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NIR-LUMINESCENCE OF YTTERBIUM IONS IN ISOMERIC TETRAPHENYLPORPHYRIN MODIFIED EDTA COMPLEXES

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Abstract

New ytterbium complexes were synthesized on the base of tetraphenylporphyrin modified with ethylenediaminetetraacetic acid at the *ortho*- and *para*-positions of only one phenyl ring. Such a modification allows the sensitization function of the porphyrin to be retained with respect to the Yb^{3+} ion and eliminates the problem of lability of traditional lanthanide-porphyrin core-coordinated complexes. A new selective synthetic route for the mono *para*-nitro-derivative of tetraphenylporphyrin (the main precursor of the target compound) has been proposed. *4f*-Luminescence in the near-infrared range as well as non-quenched molecular fluorescence of porphyrin, are observed in all synthesized complexes, which makes these complexes dual-emissive. Since the obtained results show that both Yb-porphyrin isomers have no changes in terms of fluorescence effectiveness in comparison to their corresponding ditopic edta-porphyrins, it proves the absence of ISC and ISD acceleration in these systems. It was also found that the *4f*-luminescence intensity of the *ortho*-isomer is higher compared to the *para*-isomer. This is due to changes in the spatial structure, leading to the edta-Yb fragment being closer to the porphyrin core. Additional experiment of luminescence quenching by strong paramagnetic ion was performed. When the copper (II) acetate was added to the modified edta-porphyrin isomers, a significant difference in the efficiency of luminescence quenching was observed as the result of non-core interaction; thus, the luminescence intensity decreased more for the *ortho*-isomer than for the *para*-isomer. This also proves that the efficiency of interaction between porphyrin and the peripheral substituent is very sensitive to the distance changes between them. Enhancing of *4f*-luminescence effectiveness can be explained simultaneously by both decreasing the donor-acceptor distance and the absence of notable ISD acceleration, which is typical for core-coordinated compounds.

Keywords: porphyrins; lanthanides; luminescence; energy transfer.

ІЧ-ЛЮМІНЕСЦЕНЦІЯ ІОНІВ ІТЕРБІЮ В ІЗОМЕРНИХ КОМПЛЕКСАХ ЕДТА МОДИФІКОВАНИХ ТЕТРАФЕНІЛПОРФІРИНОМ

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Анотація

Синтезовано нові комплекси ітербію на основі тетрафенілпорфірину, модифікованого етилендіамінтетраоцтовою кислотою по *орто*- і *пара*-положенням одного фенільного циклу. Така модифікація дозволяє залишити сенсибілізаційну функцію порфірину відносно іону Yb^{3+} та усуває проблему лабільності традиційних лантанід-порфіринових core-координованих комплексів. Запропоновано новий селективний спосіб синтезу моно *пара*-нітропохідної тетрафенілпорфірину (основного прекурсору цільової сполуки). В усіх синтезованих комплексах спостерігається *4f*-люмінесценція в ближньому ІЧ-діапазоні, а також непогашена молекулярна флуоресценція порфірину, що робить ці комплекси двоемісійними. Отримані результати показують, що обидва ізомери Yb-порфірину мають таку ж ефективність флуоресценції, як і відповідні дитопні едта-порфірини, й це доводить відсутність прискорення процесів інтеркомбінаційної конверсії (ISC) та інтеркомбінаційної деградації (ISD) у цих системах. Було виявлено, що інтенсивність *4f*-люмінесценції *орто*-ізомеру вища порівняно з *пара*-ізомером. Це пов'язано зі змінами просторової структури, що призводить до наближення фрагменту edta-Yb до ядра порфірину. Гасіння люмінесценції сильним парамагнітним іоном показало, що додавання до модифікованих ізомерів едта-порфірину ацетату міді (II) приводить до істотної різниці в ефективності гасіння люмінесценції в результаті non-core взаємодії; таким чином, зменшення інтенсивності люмінесценції більше для *орто*-ізомеру, ніж для *пара*-ізомеру. Це доводить, що ефективність взаємодії між порфірином і периферичним замісником дуже чутлива до зміни відстані між ними. Підвищення ефективності *4f*-люмінесценції можна пояснити одночасно як зменшенням відстані донор-акцептор, так і відсутністю помітного прискорення ISD, характерного для core-координованих сполук.

Ключові слова: порфірини; лантаніди; люмінесценція; перенос енергії.

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Introduction

The near-infrared region (NIR) is widely used in optical applications [1-5] and biomedical practice [6-9]. This is due to its safety when interacting with biological objects, minimal scattering, and the ability to easily penetrate biological tissues, compared to ultraviolet and visible light [10].

Macrocyclic tetrapyrrole compounds, along with their metal complexes, are the subject of widespread research. This is primarily due to their characteristic and powerful light absorption and emission properties. Moreover, they are of significant interest for their efficacy as catalysts and as a fundamental component in various applications, including sensors and solar panels [11-13].

Considering these perspectives, the use of lanthanide complexes with porphyrins shows considerable potential because of both their low-resonance energy levels, which enable them to emit in the NIR, and the low triplet levels (T_1) of porphyrins, which are responsible for the sensitization mechanism [14]. For example, Nd (III) emits at 850–1850 nm due to $^4F_{3/2}\rightarrow{}^4I_{9/2\text{-}15/2}$ transitions, and Yb (III) emits at 950–1050 nm due to $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transitions.

