Фталоцианины
Phthalocyanines

Макрогетероциклы
http://macroheterocycles.isuct.ru

Статья
Paper

The First Example of Near−Infrared 4*f* Luminescence of Sandwich−Type Lanthanide Phthalocyaninates

Sergey S. Smola,[a] Olga V. Snurnikova,[a] Evgeniy N. Fadeyev,[a]
Anna A. Sinelshchikova,[b] Yulia G. Gorbunova,[b,c] Lyudmila A. Lapkina,[c]
Aslan Yu. Tsivadze,[b,c] and Nataliya V. Rusakova[a@]

[a]*A.V. Bogatsky Physico-Chemical Institute of National Academy of Sciences of Ukraine, 65080 Odessa, Ukraine*
[b]*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, 119071 Moscow, Russia*
[c]*N.S. Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, 119991 Moscow, Russia*
[@]*Corresponding author E-mail: lanthachem@ukr.net*

A detailed analysis of photophysical characteristics of mono-, double- and triple-decker complexes of Er[III], Yb[III] and Lu[III] with 2,3,9,10,16,17,24,25-tetrakis(15-crown-5)phthalocyanine (L) was performed. The values of the quantum yields and the rate constants of molecular fluorescence and intersystem crossing of the compounds were estimated. It was discovered that the solutions of the sandwich Er[III] and Yb[III] double- and triple-decker phthalocyaninates possess 4f luminescence in near-infrared range (NIR) at 1540 nm and 980 nm, respectively. It was demonstrated that Yb[III] mono-phthalocyaninate also exhibits 4f luminescence. The proposed mechanism of excitation energy transfer is discussed.

Keywords: Phthalocyanine, lanthanides, luminescence, 4*f* luminescence, energy transfer, erbium(III), ytterbium(III).

Первый пример 4*f* люминесценции сэндвичевых фталоцианинатов лантанидов в ближней ИК−области

С. С. Смола,[a] О. В. Снурникова,[a] Е. Н. Фадеев,[a] А. А. Синельщикова,[b]
Ю. Г. Горбунова,[b,c] Л. А. Лапкина,[c] А. Ю. Цивадзе,[b,c] Н. В. Русакова[a@]

[a]*Физико-химический институт им. А.В. Богатского Национальной академии наук Украины, 65080 Одесса, Украина*
[b]*ФГБУН Институт физической химии и электрохимии им. А.Н. Фрумкина Российской академии наук, 119071 Москва, Россия*
[c]*ФГБУН Институт общей и неорганической химии им. Н.С. Курнакова Российской академии наук, 119991 Москва, Россия.*
[@]*E-mail: lanthachem@ukr.net*

Проведен детальный анализ фотофизических характеристик моно-, двух- и трехпалубных тетра(15-краун-5) фталоцианинатов Er[III], Yb[III] и Lu[III]. Оценены значения квантовых выходов и вероятностей молекулярной флуоресценции и интеркомбинационной конверсии соединений. Для сэндвичевых фталоцианинатов Er[III] и Yb[III] впервые обнаружена 4f люминесценция в ближнем ИК-диапазоне в области 1540 нм и 980 нм, соответственно. Установлено, что 4f люминесценция ионов Yb[III] реализуется также в случае монофталоцианината. Предложены варианты механизма переноса энергии возбуждения.

Keywords: Фталоцианин, лантаниды, 4*f* люминесценция, перенос энергии, эрбий(III), иттербий(III).

Luminescence Properties of Sandwich-Type Lanthanide Phthalocyaninates

Introduction

The investigation of near-infrared 4*f* luminescence of lanthanide-based systems is one of the most promising research areas owing to their attraction for multiple applications in high technology, first of all in biomedicine.[1-3] Such factors as low background signal of bio-objects in this spectral range (high when measured in visible region of spectrum), possibility of excitation of luminescence in a wide range of wavelengths, including soft visible light irradiation, high values of luminescence lifetimes are factors, responsible for possible applications.[4,5] The values of resonance energy levels of the lanthanide ions emitting in NIR spectral range are at about 10800-11500 cm^{-1}, 6490 cm^{-1} and 10000-10200 cm^{-1}, for Nd^{III}, Er^{III} and Yb^{III}, respectively,[6] that allows to study 4*f* luminesence of lanthanide containing complexes with organic ligands with low triplet levels. Among such organic ligands the macrocyclic tetrapyrroles are most attractive. Indeed, a large number of studies are devoted to luminescence of lanthanide complexes with various porphyrins, which triplet levels are about 14000-15000 cm^{-1}. [7-9] The lanthanide ion in investigated complexes can be located directly at porphyrin N$_4$ coordination cavity[10-12] or bound by chelating peripheral substituents of a porphyrin.[13] Although there are many reports on the synthesis and physico-chemical properties of lanthanide complexes with phthalocyanines – analogues of porphyrins,[14-18] but number of works devoted to investigation of 4*f* luminescence in these compounds are limited.[19-21]

Higher thermal stability of phthalocyanines compared to porphyrins, ability of these molecules to self-assembling due to stacking interactions between aromatic rings makes them attractive for spectroscopic investigations and optical applications. From the other side sandwich lanthanide-based phthalocyaninato complexes possess a wide set of unique spectral, electrochemical, semiconductor and catalytic properties.[17-18] Such peculiarities of sandwich phthalocyaninates combined with unique luminescent properties of lanthanide ions stimulate the appearance of new fields of investigations and application of sandwich lanthanide phthalocyanines.

