of sodium Sal and Anthr salts, and europium Benz and 4-OHBenz salts, where only wide ligand bands were registered [31]. In the paper cited, LM CTB were detected in compounds with ligands having electron-donating groups in *ortho*-position to carboxylic group. The bands analogous to ligand bands and LM CTB indicated are not observed in the excitation spectra of europium Sal, MSal, SSal (Fig. 8) and Anthr salts, probably, due to the excitation energy dissipation through the LM CTS. This quenching channel is widened at heating of the samples. Feeble luminescence of the EuSal and EuAnthr compounds depends noticeably on temperature; so, it is not registered at 300 K. One of two europium sulfosalicylates investigated, EuSSal{1}, has the same excitation and luminescence properties as the latter two compounds. The other europium sulfosalicylate, EuSSal{2}, has stronger luminescence. The $Eu^{3+}$ states above $^5D_2$ do not participate in the excitation of EuSal luminescence because of the energy transfer to LM CTS. Therefore, the LM CTS in this compound has the lowest energy. Low energy of LM CTS in the EuAnthr, EuSal and EuSSal{1} salts should be conditioned by strong “metal–ligand” bonds. Hypothetically, the presence of the protonated OH-group in EuSSal{2} can give rise to weakening of the “metal–ligand” bonds and to increase of the LM CTS energy. It is known (for example, from [32]), that the deprotonation of sulfosalicylate hydroxy-group is the most difficult; pK for OH-group is much higher than pK for carboxylic and sulfo-groups. So, the presence of the protonated OH-group in $Eu_2(5\text{-}SO_3Sal)_3\cdot 10H_2O$ is very feasible.

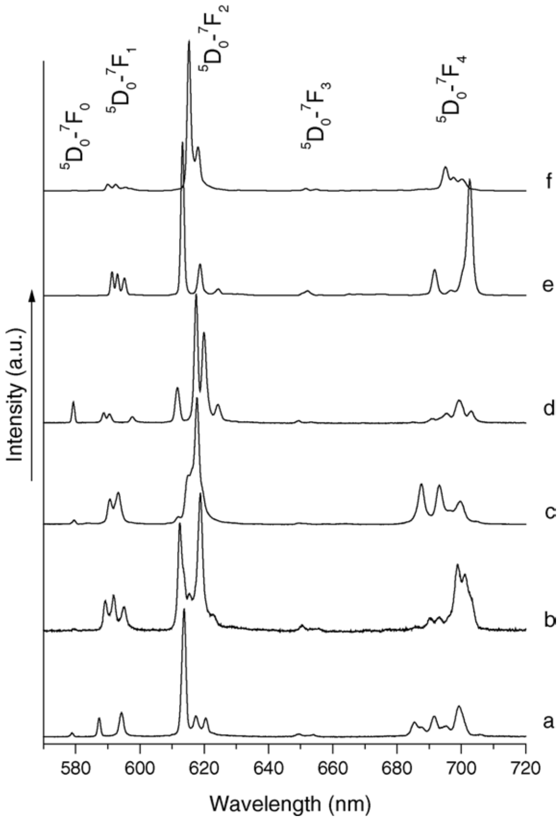

Fig. 7. Luminescence spectra of EuSal (a), EuMSal (b), EuSSal{2} (c), EuSSal{1} (d), EuDNSal (e), EuSalPhen (f) at 77 K (monochromator UM-2).

