

4f-LUMINESCENCE OF LANTHANIDE IONS IN REGIOISOMERIC CORROLE COMPLEXES

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Isomeric ditopic corroles and complexes of Yb (III), Nd (III) and Er (III) based on them were synthesized and corrole-photosensitized 4f-luminescence in near infrared region was revealed. The structure of isomeric complexes allows adjusting the distance between the corrole core and lanthanide ion. The obtained results show that the sensitization mechanism changes drastically for both different lanthanides and isomeric forms.

Keywords: lanthanides; corroles; isomers; 4f-luminescence; sensitization.

INTRODUCTION. In recent years, corroles and porphyrins, as separate classes of macrocyclic tetrapyrrole compounds, and their metal complexes are widely studied due to the characteristic and very intense light absorption and emission; they are also interesting as effective catalysts, as a basis for various sensors, solar panels, etc [1]. On the other hand, lanthanide compounds are in high demand primarily due to their emission features. 4f-Luminescence (as a result of *f-f* radiative transitions) is a particular kind of emission due to its strongly specific wavelengths for each lanthanide ion, to its lifetime (as a rule 4f-luminescence is a slow kind of emission and can be admitted as phosphorescence) and to a variety of regions of its appearance (UV, VIS, IR).

One of the main features of lanthanide spectroscopy is the impossibility of direct excitation of the lanthanide ion, because the *f-f* absorption of any lanthanide ion is very weak according to the Laport rule [2]. This limitation can be easily overcome by using organic chromophores, which have efficient light absorption and the ability to transfer energy to lanthanide ions.

Macrocyclic tetrapyrroles were the first among macrocyclic compounds to reveal 4f-luminescence sensitization in the early 1970s [3–4]. Lanthanide complexes with macrocyclic tetrapyrroles are promising as agents for luminescent diagnostics (LD) [5], photodynamic therapy (PDT) [6] and magnetic resonance imaging (MRI) [7] due to their

specific luminescent and magnetic properties. Note that 4*f*-luminescence in these complexes is possible in near-infrared (NIR) region only. Lower triplet state (T_1), which is responsible for the sensitization mechanism, can serve as an energy donor for lanthanide ions Yb^{3+} , Nd^{3+} and Er^{3+} , which have low-lying resonant energy levels. Sensitized 4*f*-luminescence is a quite important phenomenon, which is already used in medicine (drugs, markers, assay) [8], technology (fiber-optics, OLED), etc. NIR 4*f*-luminescence is highly demanded for several important reasons: the light of NIR region can penetrate biological tissues much more effectively in comparison to UV/VIS ranges (UV = ultraviolet, VIS = visual) due to very poor overlapping with absorption of bioobjects; NIR light is absolutely safe for human in comparison to UV/VIS ranges whose action can generate dangerous radical species; NIR photons undergo much less scattering in comparison to UV/VIS light [9].

Since the core-coordinated complexes of lanthanides with porphyrins, corroles and phthalocyanines are somewhat less stable in comparison with cyclic and acyclic lanthanide aminopolycarboxylates, it was proposed to obtain tetrapyrrole-based ditopic compounds, which allow the lanthanide ion to be substantially coordinated by aminopolycarboxylate site [10,11]. This approach gave two very important achievements – outstanding stability of lanthanide-porphyrins and lanthanide-corroles and similarity in the effectiveness of both core-coordinated and side-coordinated lanthanide complexes, despite noted difference in distance between chromophore and lanthanide ion.

EXPERIMENT AND DISCUSSION OF THE RESULTS. The spectra of molecular fluorescence, 4*f*-luminescence and excitation

spectra were recorded on a spectrofluorimeter Fluorolog FL 3–22 (Horiba Jobin Yvon) using a 450 W Xe-lamp. The spectra of 4*f*-luminescence of Er(III) complexes were registered in the 1500–1600 nm range (transition ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$). The spectra of molecular fluorescence of porphyrins, corroles and phthalocyanines were registered at 550–800 nm (S_1 - S_0 transitions). The integral intensity of luminescence was measured using the software of the device. The relative quantum yield of molecular fluorescence (φ_{ML}) was determined using a solution of Zn-*tpp* ($\text{H}_2\text{tpp} = 5,10, 15, 20$ -tetraphenylporphyrin) in ethanol as a primary standard (0.022). The determination of φ_{ML} (accuracy $\pm 10\%$) was made using the formula:

$$\Phi_{\text{ML}} = \varphi_0 I_x A_0 n_x^2 / (I_0 A_x n_0^2),$$

where φ_0 and φ_x – luminescence quantum yield of the standard and of the sample respectively, A_0 and A_x – absorption at the wavelength of Soret band of the standard and of the sample respectively,