Although lanthanide spectroscopy offers numerous benefits, a notable characteristic is the inability of lanthanide direct excitation, as per Laporte's rule, due to the inherently weak f-f absorption of these ions. Nevertheless, this limitation can be readily overcome by employing organic chromophores capable of efficient light absorption and energy transfer to lanthanide ions [15]. Porphyrins, for example, can serve as effective chromophores for NIR *4f*-luminescence sensitization.

It is known that the stability of lanthanide core-coordinated complexes with porphyrins is lower in comparison to cyclic and acyclic aminopolycarboxylates of lanthanides. Even a recent study on obtaining huge quantum yields of Yb^{3+} luminescence up to 69 % in special conditions does not solve the main stability issue of this class of compounds [16]. Consequently, different researchers [17–20] suggested producing porphyrins that have been modified with aminopolycarboxylic acids (e.g. ethylenediaminetetraacetic acid, H_4edta) along their periphery. This strategy has resulted in notably improved stability of lanthanide-porphyrin systems, which does not have direct chemical bonding between porphyrin and lanthanide, but reveal sensitization mechanism between porphyrin and lanthanide ion.

Previous numerous studies have shown that the direct core interaction of paramagnetic lanthanide ion with porphyrin leads to complete molecular fluorescence quenching as a result of significantly accelerated intersystem processes – both ISC (intersystem crossing, $S_1\rightarrow T_1$) and ISD (intersystem degradation, $T_1\rightarrow S_0$) [21]. Although 100 % ISC should provide more effective *4f*-luminescence sensitization process (through T_1 donor level), nevertheless, accelerated ISD competes with sensitization process ($T_1\rightarrow Ln^{n+}$) and this can be one of the reasons of relatively low *4f*-luminescence efficiency in lanthanide-porphyrins. Lanthanide ion transfer to the porphyrin periphery (edta-fragment at *para*-position of phenyl) restores values of intersystem processes, which results in fluorescence recovery. Moreover it was demonstrated that under such sensitization circumstances lanthanide-porphyrin systems have comparable efficiency with lanthanide core-coordinated complexes [22], although the first ones do not have direct chemical bonding between lanthanide and porphyrin.

Since any known sensitization mechanism is sensitive to the donor-acceptor distance and there is still no clear proof for exact type of porphyrin *4f*-luminescence sensitization mechanism for such systems, so this work deals with the dependence of the emission features on the distance between the lanthanide ion and the porphyrin core. Thus, we study the emission of edta-lanthanide complexes with *ortho-* and *para*-isomers of H_2tpp-modified edta. The idea of such approach is to find optimal Ln-porphyrin distance, which has balanced contributions of as efficient as possible $T_1\rightarrow Ln^{n+}$ transfer and as low as possible ISD to reach the highest *4f*-luminescence efficiency.

Experimental section

Both *4f*-luminescence excitation and emission spectra (*4f*-luminescence and molecular fluorescence) were recorded on a spectrofluorimeter "Fluorolog FL 3-22" ("Horiba Jobin Yvon") using Xe-lamp (450 W). Integral intensity of emission was measured using software of the device [21].

All reagents used were laboratory grade and were not further purified, except for DMF and red-fuming nitric acid. To purify and absolutize DMF, KOH was first added and shaken well. When the 2 phases (DMF and water with KOH) were separated in the flask, the DMF phase was transferred to the flask and subjected to vacuum distillation. The first collected fraction corresponds to absolute DMF. To obtain red-fuming nitric acid, equal volumes of sulfuric and nitric acids were added to a 500 mL flask, after which a simple distillation was carried out. The first fraction at 83 °C corresponds to fuming nitric acid.

Synthesis of para-isomers of tetraphenylporphyrin (in accordance with [18], Scheme 1)

*5,10,15,20-tetraphenylporphyrin (**1a**)*

The synthesis was carried out according to the Adler-Longo method. Pyrrole (3.12 mL, 45 mmol) and benzaldehyde (4.78 g, 45 mmol) were added to boiling propionic acid in a round-bottom flask with a reflux condenser. After heating for 30 minutes, the reaction mixture was cooled to room temperature. The mixture was filtered and washed first with methanol and then with hot water. The obtained violet crystals (1 g, 1.63 mmol) of tetraphenylporphyrin were used for the synthesis of substance **2a**.

*5-(4-nitrophenyl)-10,15,20-triphenylporphyrin (**2a**)*

The crude product from the previous step was dissolved in 150 ml of chloroform and cooled to -20°C, then fumed nitric acid (1 g, 15.8 mmol) was added and this mixture was kept at –20 °C for 24 hours. After washing with water (3×150 ml) the solution was concentrated for further passage through silica gel with chloroform as an eluent.

*5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**3a**)*

The crystals of the substance **2a** obtained after drying were dissolved in 40 ml of concentrated hydrochloric acid in an N_2 atmosphere. Metallic tin (3 g) was added and the reaction mixture was heated to 65 °C. Every hour, with the help of TLC, the percentage of substance conversion was monitored, and a few more grams of metallic tin were added. After ≈2 hours, when the conversion of the substance was complete, the reaction mixture was cooled to room temperature, and 300 ml of cold water was added. The pH of the solution was adjusted to 8 using a concentrated ammonia solution. The aqueous phase was extracted with 300 ml portions of chloroform and dried on a rotary evaporator. Purification of the substance for the next stage of synthesis was carried out by the PTLC method, using chloroform : petroleum ether (1 : 1) as an eluent. The total yield of the two stages was 45 % (0.45 g, 0.72 mmol). UV-vis (DMF): λ_{max}, nm 418, 517, 556, 592, 648.

