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LANTHANIDE COMPLEXES WITH REGIOISOMERS OF CHLORO-SUBSTITUTED TETRAPHENYLPORPHYRIN

Several isomeric complexes of Yb (III) and Lu(III) with H_2tpp and its tetrachloro-substituted derivatives were synthesized. Symmetrical *ortho*-, *meta*- and *para*-positioning of four heavy atoms allows to study their effect on emission features of complexes. Obtained results show the rise of *4f*-luminescence effectiveness in the row *ortho*-*meta*-*para* isomers.

Keywords: lanthanides; porphyrins; isomers; *4f*-luminescence; sensitization.

Macrocyclic tetrapyrroles were the first among macrocyclic compounds, which reveal *4f*-luminescence sensitization in the early 1970s [1-2]. Lanthanide complexes with macrocyclic tetrapyrroles are promising as agents for luminescent diagnostics (LD),[3] photodynamic therapy (PDT) [4] and magnetic resonance imaging (MRI) [5] due to their specific luminescent and magnetic properties. Note that *4f*-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 energy donor for lanthanide ions Yb^{3+}, Nd^{3+} and Er^{3+} that have low-lying resonant energy levels. Sensitized *4f*-luminescence is a quite important phenomenon, which is already used in medicine (drugs, markers, assay) [6], technology (fiber-optics, OLED), etc. NIR4*f*-luminescence is highly demanded due to several important reasons: 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 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 [7].

Initially, only free bases of porphyrins were used as markers for fluorescence diagnostics and agents for photodynamic therapy [8]. Mainly, these were substances of natural origin, in particular, natural hematoporphyrin. These substances tend to accumulate in tumor tissues and are capable of luminescence [9]. However, the practical use of such markers is associated with two main drawbacks: 1. The luminescence of porphyrins is observed in the visible range (600-750 nm) and the luminescent contrast of the image of tumors and other objects obtained with their help is reduced due to the masking effect of the background luminescence of substances, which present in biological tissues. 2. An inevitable drawback of natural and closely related porphyrins is the phototoxicity of these drugs, which makes it necessary to protect patients from exposure to bright light on the skin for several weeks [10].

So, the present work is devoted to study of emission properties of Yb^{3+} with *ortho*-, *meta*- and *para*-isomers of tetrachlorosubstituted *meso*-tetraphenylporphyrin (H_2tpp).

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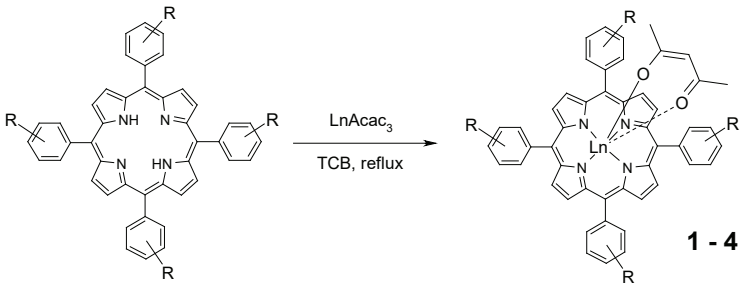
DISCUSSION OF THE RESULTS

There are three methods for the synthesis of lanthanide porphyrinates (Scheme 1): using 1,4-dichlorobenzene (DCB) [11], 1,2,4-trichlorobenzene (TCB) [3], or imidazole (Im) [12] as a solvent. It should be emphasized that the use of the imidazole method led to a rapid resinification of some porphyrins even in an inert medium in the very first minutes of the synthesis. Thus, the complexes were prepared using TCB and DCB.



Scheme 1

Synthesis of tetraphenylporphyrinates of lanthanides (Ln=Yb, Lu; R=H, Cl).
1 – Ln=Yb, R=H. **2** – Ln=Yb, R= *o*-Cl. **3** – Ln=Yb, R= *m*-Cl. **4** – Ln=Yb, R=*p*-Cl.

Acetylacetonate was used as the starting lanthanide compound. This choice is based on the fact that, as was shown earlier, in the case of β-diketones as extra ligands, the efficiency of *4f*-luminescence is higher than in the case of halides [3]. In this case, the use of acetylacetonate as an extra ligand in the series of lanthanide porphyrins of the same type with various β-diketones leads to higher values of the quantum yields of *4f*-luminescence.

