

## Infrared 4f–Luminescence of Erbium(III) Complexes with Tetrapyrrole Ligands

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*The luminescent properties of the series of erbium(III) complexes of various coordination types with different tetrapyrrole macrocycles (porphyrins, phthalocyanines and corroles) are discussed in this paper. The investigated series of compounds include mononuclear porphyrinato complexes (metal-ligand ratio 1:1, **tppEr(acac)**), sandwich phthalocyaninato-porphyrinato type complexes (metal-ligand ratio 1:2 [**(15C5)<sub>4</sub>PcJEr[(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Por]** or 2:3 – (**Pc)Er[(15C5)<sub>4</sub>PcJEr(Pc)** and [**(15C5)<sub>4</sub>PcJEr[(15C5)<sub>4</sub>PcJEr(Pc)**], ditopic porphyrins and corroles possessing peripheral lanthanides binding (metal-ligand ratio 1:1, **Er-edta-H<sub>2</sub>atpp·2H<sub>2</sub>O**, **Er-Hdtpa-H<sub>2</sub>atpp**, **Er-edta-H<sub>3</sub>dpfc·2H<sub>2</sub>O** and **Er-Hdtpa-H<sub>3</sub>dpfc**). 4f-Luminescence in the near-infrared region is observed in all studied Er-complexes as a result of intramolecular transfer of excitation energy. The unique features of each type of complexes are discussed in details. The peripheral complexes are dual-emissive: they display both erbium(III) 4f-emission in near-infrared and molecular fluorescence in the visible spectral region. The values of quantum yield of molecular fluorescence as well as the intensity of 4f-luminescence are estimated. It was found that the binding type of erbium(III) plays a key role in the macrocycle excited state relaxation. The double-decker heteroleptic complex [**(15C5)<sub>4</sub>PcJEr[(4-BrPh)<sub>4</sub>Por]** possesses unusual emission behaviour.*

**Keywords:** Tetrapyrrole, luminescence, erbium, porphyrin, phthalocyanine, corrole.

## Инфракрасная 4f–люминесценция комплексов эрбия(III) с тетрапиррольными лигандами

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*В настоящей работе обсуждаются люминесцентные свойства ряда комплексов эрбия(III) разных координационных типов с различными тетрапиррольными макроциклами (порфирины, фталоцианины и корролы). Исследованные ряды соединений включают моноядерные комплексы порфиринов (соотношение металл-лиганд 1:1, **tppEr(acac)**), сэндвичевые фталоцианин-порфириновые комплексы (соотношение металл-лиганд 1:2 [**(15C5)<sub>4</sub>PcJEr[(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Por]** или 2:3 – (**Pc)Er[(15C5)<sub>4</sub>PcJEr(Pc)** и [**(15C5)<sub>4</sub>PcJEr[(15C5)<sub>4</sub>PcJEr(Pc)**], дитопные порфирины и корролы, связанные с лантанидами на периферии молекулы (отношение металл-лиганд 1:1, **Er-edta-H<sub>2</sub>atpp·2H<sub>2</sub>O**, **Er-Hdtpa-H<sub>2</sub>atpp**, **Er-edta-H<sub>3</sub>dpfc·2H<sub>2</sub>O** и **Er-Hdtpa-H<sub>3</sub>dpfc**). 4f-Люминесценция в ближней инфракрасной области наблюдается во всех изученных комплексах эрбия в результате внутримолекулярного*

переноса энергии возбуждения. Подробно обсуждаются уникальные особенности каждого типа комплексов. Периферические комплексы являются двухэмиссионными: они проявляют как эрбиевое(III) 4*f*-излучение в ближней ИК-области, так и молекулярную флуоресценцию в видимой области спектра. Оценены значения квантового выхода молекулярной флуоресценции, а также интенсивности 4*f*-люминесценции. Было обнаружено, что тип связывания эрбия(III) играет ключевую роль в релаксации энергии возбужденного состояния макроцикла. Двухядерный гетеролептический комплекс  $[(15C5)_4Pc]Er[(4-BrPh)_4Por]$  обладает необычным характером эмиссии.

**Ключевые слова:** Тетрапиррол, люминесценция, эрбий, порфилин, фталоцианин, коррол.

## Introduction

Near-infrared (NIR) region is one of the most demanded ranges of light for optical applications in biomedical practice due to its safety for body, low scattering and easy penetration through biological tissues in comparison with ultraviolet and visible light. From these viewpoints, application of lanthanide-containing compounds and composites is promising due to their low-lying resonant energy levels which allow them to emit in NIR region.<sup>[1]</sup> For example, Nd<sup>3+</sup> ions emit at 850–1850 nm due to  ${}^4F_{3/2} \rightarrow {}^4I_{9/2-15/2}$  transitions, Yb<sup>3+</sup> ions emit at 950–1050 nm due to  ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$  transitions.