*{Carboxymethyl-[2-(carboxymethyl-{[4-(10,15,20-triphenyl-porphyrin-5-yl)-phenylcarbamoyl]- methyl}-amino)-ethyl]-amino}-acetic acid (**4a**)*

The substance **3a** was dissolved in absolute DMF and then added dropwise to a solution of EDTA dianhydride (0.35 g, 1.36 mmol), which was mixed in absolute DMF with a catalytic amount of triethylamine at 80 °C. The reaction proceeded for 1 hour until the starting substance was detected by TLC, after which the product was precipitated with water, filtered, and dried. Purification of the substance was carried out using PTLC, using chloroform: methyl alcohol (10:1) as an eluent. After completion of the reaction, the product was precipitated with water, filtered, and dried. UV-vis (DMF): λ_{max}, nm 418, 516, 551, 592, 647. MS (TSQ): *m/z* anal. calcd. for $C_{54}H_{45}N_7O_7$ 904.345; found: 904.65.

*Yb-para-edta-$H_2tpp \cdot xH_2O$ (**5a**)*

The complex was synthesized at room temperature by adding a solution of $YbCl_3 \cdot xH_2O$ to a solution of compound **4a** in absolute DMF. The yield was 95% (0.63 g, 0.59 mmol). UV-vis (DMF): λ_{max}, nm 418, 516, 551, 592, 647. MS (TSQ): *m/z* anal. calcd. for $C_{54}H_{42}N_7O_7Yb$ 1074.26; found: 1074.89.

Synthesis of ortho-isomers of tetraphenylporphyrin (**2b** and **3b** as in [23, 24], Scheme 1)

*5-(2-nitrophenyl)-10,15,20-triphenylporphyrin (**2b**)*

Benzaldehyde (7 g, 66 mmol) and ortho-nitrobenzaldehyde (5 g, 33.1 mmol) were dissolved in 200 ml of glacial acetic acid. Pyrrole (6.9 mL, 99.6 mmol) was quickly added to the reaction mixture, which was already heated in a round-bottom flask with a reflux condenser. The reaction continued for 20 minutes under the same conditions. After cooling the reaction mixture, it was filtered and washed with water, ammonia, methanol, and then dried in air at 100 °C. The concentrated solution was then passed through silica gel (60–100 mesh) with chloroform as an eluent.

*5-(2-aminophenyl)-10,15,20-triphenylporphyrin (**3b**)*

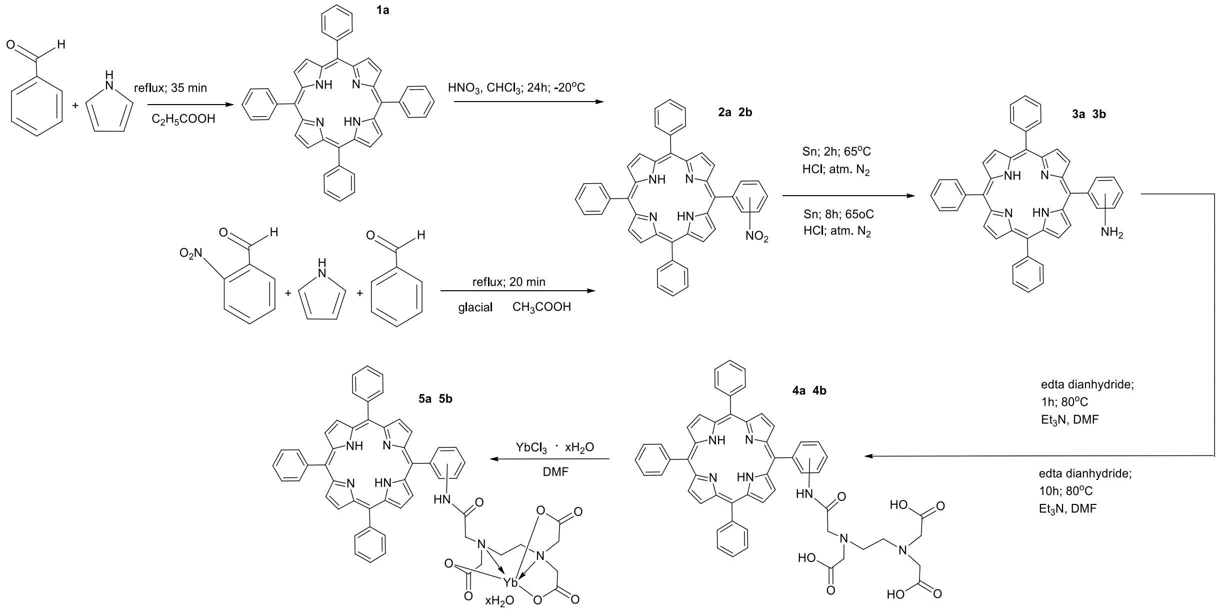
The final product of the previous was dissolved in 100 ml of concentrated hydrochloric acid in an N_2 atmosphere. After adding metallic tin (5 g), the reaction mixture was heated to 65°C for ≈8 hours. Every hour, with the help of TLC, the percentage of substance conversion was monitored, and a few more grams of metallic tin were added. After the reaction, the reaction mixture was cooled to room temperature, and 300 ml of cold water was added. The pH of the solution was adjusted to 8 using a concentrated ammonia solution. The aqueous phase was extracted with 300 ml portions of chloroform and dried on a rotary evaporator. Purification of the substance was carried out by the PTLC method, using chloroform : petroleum ether (1 : 1) as an eluent. The total yield of both stages was 2 % (0.38 g, 0.66 mmol). UV-vis (DMF): λ_{max}, nm 418, 515, 549, 590, 646.

