Porphyrins
Порфирины

Макрогетероциклы
http://macroheterocycles.isuct.ru

Paper
Статья

DOI: 10.6060/mhc160425r

Study of Structure–Properties Relationship for Lanthanide Tetrapyrrolic Macrocycles Modified with Aminopolycarboxylate Substituents

Nikolay N. Semenishyn and Natalia V. Rusakova@

A. V. Bogatsky Physico-Chemical Institute, 65080 Odessa, Ukraine
@Corresponding author E-mail: lanthachem@ukr.net

The structure of lanthanide complexes based on ditopic corroles and porphyrins is studied in details. Fluorescence and 4f-luminescence features of corrole-based and porphyrin-based lanthanide systems are compared. It was found out, that porphyrin derivatives have three types of emission (fluorescence, phosphorescence and 4f-luminescence) in two ranges (visual and near infrared) and corrole derivatives have two types of emission (fluorescence and 4f-luminescence) in two ranges (visual and near infrared). It is shown that sensitization mechanism of luminescence of Nd and Yb ions has different pathways in corroles.

Keywords: Corroles, porphyrins, lanthanides, 4*f*-luminescence, fluorescence.

Изучение связи структура–свойства в комплексах лантанидов с тетрапиррольными макроциклами, модифицированными аминополикарбоксилатными заместителями

Н. Н. Семенишин, Н. В. Русакова@

Физико-химический институт им. А.В. Богатского, 65080 Одесса, Украина
@E-mail: lanthachem@ukr.net

В работе проведен синтез периферических комплексов лантанидов с порфиринами и корролами и проведено детальное исследование их структуры. Проведено сравнение флуоресцентных и 4f-люминесцентных свойств данных соединений. Показано, что для периферических комплексов лантанидов с порфиринами характерно наличие трёх видов эмиссии (флуоресценция, фосфоресценция и 4f-люминесценция), а для периферических комплексов лантанидов с корролами характерно наличие двух видов эмиссии (флуоресценция и 4f-люминесценция), причём флуоресценция макроцикла остаётся непогашенной в обоих случаях. Механизм сенсибилизации 4f-люминесценции ионов Nd и Yb хромофором коррола отличается от такового в случае порфирина.

Ключевые слова: Корролы, порфирины, лантаниды, 4*f*-люминесценция, флуоресценция.

Introduction

Corolles are the closest structural analogues of well-known macrocyclic tetrapyrrole compounds – porphyrins. Many derivatives of porphyrins and corroles are the basis of numerous natural compounds such as heme, vitamin B12, *etc.*[1] Corolles consist of completely unsaturated ring, and their main difference from porphyrins is the absence of one methine bridge between the pyrroles. Therefore, the number of carbon atoms in the aromatic chain changes and this macrocycle becomes tribasic (Figure 1).

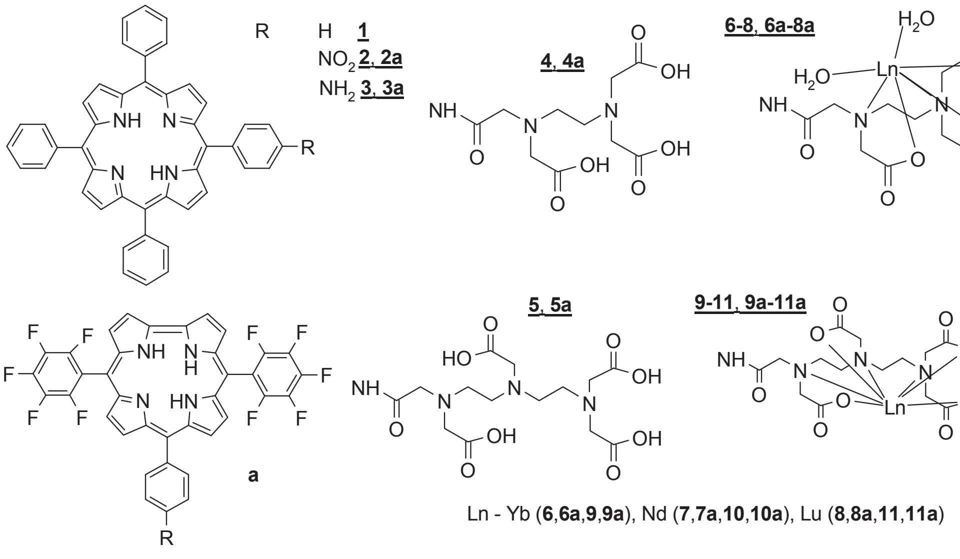

Figure 1. Structure of porphyrins and corroles (number marked with **a**) studied.