Erbium(III) ions are of particular interest due to the  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  transition in their 4*f*-shell. This transition gives rise to emission in the region of 1540 nm, which is characterized by minimal absorption in quartz-based optical systems. It is expected that semiconductor laser diodes and optical amplifiers that emit in this region will be less sensitive to temperature variations than devices using interband recombination since 4*f*-level is effectively shielded by external filled shells. Therefore the interaction of the erbium ion with the surrounding matrix is weak and the wavelength of the luminescence is virtually independent from the semiconductor material.

The main drawback of erbium-doped glass fibre amplifiers arises from the requirement in application of high power pump lasers for relatively long fibre.<sup>[2]</sup> It derives from the limited concentration of erbium ions in erbium-doped glass (10<sup>20</sup> ions/cm<sup>3</sup>) and low extinction coefficients of *f*-*f* absorption of lanthanides (typically less than 10 M<sup>-1</sup>cm<sup>-1</sup>). Altogether it leads to very poor 4*f*-emission. Both these reasons can be overcome by using organic chromophores, which act as ligands forming stable coordination compounds with Er<sup>3+</sup> ions and as efficient sensitizers of their NIR emission.

4*f*-Luminescence of Er<sup>3+</sup> complexes in solution was observed for the first time in 1997 using eosin and fluorescein chelating derivatives as NIR emission sensitizers.<sup>[3]</sup> It was also shown that lanthanide complexes with tetrapyrrolic ligands can be efficient NIR emitters. These ligands have appropriate donor triplet (T) levels for intramolecular energy transfer to the resonant levels of lanthanide ions; moreover, these macrocycles have very strong absorption in near-UV region and visible regions. Described approach included synthesis of Yb(III) and Nd(III) complexes based on ditopic tetrapyrrolic ligands bearing external chelating sites.<sup>[4,5]</sup> Recently the first examples of 4*f*-luminescence in the series of Nd(III) complexes with different tetrapyrrolic macrocycles (porphyrins, phthalocyanines and corroles) as

well as Er(III) and Yb(III) mono-, bis- and trisphthalocyanines were demonstrated.<sup>[6,7]</sup>

Thus, in the present work we have continued the study of photoluminescent properties of Er(III) complexes depended on the nature of tetrapyrrolic macrocycles (porphyrin, phthalocyanine and corrole) and types of metal coordination.

## Experimental

Synthesis of the corroles, porphyrin and phthalocyanine derivatives, as well as their complexes except  $[(15C5)_4Pc]Er[(4-BrC_6H_4)_4Por]$  was performed following the published procedures.<sup>[5,8-14]</sup>

*Preparation of  $[(15C5)_4Pc]Er[(4-BrC_6H_4)_4Por]$ .*  $[(4-BrC_6H_4)_4Por]H_2$  (47 mg, 0.05 mmol) and Er(acac)<sub>3</sub>·xH<sub>2</sub>O (46 mg, 0.1 mmol) were mixed in 4 mL of 1-octanol and heated at 200 °C for 4 h under slow flow of dry argon. After complete conversion of the porphyrin to the corresponding erbium monoporphyrinate the mixture was cooled to ambient temperature and dicyanobenzene (15-crown-5) (128 mg, 0.4 mmol) and DBU (50 μl, 0.33 mmol) were added subsequently. The resulting mixture was heated at 200 °C on the oil bath for 24 h under slow flow of dry argon. Further the mixture was cooled and added dropwise to 50 ml of hexane. The precipitate was filtered and washed successively with hexane. The crude product was applied to column packed neutral alumina in chloroform and eluted with CHCl<sub>3</sub>-MeOH mixtures (0→6 % of MeOH), containing 0.1 % of Et<sub>3</sub>N. The evaporation of fractions, eluted with 4–6 % of MeOH in CHCl<sub>3</sub>, provided the target complex as green solid (43 mg, 36 %). *m/z* (MALDI-TOF MS) calcd. for C<sub>108</sub>H<sub>96</sub>Br<sub>4</sub>ErN<sub>12</sub>O<sub>20</sub> 2362.3, found 2362.7. UV-Vis (CHCl<sub>3</sub>) λ<sub>max</sub> (rel. int.) nm: 293 (0.483), 338 (0.609), 372 (0.770), 415 (1.000), 484 (0.473), 591 (0.165), 613 (0.177), 834 (0.099).