*{Carboxymethyl-[2-(carboxymethyl-{[2-(10,15,20-triphenyl-porphyrin-5-yl)-phenylcarbamoyl]- methyl}-amino)-ethyl]-amino}-acetic acid (**4b**)*

The previously obtained substance 2b was dissolved in absolute DMF and then added dropwise to a solution of EDTA dianhydride (0.26 g, 1 mmol), which was mixed in absolute DMF with a catalytic amount of triethylamine at 80°C. The reaction proceeded for ≈10 hours, the degree of conversion of the substance was checked by TLC every hour, and a small amount of EDTA dianhydride and a few drops of triethylamine were added. After completion of the reaction, the product was precipitated with water, filtered, and dried. Purification of the substance was carried out using PTLC, using chloroform : methyl alcohol (10 : 1) as an eluent. The yield was 83% (0.49 g, 0.55 mmol). UV-vis (DMF): λ_{max}, nm 419, 515, 551, 591, 646. ^{1}H NMR (dmso-d$_6$) δ 8.85 (s, 6H), 8.23 (m, 6H), 7.85 (m, 9H), 7.60 (m, 3H), 7.51 (m, 3H), 3.5 (br, 12H). MS (TSQ): *m/z* anal. calcd. for $C_{54}H_{45}N_7O_7$ 904.345; found: 904.49.

*Yb-ortho-edta-H_2tpp·xH_2O (**5b**)*

The synthesis of complexes with Yb(III) was carried out at room temperature by adding a solution of **4b** to a solution of $YbCl_3 \cdot xH_2O$ crystal hydrate in DMF. The yield was 95 % (0.56, 0.52 mmol). UV-vis (DMF): λ_{max}, nm 419, 515, 551, 591, 646. MS (TSQ): *m/z* anal. calcd. for $C_{54}H_{42}N_7O_7Yb$ 1074.25; found: 1074.94.



Scheme 1. Synthetic routes to the target compounds

Results and discussion

Synthetic procedures (Scheme 1) are well-known and standard for this kind of compounds, but one step needs to be discussed since we propose its improvement. Nitration of H_2tpp is known to be performed by several different approaches to reach *para*-nitrophenyl derivatives – mono-, bis- (*cis*- and *trans*-), tris- and tetrasubstituted porphyrins. If the latter can be obtained selectively as a result of full nitration (*para*-positions of phenyls only) of H_2tpp, so all other products can be obtained only in a mixture with other nitrated products. Of course, it is possible to reach certain nitro-derivatives through the dipyrromethane technique, but it does help for only *trans*-di-nitroderivative of H_2tpp. Here we'd like to propose selective nitration of H_2tpp, which gives high-yielded mono-nitro-derivative. Thus, we propose to use the well-known old approach of H_2tpp nitration by red fuming nitric acid in $CHCl_3$, but in contrast to authors [25], we propose to use deep freeze (–20 °C). Using the temperature, which is 20–25 °C smaller than in the original approach, prevents further nitration of mono-nitro-porphyrin. It can be explained by the deactivation of the macrocycle by a strong electron-withdrawing group, which leads to the inability of further nitration at such low temperatures in contrast to temperatures higher than 0 °C.

A special attention should be paid to the initial stages when discussing the differences in the synthesis of the *ortho*- and *para*-derivatives. The synthesis of the *para*-derivative was carried out using the well-known classical Alder-Longo method. However, the subsequent nitration of porphyrin **1a** differs from the standard methodology, as noted earlier. Regarding the *ortho*-derivative, the synthesis of compound **2b** occurred in a single step through the cross-synthesis of *ortho*-nitrobenzaldehyde, pyrrole, and benzaldehyde, taken in a 1 : 3 : 2 ratio. During cross-synthesis, undesirable competing reactions may occur, leading to the formation of by-products, which results in a low yield of product **2b**.

As seen in Scheme 1, the following stages are similar for both the *ortho*- and *para*-derivatives. The only difference is the reaction rate – In the case of the *ortho*-derivative the synthesis time is significantly longer due to the sterically hindered *ortho*-group. Special attention should also be given to the purification of the compound from by-products. This stage is carried out only after obtaining the amino derivatives (**3a**, **3b**). This specificity is due to the challenging separation of the nitro derivatives by chromatography, as the Rf values of the target product and the main by-product H_2tpp are too close. The only purification that can be performed at this stage is the removal of some by-products (mainly – tar with Rf=0) of the cross-synthesis, which is achieved by passing the reaction mixture through silica gel.

Synthesized edta-porphyrins have a standard 5-band absorption spectrum profile – 1 band at the near UV region (Soret band) and 4 *Q*-bands at the visual range. Note, that there are no spectrum distortions under complexation reaction. Both edta-porphyrins and their coordination derivatives have an intensive emission at 600–800 nm. The fluorescence profile of both isomers has two bands with maxima at 650 (0-0 band) and 720 nm (0-1 band). Note, that there are no perceptible changes in the fluorescence profile under the formation of edta-coordinated porphyrins with Yb^{3+}, *i.e.* neither band positioning nor their intensities.

