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Luminescence Features of Neodymium(III) Compounds with Various Tetrapyrrole Macrocycles

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We considered the changes in the luminescent properties in the series of neodymium(III) complexes of various coordination types with different tetrapyrrole macrocycles (porphyrins, phthalocyanines and corroles): mononuclear complexes (metal-ligand ratio 1:1), sandwich type complexes (metal-ligand ratio 1:2 or 2:3), peripheral binding (on the basis of ditopic tetrapyrrole, metal-ligand ratio 1:1). 4f-Luminescence in the near infrared region is observed in all studied Nd-complexes as a result of intramolecular transfer of excitation energy. Each kind of complexes has its unique features, which are discussed. The peripheral complexes are dual-emissive: they display both neodymium(III) 4f-emission and molecular fluorescence. The values of quantum yield of molecular fluorescence as well as 4f-luminescence are estimated. It was found that binding type plays a key role in excited state relaxation pathways in the molecule. Corroles have unusual behaviour in terms of Nd sensitization.

Keywords: Tetrapyrroles, luminescence, neodymium, porphyrin, phthalocyanine, corrole.

Люминесцентные свойства соединений неодима(III) с различными тетрапиррольными макроциклами

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Мы изучили изменения люминесцентных свойств класса комплексов неодима(III) различных координационных типов с несколькими тетрапиррольными макроциклами (порфиринами, фталоцианинами и корролами): моноядерных комплексов (соотношение металл-лиганд 1:1), комплексов сэндвич-типа (соотношение металл-лиганд 1:2 или 2:3), периферического связывания (на основе дитопического тетрапиррола, соотношение металл-лиганд 1:1). 4f-Люминесценция в ближней инфракрасной области наблюдается во всех изученных Nd-комплексах в результате внутримолекулярного переноса энергии возбуждения. Обсуждаются уникальные особенности каждого вида комплексов. Периферические комплексы являются двухэмиссионными: они проявляют, как 4f-эмиссию, так и молекулярную флуоресценцию. Были оценены значения квантового выхода молекулярной флуоресценции, а также 4f-люминесценции. Было обнаружено, что тип связывания катиона неодима играет ключевую роль в формировании энергетических путей релаксации возбужденных состояний в молекуле. Корролы характеризуются необычным поведением с точки зрения сенсибилизации неодима.

Ключевые слова: Тетрапирролы, люминесценция, неодим, порфирин, фталоцианин, коррол.

Introduction

One of the most important parts of investigations in the field of lanthanides is their opportunity to form luminescent compounds with different organic chromophores. Luminescence properties of such compounds always depend on the nature of the lanthanide ion and the chromophore, which are included in the structure of such complexes, theirs quantity, medium and other factors.[1]

Note that 4f-luminescence (luminescence of 4f-elements) in the near infrared (NIR) region is one of the most demanded for medicine (as markers) and technology (as a base for optical devices like fiber-optics, *etc.*) due to several very important reasons:

- light of NIR range can penetrate biological tissues much more effectively in comparison to UV/VIS ranges (UV – ultraviolet, VIS – visual) due to the weak overlapping with absorption of bioobjects;
- NIR light is absolutely safe for human in comparison to UV range, which action can generate dangerous radical species;
- NIR photons undergo much less scattering in comparison to UV/VIS light.

Tetrapyrroles are the best candidates for obtaining NIR emitting objects. Their low-energy donor triplet (T) levels are suitable for intramolecular energy transfer to the resonant levels of such NIR emitting lanthanide ions like Nd^{3+}, Ho^{3+}, Er^{3+}, and Yb^{3+}. These macrocycles have a very strong absorption in near UV region and in visual region.

Lanthanide porphyrins as NIR-emitting agents have been studied starting from 1974.[2] It is interesting that porphyrins were the first macrocyclic compounds that showed sensitization of 4f-luminescence. The investigation of these compounds always deals with several main drawbacks such as relative lability (a result of discrepancy of the core of porphyrins and lanthanide ions radii; only some lanthanide ions have stable complexes with porphyrins due to lanthanide compression) and relatively low efficiency of NIR emission of lanthanide ion. To avoid the problem of stability of complexes there were presented different approaches of external porphyrin-lanthanide binding, reviewed in [3]. It is very important to mention that there is no any significant decreasing of 4f-emission efficiency under such conditions of sensitization.[4] Recently the first example of near-infrared 4f-luminescence of sanswich type lanthanide phthalocyanines was demonstrated using Er(III) and Yb(III) complexes.[5]

Many systems containing Nd^{3+} have been regarded as the most popular luminescent materials for laser system applications.[6] Thus, we have investigated influence of different parameters of the structure on their luminescent properties and stability: *e.g.* nature of tetrapyrrole, quantity of metal ions and the type of coordination.