I_x and I_0 – integral luminescence intensity of the standard and of the sample respectively, n_0 and n_x – refractive index of the standard solvent and of the sample solvent respectively.

Fluorescence lifetime (τ) was measured under excitation at the Soret band.

The synthesis of starting corroles **1**, **2**, **4** and complexes **6**, **8** and **10** was performed previously [10, 12]. The purity of the obtained compounds was checked by TLC Sorbfil plates (grain 5–17 μm , UV-254, thickness 0.1 mm) by Imid Ltd. ${}^1\text{H}$ NMR and ${}^{19}\text{F}$ NMR spectra were recorded using Bruker Avance 600 or 400 MHz in CD_3OD . Mass spectra (MS) were registered on the spectrometer Waters ESI TOF Premier

and the Varian MAT CH-112 spectrometer. The elemental analysis was performed on the CHNS analyzer Flash 2000 Thermo Scientific.

{Carboxymethyl-[2-(carboxymethyl-[[3-(5,10-diphenyl-corrol-5-yl)-phenylcarbamoyl]-methyl]-amino)-ethyl]-amino}-acetic acid (*m*-H₃edta-corrole 3).

A solution of **1** (150 mg, 0.14 mmol) in dry DMF (5 ml) was added dropwise to a stirred solution (80°C) of H₄edta dianhydride (52 mg, 0.2 mmol) in dry DMF (5 ml), containing a catalytic amount of triethylamine (1 drop), during 10 minutes. After adding, the reaction was continued at the same conditions for 1 hour until the starting corrole was determined by TLC in the reaction mixture. Crude product was precipitated with water, filtered and dried to provide the title compound as a purple powder in 90% yield (185 mg). ¹H NMR (MeOD) δ 9.03 (d, 2H, J=4.16Hz), 8.83 (d, 2H, J=4.4Hz), 8.69 (d, 2H, J=4.65Hz), 8.60 (d, 2H, J=4.16Hz), 8.58 (s, 1H), 7.93 (d, 1H, J=8.07Hz), 7.91 (d, 1H, J=7.46Hz), 7.64 (t, 1H, J=7.83Hz), 3.67 (s, 4H), 3.58 (s, 2H), 3.47 (s, 2H), 3.21 (s, 2H), 3.05 (s, 2H). ¹⁹F NMR (MeOD) -140.67 (d, 2F, J=23.16Hz), -140.93 (d, 2F, J=18Hz), -155.67 (t, 2F, J=17.7Hz), -164.65 (t, 2F, J=17.7Hz), -164.79 (t, 2F, J=20.44Hz). ESI-MS obsd 994 [M-H⁺]; λ_{abs.} (nm(lgε), methanol) 410(5.08), 568(4.38), 615(4.26). Calc for C₄₇H₃₁N₇O₇F₁₀: C 56.69%, H 3.14%, N 9.85%. Found: C 56.52%, H 3.03%, N 9.68%.

Inspired by our recent findings regarding the structure features of corroles [12] and our discovery of 4*f*-sensitizing activity of corroles [10], in the present work we continue the synthesis and study of lanthanide complexes with these porphyrinoids, which contain strongly bound Ln³⁺ ion by aminopolycarboxylic site. Thus, the main idea of the present investigation is synthesis of stable lanthanide-porphyrinoids

with acceptable photo-physical parameters avoiding the challenging synthesis of *per*-deuterated and/or *per*-fluorinated compounds.