The $NO_2$-groups bound to the aromatic ring of salicylic salt may “sensitize” $Eu^{3+}$ luminescence by means of withdrawing the $\pi$-electron density from the aromatic ring and decreasing the quenching through LM CTS. A similar decrease of degradation rate of the $Eu^{3+}$ excitation energy

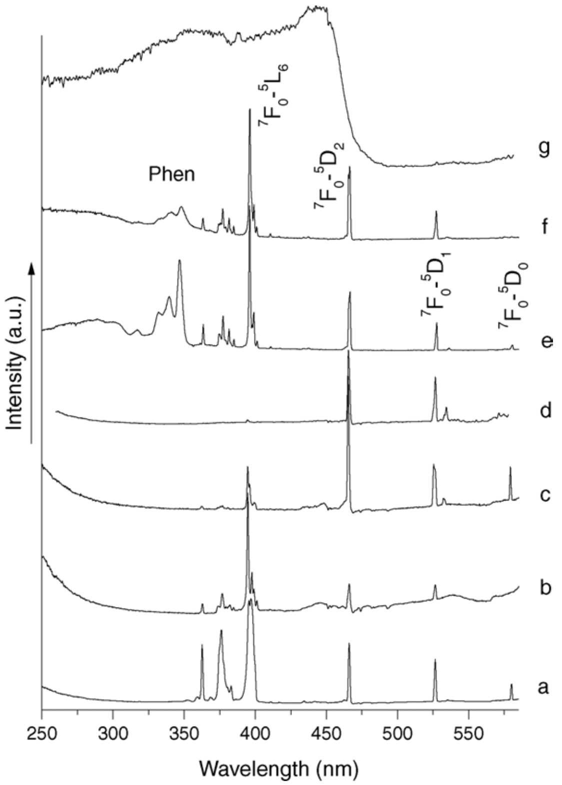

Fig. 8. Luminescence excitation spectra of EuSSal{2} (a), EuMSal (b), EuSSal{1} (c), EuSal (d), EuMSalPhen (e), EuSalPhen (f), EuDNSal (g) at 77 K.

through the LM CTS at weakening the “metal–ligand” bonds was observed in europium β-diketonates [12,13]. Besides, the energy of LnDNSal triplet state (it is ∼18800 $cm^{-1}$ by our estimation) is lower than ones of LnSal (23800 $cm^{-1}$ [20]) and LnSSal (24300 $cm^{-1}$ [33]). The LnDNSal triplet is situated higher than $^5D_0$ level of $Eu^{3+}$ (17227 $cm^{-1}$), but lower than $^5D_4$ level of $Tb^{3+}$ (∼20500 $cm^{-1}$); so, $Tb^{3+}$ luminescence in TbDNSal is absent. To be certain that the TbDNSal complex has the same composition and structure as the EuDNSal, $Eu^{3+}$ ions were admixed as a luminescent probe. In this case, wide-band yellow phosphorescence of the ligand and a weak $Eu^{3+}$ luminescence of Tb(Eu)DNSal were observed. Decrease of the DNSal triplet energy in comparison with Sal and SSal increases the rate of the excitation energy transfer to $Eu^{3+}$ ion. Weakening the ligand–metal bonds in the EuDNSal by two acceptor nitro-groups raises LM CTS energy that diminishes the participation of this state in quenching of $Eu^{3+}$ levels. Two factors indicated may explain high luminescence efficiency of EuDNSal compound.

The introduction of Phen or Bpy into the structures of EuPhAnthr, EuAnthr, EuSal, EuMSal, and EuSSal having poor emission (0–3) leads to increase of the luminescence quantum yield. Luminescence efficiency improves to 5–15 for europium compounds with PhAnthr and Anthr, to 35–70 for compounds with SSal, MSal and Sal ligands. Higher luminescence efficiency of the europium compounds with heterocyclic diimines is conditioned, mainly, by participation of the Phen and Bpy triplet states in the excitation of $Eu^{3+}$ ion. The Phen triplet state (∼22100 $cm^{-1}$) is lower in energy than the triplets of Anthr, PhAnthr and Sal lying at 25200–23800 $cm^{-1}$ [20]. Still the lowest triplet state of two ligands gives the most significant contribution in the processes of excitation energy transfer and quenching [20].