It seems like the paramagnetic metal ion in the edta fragment does not affect porphyrin emission, but we have performed a separate experiment with the formation of Cu^{2+} coordination compounds with both ditopic edta-porphyrin isomers to ensure that the strong fluorescence quencher (Cu^{2+} ion) can affect the emission without direct covalent bonding to the porphyrin chromophore (Fig. 1). Therefore, this experiment is based on the interaction of free ditopic edta-porphyrins with Cu^{2+} ion. Since the formation of core-coordinated copper complexes with porphyrins needs much tougher conditions than room temperature, so under the circumstances of the present experiment there is no formation of the core-coordinated copper complexes (UV-Vis checking shows no formation of the core-coordinated complex).

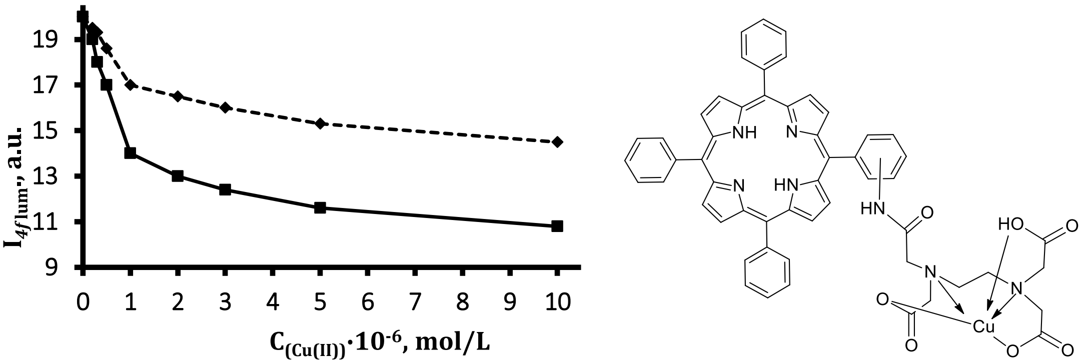


Fig. 1. Luminescence quenching curve of the *ortho*-isomer (—) and *para*-isomer (---) edta-tpp by adding Cu(II)

Points, which correspond to 1 : 1 ratio of metal : poprhyrin are transition points between static (intramolecular interaction) and dynamic (intermolecular interaction) fluorescence quenching. The presumed composition of the complexes is 1 : 1 due to the fact that the bends in the curves correspond to this point. Expectedly, the *ortho*-isomer of copper complex notably higher affects fluorescence effectiveness. Fluorescence of *ortho*-isomer is quenched by 30 % and *para*-isomer fluorescence is quenched by only 20 %.

Synthesis of Yb^{3+} complexes with *ortho*- and *para*-H_3edta-H_2tpp was performed *in situ* by the interaction of the corresponding edta-porphyrin with $YbCl_3$aq. at room temperature in methanol.

As it was mentioned above, in contrast to Cu^{2+} the ion Yb^{3+} does not have a quenching effect in these systems, and the fluorescence profile remains unchangeable (Fig. 2). Both isomeric forms of the Yb^{3+} complex have emission in the NIR with maxima at *ca.* 980 nm. Both types of radiation (fluorescence and *4f*-luminescence) can be realized upon excitation at the maximum of any band (Soret band and 4 visual bands), *i.e.* these systems are capable of simultaneous dual-band radiation. *4f*-Excitation spectra of both isomeric complexes of Yb^{3+} demonstrate full identity with porphyrin absorption spectra, which proves the participation of the porphyrin chromophore in the *4f*-sensitization process in both cases.

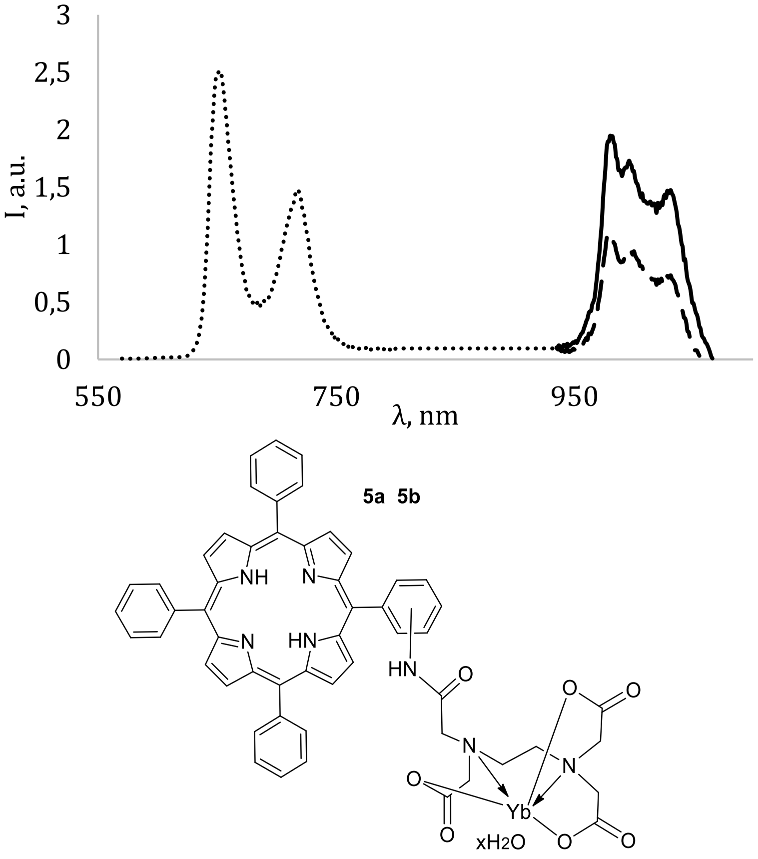


Fig. 2. Emission profile of isomeric Yb complexes: molecular fluorescence (•••) of both porphyrin-edta isomers and their Yb-complexes, *4f*-luminescence of *ortho*- (—) and *para*-isomer (- - -)