Intensive study of corroles was started in 1999, when their one-step synthesis was discovered. [2] Until that time corroles had obtained by complexed multi-step pathway, with a total yield of compounds (even the most simple structure) less than 0.1 %.[3]

Both porphyrins and corroles already prove itself as efficient catalysts for oxidation [4] and reduction reactions,[5] as a basis for carbon monoxide sensors, [6] as optodes for determination the p*H*,[7] as ion-selective electrodes,[8] as dye-sensitized solar cells[9] and also in medicine as fluorescent markers.[10]

Application of corroles in most cases is based on their fluorescent properties. These macrocycles have the characteristic absorption and emission of light (like porphyrins) due to 18-membered aromatic π-systems. It should be noted that in comparison to porphyrins, corroles in some cases have an abnormally high fluorescence efficiency – a quantum yield of 76 %.[11]

The present work describes a study of spectral-luminescent properties of corroles and porphyrins and their complexes with *f*-metals. 5,10,15,20-tetraphenylporphyrin (H_2tpp, **1**) was used as a standard for the studied porphyrins, and 5,10,15-tris-(pentafluorophenyl)-corrole (H_3tpfc, **12**) was used as a standard for corroles. The choice of these standards based on their stability, their ease of preparation and their good scrutiny. In addition H_2tpp is a starting material in the synthesis of studied porphyrins and H_3tpfc is a close structural analogue of the studied corrole series.

Experimental

Synthesis of all porphyrins, corroles and their derivatives was performed accordingly to the known procedures.[12,13] 5-(Pentafluorophenyl)-dipyrromethane (DPM) was synthesized accordingly to the reaction.[14] Synthesis of H_3tpfc (**12**) was carried out according to the most convenient method for the preparation.[15] Purity of the obtained compounds was checked by TLC Sorbfil plates (grain 5-17 μm, UV-254, thickness 0.1 mm) by Imid Ltd. ^{1}H NMR and ^{19}F NMR spectra were recorded using Bruker Avance 600 or 400 MHz in $CDCl_3$ and CD_3OD. Mass-spectra (MS) were registered on spectrometer Waters ESI TOF Premier and Varian MAT CH-112 spectrometer. Elemental analysis was performed on CHNS analyzer Flash 2000 Thermo Scientific.

Spectra of 4*f*-luminescence, molecular fluorescence and excitation spectra were recorded on spectrofluorimeter “Fluorolog FL 3-22” “Horiba Jobin Yvon” (Xe-lamp 450 W). Spectra of 4*f*-luminescence of Yb^{3+} ions (transition $^2F_{5/2}\rightarrow{}^2F_{7/2}$) were registered at 950–1050 nm region and of Nd^{3+} at 850–1350 nm (transitions $^4F_{3/2}\rightarrow{}^4I_{13/2}$, $^4F_{3/2}\rightarrow{}^4I_{11/2}$ and $^4F_{3/2}\rightarrow{}^4I_{9/2}$). Spectra of molecular fluorescence of porphyrins and corroles were registered at 550–800 nm (S-S transitions).

Luminescence integral intensity was measured using software of the device. Fluorescence lifetime (τ) was measured under excitation at the Soret band. The relative quantum yield of molecular fluorescence was determined using solution of Zn-tpp in ethanol as a primary reference. Determination of the relative quantum yield of molecular fluorescence and 4*f*-luminescence was made using formula:

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

where: φ_0 and φ_x – luminescence quantum yield of the reference and of the sample respectively; A_0 and A_x – absorption at the Soret band of the reference and of the sample respectively; I_x and I_0 – integral luminescence intensity of the reference and of the sample respectively; n_0 and n_x – refractive index of the reference solvent and of the sample solvent respectively.