Herein we describe the photophysical characteristics of mono, double- and triple-decker complexes of Er^{III}, Yb^{III} and Lu^{III} with tetra(15-crown-5)phthalocyanine, including NIR 4*f* luminescence.

Experimental

The monophthalocyaninates [LuL·OAc·Phen] (Phen – 1,10-phenanthroline), [LnL·OAc·DBU] (Ln = Er, Yb, DBU - 1,8-diazabicyclo[5.4.0]undec-7-ene), as well as sandwich type complexes LnL$_2$ and Ln$_2$L$_3$ (Ln = Er, Yb, Lu) were investigated in this study (Figure 1). Tetra(15-crown-5)phthalocyanine (L), Er^{III}, Yb^{III}, Lu^{III} complexes were synthesized and characterized using previously described methods.[15,22-24]

Spectroscopic measurements were performed in absolute CHCl$_3$ in concentration of 10^{-5} M using quartz cells with optical path of 1 cm. Ln$_2$L$_3$ complexes were dissolved in CHCl$_3$ with addition of 2 vol.% of CH$_3$OH to prevent the oxidation of phthalocyaninates. [25] Electronic absorption spectra in the UV- and visible range were recorded on Specord M40 and Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometers.

Excitation, molecular and 4*f* luminescence spectra were registered on a Fluorolog 3-22 (Horiba Jobin Yvon) spectrofluorimeter.
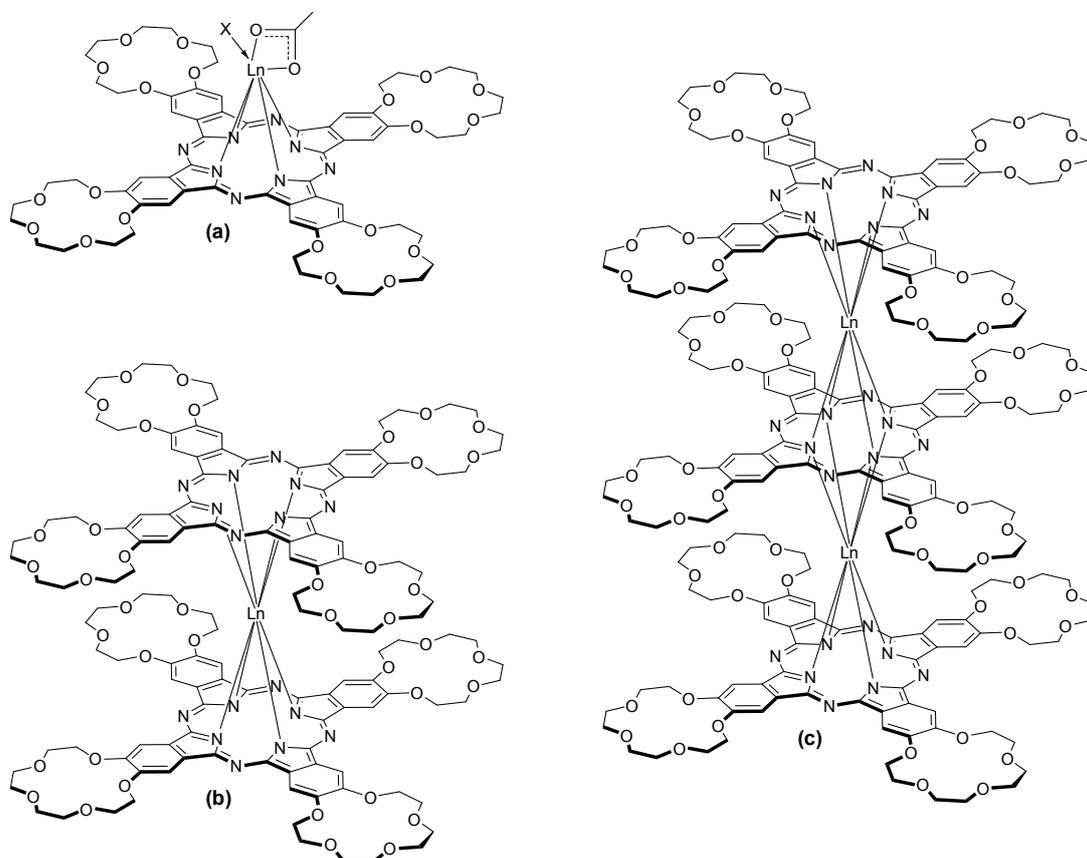
Figure 1. Investigated complexes (a) [LnL·OAc·X], Ln = Lu, X = Phen; Ln = Yb, Er X = DBU; (b) LnL$_2$ and (c) Ln$_2$L$_3$, Ln = Lu, Yb, Er.