NIR 4*f*-luminescence in coordination compounds always has poor effectiveness. Traditionally, this problem is caused by the external quenching of NIR luminescence – the overlap of NIR luminescence bands with vibrating quanta of CH and OH bonds, which are always present in the structure of the complex and the environment [13]. It is very difficult to create a system that does not contain the already mentioned chemical bonds in both the structure of the molecule and the solvent. On the other hand it is important to note that the complete removal of CH and OH bonds from the coordination environment of the lanthanide ion does not notably solve this problem [14]. The use of fully deuterated solvents does not solve this problem, too. Moreover, solutions of Er compounds in dmsO and dmsO-d₆ do not reveal any difference in luminescence effectiveness [15]. The simultaneous use of both fully deuterated chromophores (cryptates) and fully deuterated solvents provides mediocre quantum yields of 6.1–6.6% for Yb³⁺ and 0.66–1.7% for Nd³⁺ [16]. On the other hand, fluorinated or/and deuterated ytterbium-porphyrins reveal very imposing 4*f*-luminescence quantum yields of up to 23% even in non-deuterated solvents (there is no data for deuterated ones) [17]. This finding does not solve the above-mentioned problem regarding stability issues. According to this study, ytterbium porphyrins decompose under irradiation with 405 nm light and this fact is still a remaining obstacle for *in vivo* use.

Since stability and luminescence effectiveness are two major requirements for lanthanide-tetrapyrroles, the above-mentioned

approach [10–11] is the only way of solving stability issues for *in vivo* use.

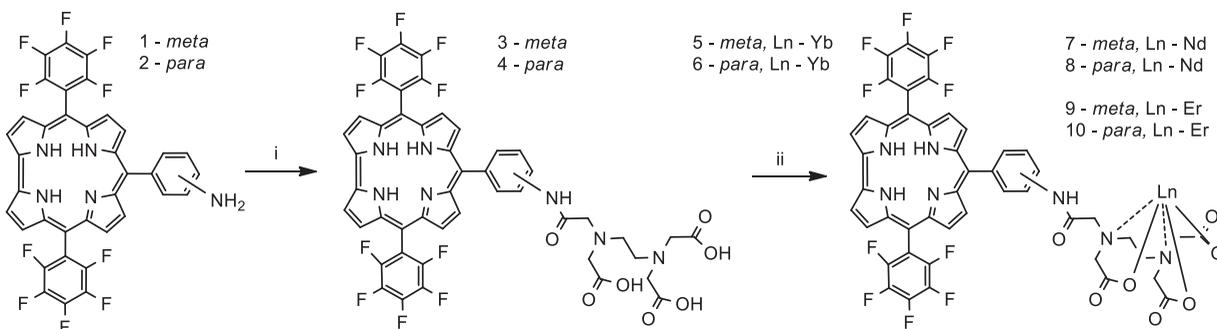
The corrole analogue of 5,10,15,20-tetra-phenylporphyrin (H_2tpp , which is widely used as synthetically accessible and most stable) – 5,10,15-triphenylcorrole (H_3tpc) is a very photosensitive compound and since electron-withdrawing aryl groups increase the photostability of corroles [18], so we used a corrole with two C_6F_5 groups and one aryl group, which could be further easily modified (Scheme 1).

5,15-Bis-(pentafluorophenyl)-10-(3-aminophenyl)-corrole **1** and 5,15-bis-(pentafluorophenyl)-10-(4-aminophenyl)-corrole **2** were obtained according to the previous data [10, 12]. Acylation of **1** and **2** with dianhydride of H_4edta , provides compounds **3** and **4** respectively in about 90% yield. The last step of the synthesis did not require column chromatography (Fig. 1). Ethylenediaminetetraacetic acid was chosen as binding site, since it forms very stable complexes with lanthanides, $lg\beta=15-19$ [19].

The complexation reactions of **3** and **4** with lanthanides were performed quantitatively. Note that MALDI MS and ESI MS revealed two peaks in the molecular ion region that cor-

respond to molecules with mono- and bis-adducts of H_2O [10], hence corrole-edta forms peripheral complexes with two coordinated water molecules to provide the total coordination number (CN) of lanthanide ion $CN=7$. It is important to know the quantity of water molecules coordinated to the lanthanide ion since direct coordination of water to Ln^{3+} leads to the above energy dissipation due to overlapping of the ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ transition (5400 cm^{-1}) of Nd^{3+} emission with O-H bond vibrational quanta $\nu=2$ (6900 cm^{-1}), and such excitation of vibrational state leads to effective quenching of the ${}^4F_{3/2}$ -state of Nd^{3+} ion. Overlapping of O-H bond vibrational quanta $\nu=3$ with the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition (10200 cm^{-1}) of Yb^{3+} emission leads to the same energy dissipation.