Results and Discussion

Synthesis of 10-(4-aminophenyl)-5,15-bis-(pentafluorophenyl)-corrole (**3a**), 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**3**) and their further modification (Figure 1) was performed according to the previous works.[12-13] It should be noted that the presence of fluorine atoms in corrole structure is desirable in terms of photo- and thermo stability of corroles.[16]

The step of formation of peripheral complexes on the base of ditopic ligands can not be administrated by absorption spectra in contrast to classical systems. Therefore, NMR and

MS was used in this case. The formation of complexes with paramagnetic ions Yb^{3+} and Nd^{3+} can be fixed only by the methods ^{19}F NMR and MS. Complexes with diamagnetic Lu^{3+} additionally can be identified with ^{1}H NMR. In the case of the latter, a linear NMR spectrum becomes extremely complicated in strong fields. Fragment of ^{1}H NMR spectrum reveals that the protons of the same methylene and ethylene groups are not equivalent due to a different location relative to the Lu^{3+} ion (Figure 2).

All signals in the aliphatic proton region 3.5–4.5 ppm appear in the form of doublets, with the integrated intensity corresponding to one proton. High values of J confirm that the spin-spin interaction constants are geminal ($^{2}J_{H\text{-}H}$). Thus, signals at 4.34 and 4.15 ppm have $^{2}J=16.8$ Hz, signals at 3.96 and