The Xe-lamp (450 W), detectors R928P (Hamamatsu, Japan) was used for visible range and InGaAs photoresistor DSS-IGA020L (Electro-Optical Systems, Inc, USA), cooled by liquid nitrogen was applied for NIR range. The excitation and emission spectra were corrected taking into account distribution of Xe lamp emission and sensitivity of photoelectric multiplier.

The relative quantum yields were determined as described in [26]. Zn^{II} tetraphenylporphyrinate (ZnTPP, $\phi = 0.03$[27]) in ethanol and Yb^{III} tris-(2-thenoyltrifluoroacetonate) in toluene (Yb(TTA)$_3$, $\phi = 0.0035$[28]) were used as a reference in determination of fluorescence and $4f$ luminescence quantum yields, respectively.

Fluorescence lifetime measurements were performed with the same Fluorolog 3-22 instrument using TCSPC technique. A pulsed NanoLED-370 (Horiba Jobin Yvon, λ_{ex} = 370 nm, repetition rate 500 KHz, pulse duration 1.3 ns) was used as a light source, and R928P (Hamamatsu, Japan) as a detector in photon counting mode, resolution of a time-to-amplitude converter - 0.112 ns per channel. The instrumental response function was measured with the use of Ludox® (Sigma-Aldrich) colloidal solution at monochromator wavelength set to 370 nm. Signals were acquired using an IBH Datastation HUB photon counting module and data analysis was performed using the commercially available DAS 6 decay analysis software package from Horiba Jobin Yvon. Goodness of fit was assessed by minimizing the reduced chi squared function, each trace contained 10000 points and the reported lifetime values are the result from at least three independent measurements.

Results and Discussion

Electronic Absorption Spectra

The UV-visible absorption spectrum of free-base tetra(15-crown-5)phthalocyanine consists of a Soret band with maximum at 348 nm and two Q-bands at 662 and 702 nm (Table 1). During the formation of lanthanide phthalocyaninates a typical changes were observed in UV-visible spectrum, namely, conversion of two Q-bands into one due to increasing of molecule symmetry.

The electronic absorption spectra of mono-phthalocyaninates solutions consist of typical set of absorption bands in UV and visible region; the most intensive are narrow Q-band with maxima at 679 or 685 nm with vibrational satellites and Soret band in the range of 350-370 nm (Table 1).

The position of the absorption bands in the spectra of mono-phthalocyaninates solutions does not depend on radius of the metal ion, however the influence of the nature of axial ligands in Ln^{III} coordination sphere is observed. Thus, the UV-visible absorption spectra of Er^{III} and Yb^{III} mono-phthalocyaninates [LnL·OAc·DBU] solutions completely coincide while there is a shift of all of the absorption bands in spectrum of chloroform solution of Lu^{III} complex that contains according to NMR data axially coordinated phenanthroline molecule.

In contrast to mono-phthalocyaninates the position of the absorption bands in the spectra of sandwich compounds solutions depends on radius of the lanthanide ion as far as the value of the radius defines distance between decks and as a results degree of $\pi-\pi$ interaction. The intensive Q-band at 665-669 nm and Soret band around 370 nm (Table 1) are observed in the UV-visible absorption spectra of solution of double-decker complexes $LnL_2^{0\bullet}$ in chloroform. Less intensive absorption band is observed also in the range of 476-480 nm, that is typical for electroneutral radical forms of the complexes $[L^{2-}]Ln^{3+}[L^{\bullet-}]$. This band corresponds to electron transfer from LUMO-1 to semi-occupied LUMO orbital. Main absorption bands undergo a small bathochromic shifts passing from Lu^{III} to Er^{III}.

The electronic absorption spectra of triple-decker complexes Ln_2L_3 reveals two Q-bands (intensive Q_1 at 638-640 nm and less intensive Q_2 at 707-718 nm), as well as Soret band at 362 nm (Table 1). The absorption band Q_1 undergoes hypsochromic shift relatively to Q-band of monophthalocyaninate and has additional less intensive Q_2 band. The splitting of Q-bands is increased according to decrease of lanthanide ionic radius passing from Er^{III} to Lu^{III}. Such spectral transformations are determined by exciton interactions between three L^{2-} ligands in contrast to monophthalocyaninate.[15,29] Position of Q_1 absorption band also undergoes a small bathochromic shift passing from Lu^{III} to Er^{III}.