4f-Emission of *ortho*-isomer is about 50 % more efficient than for *para*-isomer (Fig. 2). Efficiency is expectedly differing since the *4f*-sensitization process previously has been shown as distance-sensitive as occurring through both Förster and Dexter mechanisms, which effectiveness strongly depends on the donor-acceptor distance [26]. On the other side, it was proposed that sensitized Yb^{3+} luminescence occurs via a long-range electron transfer (ET) process as photoinduced electron transfer (PET) [27]. Similar conclusions were made in early 1984 – authors studied edta-lanthanide complexes modified by different chromophores without chemical bonds between them and lanthanides [28]. The most powerful argument for the last one is the absence of any overlapping between porphyrin emission and absorption of Yb^{3+} ion. Note, that porphyrin-free edta-Yb complex does not reveal 4f-luminscence at all since ther are no appropriate sensitization pathways in this case.

The optimal donor-acceptor distance for the effective energy transfer is zero angstroms, *i.e.* direct covalent bonding of Ln ion to the chromophore. On the other side, the distance between the lanthanide ion and the porphyrin core drastically affects the kinetic features of intramolecular transfers. Previously it has been proved [29] that heavy atoms cause acceleration of the intersystem processes both ISC (intersystem crossing, $S_1 \rightarrow T_1$) and ISD (intersystem degradation, $T_1 \rightarrow S_0$). Thus, both ISC and ISD endure significant acceleration in core-coordinated lanthanide-porphyrins in comparison to any other non-core (peripheral) lanthanide-porphyrin systems or free porphyrin molecules. Thus, core-coordinated lanthanide-porphyrins reveal almost 100 % effectiveness of $S_1 \rightarrow T_n$

transfer, which should make the whole pathway of *4f*-sensitizing ($S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow Ln^{n+}$) almost quantitative. However, since ISD is accelerated too, it should compete with $T_1 \rightarrow Ln^{n+}$ process and the rate of ISD should reduce the efficiency of *4f*-sensitization.

The structure of *ortho*- and *para*-isomers differs not only by the orientation of the Yb-edta fragment relative to the phenyl group but also primarily by its spatial position relative to the porphyrin chromophore. It is known that the interplanar angle between the phenyl group and the porphyrin cycle in *meso*-phenyl porphyrins can be approximately within an interval of 60–90° depending on the nature of the *ortho*- and *meta*-groups in the phenyl ring [30]. Thus, Yb^{3+} should be spatially located directly above the porphyrin ring. Calculations of respective optimized structures have confirmed these suggestions (Fig. 3). The calculated distances between the center of the porphyrin core and the lanthanide ion in *ortho*- and *para*-isomers are respectively 6 and 12 Å.

Since there is no overlapping between porphyrin emission and absorption of Yb^{3+} ion, so there can be no through space transfer and, presumably, only PET can be only one possible mechanism of sensitization. Thus, in frames of the present work, we show that halving the distance between porphyrin and lanthanide ion results in half increase of Yb^{3+} luminescence supposedly as a consequence of more efficient PET and the absence of ISD.

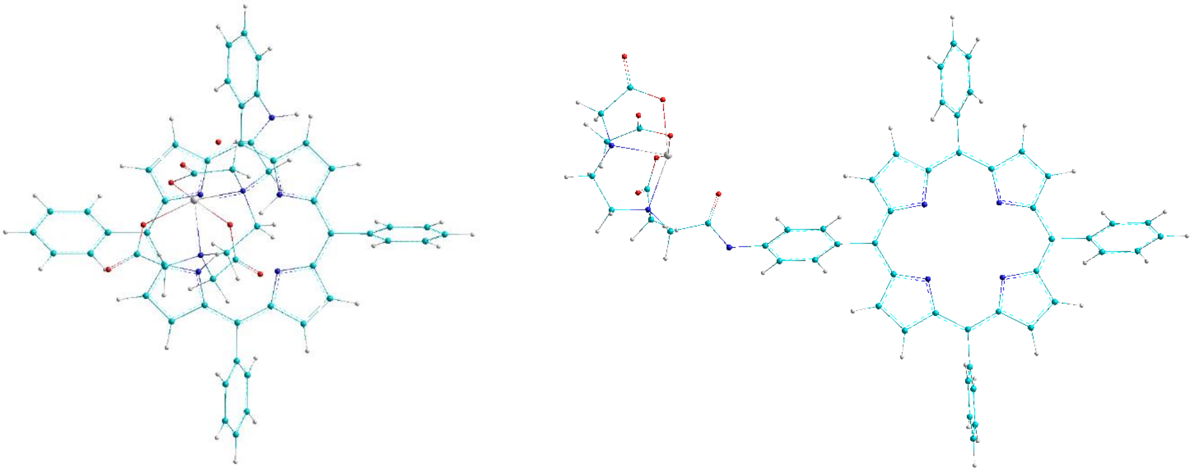


Fig. 3. Optimized structures (HyperChem, MM+) of *ortho*- and *para*-isomers of Yb-edta-tpp

Conclusions

The present study aimed to construct and study the lanthanide-porphyrin system, in which the donor and acceptor are as close to each other as possible, wherein the absence of direct covalent bonding between them will provide no (or minor) effect of ISD on the *4f*-sensitization process in contrast to core-coordinated lanthanide-porphyrins. The obtained results show that both Yb-edta-porphyrin isomers have no changes in terms of fluorescence effectiveness in comparison to their corresponding ditopic edta-porphyrins, which proves the absence of ISC and ISD acceleration. Halving the distance between porphyrin and lanthanide ion results in half increase of Yb^{3+} luminescence. Enhancing of *4f*-luminescence effectiveness can be explained simultaneously by both decreasing the donor-acceptor distance and the absence of notable ISD acceleration which is typical for core-coordinated compounds.