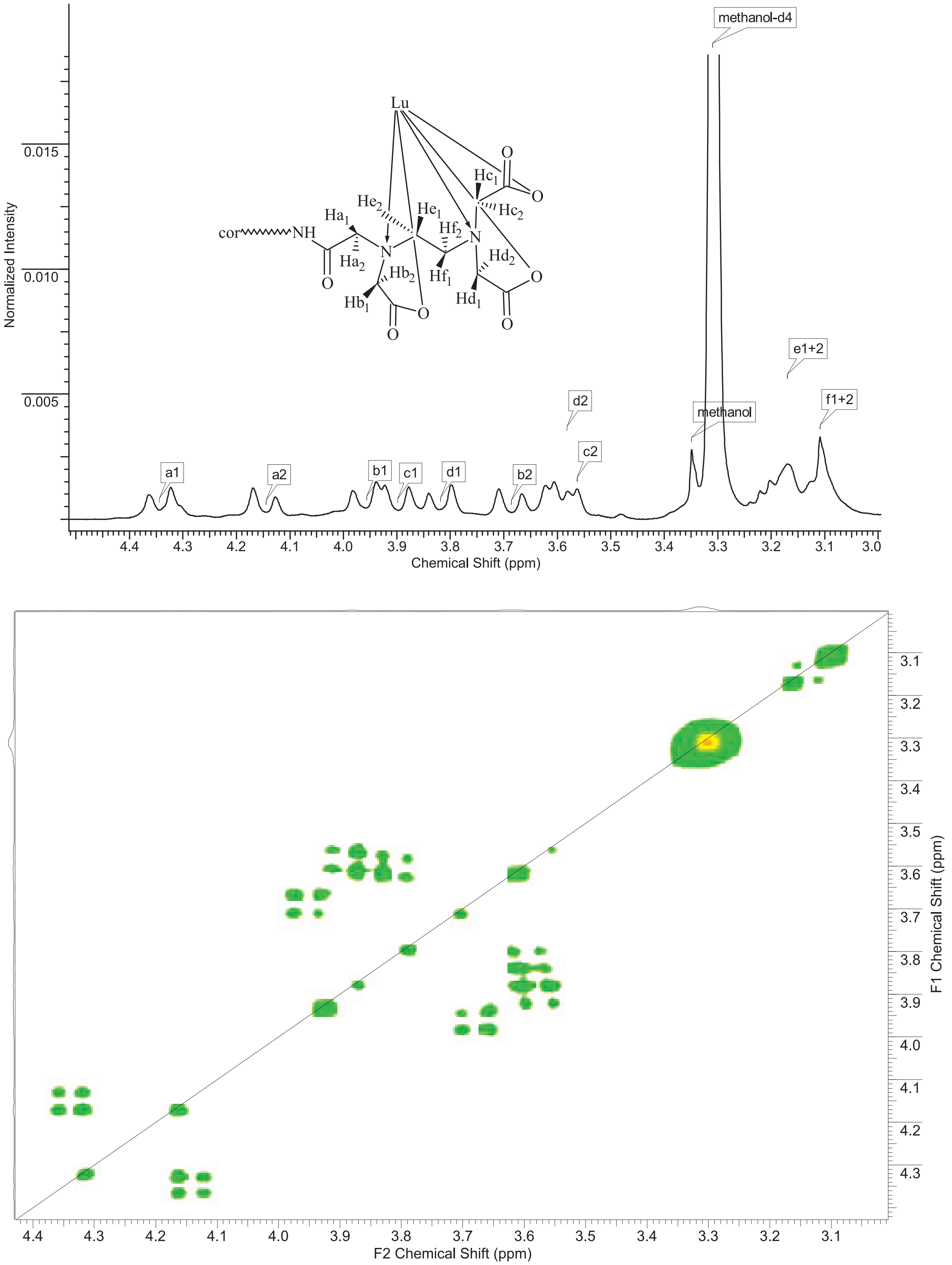

Figure 2. 1D ^{1}H NMR (top) and 2D ^{1}H NMR (bottom) spectra of **8a**.

3.69 ppm have ^2J=17.6 Hz, signals at 3.90 and 3.58 ppm have ^2J=17.4 Hz, signals at 3.82 and 3.60 ppm have ^2J=16.7 Hz.

For identification of the aliphatic protons 2D COSY NMR method was also used. Four protons of ethylene groups have two broad signals. The multiplicity and position of each proton signal is difficult to determine, however, due to the appearance of appropriate cross-peaks, these signals are readily identified as an ethylene group protons.

The protons of the methylene groups were also able to identify, despite the overlapping of the signals. Most shifted downfield doublet at 4.34 and 4.15 ppm correspond to the protons H^{a1} and H^{a2} near amide bond, doublets at 3.96 and 3.69 ppm are proton signals of carboxymethylene group H^{b1} and H^{b2}. Couples H^{c1} and H^{c2} protons, H^{d1} and H^{d2} are equal in their surroundings, but due to the additional coordination of water molecules by lutetium ion (*vide infra*), they differ slightly in the position, and in the values of $^2J_{H\text{-}H}$.

The absorption spectra of the porphyrins and corroles are characteristic and consist of intense Soret band in the region of 400-420 nm and four Q-bands in the region of 500-600 nm for porphyrins and two Q-bands in the region of 500-600 nm for corroles (Figure 3).

Absorption spectrum does not undergo significant changes under consequent modification of the starting H_2tpp to form the nitro derivative (**2**), the amino derivative (**3**) ditopic derivatives substituted with fragments of aminopolycarboxylic acids (APC) - ethylenediamine-*N,N,N',N'*-tetraacetic (H_4EDTA) acid (**4**) and diethylenetriamine-*N,N,N',N",N"*-pentaacetic (H_5DTPA) acid (**5**), as well as peripheral mononuclear metal complexes based on them (**6-11**). However, under modification of the substituent at *para*-position of the phenyl with APC resulting in formation of ditopic ligands **4** and **5**, there is a slight bathochromic shift of the first absorption band (2-4 nm) in contrast to H_2tpp. This band is known[17] to be the most sensitive to the structural changes in porphyrin. The optical density of all bands increases in the spectra of **4** and **5** in comparison to monotopic porphyrins.

The quantity of absorption bands, wavelengths of their maxima and molar absorption coefficients do not undergo significant change under the introduction of ions of heavy f-metals on the molecule periphery. Apparently, this fact is explained by a significant distance from the metal ion to the chromophore.

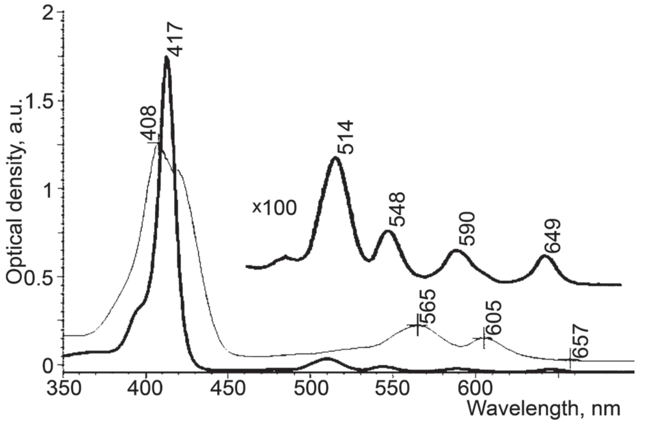

Figure 3. Absorption spectra of the H_2tpp (**1**, bold line) and H_3tpfc (**12**, thin line).