As in salts, LM CTS may hinder an essential growth of the $Eu^{3+}$ luminescence efficiency of europium anthranylates and salicylates with heterocyclic diimines. The excitation spectrum of EuAnthrPhen (Fig. 9a) does not have noticeable ligand bands. The weak wide band in EuPhAnthrBpy spectrum (Fig. 9b) can be attributed to the phenylamino-radical of the ligand. Weak Phen bands appear in the excitation spectra of related EuSalPhen and EuMSalPhen compounds (Fig. 8f and e). The energy adsorbed by heterocyclic diimine molecules can be dissipated through anthranylate-europium and salicylate-europium LM CTS. This effect resembles the Phen energy degradation through $NO_2$-group of nitrobenzoates.

One should note, that a wide salicylate ligand band with maximum at 340 nm appears in the excitation spectrum of europium salicylate salt presented in the paper [34], testifying to possibility of the effective energy transfer from Sal ligand to $Eu^{3+}$.

In contrast to redox-sensitive $Eu^{3+}$ cation, which may take the ligand electron and become $Eu^{2+}$, $Tb^{3+}$ cation have dif-

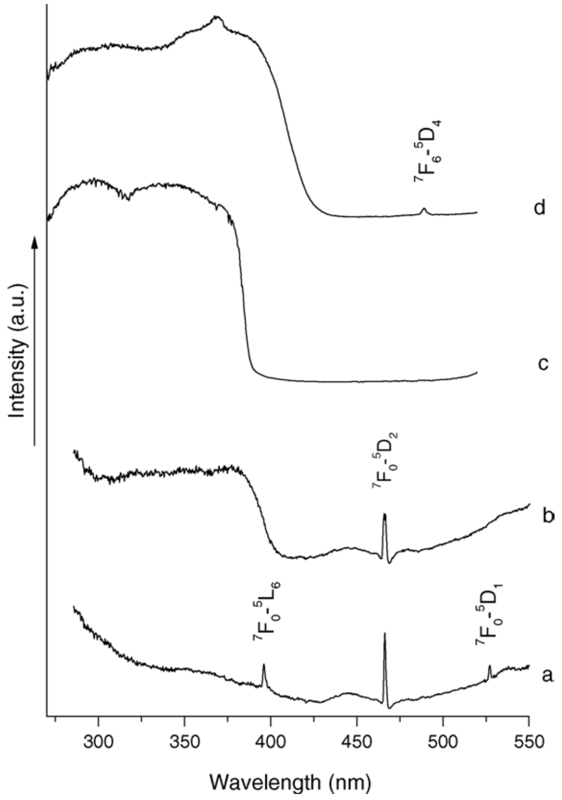

Fig. 9. Luminescence excitation spectra of EuAnthrPhen (a), EuPhAnthrBpy (b), TbAnthr (c), TbAnthrPhen (d) at 77 K.

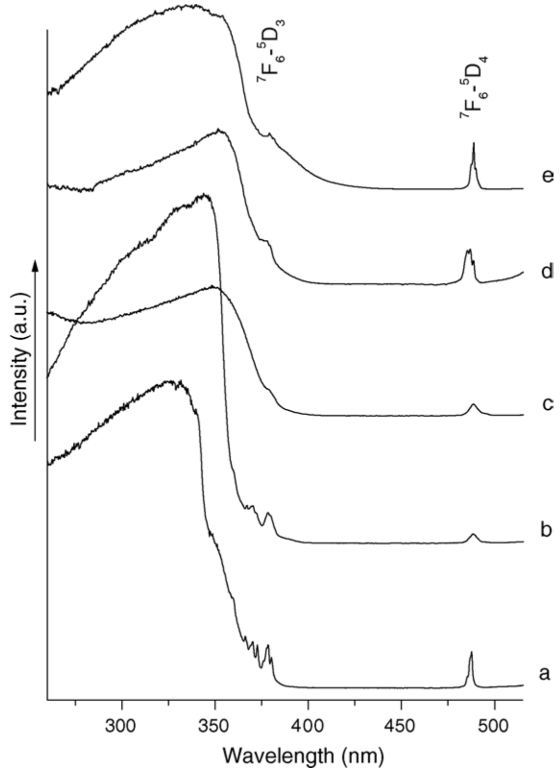

Fig. 10. Luminescence excitation spectra of TbSal (a), TbMSal (b, c), TbSSal{1} (d), TbMSalPhen (e) at 77 (a, b, d, e) and 300 K (c).