A diagram of the dependence of the yield on the temperature and synthesis time was obtained (Fig. 1). Obtained graph shows that the long synthesis time is accompanied by the pyrolysis of the starting lanthanide acetylacetonates (gray zone: yield < 50%); therefore, long-term syntheses are not preferable. It should be noted that although TCB is an optimal synthesis medium, there are nevertheless certain limitations for its use. Firstly, inorganic salts of lanthanides are insoluble in either TCB or DCB; therefore, imidazole is used in this case. Secondly, some porphyrinates cannot be obtained in TCB due to their low thermal stability, such as modified porphyrins. An attempt to use DMF as a synthesis medium did not lead to satisfactory results, since during 48 hours of synthesis, no complex appeared in the system, and after this time, it was not possible to detect the starting acetylacetonate, which completely underwent pyrolysis.

Thus, we used the procedure for preparing complexes in TCB, since the yield in this case is highest. The synthesis was carried out using lanthanide acetylacetonate as salt according to the scheme (Scheme 1) with the formation of complexes with the ratio lanthanide: porphyrin: extra-ligand = 1:1:1. In the FAB mass spectra of all complexes, the molecular ion peak is absent. The most intense peak belongs to the fragment Ln-Porph$^+$. NMR spectra recorded for Lu-complexes only (other lanthanide ions act as strong shift

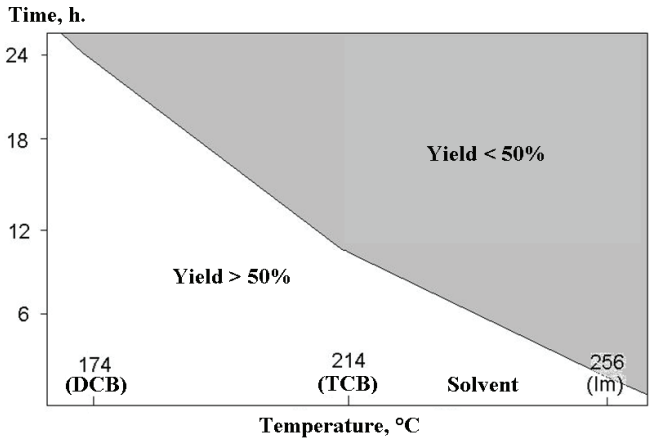


Fig. 1. Diagram: yield of the complexes – temperature – synthesis time

agents and NMR spectra became quite hard for the interpretation). Phosphorescence spectra of Lu-complexes were recorded to determine the T_1 (lower triplet) levels.

meso-Tetraarylporphyrins are characterized by the etio-type of the absorption spectrum – the increase in the intensities of the *Q*-bands occurs in the following order: I <II <III <IV. Data on the absorption spectra of the studied ligands and their complexes are presented in Table 1. The introduction of phenyl substituents (**1**) leads to a bathochromic shift of all four *Q*-bands, as well as the Soret band, in comparison with porphine (Por). The electron-withdrawing substituent -Cl in *para*-position (compound **4**) has practically no effect on the position of the bands in the absorption spectra of ligands in comparison with H_2tpp.

The study of regioisomers **2**, **3** and **4** with different spatial arrangements of substituents in the structure of porphyrins and their complexes allows finding dependence of both absorption spectra and luminescence properties on its location in the structure.

The introduction of the Cl-substituent into the phenyl rings changes the absorption spectra of the ligands: the greatest changes are observed for *ortho*-derivatives – the bathochromic shift of the first band is 38 nm compared to porphine and 5 nm compared to H_2tpp. The substituents in the *meta*- and *para*-positions change the absorption spectra lesser.

The results confirmed that *ortho*-substitution has the most significant effect on the absorption spectra due to a change in the conformation of the C-C bond of the *meso*-carbon atom and the carbon atom in the first position of the phenyl group. In this case, the phenyl rings are almost at a right interplanar angle to the macroring.

Molecular fluorescence of tetraarylporphyrins is realized due to the radiative transition $S_1 \rightarrow S_0$. The luminescence parameters of all H_2tpp derivatives have comparable values (Table 1). Substitution in the *para*-position of phenyl has practically no effect on the quantum yield and the luminescence lifetime of the porphyrins. A decrease in these values for halogen derivatives is associated with the internal effect of a heavy atom, which leads to an increase in the probability of intramolecular intercombination transi-