In contrast to the porphyrins, a similar modification of *para*-aminophenyl derivative of corrole with APC fragments leads to a noticeable hypsochromic shift of the Soret band (Table 1). The remaining bands keep unchanged. The complexation of *f*-metal ions with the periphery of ditopic corrole is similar to porphyrins – there is no change in the absorption spectra in this case.

Table 1. Absorption spectra of the studied macrocyclic tetrapyrroles for solutions of **1-11** in DMF, **2a-11a** and **12** in ethanol, λ, nm (lgε).

Sample	Soret	IV	III	II	I
1	417(5.1)	514(3.7)	548(3.3)	590(3.1)	649(3.1)
3	419(5.28)	517(4.08)	558(3.99)	592(3.72)	652(3.71)
4	419(5.57)	514(4.36)	551(4.15)	593(3.93)	648(3.93)
5	418(5.60)	515(4.30)	552(4.11)	591(3.91)	650(3.91)
6	419(5.56)	515(4.36)	550(4.16)	591(4.05)	648(4.03)
7	419(5.46)	515(4.31)	550(4.17)	591(4.08)	648(4.05)
8	419(5.49)	515(4.32)	550(4.11)	591(4.05)	648(4.02)
9	418(5.53)	514(4.37)	551(4.19)	592(4.03)	647(4.04)
10	418(5.54)	514(4.32)	551(4.17)	592(4.04)	647(4.01)
11	418(5.53)	514(4.35)	551(4.19)	592(4.03)	647(4.04)
2a	412(5.08)	–	–	568(4.38)	615(4.26)
3a	415(5.08)	–	–	568(4.38)	615(4.26)
4a-11a	410(5.08)	–	–	568(4.38)	615(4.26)
12	408(5.08)	–	–	565(4.25)	605(4.02)

All of the compounds have intense molecular fluorescence in the region of 600–800 nm. It should be noted that all of the investigated corroles do not show any phosphorescent properties. This fact is in accordance with the literature data and it is due to the rapid relaxation of triplet (T) levels in these macrocycles with the exception of some complex compounds, such as germanium-corroles, which phosphorescence was discovered for the first time recently.[18]

Molecular fluorescence of porphyrin appears as two Q-bands (0-0) in the region of 650–705 nm, and (0-1) – 715–765 nm. Position of Q-bands in fluorescence spectra of mono-*meso*-amino derivative, as well as its APC-derivatives **4** and **5**, are slightly different from the spectrum of the H_2tpp. This is probably due to the fact that the covalent bond in the porphyrin-modified systems is realized through the *para*-position of the phenyl spacer, so in this case a steric factor does not play a significant role. At the same time it was found that the formation of modified porphyrins (through the phenyl spacer) leads to significant changes in T_1-states without affecting of lower singlet levels of macrocycle.

meso-(4-Phenyl) substitution of porphyrin with APC fragments, results (similarly to the absorption spectra) in a slight bathochromic (30–70 cm^{-1}) and hypsochromic shifts of Q (0-0) band and does not affect (Table 2) the position of the excited singlet level (E_{S1}=15270–15310 cm^{-1}). The Stokes shift increases slightly from H_2tpp to APC-modified ligands and it is 110–140 cm^{-1} (Tables 1 and 2), which is characteristic for porphyrins with asymmetric substitution on the phenyl ring. It should be noted that the substitution of H_2tpp reduces the molecular fluorescence quantum yield (φ_F).

Phosphorescence spectra of free base porphyrins undergo a significant change in contrast to fluorescence spectra. Introduction of APC fragments leads to the hypsochromic shift (more than 450 cm^{-1}) of phosphorescence band 0-0, due to increase of triplet level energy (E_{T1} = 12060-12170 cm^{-1}). Further interaction with metal ions doesn't affect the phosphorescence characteristics.