ferent properties, in particular, may donate an electron. The high efficiency of the $Tb^{3+}$ excitation through the ligand absorption bands provides high brightness of the TbAnthr, TbSal, TbMSal, TbSSal{1} compounds (Table 2). The excitation spectrum of TbAnthr is presented in Fig. 9c. The excitation spectra of three terbium salicylates TbSal, TbMSal and TbSSal{1} at 77 K are given in Fig. 10a, b and d. The ligand bands in these spectra agree with bands in the terbium absorption and excitation spectra of anthranylate, salicylate and sulfosalicylate investigated in [31,34,35]. An increase of luminescence intensity of TbSSal{1} salt under UV excitation used is induced by the long-wavelength shift of the excitation band. The luminescence efficiency measured grows sometimes at heating of sample from 77 to 300 K due to expansion of the ligand band to long-wavelengths, for example, in the case of TbMSal (Fig. 10b and c).

The excitation spectra of the adducts TbAnthrPhen and TbMSalPhen have wider bands in UV region in comparison with the spectra of salts (Figs. 9 and 10). If the long-wavelength edge of Phen band lies usually at ∼350 nm, the long-wavelength edges of TbAnthr and TbMSal bands lie at ∼385 and ∼355 nm, then the widening of the excitation band of TbAnthrPhen to ∼420 nm (Fig. 9d) and of the band of TbMSalPhen to ∼370 nm (Fig. 10e), probably, may be attributed to $Tb^{3+}$ f–d transitions [36].

Thus, as a consequence of the strong enough “metal–ligand” bonds, the low-energy LM CTS take part in degradation of the excitation energy in europium anthranylates and salicylates. The emission of majority of europium anthranylates and salicylates is low (0–15 and 0.5–70, respectively). On the contrary, all terbium anthranylates and salicylates have high emission intensity (120–200 and 100–400). This is vice versa for EuDNSal and TbDNSal compounds. The important role in these effects belongs to amino- and hydroxy-groups in *ortho*-position. Possibility of involving of these groups in chelate formation of lanthanide with the carboxylate group is not excluded [31,37,38]. Confirmative arguments of the presence of such chelate cycles in some lanthanide compounds investigated were obtained from the vibrational IR spectra.

### 3.3. 8-Oxyquinolinates

The lanthanide 8-oxyquinolinates form the third group of compounds with aromatic ligands under investigation. Optical properties of oxinates of light and heavy metals were reported in many papers, for example, in [39–44]. Two bands of green fluorescence and red phosphorescence, which relative intensities are dependent on metal ion coordinated and on temperature, can be observed in emission spectra. These bands are related to the $\pi^*$–$\pi$ transitions (with admixture of $\pi^*$–n ILCT) from the lowest excited singlet and triplet states. The aluminium 8-oxyquinolinate $Al(Oxin)_3$ is prevailing among materials with green fluorescence used in light-emitting layer of OLEDs. The phosphorescence band does not appear in $Al(Oxin)_3$ spectrum because of long radiative lifetime of the lowest triplet and fast relaxation processes. Conditions for phosphorescence arise in 8-oxyquinolinates of heavy metals due to the strengthening of spin-orbital interaction. However, the quenching of red phosphorescence by oxygen is often observed at room temperature, in particular, in $Gd(Oxin)_3$ [45].