Molecular Fluorescence

It was found that molecular fluorescence of lutetium phthalocyaninates is observed in the visible region under excitation at the absorption maximum at 298 K. The fluorescence band maxima (λ_F), lifetimes (τ_F), the rate constants (k_F), the fluorescence quantum yields (ϕ_F), as well as the rate constants (k_{ST}) and quantum yields (ϕ_{ST}) of intersystem crossing of tetra-(15-crown-5)-phthalocyanine and its lutetium complexes are presented in Table 2.

Table 1. UV-visible spectral data of investigated compounds in CHCl$_3$ solution.

Compound	λ_{max}, nm					
H$_2$L	701	662	601	422	348	
[ErL·OAc·DBU]		679	612		359	290
[YbL·OAc·DBU]		679	612		359	290
[LuL·OAc·Phen]		685	612		357	
ErL$_2$		669	605	480	368	291
YbL$_2$		667	605	479	369	292
LuL$_2$		665	603	476	367	290
Er$_2$L$_3^*$	707	640			362	293
Yb$_2$L$_3^*$	715	638			362	294
Lu$_2$L$_3^*$	718	638			362	294

*Measurements were performed in CHCl$_3$ with 2% of CH$_3$OH in order to avoid the oxidation

Table 2. Photophysical characteristics of tetra(15-crown-5)phthalocyanine and its complexes with lutetium.

Compound	λ_F, nm (intensity ratio)	τ_F, ns	ϕ_F	k_F, 10^6 s^{-1}	k_{ST}, 10^6 s^{-1}	ϕ_{ST}
H_2L	708, 738, 784 (4.7 : 1.4 : 1.0)	7.64	0.740	96.85	34.03	0.260
[LuL·OAc·Phen]	704, 734, 775 (5.9 : 1.6 : 1.0)	6.07	0.064	10.54	154.15	0.936
LuL_2	704, 737, 784 (9.2 : 1.3 : 1.0)	6.13	0.010	1.63	161.37	0.989
Lu_2L_3	702, 736, 785 (4.9 : 1.4 : 1.0)	5.81	0.001	0.17	169.83	0.986

The fluorescence spectrum of free-base ligand consists of the intense band with a maximum at 708 nm and shoulders at 738 nm and 784 nm. In the spectra of Lu^{III} complexes solution (Figure 2) these bands undergo insignificant changes, but the general view of the fluorescence spectrum is remain the same for all Lu^{III}-phthalocyaninates. The spectral distribution of the radiation energy remains constant under excitation in both cases: at Soret band (350-360 nm) and Q-band (~600 nm).
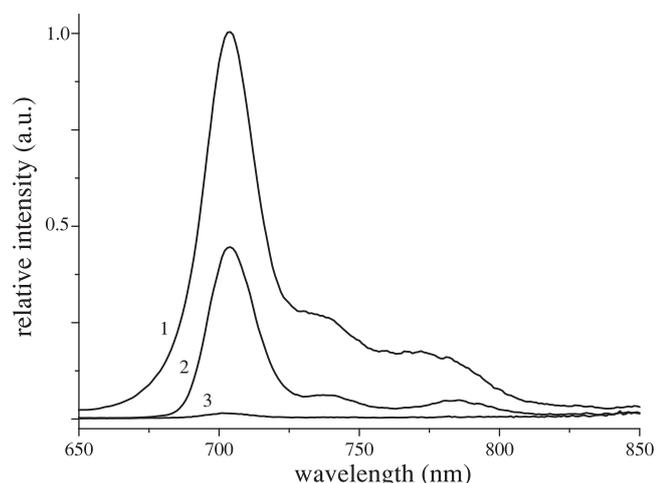
Figure 2. Molecular fluorescence spectra of lutetium III complexes [LuL·OAc·Phen] (1), LuL$_2$ (2) and Lu$_2$L$_3$ (3) (λ_{ex} = 350-360 nm, c = 10^{-5} M, CHCl$_3$).

The kinetics of fluorescence decay for all Lu^{III} complexes are described by mono-exponential curve fitting indicating the presence of one type of compounds in solution. The lifetimes are in the range of 5.8 - 6.0 ns (Table 2), these values are typical for fluorescence of tetrapyrrolic ligands. The quantum yields of fluorescence and intersystem crossing S$_1 \rightarrow$ T$_1$ were calculated based on the obtained data and their rate constants were estimated. Notwithstanding, the processes of internal conversion S$_1 \rightarrow$ S$_0$ formally should not be neglected. The formation of metallocomplexes lead to quenching of molecular fluorescence (Table 2), moreover fluorescence quantum yield decreases with each subsequent addition of the phthalocyanine ligand. At the same time, the probability of intersystem crossing increases as compared to the ligand. Quenching of sandwich compounds fluorescence compared to monophthalocyaninates may be caused mainly by two factors. At first, probability of S$_1 \rightarrow$ S$_0$ transition (k_F) decreases with the increase of number of tetrapyrrolic