## Luminescent measurements

Spectra of molecular fluorescence, 4*f*-luminescence and excitation spectra were recorded on a spectrofluorimeter "Fluorolog FL 3-22" ("Horiba Jobin Yvon") using 450 W Xe-lamp. Spectra of 4*f*-luminescence of Er(III) complexes were registered in 1500–1600 nm range (transition  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ ). Spectra of molecular fluorescence of porphyrins, corroles and phthalocyanines were registered at 550–800 nm (S<sub>1</sub>-S<sub>0</sub> transitions). Integral intensity of luminescence was measured using software of the device. The relative quantum yield of molecular fluorescence (φ<sub>ML</sub>) was determined using solution of Zntpp (H<sub>2</sub>tpp – 5,10,15,20-tetraphenylporphyrin) in ethanol as a primary standard (0.022).<sup>[8,15]</sup> Determination of the φ<sub>ML</sub> (accuracy is ±10 %) was made using formula:

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

where φ<sub>0</sub> and φ<sub>x</sub> – luminescence quantum yield of the standard and of the sample; A<sub>0</sub> and A<sub>x</sub> – absorption at the wavelength of Soret

band of the standard and of the sample;  $I_x$  and  $I_0$  – integral luminescence intensity of the standard and of the sample;  $n_0$  and  $n_x$  – refractive index of the standard solvent and of the sample solvent.

Fluorescence lifetime ( $\tau$ ) was measured under excitation at the Soret band.

## Results and Discussion

In this work we studied properties of several types of Er(III) complexes. The structures of all studied compounds are represented in Figure 1.

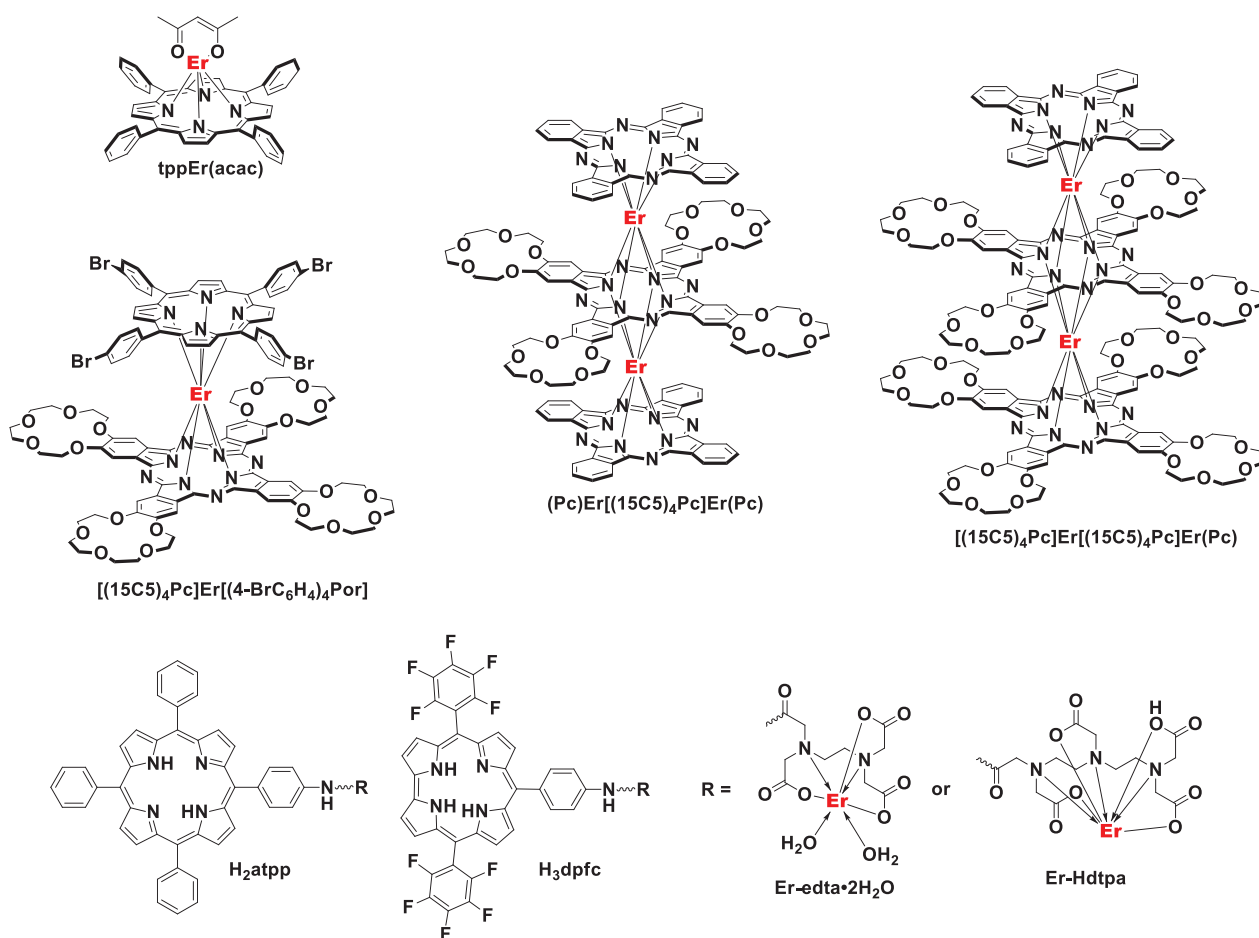
The studied complexes included ones with erbium(III) ions placed in the cavities of tetrapyrrolic macrocycles – mononuclear erbium(III) porphyrinate **tppEr(acac)**, heteroleptic double-decker porphyrinato-phthalocyaninato complex **[(15C5)<sub>4</sub>Pc]Er[(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Por]**, heteroleptic trisphthalocyaninato-complexes with metal-ligand ratio 2:3 – **(Pc)Er[(15C5)<sub>4</sub>Pc]Er(Pc)** and **[(15C5)<sub>4</sub>Pc]Er[(15C5)<sub>4</sub>Pc]Er(Pc)**. These complexes were synthesized following the previously published procedures.<sup>[5,12,13]</sup>