Molecules of Oxin derivatives are coordinated by $Ln^{3+}$ ion through nitrogen atom and oxy-group. SOxin may also be coordinated by $Ln^{3+}$ through sulfo-group that strengthens acceptor properties of this group in relation to the ligand. Vibrational IR spectra and vibronic sidebands of the $Eu^{3+}$ electronic transitions testify to the coordination of $SO_3^-$-group in compound under investigation. An increase of the $Eu^{3+}$ luminescence efficiency of EuNOxin (up to 7) and especially of EuSOxin (to 55) is observed at 77 K in comparison with very weak luminescence of EuOxin (0.5). At the same time, corresponding terbium compounds do not luminesce. The luminescence spectra of three europium 8-oxyquinolinates are presented in Fig. 11. One should pay attention to high luminescence monochromaticity of EuSOxin. The maximum deviation of the position symmetry of $Eu^{3+}$ ion from the centrosymmetric one in this compound can be conditioned by distortions of the structure at coordination of sulfo-groups.

It is known, that the energies of the first triplet level of $Al(Oxin)_3$ and $Gd(Oxin)_3$ are very low [45–48]. Recently, the time-delayed spectra of low-temperature photo- and electroluminescence of the $Al(Oxin)_3$ thin films were investigated

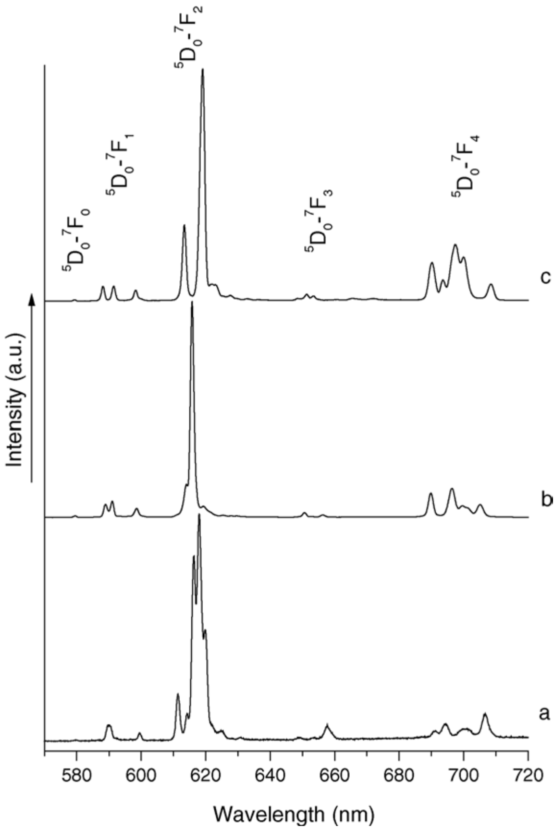

Fig. 11. Luminescence spectra of EuOxin (a), EuSOxin (b), EuNOxin (c) at 77 K (monochromator UM-2).

[48]. It was found, that the energy of triplet level of Al(Oxin)$_3$ at 30 K is 16810 cm$^{-1}$ (2.09 eV). The position of zero-phonon line of T–S transition in emission spectrum of Gd(Oxin)$_3$ in a rigid glass solvent is 17200 cm$^{-1}$ at 77 K [47]. So, the Oxin triplet level in our compounds must be lower than $^5D_0$ level of Eu$^{3+}$ and much lower than $^5D_4$ level of Tb$^{3+}$. The excitation energy reaches Oxin triplet missing the first metastable excited level of both lanthanide ions. Just the same occurs in case of europium and terbium NOxin compounds. Excitation spectrum of EuOxin was not recorded because of very weak monitoring signal. However, the signal was sufficient for the registration of EuNOxin excitation spectrum presented in Fig. 12. An increase of luminescence intensity of EuNOxin in comparison with one of EuOxin can not be explained by position of the lowest NOxin triplet, which must be lower than Oxin triplet. Probably, the LM CTS may participate in processes of dissipation of the excitation energy in EuOxin. This participation is reduced in EuNOxin because of the influence of the acceptor NO$_2$-group in the same way, as it was supposed in case of EuDNSal.