Table 1

Absorption and emission properties of studied compounds

#	$\lambda_{max.}$ (nm) (lgε)					φ_F	φ_{4f} ×10^3	$\Delta E_{(S1-T1)}$, cm^{-1}	$\Delta E_{(T-Yb)}$, cm^{-1}	λ_f, nm		λ_p, nm	τ_F, ns	τ_P, ns 77K	φ_T	φ_P ×10^5 77K
	Soret band	*Q*-bands														
		IV	III	II	I					0-0	0-1					
1	417 (5.1)	514 (3.7)	548 (3.3)	590 (3.1)	649 (3.1)	0.12	-	3860	-	645	715	859	13.6	5.6	0.88	6.7
Yb**1**	424 (5.5)	-	-	556 (4.4)	594 (4.0)	-	4.2	-	1440	-	-	-	-	-	-	-
2	419 (5.3)	511 (3.3)	540 (2.8)	593 (2.3)	654 (2.0)	0.02	-	3820	-	640	710	847	5.3	3.3	0.98	66
Yb**2**	426 (5.4)	-	-	554 (2.4)	598 (2.0)	-	3.4	-	1610	-	-	-	-	-	-	-
3	416 (5.2)	515 (3.3)	547 (2.6)	588 (2.4)	648 (2.1)	0.07	-	3870	-	643	713	856	9.7	3.7	0.93	20
Yb**3**	428 (5.4)	-	-	557 (2.6)	600 (2.1)	-	4.3	-	1480	-	-	-	-	-	-	-
4	418 (5.4)	514 (3.1)	549 (2.8)	590 (2.8)	647 (2.8)	0.09	-	3830	-	648	718	862	10.5	4.2	0.91	9.4
Yb**4**	426 (5.5)	-	-	561 (3.3)	602 (3.1)	-	4.1	-	1400	-	-	-	-	-	-	-
Por	395 (5.4)	490 (4.2)	520 (4.5)	563 (3.7)	616 (3.0)	-	-	-	-	-	-	-	-	-	-	-

tions (IIT). This results in quenching of fluorescence and a reduction in the lifetime of the T_1-state. Despite the fact that, due to the non-coplanarity of phenyl rings with porphyrin, chlorine atoms are largely isolated from the conjugated chromophore system, in the studied systems the phosphorescence quantum yield (φ_P) sharply increases as the halogen atom moves from *para*- to *ortho*-position from $9.4 \cdot 10^{-5}$ to $6.6 \cdot 10^{-4}$. This means that the singlet states are mixed with the T_1 state under the influence of heavy atoms. Thus, a decrease in the fluorescence quantum yield (φ_F) and an increase in the quantum yield of intercombination conversion (φ_T) are in good agreement with an increase in the phosphorescence efficiency (φ_P –phosphorescence quantum yield) in the series of *para*-, *meta*-, and *ortho*-chloro-substituted H_2tpp derivatives.

The lifetime of molecular fluorescence (τ_F) decreases like the quantum yield in the series of *para*-, *meta*-, and *ortho*-chloro-substituted H_2tpp derivatives and does not change in the series of various substituted *para*-H_2tpp derivatives (Table 1).

The shift of the phosphorescence band maximum is observed in the case of a change in the position (Table 1). Thus, upon going from the *para*- to *meta*-position, the hypsochromic shift is 6 nm, and from the *meta*- to *ortho*-position, 9 nm. This is a consequence of the close location of the chlorine substituent to the porphyrin chromophore, which causes a redistribution of the electron density and consequently affects the position of the triplet emitting level.

Luminescence of Yb^{3+} ions is observed in all studied complexes (Fig.2) in the region of 980 nm upon excitation in a wide spectral range (300-600 nm); however, it is most efficiently realized upon excitation at the maximum of the Soret band. The almost complete similarity of the *4f*-luminescence excitation spectra of Yb^{3+} in porphyrinates with their absorption spectra indicates that Yb^{3+} ions serve as acceptors of the excitation energy from the organic part of the complex.

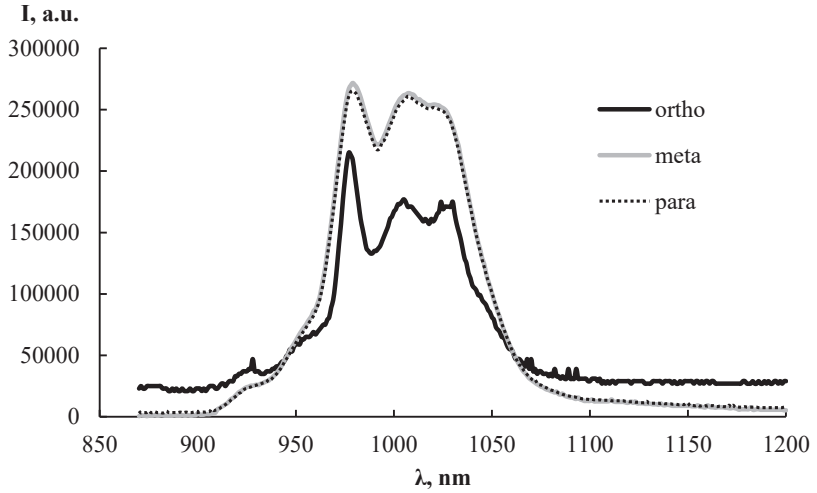


Fig. 2. Non-smoothed (original) *4f*-luminescence spectra of Yb-complexes **2**, **3** and **4** (*ortho*-, *meta*- and *para*-isomers of tetrachloro-substituted Yb-tpp)