Molecular fluorescence lifetime (τ_S) decreases under modification of the H_2tpp. Moreover, the complexation reaction of the ditopic ligand periphery with metal ions Yb(III) and Nd(III) reduces this parameter intensively than Lu(III), due to the paramagnetic properties of lanthanide ions with unfilled *f*-shells, in contrast to the diamagnetic ion Lu (III).

From the other side, phosphorescence lifetime (τ_p) reacts to the modification of the porphyrin as follows: the introduction of the amino group, the covalent binding fragments of APC and complexation reaction with lanthanide ions lead to its increase.

S-Levels of corroles are higher than those of the porphyrins because of the degradation of the symmetry from D_{4h} to C_{2v} in porphyrins and corroles, respectively. The τ_S of corroles lower than τ_S for all relevant porphyrins.

The energies of T_1-levels of studied porphyrins (Table 2) consider them as potential 4*f*-luminescence sensitizers for lanthanide ions emitting in the near-infrared (IR) spectral range – such as Yb(III), Nd(III) and Er(III). It is known that their resonant levels are respectively equal to 10200 cm^{-1}, 11500 cm^{-1}, 6500 cm^{-1}, which enables them to act as acceptor energy levels from higher donor T_1-levels of tetrapyrroles.

T-Corroles levels can not be determined due to the absence of phosphorescence in the metal-free compounds.[19] Nonetheless, the values of their energy of some germanium complexes,[18] gold,[20] rhodium,[21] iridium[22] found that their T_1-levels are also suitable for sensitizing 4*f*-luminescence.

Sensitization of 4*f*-luminescence of ytterbium and neodymium ions (coordinated by APC fragment) by porphyrin macrocycle is confirmed by the coincidence of the absorption spectrum of the complexes and excitation spectra of 4*f*-luminescence.

A distinctive feature of the peripheral lanthanide complexes is that 4*f*-luminescence appears without any affecting both the fluorescence and the phosphorescence of the porphyrin (Figure 4). 4*f*-Luminescence efficiency of Yb(III) and Nd(III) ions in all peripheral studied complexes is lower than for porphyrinates of these metals. This is easily explained by the lack of direct covalent interaction between the chromophore and the emitting ion. On the other hand the present approach for the creation of a lanthanide-porphyrin systems solves the stability issue for a practical application – for example lg*K*(Lu-EDTA) = 19.8.[23] In fact lanthanide-porphyrins are relatively labile systems.

4*f*-Emission efficiency of Nd ions in complexes with porphyrins is lower than that for Yb in isostructural complexes. This is due to the presence of several transitions from the resonance level of the neodymium ion ($^4F_{3/2} \rightarrow ^4I_{13/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$ and $^4F_{3/2} \rightarrow ^4I_{9/2}$). From the other side ytterbium ion has only one transition ($^2F_{5/2} \rightarrow ^2F_{7/2}$), therefore energy dissipation in this case is less probable.

4*f*-Luminescence of Yb ion has a higher quantum yield in the dtpa-derivative of porphyrin than in edta-derivative. It can be explained with a greater saturation of the coordination number of lanthanide ion. The remaining coordination sites in edta-derivative is occupied by water molecules, which is confirmed for a similar derivative of corrole previously using MS technique.[12] Further coordination of the solvent molecules by lanthanide ion results in a dissipation of energy due to overlapping of 4*f*-transitions bands with the vibrational quanta of O-H- and C-H-bonds.

4*f*-Luminescence sensitization by corrole chromophore confirmed by complete coincidence of the absorption spectra and 4*f*-luminescence excitation spectra of the corresponding complexes. However, obtained values of the 4*f*-luminescent characteristics are substantially different from complexes with porphyrins. Thus, the quantum yield

Table 2. Emission properties of corroles and porphyrins studied.