We do not know the position of the triplet of SOxin ligand, but in analogy to Sal and SSal, one should wait for increase of its energy in comparison with Oxin. Judging from the papers [20,33,49], the SSal triplet is higher by ~400 cm$^{-1}$ than the Sal triplet. If our assumption is correct, the energy transfer from SOxin triplet to Eu$^{3+}$ $^5D_0$ level in EuSOxin must arise. This will result in relatively high intensity of luminescence of this compound. The excitation spectra of EuNOxin and EuSOxin compounds (Fig. 12) resemble the spectrum of EuDNSal; the efficiency of the Eu$^{3+}$ excitation through the ligand bands is high. In analogy to [41], the band with maximum at ~350 nm in the excitation spectrum of EuSOxin is assigned to π–π$^*$ intraligand transition, the band at ~390 nm is attributed to π–π$^*$ transition with admixture of ILCT (π–π$^*$/n–π$^*$). The long-wavelength spread of the wide ligand band to 445 nm in the spectrum of EuNOxin is conditioned by participation of NO$_2$-group in ILCT.

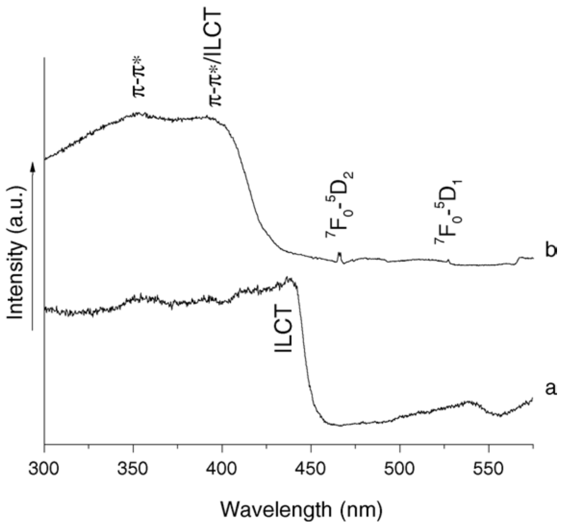

Fig. 12. Luminescence excitation spectra of EuNOxin (a), EuSOxin (b) at 77 K.

So, the increase of the luminescence efficiency of europium 8-oxyquinolinates (as well as salicylates) at introduction of the electron-withdrawing nitro-and sulfo-groups can be explained by proper regulation of positions of triplet and ligand–metal charge transfer states.

## 4. Conclusion

The influence of different radicals of the ligands on spectroscopic characteristics of europium and terbium compounds with aromatic carboxylic acids and with 8-hydroxyquinoline derivatives was examined at 77 and 300 K. The Eu$^{3+}$ and Tb$^{3+}$ luminescence and luminescence excitation spectra were investigated. The luminescence efficiencies were estimated.

It was demonstrated, that the luminescence efficiencies of europium and terbium benzoates and furancarboxylates are high, in contrast to very low efficiencies of europium and terbium nitrobenzoates. The luminescence intensities of compounds can be regulated by choice of the relative positions of the triplet levels at modification of ligands. In europium and terbium nitrobenzoates a channel of dissipation of the excitation energy through the NO$_2$-group π$^*$–n transition with participation of ILCT was found.

The luminescence efficiencies of majority of europium anthranylates and salicylates are low, in contrast to high efficiencies of terbium anthranylates and salicylates. Weak luminances of europium anthranylates and salicylates are caused by energy dissipation through the low-energy LM CTS. Effect of increasing the luminescence efficiency of europium compounds due to introduction of the electron-withdrawing nitro- and sulfo-groups in the aromatic ligands was revealed. An increase of luminescence efficiencies of europium 5-sulfo-8-oxyquinolinate and 3,5-dinitrosalicylate by factors of $10^2$ and $10^3$, respectively, was obtained.

The influence of radicals on quantum yield of luminescence should be taken into consideration at engineering of red and green luminophores.

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