Difference between the values of the triplet and singlet levels of the complex, as well as the triplet and resonance levels of the ytterbium ion $^2F_{5/2}$, does not undergo significant changes in the series of complexes with *para*-substituted H_2tpp derivatives. For complexes with *meta*- and *para*-isomers of *meso*-tetrachlorophenylporophyrin, the values of *4f*-luminescence quantum yields also hardly differ, in contrast to the complex with the *ortho*-isomer (φ_{4f} = 3.4 is the minimum value in the presented series). It is obvious that the effect of the heavy atom is most pronounced in this isomer, since the distance from the chlorine atom to the emitting ion in this case is minimal. Recently, it was shown that such *ortho*-positioning of substituent in macrocyclic tetrapyrroles even can lead to formation of prototropic isomers due to electronic redistribution [13]. It should also be noted that the difference between the lower triplet state of the complex and the resonance level $^2F_{5/2}$ in this case is maximum, which suggests the presence of additional ways of deactivation of the excitation energy.

It should be emphasized that the values of the quantum yield for all the studied Yb-tetraarylporphyrinates are significantly higher than for all Yb-tetraalkylporphyrinates, which were studied earlier [14]. This effect is associated with the presence of partial conjugation of the phenyl rings at the *meso*-positions, and, as a consequence, a higher population of all energy levels, including the T_1 level, from which the energy is transferred to the resonance level of the Yb^{3+} ion. Another possible explanation is that the first carbon atom of the *meso*-substituent does not contain C-H bonds, the vibrational absorption bands of which are close to the value of the $T_1 \rightarrow {}^2F_{7/2}$ transition. In *meso*-tetraalkylporphyrins, on the contrary, the first carbon atom contains two such bonds, which, apparently, is reflected in a sharp decrease in the *4f*-luminescence intensity.

To conclude, we synthesized several regioisomeric complexes of Yb(III) and Lu(III) on the base of chloro-substituted H_2tpp. It was found out, that values of the quantum yield of arylporphyrinates of ytterbium are significantly higher than for alkylporphyrinates. Position of the heavy atoms in four phenyl rings of Yb-tpp affects its photophysical features drastically, thus in the row *ortho-meta-para* isomers IIT slows down, which leads to increase of φ_F, φ_{4f}, τ_F, and, on the other hand to decrease of φ_T and φ_P.

EXPERIMENTAL PART

Spectra of molecular fluorescence, *4f*-luminescence and excitation spectra were recorded on a spectrofluorimeter "Fluorolog FL 3-22" ("Horiba Jobin Yvon") using 450 W Xe-lamp. Spectra of molecular fluorescence of porphyrins, corroles and phthalocyanines were registered at 550-800 nm (S_1-S_0 transitions). Integral intensity of luminescence was measured using software of the device. The relative quantum yield of molecular fluorescence (φ_F) was determined using solution of Zn-tpp in ethanol as a primary standard (0.022). Determination of the φ_F (accuracy is ±10%) was made using formula:

$$\varphi_F = \varphi_0 I_x A_0 n_x^2 / (I_0 A_x n_0^2),$$

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.

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}H NMR-spectra were recorded using Bruker Avance 600 or 400 MHz in CD_3OD. Mass spectra FAB were recorded on a Varian MAT CH-112 spectrometer (Varian BV, Middelburg) using m-nitrobenzylalcohol as the matrix. Elemental analysis was performed on CHNS analyzer Flash 2000 Thermo Scientific.

Synthesis of starting porphyrins and complexes was performed accordingly to known procedures for these compounds [15-18].