fragments in the complex. Second, due to the relatively small Stokes shift and overlapping of the absorption and fluorescence spectra, reabsorption of photons emitted by the phthalocyanine molecules occurs,[30] especially in the case of triple-decker complexes, where photons emitted by the central ligand can be absorbed by two peripheral macrocycles. Efficiency of intersystem crossing process of studied phthalocyanine complexes is high and comparable to Zn^{II} porphyrinates.[31,32] Thus, intersystem crossing is the main route of S$_1$-state deactivation in Lu^{III} phthalocyaninates. Phosphorescence spectra and the position of the triplet level of studied compounds could not be observed, but because there is quite effective intersystem crossing, the energy difference between the singlet and the triplet state is probably not less than 5000 cm^{-1}.[33] It should be noted, that the photogeneration of singlet oxygen is typical for lanthanide phthalocyaninates.[20,34] Thus, it can be assumed that in the studied compounds the quenching of ligand phosphorescence occurs through the deactivation of the triplet state by singlet oxygen molecules, but in this research, such studies were not carried out.

In contrast to Lu^{III} phthalocyaninates the complexes with Er^{III} and Yb^{III} may exhibit not only the molecular fluorescence in the visible region, but infrared 4f luminescence can also occur. Therefore, for all complexes of Er^{III} and Yb^{III} with tetra(15-crown-5)phthalocyanine intrinsic 4f luminescence was studied.

4f Luminescence

It was found that in the solution of ytterbium complexes molecular fluorescence is not completely quenched. Fluorescence quantum yields are 0.0380, 0.0012 and 0.0009 for [YbL·OAc·DBU], YbL$_2$ and Yb$_2$L$_3$, respectively. For effective excitation energy transfer to the emitting levels of lanthanide ions, the spectral overlapping between the energy levels of the donor, in this case, tetra(15-crown-5) phthalocyanine, and the acceptor – lanthanide must exist. It is known[35,36] that the values of the triplet levels of phthalocyanines and resonance $^2F_{5/2}$-level of Yb^{III} ion are close enough. The 4f luminescence of Yb^{III} was registered in the range of 920-1060 nm in all studied Yb^{III} complexes under excitation in the region of Soret band absorption as well as in the region of the intense Q-band (Figure 3). Therewith the excitation spectra in the region of 300 - 600 nm are almost identical to absorption spectra of the corresponding complexes.

The most intensive 4f luminescence is observed in the spectrum of solution of triple-decker complex Yb$_2$L$_3$.
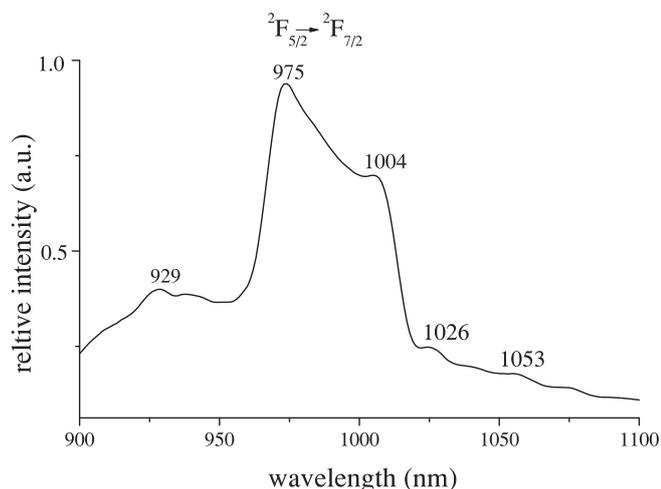
Figure 3. *4f* Luminescence spectrum (λ_{ex} = 350-360 nm) of Yb_2L_3 complex ($c = 10^{-5}$ M, $CHCl_3$)

The quantum yield values are less than $0.06 \cdot 10^{-4}$ for mono- and diphthalocyaninate, within $0.59 \cdot 10^{-4}$ for Yb_2L_3, that is one order less compared to Yb^{III}-monoporphyrinate.[37,38] The band corresponding to the transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$ in the luminescence spectrum of triple-decker complex is splitted by the crystal field on five components. Peaks with maxima at 920-980 nm correspond to the transitions between the lower Stark components of the $^2F_{5/2}$ and $^2F_{7/2}$ levels, and bands in the region of 1000-1060 nm caused by the transitions from the lower Stark components of the $^2F_{5/2}$. Peak with a maximum at 1053 nm corresponds to the Stark component of the ground state, the splitting of which is about 760 cm^{-1}.