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References

[1] Puccini, A., Liu, N., Hemmer, E. (2024). Praseodymium-Doped Nanoparticles: Candidates for Near-Infrared-II Double- and Single-Band Nanothermometry. *ACS Materials Letters*, *6*(4), 1327–1337. https://doi.org/10.1021/acsmaterialslett.3c01554

[2] Malhotra, K., Hrovat, D., Kumar, B., Qu, G., Houten, J. V., Ahmed, R., Piunno, P. a. E., Gunning, P. T., Krull, U. J. (2023). Lanthanide-Doped Upconversion Nanoparticles: Exploring A Treasure Trove of NIR-Mediated Emerging Applications. *ACS Applied Materials & Interfaces*, *15*(2), 2499–2528. http://dx.doi.org/10.1021/acsami.2c12370

[3] Li, J., Li, Y., Selishchev, D., Zhang, G. (2024). Near-infrared responsive photocatalysts for environmental remediation and energy conversion: A review. *Chemosphere*, 367, 143599. https://doi.org/10.1016/j.chemosphere.2024.143599

[4] Liu, Y., Wang, H., Qu, S. (2025). Review on near-infrared absorbing/emissive carbon dots: From preparation to multi-functional application. *Chinese Chemical Letters*,

36(5), 110618. https://doi.org/10.1016/j.cclet.2024.110618

[5] Khan, M. A., Asadi, H., Zhang, L., Qazani, M. R. C., Oladazimi, S., Loo, C. K., Lim, C. P., Nahavandi, S. (2024). Application of artificial intelligence in cognitive load analysis using functional near-infrared spectroscopy: A systematic review. *Expert Systems with Applications*, 249, 123717. https://doi.org/10.1016/j.eswa.2024.123717

[6] Du, Y., Ni, S., Ma, Q., Song, X., Yang, H. (2023). Engineering NIR-II luminescent lanthanide nanoprobes for imaging brain diseases in vivo. *Coordination Chemistry Reviews*, 496, 215401. https://doi.org/10.1016/j.ccr.2023.215401

[7] Luo, X., Zhang, C., Yu, Z., Wen, S., Xian, Y. (2023). Recent advances in responsive lanthanide-doped luminescence nanoprobes in the near-infrared-II window. *TrAC Trends in Analytical Chemistry*, *169*, 117368. https://doi.org/10.1016/j.trac.2023.117368

[8] Falsaperla, R., Leone, G., Giallongo, A., Giacchi, V., Lombardo, G., Polizzi, A., Romano, C., Ruggieri, M. (2025). Near-infrared spectroscopy (NIRS) as a tool to prevent cerebral desaturation in newborns with bradycardia events: A systematic review. *Pediatrics & Neonatology*, *66*(2), 94–101. https://doi.org/10.1016/j.pedneo.2024.07.011

[9] Gan, Y., Ying, J., Qiu, X., You, S., Zhang, T., Ruan, T., Zhou, R., Ye, Y., Yue, Y., Zhang, L., Mu, D. (2024). Value of near-infrared spectroscopy in evaluating the risk of neonatal necrotizing enterocolitis: A systematic review and meta-analysis. *Early Human Development*, *195,* 106083. https://doi.org/10.1016/j.earlhumdev.2024.106083

[10] Wang, T., Wang, S., Liu, Z., He, Z., Yu, P., Zhao, M., Zhang, H., Lu, L., Wang, Z., Wang, Z., Zhang, W., Fan, Y., Sun, C., Zhao, D., Liu, W., Bünzli, J.-C. G., Zhang, F. (2021). A hybrid erbium(III)–bacteriochlorin near-infrared probe for multiplexed biomedical imaging. *Nature Materials*, *20*(11), 1571–1578. https://doi.org/10.1038/s41563-021-01063-7

[11] Altmann, A., Eden, M., Hüttmann, G., Schell, C., Rahmanzadeh, R. (2023). Porphyrin-based sensor films for monitoring food spoilage. *Food Packaging and Shelf Life*, 38, 101105. https://doi.org/10.1016/j.fpsl.2023.101105

[12] Li, L.-L., Diau, E. W.-G. (2013). Porphyrin-sensitized solar cells. *Chem. Soc. Rev.*, *42*(1), 291–304. https://doi.org/10.1039/c2cs35257e

[13] Duc La, D., Khong, H.M., Nguyen, X.Q., Dang, T.-D., Bui, X.T., Nguyen, M. K., Ngo, H. H., Nguyen, D. D. (2024). A review on advances in graphene and porphyrin-based electrochemical sensors for pollutant detection. *Sustainable Chemistry One World*, 3, 100017. https://doi.org/10.1016/j.scowo.2024.100017

[14] Atal, K., Phageria, U., Kumari, S., Dhayal, Y., Bugalia, S. (2024). A review on designing and synthesis of lanthanide based macrocyclic complexes and their potential applications. *Inorganica Chimica Acta*, *561,* 121857. https://doi.org/10.1016/j.ica.2023.121857