Heteroleptic double-decker phthalocyaninato-porphyrinato double-decker complex **[(15C5)<sub>4</sub>Pc]Er[(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Por]** was prepared in 36 % yield by interaction of generated in situ erbium monoporphyrinate **[4-BrC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Por]Er(acac)** and dicyanobenzo-(15-crown-5).

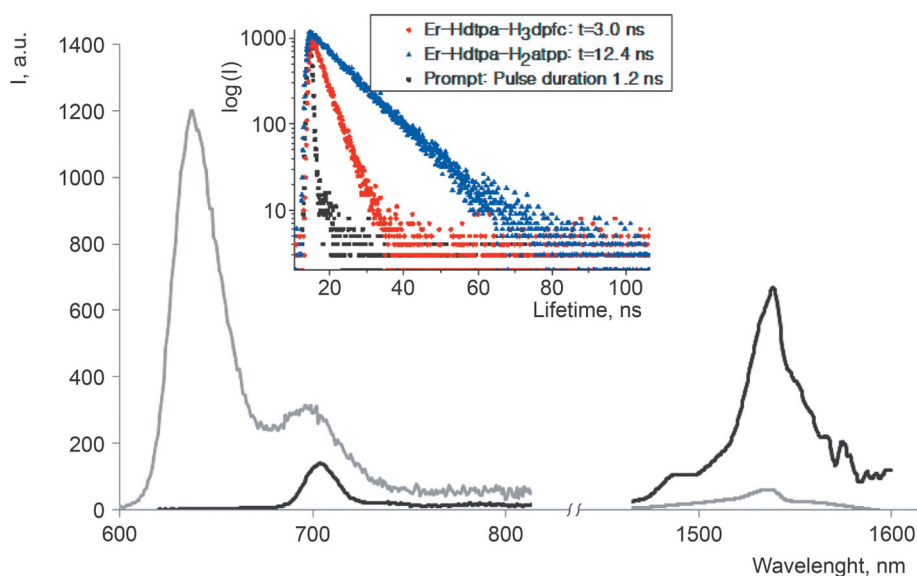
Purity of all complexes was confirmed by MALDI-TOF mass-spectrometry, NMR, FTIR and UV-Vis spectroscopy. The obtained data were found to be consistent with the predicted structures. NMR analysis of paramagnetic Er complexes was performed using previously described approaches.<sup>[16,17]</sup>

We also have studied mononuclear complexes formed by Er(III) with ditopic porphyrins and corroles bearing peripheral binding sites as convenient building blocks which can be used to form polynuclear tetrapyrrole-based complexes.<sup>[18-20]</sup> These ditopic porphyrins and corroles were synthesized through the acylation of parental aminoderivatives (**H<sub>2</sub>atpp** – 5-(4-aminophenyl)-10,15,20-triphenylporphyrin and **H<sub>3</sub>dpfc** – 10-(4-aminophenyl)-5,15-di(pentafluorophenyl)corrole) by bis-anhydrides of aminopolycarbonic acids (ethylenediamine-*N,N,N',N'*-tetraacetic acid, **H<sub>4</sub>edta** and diethylenetriamine-*N,N,N',N',N''*-pentaacetic acid, **H<sub>5</sub>dtpa**). The erbium complexes with these functionalized porphyrins and corroles were formed with ratio Er:L = 1:1, erbium ions were located in peripheral binding centers.

All studied complexes containing Er(III) were 4*f*-luminescent compounds. The coincidence of the absorption and excitation spectra of these compounds clearly showed that the 4*f*-luminescence of Er<sup>3+</sup> was a result of ligand-to-



**Figure 1.** Structures of studied erbium(III) complexes – monoporphyrinate **tppEr(acac)**, heteroleptic double-decker complex **[(15C5)<sub>4</sub>Pc]Er[(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Por]**, heteroleptic triple-decker complexes **(Pc)Er[(15C5)<sub>4</sub>Pc]Er(Pc)** and **[(15C5)<sub>4</sub>Pc]Er[(15C5)<sub>4</sub>Pc]Er(Pc)**, peripherally-metallated complexes of porphyrins (**Er-edta-H<sub>2</sub>atpp·2H<sub>2</sub>O** and **Er-Hdtpa-H<sub>2</sub>atpp**) and corroles (**Er-edta-H<sub>3</sub>dpfc·2H<sub>2</sub>O** and **Er-Hdtpa-H<sub>3</sub>dpfc**).