It can be proposed that, the observed *4f* luminescence of Yb^{III} in phthalocyaninates may be due to one of the following factors. The Förster-type of energy transfer is forbidden by the selection rule $|\Delta J| = 2, 4, 6$ for $^{2S+1}L_J$-levels for the resonance $^2F_{5/2}$-level of Yb^{III} ion,[39,40] moreover, the spectral overlapping of the energy levels of the donor and acceptor is minimal. Therefore, this mechanism of energy transfer (from both singlet and triplet levels of phthalocyanine) is impossible, unlike Dexter migration, because $|\Delta J| = 1$. Dexter energy transfer is effective only at distances less than 10 Å and may be observed in the studied systems.

It is also necessary to take into account that among of the lanthanide ions Yb^{3+} is one of the easily reduced to Yb^{2+}; the redox potential of Yb^{3+}/Yb^{2+} is -1.05 V.[41,42] It was shown that the ligand cannot reduce ion Yb^{III} in the ground state of double- and triple-decker Yb^{III} phthalocyaninates. However, in the excited state this process can occur as it has been described for complexes of Yb^{III} with organic ligands containing conjugated aromatic moieties.[43,44] In this case, the observed fluorescence quenching may be due to a rapid transition from S_n state to the charge transfer state, that corresponds to the transition of π-electron from the phthalocyanine orbitals to the lanthanide orbital with the reduction of the Yb^{III} to divalent state. In addition, the intensity of the *4f* luminescence under excitation in both S_1 and S_n state is almost the same. This means that the complex goes from the charge-transfer state to the $^2F_{5/2}$, but it is difficult to estimate the participation of S_1 and T_1 states in this process.

Thus, the *4f* luminescence of Yb^{III} phthalocyaninates may be caused also by photoinduced electron transfer.

It is well known that the NIR-luminescence of Er^{III} complexes is generally observed in non-aqueous media or deuterated solvents.[45,46] Low-lying emissive level of Er^{III} $^4I_{13/2}$ is extremely sensitive to quenching effects of the OH-, NH and C-H bonds oscillations. However, the position of the energy levels of phthalocyanine ligands is favorable for the implementation of the intramolecular energy transfer to Er^{III} ion to a greater extent than other lanthanides. The absorption spectrum of Er^{III} ion is characterized by a large number of bands in the UV and visible region. The most efficient spectral overlap is observed for levels $^4F_{9/2}$ (15500 cm^{-1}), $^4I_{9/2}$ (12500 cm^{-1}) and $^4I_{11/2}$ (10200 cm^{-1}). For the latter, the selection rule of Förster-type of energy transfer ($|\Delta J| = 2$) is valid, and for the emissive level $^4I_{13/2}$ it is the conditions of exchange mechanism ($|\Delta J| = 1$).

It has been shown that for Er^{III} mono-phthalocyaninate solution *4f* luminescence is absent in conditions of our experiments. This compound exhibits molecular fluorescence in solution with quantum yield equal 0.0148. As for the double- and triple-decker erbium complexes, they are also characterized by molecular fluorescence, but it is signally quenched; its intensity is only 14-15 % of mono-phthalocyaninate.

In contact to mono-phthalocyaninate, *4f* luminescence of Er^{III} in sandwich complexes with tetra(15-crown-5)-phthalocyanine is observed under excitation in the ligand absorption region (Figure 4). Its absence in the case of Er^{III} monophthalocyaninate solutions is probably may be explained by quenching by the solvent molecules oscillations, because of the higher availability of the central ion, in contrast to the sandwich complexes, where the central complexing ion is "closed" by phthalocyanine ligands.

4f Luminescence spectra profile and intensity of the double- and triple-decker phthalocyaninates solutions are almost identical. Similar to ytterbium complexes in erbium-containing sandwich complexes luminescence spectra are splitted into a number of components with maxima at 1487 nm, the most intensive at 1538 nm, 1548 nm, 1564 nm and 1576 nm.

The luminescence observed in this spectral region is of great interest for the development of signal amplifiers in
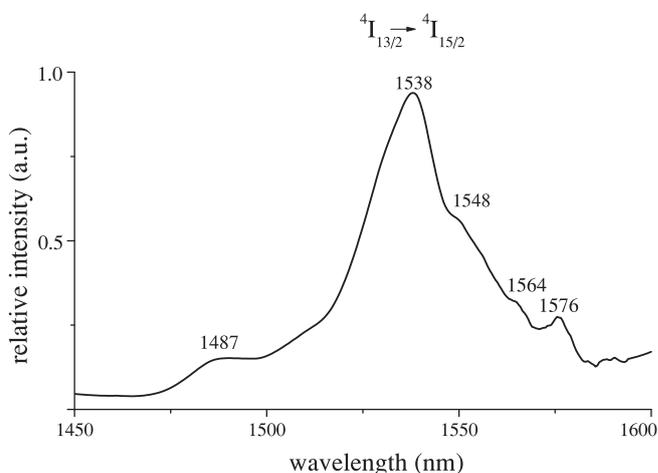
Figure 4. *4f* Luminescence spectrum Er_2L_3 (λ_{ex} = 350-360 nm, $c = 10^{-5}$ M, $CHCl_3$).