	E_{S1}, cm^{-1}	φ_F*	τ_S, ns**	λ_p, nm	E_{T1}, cm^{-1}	τ_p, ms***	$\varphi_{Nd}\times10^4$*	$\varphi_{Yb}\times10^3$*
1	15340	0.12	10.4	859	11640	5.1	2.4	4.8
3	15310	0.11	9.80	862	11600	6.3		
4	15290	0.11	9.56	829	12060	12.8		
5	15270	0.11	9.94	822	12170	13.5		
6	15290	0.11	8.82	828	12070	12.9		1.1
7	15290	0.11	8.98	830	12050	12.6	2.0	
8	15290	0.11	9.55	830	12050	12.4		
9	15270	0.11	9.01	823	12150	13.1		1.5
10	15270	0.11	9.04	820	12200	12.8	2.0	
11	15290	0.11	9.79	821	12180	12.7		
3a	15380	0.08	3.47					
4a	15580	0.08	3.72					
5a	15580	0.08	3.46					
6a	15670	0.10	3.21					<0.1
7a	15650	0.08	3.43				27.9	
9a	15630	0.09	3.57					0.3
10a	15650	0.08	3.34				14.4	
12	15850	0.17	4.29					

All solutions in DMF. *C*=10^{-5}M. * ±10 %; ** ±0.02 ns; *** 77 K, ±0.02 ns.

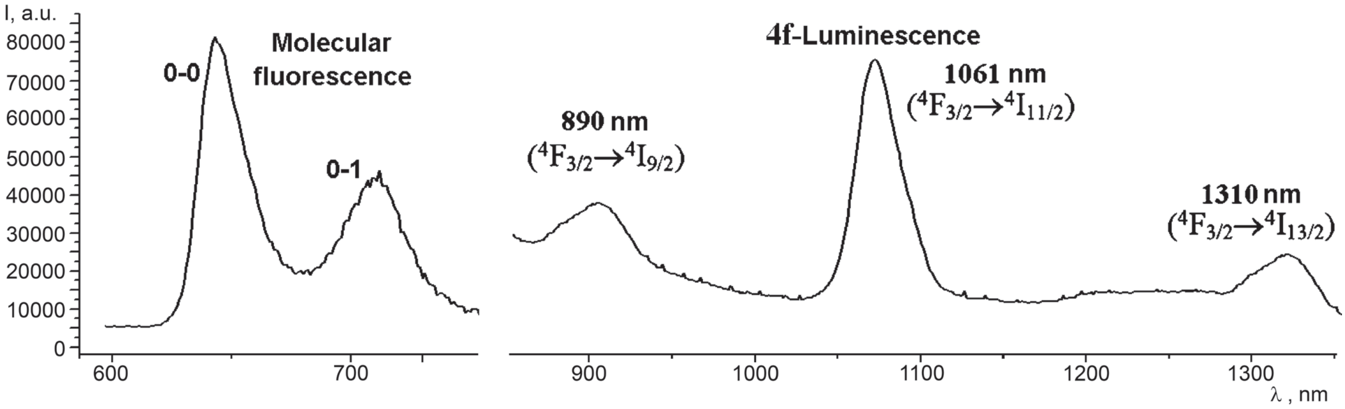

Figure 4. Emisson of **10** in two ranges.

of luminescence of neodymium complexes is much higher than for ytterbium complexes (Table 2). As it was mentioned above, according to the literature,[24] the opposite pattern should be observed. Furthermore, in the case of compound **6a**, for example, a luminescent signal was so weak that calculation of φ_{Yb} was impossible.

Comparison of the effectiveness of neodymium emission in the complexes shows that φ_{Nd} in corroles is an order of magnitude higher than in porphyrins. Apparently, these facts suggest an alternative way of excitation energy transfer in corrole-lanthanides – the excitation energy is transferred directly from the S_1-level of corrole.

Currently, it can be assumed that the sensitization passes through two transitions: the traditional $T_1\rightarrow{}^4F_{3/2}$, and $S_1\rightarrow{}^4F_{3/2}$.

Such a mechanism may be well realized due to the effective overlap of the 0-0 and 0-1 molecular fluorescence bands of corrole and *f-f* transitions of Nd(III) ion.

Note, that as in the case of porphyrins, 4*f*-luminescence in corrole derivatives appears without any affecting the fluorescence characteristics of the corrole, but the phosphorescence is still absent.

Conclusions

Thus, we analized the structure of peripheral lanthanide complexes based on ditopic corroles and porphyrins using NMR and MS techniques. We compared such fluorescence and 4*f*-luminescence features of corrole-based and porphyrin-based lanthanide systems, as quantum yield, luminescence lifetime, and energy levels. Finally, obtained results show that sensitization mechanism of luminescence of Nd and Yb ions has different pathways in corrole systems. Porphyrin derivatives have three types of emission, from the other side corrole derivatives have only two types of emisson.