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КОМПЛЕКСИ ЛАНТАНІДІВ З РЕГІОІЗОМЕРАМИ ХЛОРОЗАМІЩЕНОГО ТЕТРАФЕНІЛПОРФІРІНУ

В роботі було синтезовано декілька регіоізомерних комплексів ітербію (III) та лютецію (III) з мезо-тетрафенілпорфірином та його тетрахлор-заміщеними похідними. Вивчено особливості протікання синтезу комплексів лантанідів з похідними мезо-тетрафенілпорфірину. Показано, що серед існуючих одностадійних процесів синтезу 1,4-дихлобензол та 1,2,4-трихлорбензол є оптимальними середовищами для проведення синтезу. Головним чином це пов'язано з деструкцією/піролізом як деяких вихідних порфіринів, так і багатьох вихідних сполук лантанідів у разі використання імідазолу в якості середовища. Власна флуоресценція хлорпохідних порфіринів спостерігається в звичайному діапазоні 600-750 нм, але її ефективність помітно знижується у ряду пара-мета-орто-ізомерів. На відміну від комплексів ітербію з мезо-тетраалкілпорфіринами, всі представлені комплекси на основі похідних мезо-тетрафенілпорфірину мають доволі високу ефективність *4f*-люмінесценції іону ітербію. Симетричне орто-, мета- та пара-позиціонування чотирьох «важких» атомів хлору дозволяє вивчити їх вплив на емісійні особливості комплексів в залежності від відстані до хромофору порфірину та іону-випромінювачу. Основний фактор, який чинить «важкий» атом емісійній системі комплексу це прискорення внутрішньомолекулярної інтеркомбінаційної конверсії. Про це, зокрема, свідчить підвищення квантового виходу інтеркомбінаційної конверсії з 0.88 до 0.98 яка, внаслідок дії «важких» атомів може краще конкурувати з іншими фотофізичними процесами у молекулі. З іншого боку наслідком такого явища є підвищення квантового виходу фосфоресценції порфірину на порядок (з $6.7 \cdot 10^{-5}$ до $6.6 \cdot 10^{-4}$). Отримані результати демонструють зростання ефективності *4f*-люмінесценції іону ітербію при переході з орто- до мета- та пара-ізомерів комплексів з $3.4 \cdot 10^{-3}$ до $4.3 \cdot 10^{-3}$.

Ключові слова: лантаніди; порфірини; ізомери; *4f*-люмінесценція; сенсибілізація.

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КОМПЛЕКСЫ ЛАНТАНИДОВ С РЕГИОИЗОМЕРАМИ ХЛОРОЗАМЕЩЕННОГО ТЕТРАФЕНИЛПОРФИРИНА

В работе были синтезированы несколько региоизомерних комплексов иттербия (III) и лютеция (III) с мезо-тетрафенилпорфирином и его тетрахлоро-замещенными производными. Изучены особенности протекания синтеза комплексов лантанидов с производными мезо-тетрафенилпорфирина. Показано, что среди существующих одностадийных процессов синтеза, 1,4-дихлобензол и 1,2,4-трихлорбензол являются оптимальными средами для проведения синтеза. Главным образом это связано с деструкцией/пиролизом как некоторых исходных порфиринов, так и многих исходных соединений лантанидов при использовании имидазола в качестве среды. Собственная флуоресценция хлорпроизводных порфиринов наблюдается в обычном диапазоне 600-750 нм, но её эффективность заметно снижается в ряду пара-мета-орто-изомеров. В отличие от комплексов иттербия с мезо-тетраалкилпорфиринами, все представленные комплексы на основе производных мезо-тетрафенилпорфирину имеют достаточно высокую эффективность *4f*-люминесценции иона иттербия. Симметричное орто-, мета- и пара-позиционирование четырех «тяжёлых» атомов хлора позволяет изучить их влияние на эмиссионные особенности комплексов в зависимости от расстояния до хромофора порфирина и иона-излучателя. Основной фактор, который оказывает «тяжёлый» атом эмиссионной системе комплекса, это ускорение внутримолекулярной интеркомбинационной конверсии. Об этом, в частности, свидетельствует повышение квантового выхода интеркомбинационной конверсии с 0.88 до 0.98, которая, вследствие действия «тяжелых» атомов, может лучше конкурировать с другими фотофизическими процессами в молекуле. С другой стороны, как следствие этого явления, наблюдается повышение квантового выхода фосфоресценции порфирина на порядок (с $6.7 \cdot 10^{-5}$ до $6.6 \cdot 10^{-4}$). Полученные результаты демонстрируют рост эффективности *4f*-люминесценции иона иттербия при переходе с орто- к мета- и пара-изомерам комплексов с $3.4 \cdot 10^{-3}$ до $4.3 \cdot 10^{-3}$.

Ключевые слова: лантаниды; порфирины; изомеры; *4f*-люминесценция; сенсибилизация.

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