telecommunication systems, since the lowest attenuation of the radiation is observed in the third transmission window of optical fibers at 1550 nm. Herewith, the value of full-width half-maximum (FWHM) of the band has a great importance for optical amplification. The FWHM values of $4f$ luminescence band in the solutions of studied complexes are 16 nm and 32 nm for ErL_2 and Er_2L_3, respectively. This is comparable with the data obtained for the Er^{III} compounds in rigid inorganic matrix, for example, it is 25 nm for Er^{III} containing phosphosilicate glasses, 11 nm - in SiO_2 and 55 nm - in Al_2O_3.[47]

Conclusions

Thus, the features of spectral (absorption and luminescent) properties of mono-, double- and triple-decker complexes of erbium(III), ytterbium(III) and lutetium(III) with tetra(15-crown-5)phthalocyaninates were determined. The basic photophysical parameters of fluorescence and intersystem crossing of lutetium-containing compounds were evaluated; their values are comparable with porphyrinates of d-metals. The $4f$ luminescence of sandwich Er^{III}- and Yb^{III}-phthalocyaninates in the near-infrared region was discovered for the first time. All complexes of Yb^{III} with tetra(15-crown-5)phthalocyanine exhibit near-infrared $4f$ luminescence (980 nm). The mechanism of this process was proposed. This luminescence can occur probably due to Dexter energy transfer or it can be caused by photoinduced electron transfer with the reduction of Yb^{III} to Yb^{II} in the electronically excited state of the complex. The intensive $4f$ luminescence in the NIR-region with maximum at 1535-1540 nm is also observed for the solutions of double- and triple-decker complexes of erbium(III). The found parameters of $4f$ luminescence are comparable to the erbium-containing inorganic compounds.