**Figure 2.** Luminescence spectra of double-decker heteroleptic complex  $[(15C5)_4Pc]Er[(4-BrC_6H_4)_4Por]$  (black line) and peripheral complex  $Er-Hdtpa-H_3dpfc$  (grey line). Inset – measurement of molecular fluorescence lifetimes for **dtpa**-derived peripheral complexes with corrole and porphyrin.

lanthanide energy transfer. Thus, all macrocyclic tetrapyrroles under study were able to sensitize the *4f*-luminescence of erbium (Figure 2).

Notably, it is impossible to calculate the quantum yield of the *4f*-luminescence of erbium(III) ion due to the absence of the primary standard in the region 1500–1600 nm. Thus, we used the values of relative *4f*-luminescence intensity ( $I_{4f}$ ).

### Porphyrins

The absorption spectra of  $Er-edta-H_2atpp \cdot 2H_2O$  and  $Er-Hdtpa-H_2atpp$  in methanol are typical for metal-free porphyrins, and their bands are only slightly shifted to longer wavelengths with respect to the parental  $H_2atpp$ , despite the bulky substituent in one of the phenyl groups, which is coordinated with Er(III) ion. Both complexes possess equal spectra: near-UV Soret band maximum at 419 nm, and four *Q*-bands in the visible range with  $\lambda_{max} = 515, 550, 591$  and 647 nm.

The efficiency of the *4f*-luminescence in 1:1 complexes depends on denticity of the ligand: saturation of the Er(III) coordination sphere is achieved by water molecules, which provided additional energy dissipation channels because of the lack of coordinating atoms in the case of **edta** fragment.<sup>[8]</sup> In the case of the peripherally metalated complexes with **dtpa** fragment water molecules do not enter the coordination sphere of erbium ion, so these complexes revealed higher  $I_{4f}$ . Paramagnetic ion does not affect molecular fluorescence (Table 1).

In contrast, the complex  $tppEr(acac)$  does not reveal molecular fluorescence. In this case paramagnetic ion is coordinated directly to the chromophore macrocycle that results in complete molecular fluorescence quenching, however this complex reveals relatively strong *4f*-luminescence in comparison with the peripherally metalated complex.

### Corroles

Absorption spectra of ditopic corroles metalated at the peripheral polydentate binding site by Er(III) possessed a near-UV Soret band maximum at 410 nm, and two *Q*-bands in the visible range with  $\lambda_{max} = 568$  and 615 nm. Note, that there are no changes in the absorption spectra of  $Er-edta-H_3dpfc \cdot 2H_2O$  and  $Er-Hdtpa-H_3dpfc$  in comparison with the parental ditopic ligands  $H_3edta-H_3dpfc$  and  $H_4dtpa-H_3dpfc$ .

*4f*-Emission of  $Er-edta-H_3dpfc \cdot 2H_2O$  and  $Er-Hdtpa-H_3dpfc$  is characterized with 320 and 390 a.u. of intensity, respectively. The molecular fluorescence decay curves are well-fitted to a single exponential function in all cases (Figure 2).