[15] Li, L., Wang, Z., Zhao, L., Liu, H., Li, Y. (2025). Lanthanide-based photocatalysts for CO2 conversion: Are they a better choice for realizing sustainability? *Coordination Chemistry Reviews*, *522*, 216223. https://doi.org/10.1016/j.ccr.2024.216223

[16] Hu, J.-Y., Ning, Y., Meng, Y.-S., Zhang, J., Wu, Z.-Y., Gao, S., Zhang, J.-L. (2017). Highly near-IR emissive ytterbium(iii) complexes with unprecedented quantum yields. *Chemical Science*, 8, (4), 2702-2709. http://dx.doi.org/10.1039/c6sc05021b

[17] Kuznetsova, R. T., Ermolina, E. G., Gadirov, R. M., Mayer, G. V., Semenishin, N. N., Rusakova, N. V., Korovin, Y. V. (2010). Luminescence of metal complexes of chelate-substituted tetraphenylporphyrin. *High Energy Chem.*, *44*(2), 134–138. https://doi.org/10.1134/s0018143910020098

[18] Rusakova, N., Semenishyn, N., Korovin, Y. (2010). Heteronuclear lanthanide-containing complexes on the base of modified porphyrins and their luminescent properties. *J. Porphyrins Phthalocyanines*, *14*(2), 166–169. https://doi.org/10.1142/S1088424610001817

[19] Shin K., Y. D.-H. (1999). Facile synthesis of porphyrin-EDTA conjugate and porphyrin-DTPA conjugate. *J. Korean Chem. Soc.*, *43*(6), 611–613.

[20] Hofmann, B., Bogdanov Jr., A., Marecos, E., Ebert, W., Semmler, W., Weissleder, R. (1999). Mechanism of gadophrin-2 accumulation in tumor necrosis. *Journal of Magnetic Resonance Imaging*, *9*(2), 336–341. https://doi.org/10.1002/(SICI)1522-2586(199902)9:2<336::AID-JMRI28>3.0.CO;2-3

[21] Semenishyn, N. N., Smola, S. S., Rusakova, M. Y., Rusakova, N. V. (2022). 4f-Luminescence of 3d-4f heteronuclear porphyrin complexes. *Journal of Chemistry and Technologies*, 30(3), 363–369. https://doi.org/10.15421/jchemtech.v30i3.261538

[22] Semenishyn, N. N., Smola, S. S., Rusakova, N. V., Martynov, A. G., Birin, K. P., Gorbunova, Y. G., Tsivadze, A. Y. (2018). Infrared 4f-Luminescence of Erbium(III) Complexes with Tetrapyrrole Ligands. *Macroheterocycles*, 11(3), 262–268. https://doi.org/10.6060/mhc180691r

[23] Rao, T. A., Maiya, B. G. (1994). Spectroscopic, redox and emission properties of 2-nitro-substituted free base- and metallo-tetra-aryl porphyrins. *Polyhedron*, *13*(12), 1863–1873. http://dx.doi.org/10.1016/0277-5387(94)80009-X

[24] Uemori, Y., Kitamura, A., Munakata, H., Imai, H., Nakagawa, S. (2001). Syntheses and characterization of porphyrins and their zinc complexes appending a multi-dentate ligand. *Inorganica Chimica Acta*, *325*(1), 29–35. https://doi.org/10.1016/S0020-1693(01)00630-2

[25] Kruper, W. J., Jr., Chamberlin, T. A., Kochanny, M. (1989). Regiospecific aryl nitration of meso-substituted tetraarylporphyrins: a simple route to bifunctional porphyrins. *The Journal of Organic Chemistry*, *54*(11), 2753–2756. https://doi.org/10.1021/jo00272a057

[26] Andres, J., Chauvin, A.-S. (2013). Energy transfer in coumarin-sensitised lanthanide luminescence: investigation of the nature of the sensitiser and its distance to the lanthanide ion. *Physical Chemistry Chemical Physics*, *15*(38), 15981–15994. https://doi.org/10.1039/C3CP52279B

[27] Horrocks, W. D., Bolender, J. P., Smith, W. D., Supkowski, R. M. (1997). Photosensitized Near Infrared Luminescence of Ytterbium(III) in Proteins and Complexes Occurs via an Internal Redox Process. *Journal of the American Chemical Society*, *119*(25), 5972–5973. https://doi.org/10.1021/ja964421l

[28] Abusaleh, A., Mearest, C. F. (1984). Excitation and de-excitation processes in lanthanide chelates bearing aromatic sidechains. *Photochemistry and Photobiology*, *39*(s1), 763–769. https://doi.org/10.1111/j.1751-1097.1984.tb08856.x

[29] Gastilovich, E.A., Korol'kova, N.V., Serov, S.A., Klimenko, V.G., Nurmukhametov, R. N. (2008). Effect of

the vibrational pattern of out-of-plane vibrational modes on vibronically induced spin-orbit coupling between ππ* states involved in nonradiative intersystem crossing transitions. *Optics and Spectroscopy*, *105*(2), 208–216. https://doi.org/10.1134/S0030400X08080080

[30] Rosa, A., Ricciardi, G., Baerends, E. J. (2006). Synergism of Porphyrin-Core Saddling and Twisting of meso-Aryl Substituents. *The Journal of Physical Chemistry A*, *110* (15), 5180–5190. https://doi.org/10.1021/jp060931i