References

1. Bünzli J.-C. G. *Acc. Chem. Res.* **2006**, *39*, 53-61.
2. Ivanov A.V., Rumyantseva V.D., Shchamkhalov K.S., Shilov I.P. *Laser Physics* **2010**, *20*, 2056-2065.
3. Werts M.H.V. *Science Progress* **2005**, *88*, 101-131.
4. Babu S., Cho J.H., Dowding J.M., Heckert E., Komanski C., Das S., Colon J., Baker C.H., Bass M., Self W.T., Seal S. *Chem. Commun.* **2010**, *46*, 6915-6917.
5. Fernandez-Moreira V., Song B., Sivagnanam V., Chauvin A.S., Vandevyver C.D.B., Gijs M.A.M., Hemmilä I.A., Lehr H.A., Bünzli J.-C.G. *Analyst* **2010**, *135*, 42-52
6. Bünzli J.-C.G., Eliseeva S.V. *J. Rare Earths* **2010**, *28*, 824-842.
7. Bulach V., Sguerra F., Hosseini M.W. *Coord Chem. Rev.* **2012**, *256*, 1468-1478.
8. Zhu X., Wong W.-K., Wong W.-Y., Yang X. *Eur. J. Inorg. Chem.* **2011**, 4651-4674.
9. Wong W., Zhu X., Wong W.-Y. *Coord. Chem. Rev.* **2007**, *251*, 2386-2399.
10. Korovin Yu., Zhilina Z., Rusakova N., Kuz'min V., Vodzinsky S., Ishkov Yu. *J. Porphyrins Phthalocyanines* **2001**, *5*, 481-485.
11. He H., May P. S., Galipeau D. *Dalton Trans.* **2009**, 4766-4771.
12. Fedorova L.D., Rumyantseva V.D., Roshchina N.V., Mironov A.F., Markushev V.M., Shilov I.P. *Macroheterocycles* **2011**, *4*, 122-123.
13. Rusakova N., Semenishyn N., Korovin Yu. *J. Porphyrins Phthalocyanines* **2010**, *14*, 166-169.
14. Ng D.K.P., Jiang J. *Chem. Soc. Rev.* **1997**, *26*, 433-442.
15. Gorbunova Yu.G., Lapkina L.A., Martynov A.G., Biryukova I.V., Tsivadze A.Yu. *Russ. J. Coord. Chem.* **2004**, *30*, 245-251.
16. Pushkarev V.E., Tomilova L.G., Tomilov Y.V. *Russ. Chem. Rev.* **2008**, *77*, 875-907.
17. Jiang J., Ng D.K.P. *Acc. Chem. Res.* **2009**, *42*, 79-88.
18. Ishikawa N. In: *Functional Phthalocyanine Molecular Materials* (Jiang J., Ed.), Springer-Verlag Berlin Heidelberg **2010**. p. 211.
19. Bo S., Hu J., Wang Q., Liu X., Zhen Z. *Photochem. Photobiol. Sci.* **2008**, *7*, 474-479.
20. Ke H., Wong W.-K., Wong W.-Y., Tam H.-L., Poon C.-T., Jiang F. *Eur. J. Inorg. Chem.* **2009**, 1243-1247.
21. Gerasymchuk Y., Tomachynski L., Tretyakova I., Hanuza J., Legendziewicz J. *J. Photochem. Photobiol. A: Chem.* **2010**, *214*, 128-134.
22. Lapkina L.A., Larchenko V.E., Tolkacheva E.O., Popov K.I., Konstantinov N.Yu., Nosova V.M., Tsivadze A.Yu. *Rus. J. Inorg. Chem.* **1998**, *43*, 901-909.
23. Lapkina L.A., Gorbunova Yu.G., Nefedov S.E., Tsivadze A.Yu. *Rus. Chem. Bull.* **2003**, *52*, 1633-1636.
24. Sinelshikova A.A., Gorbunova Yu.G., Lapkina L.A., Konstantinov N.Yu., Tsivadze A.Yu. *Russ. J. Inorg. Chem.* **2011**, *9*, 1370-1379.
25. Zhukov I.E, Lapkina L.A., Gorbunova Yu.G., Larchenko V.E., Tsivadze A.Yu. *J. Porphyrins Phthalocyanines* **2005**, *9*, 1-6.
26. Petoud S., Bünzli J.-C.G., Glanzman Th., Piguet C., Xiang Q. *J. Luminescence* **1999**, *82*, 69-79.
27. Shushkevich I.K., Dvornikov S.S., Kachura T.F., Solov'ev K.N. *J. Appl. Spectrosc.* **1981**, *35*, 1109-1113.
28. Tsvirko M.P., Meshkova S.B., Venchikov V.Ya., Bol'shoi D.V. *Opt. Spectrosc.* **1999**, *6*, 950-955 (in Russ.).
29. Rousseau R., Aroca R., Rodriques-Mendez M.L. *J. Molec. Struct.* **1995**, *356*, 49-62.
30. Cordón G.B., Lagorio M.G. *Photochem. Photobiol. Sci.* **2006**, *5*, 735-740.
31. Gradyushko A.T., Tsvirko M.P. *Opt. Spectrosc.* **1971**, *31*, 548-556 (in Russ.).
32. Kruk M.M., Starukhin A.S. *Macroheterocycles* **2009**, *2*, 251-254.
33. Eliseeva S.V., Bünzli J.-C. G. *Chem. Soc. Rev.* **2010**, *39*, 189-227.
34. Venediktov E.A. *Russ. J. Phys. Chem.* **2006**, *80*, 461-463.
35. Solov'ev K.N., Mashenkov V.A., Kachura T.F. *Zh. Prikl. Spectroscopii* **1967**, *5*, 773-774 (in Russ.).
36. Vincett P.S., Voigt E.M., Rieckhoff K.E. *J. Chem. Phys.* **1971**, *55*, 4131-4140.
37. He H., Sykes A.G., Stanley May P., He G. *Dalton Trans.* **2009**, 7454-7461.
38. Semenishyn N.N., Rusakova N.V., Mazepa A.V., Korovin Yu.V. *Macroheterocycles* **2009**, *2*, 57-59.
39. De Sá G.F., Malta O.L., de Mello Donegá C., Simas A.M., Longo R.L., Santa-Cruz P.A., da Silva E.F. *Coord. Chem. Rev.* **2000**, *196*, 165-195.

40. Gonçalves e Silva R.R., Malta O.L., Reinhard C., Güdel H.-U., Piguet C., Moser J.E., Bünzli J.-C.G. *J. Phys. Chem. A.* **2002**, *106*, 1670-1677.

41. Bard A.J., Parsons R., Jordan J. *Standard Potentials in Aqueous Solution.* New York: Marcel Dekker Inc., **1985**. 587 p.

42. Trifonov A.A., Fedorova E.A., Ikorskii V.N., Dechert S., Schumann H., Bochkarev M.N. *Eur. J. Inorg. Chem.* **2005**, 2812-2818.

43. Abusaleh A., Meares C.F. *Photochem. Photobiol.* **1984**, *6*, 763-769.

44. Horrocks W.D., Jr., Bolender J.P., Smith W.D., Supkowski R.M. *J. Am. Chem. Soc.* **1997**, *119*, 5972-5973.

45. Hernandez I., Tan R.H.C., Pearson J.M., Wyatt P.B., Gillin W.P. *J. Phys. Chem. B* **2009**, *113*, 7474-7481.

46. Norton K., Kumar G.A., Dilks J.L., Emge T.J., Riman R.E., Brik M.G., Brennan J.G. *Inorg. Chem.* **2009**, *48*, 3573-3580.

47. Slooff L.H., van Blaaderen A., Polman A., Hebbink G.A., Klink S.I., van Veggel F.C.J.M., Reinhoudt D.N., Hofstraat J.W. *J. Appl. Physics* **2002**, *91*, 3955-3980.