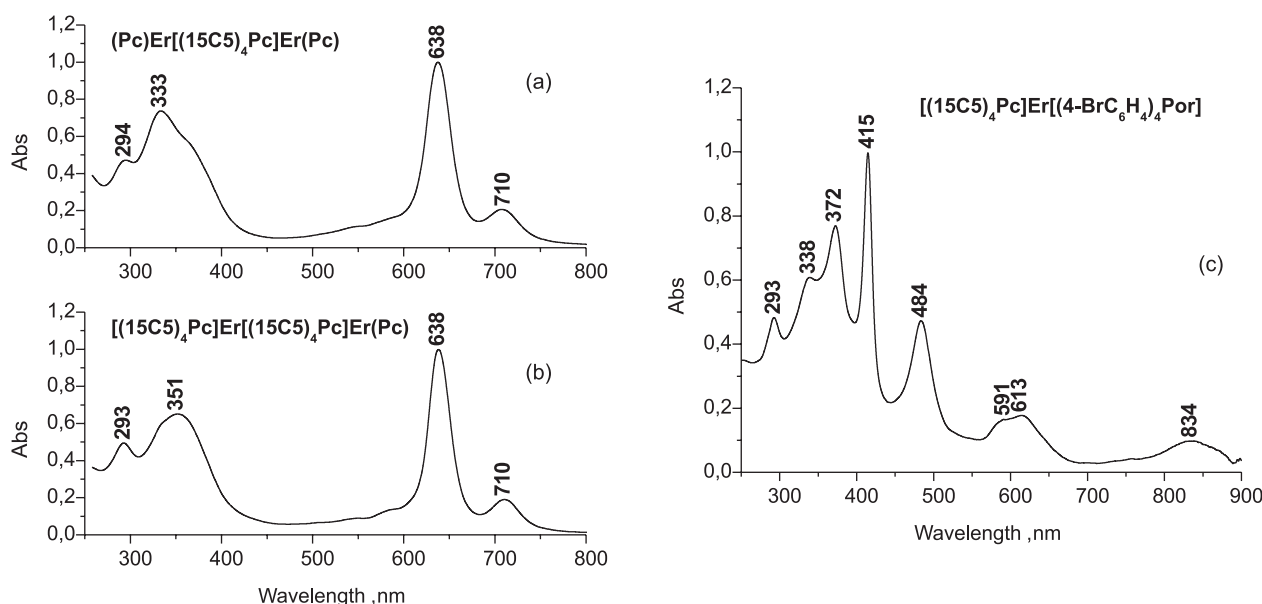
Like in the case of ditopic porphyrins, all of the studied peripheral complexes reveal two types of emission: corrole molecular luminescence with basic band  $\lambda_{max} \approx 650$  nm and *4f*-luminescence of erbium(III) ion with band  $\lambda_{max} \approx 1540$  nm.

Due to the extreme instability of the core-coordinated lanthanide-corroles<sup>[8]</sup> we cannot provide their photophysical data.

### Sandwich complexes

The absorption spectra of erbium(III) trisphthalocyanines are typical for the triple-decker complexes.<sup>[21,13]</sup> In the case of symmetrical complex  $(Pc)Er[(15C5)_4Pc]Er(Pc)$  the Soret band has a maximum at 333 nm, while in the case of asymmetric complex  $[(15C5)_4Pc]Er[(15C5)_4Pc]Er(Pc)$  its maximum shifts to 351 nm, which reflects the increase of the number of electron donating crown ether substituents. The *Q*-band is split into two components with maxima at 638 and 710 nm independently on the number and position of crown ether substituents (Figure 3a,b).





**Figure 3.** The absorption spectra of erbium(III) trisphthalocyaninates **(Pc)Er[(15C5)<sub>4</sub>Pc]Er(Pc)** (a), **[(15C5)<sub>4</sub>Pc]Er[(15C5)<sub>4</sub>Pc]Er(Pc)** (b) and heteroleptic double-decker erbium(III) complex **[(15C5)<sub>4</sub>Pc]Er[(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Por]** (c).

The molecular fluorescence of the triple-decker erbium-phthalocyaninates is observed at the noise level, so its  $\phi_{ML}$  could not be measured accurately. This was mainly because of the quenching of the fluorescence due to the presence of paramagnetic metal ion.

The maxima of 4*f*-luminescence bands of both symmetric and asymmetric triple-decker erbium-phthalocyaninates are observed at 1539 nm. The values of intensity of their signals are 5250 and 4720 a.u., respectively, which is found to be two times lower than for **tppEr(acac)** (Table 1). Such decrease of intensity can be explained with at least two reasons: 1. Non-radiative energy pathways due to increased number of C-H-oscillators in comparison to **tppEr(acac)**. 2. Overlapping of Er<sup>3+</sup> IR emission with its strong absorption in the region 1368–1660 nm.

UV-Vis spectrum of heteroleptic double-decker complex **[(15C5)<sub>4</sub>Pc]Er[(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Por]** contained additional bands corresponding to the porphyrin ring, in contrast to homoleptic triple-decker complexes. Thus, it consists of two Soret bands at 415 and at 484 nm as well as two Q-bands at 613 with the shoulder at 591 and 834 nm related to porphyrin and phthalocyanine decks, correspondingly (Figure 3c).

4*f*-Luminescence excitation of heteroleptic complex is performed at different wavelengths of UV- and Vis-range – 371, 415, 484, 600 nm (maxima of absorption bands). The maximum of Er(III) emission band does not depend on the excitation wavelength and it corresponds to the standard emissive transition of erbium  $^4I_{13/2} \rightarrow ^4I_{15/2}$  at 1538–1539 nm. The most intensive 4*f*-signal was observed under excitation at 484 nm, which can be attributed to region of simultaneous absorption of both porphyrin and phthalocyanine. Molecular fluorescence of double-decker erbium complex is quenched (its  $\phi_{ML}=0.01$ ) and it has only one band with maximum at 704 nm.