Compounds **1** and **2** have absorption spectra that are characteristic of regular corroles like 5,10,15-tris-(pentafluorophenyl)corrole (H_3tpfc). The near-UV Soret band maxima for both **1** and **2** are presented at 415 (5.08) nm ($lg\epsilon$ in parentheses), two Q-bands are in the visual range: 568 (4.38) and 615 (4.26) nm (spectra were measured in methanol). Note, that methanol solutions provide only free base forms of corroles [20].



Scheme 1. Synthesis of isomeric ditopic corroles and the corresponding lanthanide complexes. i) DMF anh., NEt_3 anh., Ar, H_4edta dianhydride, 70–80 °C, 90% yield; ii) methanol, RT, $LnCl_3$ aq.

Ditopic compounds **3** and **4** have exactly the same spectra: the Soret band maxima are the same for both compounds and presented at 410 nm. Two Q-bands are the same for both compounds, too, and presented at 568 and 615 nm. All peripheral lanthanide complexes based on **3** and **4** have the same absorption spectra: Soret band is presented at 410 nm and two Q-bands at 568 and 615 nm. These similarities in light absorption features follow from the unchangeable electronic structure of chromophore. So, peripheral modification at the *meta*- and *para*-positions of phenyl at the 10-th position by edta fragments does not affect the corrole electronic structure.

All compounds **1–10** have similar molecular fluorescence parameters: spectra, kinetic data and effectiveness. All compounds in DMF solutions provide deprotonated forms only. The maxima of S-S-emission bands are around 640–650 and 690–700 nm. The molecular fluorescence quantum yields (φ_{ML}) of the studied compounds are 6–10%. The fluorescence lifetimes (τ) of both corroles and lanthanide-corroles in DMF and methanol solutions are 3–5 ns.

4f-Luminescence was observed in DMF and methanol solutions for all Nd, Yb and Er complexes (Table 1, Fig. 1). The emission maxima are correlated with the fundamental properties of lanthanides. The 980 nm band of Yb complexes **5** and **6** were analyzed as a ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. Nd complexes **7** and **8** displayed bands corresponding to ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ (≈ 890 nm) and ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions (≈ 1060 nm), the Er-complexes **9** and **10** emitted at 1540 nm due to a ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition (1540 nm).

Both Yb complexes reveal relatively weak *4f*-luminescent signals, and it is hard to determine their φ_{4f} . An erbium signal at 1540 nm

was also detected for **9** and **10**, but because of the absence of references for such a far region only arbitrary units are presented.

The molecular fluorescence lifetime measurements showed that the values in methanol solutions were consistently found to be smaller than in DMF (for compounds **7** and **8**, Table 1), which may be attributed to more effective vibrational accepting modes for nonradiative decay in methanol. Methanol contains strong luminescence quenching O-H bonds, whose importance has earlier been emphasized for coordinated H₂O molecules.

The obtained results indicate that the studied lanthanide-corroles are dual-range emitters (Fig.1): visual corrole-based molecular fluorescence with the most intense band at $\lambda_{max} \approx 640\text{--}650$ nm and *4f*-luminescence in the NIR. This dual emission was observed at room temperature and in aerated solutions, in contrast with most other tetrapyrroles that exhibit NIR emission as phosphorescence emission only at deoxygenated conditions and usually in the frozen state (as a rule, at liquid nitrogen temperature). The distance between the paramagnetic ion and the chromophore macrocycle is so large that there is no perturbing effect of the former on the properties of the latter. Note, that this is different from the previously described core-metallated tetrapyrroles with lanthanide ions, where energy transfer from the excited chromophore to the lanthanide is quantitative and no residual fluorescence is obtained [21]. Thus, the studied side-coordinated lanthanide-corroles have non-quenched molecular fluorescence.