References

1. Zipp C.F., Michael J.P., Fernandes M.A., Mathura S., Perry C.B., Navizet I., Govender P.P., Marques H.M. *Inorg. Chem.* **2014**, *53*, 4418–4429.
2. Gross Z., Galili N., Saltsman I. *Angew. Chem., Int. Ed.* **1999**, *38*, 1427–1429.
3. Johnson A.W., Price R. *J. Chem. Soc. (Resumed)* **1960**, 1649–1653.
4. Liu H.-Y., Lai T.-S., Yeung L.-L., Chang C. K. *Org. Lett.* **2003**, *5*, 617–620.
5. Grodkowski J., Neta P., Fujita E., Mahammed A., Simkhovich L., Gross Z. *J. Phys. Chem. A* **2002**, *106*, 4772–4778.
6. Barbe J.-M., Canard G., Brandes S., Jerome F., Dubois G., Guilard R. *Dalton Trans.* **2004**, *8*, 1208–1214.
7. Li C.-Y., Zhang X.-B., Han Z.-X., Akermark B., Sun L., Shen G.-L., Yu R.-Q. *Analyst* **2006**, *131*, 388–393.
8. Radecki J., Stenka I., Dolusic E., Dehaen W. *Electrochim. Acta* **2006**, *51*, 2282–2288.
9. Walker D., Chappel S., Mahammed A., Brunschwig B.S., Winkler J.R., Gray H.B., Zaban A., Gross Z. *J. Porphyrins Phthalocyanines* **2006**, *10*, 1259–1262.
10. Agadjanian H., Weaver J., Mahammed A., Rentsendorj A., Bass S., Kim J., Dmochowski I., Margalit R., Gray H., Gross Z., Medina-Kauwe L. *Pharm. Res.* **2006**, *23*, 367–377.
11. Mahammed A., Gross Z. *J. Inorg. Biochem.* **2002**, *88*, 305–309.
12. Semenishyn N., Gross Z. *Dalton Trans.* **2013**, *42*, 3775–3778.
13. Rusakova N., Semenishyn N., Korovin Yu. *J. Porphyrins Phthalocyanines* **2010**, *14*, 166–169.
14. Laha J.K., Dhanalekshmi S., Taniguchi M., Ambroise A., Lindsey J.S. *Org. Process Res. Dev.* **2003**, *7*, 799–812.
15. Reith L.M., Stiftinger M., Monkowius U., Knör G., Schoefberger W. *Inorg. Chem.* **2011**, *50*, 6788–6797.
16. Geier G.R., Chick J.F.B., Callinan J.B., Reid C.G., Auguscinski W.P. *J. Org. Chem.* **2004**, *69*, 4159–4169.
17. Takeda J., Ohya T., Sato M. *Chem. Phys. Lett.* **1991**, *183*, 384–386.
18. Nardis S., Mandoj F., Paolesse R., Fronczek F.R., Smith K.M., Prodi L., Montalti M., Battistini G. *Eur. J. Inorg. Chem.* **2007**, *2007*, 2345–2352.
19. Ventura B., Degli Esposti A., Koszarna B., Gryko D.T., Flamigni L. *New J. Chem.* **2005**, *29*, 1559–1566.
20. Rabinovich. E., Goldberg I., Gross Z. *Chem.-Eur. J.* **2011**, *17*, 12294–12301.
21. Tanabe M., Matsuoka H., Ohba Y., Yamauchi S., Sugisaki K., Toyota K., Sato K., Takui T., Goldberg I., Saltsman I., Gross Z. *J. Phys. Chem. A* **2012**, *116*, 9662–9673.
22. Palmer J.H., Durrell A.C., Gross Z., Winkler J.R., Gray H.B. *J. Am. Chem. Soc.* **2010**, *132*, 9230–9231.
23. Alexander V. *Chem. Rev.* **1995**, *95*, 273–342.
24. Oude Wolbers M.P., van Veggel F.C.J.M., Snellink-Ruel B.H.M., Hofstraat J.W., Geurts F.A.J., Reinhoudt D.N. *J. Chem. Soc., Perkin Trans. 2* **1998**, *10*, 2141–2150.

Received 28.04.2016
Accepted 13.06.2016