The unusual emission of heteroleptic complex can be explained by several reasons. First of all, we have to mention

that the values of energy of S<sub>1</sub>- and T<sub>1</sub>-levels for *meso*-tetra(*p*-bromophenyl)porphyrin are 15500 cm<sup>-1</sup> and 12000 cm<sup>-1</sup>, respectively. Tetracrownphthalocyanine has S<sub>1</sub>-level at 13500 cm<sup>-1</sup>. Measuring of the energy of T<sub>1</sub>-level of phthalocyanine was impossible for us, but for some complexes these values are located in the region of 8500–11000 cm<sup>-1</sup>.<sup>[22]</sup>

Under excitation at 371 nm (at phthalocyanine absorption maximum) we observed 93 %-quenched phthalocyanine fluorescence. Hypersensitive *f-f*-transition  $^4I_{15/2} \rightarrow ^4G_{11/2}$  of erbium(III) was located at almost the same wavelength (379 nm).<sup>[23]</sup> Thus, 4*f*-luminescence observed under excitation at 371 nm was a result of both intramolecular transfer from phthalocyanine and in a less degree from porphyrin chromophores and direct excitation of Er(III) ion. So, this “three-component” 4*f*-luminescence had a value of 8450 a.u.

4*f*-Luminescence is slightly decreased under excitation at 415 nm (at porphyrin absorption maximum) and its intensity became 7040 a.u. This decrease could be attributed to the following reasons: absence of the direct efficient *f-f*-excitation of Er(III) ion and a heavy atom effect, caused by four bromine substituents. Under excitation at phthalocyanine absorption maximum this effect can be avoided, since phthalocyanine fragment does not contain such kind of atoms.

Curiously, under excitation at 415 nm it is possible to detect weak (quenched) fluorescence of porphyrin with maximum at 653 nm (Table 1).

The highest value of 4*f*-luminescence is observed under excitation at 484 nm – 16300 a.u., while molecular fluorescence is 98 %-quenched. S<sub>1</sub>-S<sub>0</sub>-emissive transition in the region of porphyrin and phthalocyanine is located in the region that possesses two *f-f*-transitions of Er(III) ion –  $^4I_{15/2} \rightarrow ^4F_{9/2}$  and  $^4I_{15/2} \rightarrow ^4I_{9/2}$ , correspondingly, *i.e.* quenching of the molecular fluorescence takes place not only because of perturbing action of paramagnetic ion, but also owing to a donor action of the lowest S-level. Among other things, excitation wavelength 484 nm is a maximum of another one *f-f*-absorption

**Table 1.** Luminescent data of Er(III) complexes with various tetrapyrroles.

Complex	$\lambda_{exc.}$ , nm	$\lambda_{ML}$ , nm	$\lambda_{4f}$ , nm	$\phi_{ML} \times 10^{2a}$	$I_{4f}$ , a.u.	$\tau_{ML}$ , ns <sup>b</sup>
<b>Er-edta-H<sub>2</sub>atpp·2H<sub>2</sub>O</b>	419	654, 714	1541	11	500	11.8
<b>Er-Hdtpa-H<sub>2</sub>atpp</b>	419	654, 715	1541	11	850	12.4
<b>Er-edta-H<sub>3</sub>dpfc·2H<sub>2</sub>O</b>	410	639, 695	1542	5.3	320	3.2
<b>Er-Hdtpa-H<sub>3</sub>dpfc</b>	410	640, 697	1542	6.0	390	3.0
<b>Er-tpp(acac)</b>	425	–	1539	–	10700	–
<b>(Pc)Er[(15C5)<sub>4</sub>Pc]Er(Pc)</b>	331	–	1539	–	5250	–
<b>[(15C5)<sub>4</sub>Pc]Er[(15C5)<sub>4</sub>Pc]Er(Pc)</b>	355	–	1539	–	4720	–
	371	704	1539, 1532(sh.), 1552(sh.)	<1	8450	–
<b>[(15C5)<sub>4</sub>Pc]Er[(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Por]</b>	415	653, 704	1539, 1532(sh.), 1552(sh.)	<1; <1 <sup>c</sup>	7040	–
	484	704	1539, 1532(sh.), 1552(sh.)	<1	16300	–
	600	704	1539, 1532(sh.), 1552(sh.)	<1	8000	–

RT, MeOH, C=10<sup>-5</sup>M. Complex **Er-tpp(acac)** (acac – acetylacetonate) was used for comparison.

<sup>a</sup> ±10 %; <sup>b</sup> ±0.02 ns; <sup>c</sup>  $\phi_{ML}$  for porphyrin and for phthalocyanine moiety separately.

band, which corresponds to  $^4I_{15/2} \rightarrow ^4F_{7/2}$  transition, so in this case erbium ion is partially excited directly.