Strong support for the above analysis comes from the coincidence between the *4f*-luminescence excitation spectra (Fig. 1) and the absorption spectra of the complexes. This clearly

shows that IET (intramolecular energy transfer) from the donor levels of corroles (i.e., the antenna-effect) to the resonance levels of lanthanide ions takes place. One of the most important features in sensitizing 4f-luminescence is the energy of the lowest triplet level (T_1) of the organic chromophore – traditionally, exactly this energy level serves as a donor in IET

to lanthanide ion. It can be calculated from phosphorescence spectra, and some phosphorescent metallocorroles were already reported [22–24]. Unfortunately, it was impossible to determine the T_1 levels of our compounds because free-base corroles do not phosphoresce. [25] This is also the reason that estimating the IET quantum yield is not possible at this stage.

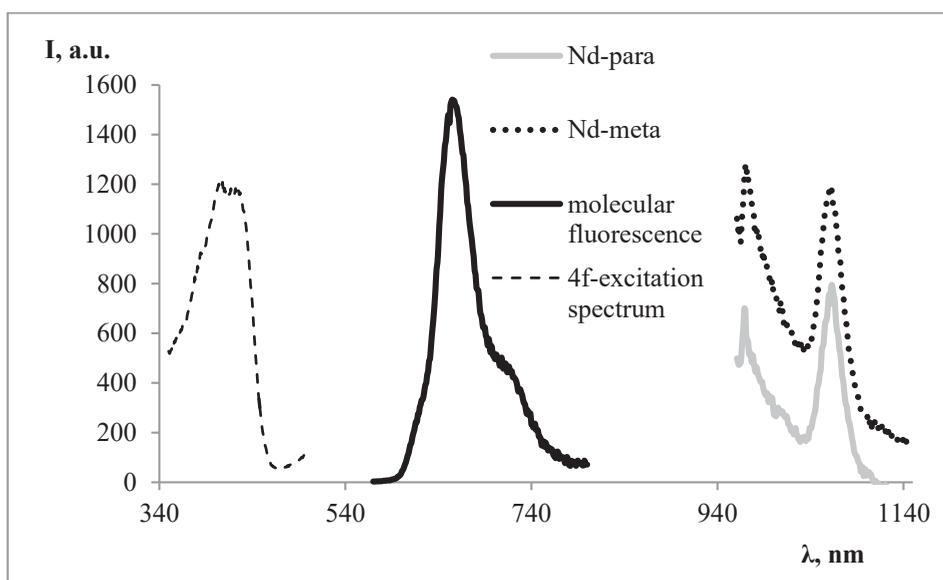


Fig.1. Excitation and emission of Nd-complexes.

Table 1

Photophysical data for studied compounds

#	UV-vis, nm (first – Soret band)	$\lambda_{ML(4f)}$, nm	E_{S1} , cm^{-1}	τ , ns	$\varphi_{ML} \times 10^{2^*}$	$\varphi_{4f} \times 10^{3^*}$
1	415,568,615	643,698	15550	4.5 ± 0.01	6.8	-
2	415,568,615	650	15380	3.47 ± 0.01	8.4	-
3	415,568,615	643,698	15550	4.48 ± 0.01	6.7	-
4	410,568,615	642,697	15580	3.72 ± 0.01	7.7	-
5	415,568,615	643,698	15550	4.51 ± 0.01	6.9	<0.1

Table 1

#	UV-vis, nm (first – Soret band)	$\lambda_{ML(4f)}$, nm	E_{S_1} , cm^{-1}	τ , ns	$\varphi_{ML} \times 10^{2^*}$	$\varphi_{4f} \times 10^{3^*}$
6	410,568,615	638,696	15670	3.21±0.02	9.7	<0.1
7	415,568,615	638,696	15670	4.2±0.01	6.8	4.7
7**	415,568,615	638,696	15670	4.1±0.01	5.9	1.0
8	410,568,615	639,695 (891,1061)	15650	3.43±0.02	7.6	2.79
8**	410,568,615	636 (890,1061)	15720	3.20±0.01	4.7	0.5
9	415,568,615	638,696	15670	4.5±0.01	6.7	1850****
10	410,568,615	639,695 (1540)	15650	3.53±0.01	9.2	20000****
Zn-tpp [#]	425	604,659	16560	2.07±0.01	2.2	-

All solutions with oxygen, DMF, RT, $\lambda_{exc.} = 410$ nm, $C=10^{-5}M$.

* $\pm 10\%$; ** methanol solution; *** φ_{4f} for Nd^{3+} was calculated for only ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition;

**** arbitrary units; # Data from [26–27].

It can be assumed that in theory, the $4f$ -sensitization of Yb^{3+} ion can pass through two transitions: the traditional $T_1 \rightarrow {}^2F_{5/2}$ and presumably $S_1 \rightarrow {}^2F_{5/2}$. [28]. The low level of the Yb^{3+} $4f$ -luminescent signal in such compounds is attributed to poor contribution of the $T_1 \rightarrow {}^4F_{3/2}$ transition in $4f$ -sensitization mechanism for both compounds **5** and **6**. On the other hand, both the molecular fluorescence and intersystem crossing lifetime of corroles (as well as for porphyrins) is too short and the transition $S_1 \rightarrow {}^2F_{5/2}$ seems to be not competitive compared to $S_1 \rightarrow S_0$ (τ is around 3–5 ns) and $S_1 \rightarrow T_n$ (τ is around 10 ns) at least because of the absence of any kind of direct chemical bonding between donor and acceptor (direct binding allows very fast transitions – just picoseconds). Another

very important reason of the very low contribution of this transition is the almost full absence of overlapping of donor emission (λ range 580–780 nm) and acceptor absorption (λ range 870–1020 nm). On the other hand neodymium-corroles **7** and **8** have perceptible φ_{4f} values. In this case, the contribution of the $S_1 \rightarrow {}^4F_{3/2}$ resonant transition should rise because of the good overlapping of donor emission (λ range 580–780 nm) $E_{S_1}=15670$ cm^{-1} and acceptor absorption (λ range 570–590 nm). We'd like to underline that like in the case of Yb^{3+} , the resonant transition $S_1 \rightarrow {}^4F_{3/2}$ is thermodynamically allowed since corrole $E_{S_1}=15670$ cm^{-1} and neodymium $E_{4F_{3/2}}=11700$ cm^{-1} . The contribution of $T_1 \rightarrow {}^4F_{3/2}$ stays unknown, but we can speculate that similarly to Yb complexes, it is very low.

Isostructural lanthanide-porphyrins (and all other complexes with lanthanides) have an opposite feature: the ϕ_{4f} values of ytterbium complexes are always higher than their isostructural neodymium analogues.

The spatial position of the energy acceptor ion relative to the corrole chromophore in the case of ytterbium (*para*- or *meta*-regioisomers) does not matter in terms of its emission effectiveness. *Per contra*, neodymium emission is sensitive to the spatial arrangement of ion relative to the chromophore, in other words, neodymium emission is sensitive to the distance between donor and acceptor. It is an additional proof for the domination of the $S_1 \rightarrow {}^4F_{3/2}$ sensitizing transition in neodymium-corroles. Thus, the *meta*-isomer of neodymium-corrole has a ϕ_{4f} value, which is 2 times higher than that for *para*-isomer.

CONCLUSIONS. Isomeric ditopic corroles and isostructural complexes of Yb (III), Nd (III) and Er (III) based on them were synthesized. The obtained results show that neodymium luminescence is particular in neodymium-corroles complexes. This work additionally confirms the previous assumption regarding the 4f-sensitization mechanism pathway in these compounds. Neodymium emission is notably sensitive to the spatial position of the ion relative to the chromophore.



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4f-ЛЮМІНЕСЦЕНЦІЯ ІОНІВ ЛАНТАНІДІВ У РЕГІОІЗОМЕРНИХ КОМПЛЕКСАХ ІЗ КОРОЛАМИ

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Синтезовано ізомерні дитопні короли та комплекси Yb (III), Nd (III) та Er (III) на їхній основі та виявлено корол-фотосенсибілізовану 4f-люмінесценцію в ближній інфрачервоній області. Структура ізомерних комплексів дозволяє регулювати відстань між ядром королю та іоном лантаноїду. Отримані результати показують, що механізм сенсибілізації різко змінюється як для різних лантаноїдів, так і для різних ізомерних форм.

Ключові слова: лантаноїди; короли; ізомери; 4f-люмінесценція; сенсибілізація.

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