Under excitation at 600 nm (region of *Q*-bands of both phthalocyanine and porphyrin) *4f*-luminescence intensity value was 8000 a.u. The molecular fluorescence in this case is 85 %-quenched. This excitation region does not include any *f-f*-transitions of erbium. Interestingly, the absence of the direct excitation of Er(III) ion (excitation at 415 nm) leads to roughly the same values of *4f*-luminescence intensity.

Analysis of the obtained results reveals that the *4f*-luminescence intensity value seemed to be in direct dependence on the number of *4f*-luminescence sensitization ways.

### Comparison of the fluorescent and *4f*-luminescent properties

The molecular fluorescence of the studied compounds demonstrates strong dependence on the type of Er(III) coordination. Thus, core-coordinated erbium porphyrin and phthalocyanine complexes including erbium porphyrinate **tppEr(acac)** and sandwich complexes possess very low quantum yields of molecular fluorescence. On the other hand, all peripheral complexes demonstrate relatively high values of the  $\phi_{ML}$ , which are comparable with  $\phi_{ML}$  of the metal-free compounds.

All the results presented so far indicate that the peripheral complexes are dual-range emitters: they reveal tetrapyrrole-based molecular fluorescence in visible range and *4f*-luminescence in the NIR range. This dual emission was observed at room temperature in aerated solutions, while macrocyclic tetrapyrroles typically exhibit NIR emission as phosphorescence only at deoxygenated conditions and usually in frozen solutions.<sup>[24]</sup> The distance between the paramagnetic ion and the chromophore is so large that there is no perturbing effect of the former on the photo-physical properties of the latter. This behavior significantly differs from the tetrapyrroles that are core-metalated with paramagnetic lanthanide ions. Energy transfer from the excited chromophore to the lanthanide is almost quan-

titative and very weak residual fluorescence is observed in such kind of systems.<sup>[25]</sup> If a lanthanide ion is remote from the sensitizing chromophore, the energy transfer step is less efficient and the deactivation of the intermediate T<sub>1</sub>-state by oxygen may compete.<sup>[20]</sup> Nevertheless, neither peripheral porphyrin complexes nor corrole ones reveal any *4f*-luminescent sensitivity to the presence of oxygen under different conditions.<sup>[26]</sup>

*4f*-Luminescence is observed in all of the studied erbium complexes as a result of the intramolecular excitation energy transfer. Mononuclear core-coordinated complexes **tppEr(acac)** and **[(15C5)<sub>4</sub>Pc]Er[(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>4</sub>Por]** have the highest luminescence efficiency especially owing to the participation of the coordinated lanthanide ion in the population of the T-state by enhancing the intersystem crossing (ISC) in the tetrapyrrole chromophore due to an external heavy atom effect. These complexes reveal a pure Dexter energy transfer mechanism because of the direct binding of Er<sup>3+</sup> ion to tetrapyrrolic macrocycle (distance of regular bond ~2 Å) and because of the extremely high ISC which almost completely quenches the molecular fluorescence. All studied peripheral erbium complexes demonstrate Förster mechanism of the energy transfer (donor-acceptor distance is more than 10 Å even for conformations of maximal proximity of lanthanide ion and chromophore). The latter can imply an additional energy transfer from S<sub>1</sub>-state to Er<sup>3+</sup> resonant levels because of the absence of perturbing action of the paramagnetic metal ion and due to overlapping of the donor emission and acceptor absorption.

Low *4f*-luminescence intensity of erbium triple-decker sandwich compound can be explained by self-quenching in lanthanide-lanthanide pair (as a result of the energy exchange between Er ions),<sup>[27]</sup> since they are located in close proximity to each other.

Low *4f*-luminescence efficiency of the peripheral **H<sub>2</sub>atpp**-complexes derives from low interaction of donor (chromophore) and acceptor (Er(III) ion) in comparison to directly-coordinated complex. On the other hand, the main advantage of such approach is keeping the value of the molecular fluorescence efficiency.

Luminescent data of the heteroleptic porphyrin-phthalocyanine Er-compound is unusual. Thus, efficiency of its 4f-luminescence and molecular fluorescence is depended on the excitation wavelength, since both porphyrin and phthalocyanine chromophores can act as energy donors for Er(III) ion.

Thus, directly coordinated complexes reveal high-intensity 4f-luminescence combined with a very weak residual molecular fluorescence of tetrapyrrole macrocycle. *Per contra*, complexes with peripherally-bound erbium ions reveal unaltered molecular fluorescence with relatively weak Er luminescence signal (Figure 2).

## Conclusions

4f-Luminescence of the erbium(III) complexes with different tetrapyrrole macrocycles (porphyrins, phthalocyanines and corroles) was compared for the first time. It was proposed that binding type of erbium(III) plays a key role in formation of energy relaxation pathways in the molecule. Presence of the different types of chromophores in heteroleptic complexes leads to unusual emission properties.

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