Experimental

Syntheses of the corrole, porphyrin and phthalocyanine derivatives, as well as their complexes were described previously.[4,7-10]

Spectra of molecular fluorescence, 4f-luminescence and excitation spectra were recorded on a spectrofluorimeter "Fluorolog FL 3-22" "Horiba Jobin Yvon" (Xe-lamp 450 W). Spectra of 4f-luminescence of Nd^{3+} were registered at 850–1150 nm (transitions $^4F_{3/2}\rightarrow{}^4I_{13/2}$, $^4F_{3/2}\rightarrow{}^4I_{11/2}$; note, that signal of the third transition $^4F_{3/2}\rightarrow{}^4I_{13/2}$ was very weak, so we did not take it into account). Spectra of molecular fluorescence of porphyrins, corroles and phthalocyanines were registered at 550–800 nm (S_1–S_0 transitions). Luminescence integral intensity was measured using software of the device. The relative quantum yield of molecular fluorescence was determined using solution of Zn-tpp (H_2tpp – 5,10,15,20-tetraphenylporphyrin) in ethanol as a primary standard (0.022).[7,11] Determination of the relative quantum yield (accuracy is ±10 %) of molecular fluorescence and 4f-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 standard and of the sample, respectively, A_0 and A_x – absorption at the wavelenght of Soret band of the standard and of the sample, respectively, I_x and I_0 – integral luminescence intensity of the standard and of the sample, respectively, n_0 and n_x – refractive index of the standard solvent and of the sample solvent, respectively.

Fluorescence lifetime was measured under excitation at the Soret band.

Results and Discussion

All polytopic porphyrins and corroles were synthesized through the acylation of parental aminoderivatives (H_2atpp – 5-(4-aminophenyl)-10,15,20-triphenylporphyrin and H_3dpfc – 10-(4-aminophenyl)-5,15-di(pentafluorophenyl)corrole) by *bis*-anhydrides (BA) of aminopolycarbonic acids (ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid, H_4edta and diethylenetriamine-*N*,*N*,*N'*,*N'*,*N''*-pentaacetic acid, H_5dtpa). The structure of all studied compounds (ligands and complexes) is presented in Figure 1. Unfortunately, neodymium-porphyrins are labile compounds, but the complex Nd-tpp(Acac) (Acac – acetylacetonate) was used only for comparison. The lanthanide complexes with the functionalized porphyrins and corroles are formed with ratio Ln:L=1:1.

Thus, in this work we consider several types of Nd-complexes: mononuclear complex (metal-ligand ratio 1:1), double-decker complex (metal-ligand ratio 1:2), peripheral binding (on the base of ditopic tetrapyrrole, metal-ligand ratio 1:1).

Previously we showed that peripheral complexes Ln-edta-tetrapyrroles have two coordinated water molecules, while the Ln-dtpa-tetrapyrroles do not contain water in their structure. This difference was attributed to the larger coordination number of the lanthanide ions in dtpa-derivatives than in edta-derivatives.[7] Note, that water is undesirable component of the inner coordination sphere of Nd^{3+}. Its presence leads to energy dissipation due to overlapping of the $^4F_{3/2}\rightarrow{}^4I_{15/2}$-transition (5400 cm^{-1}) with the O–H bond vibrational quanta $\nu=2$ (6900 cm^{-1}) and such an excitation of vibration state leads to effective quenching of the $^4F_{3/2}$-state.

4f-Emitting was fixed in all Nd-containing complexes. Full coincidence of the absorption and excitation spectra of these compounds clearly shows that the 4f-luminescence of Nd^{3+} takes place as a result of ligand-to-lanthanide energy transfer. Thus, corroles, porphyrins and phthalocyanines

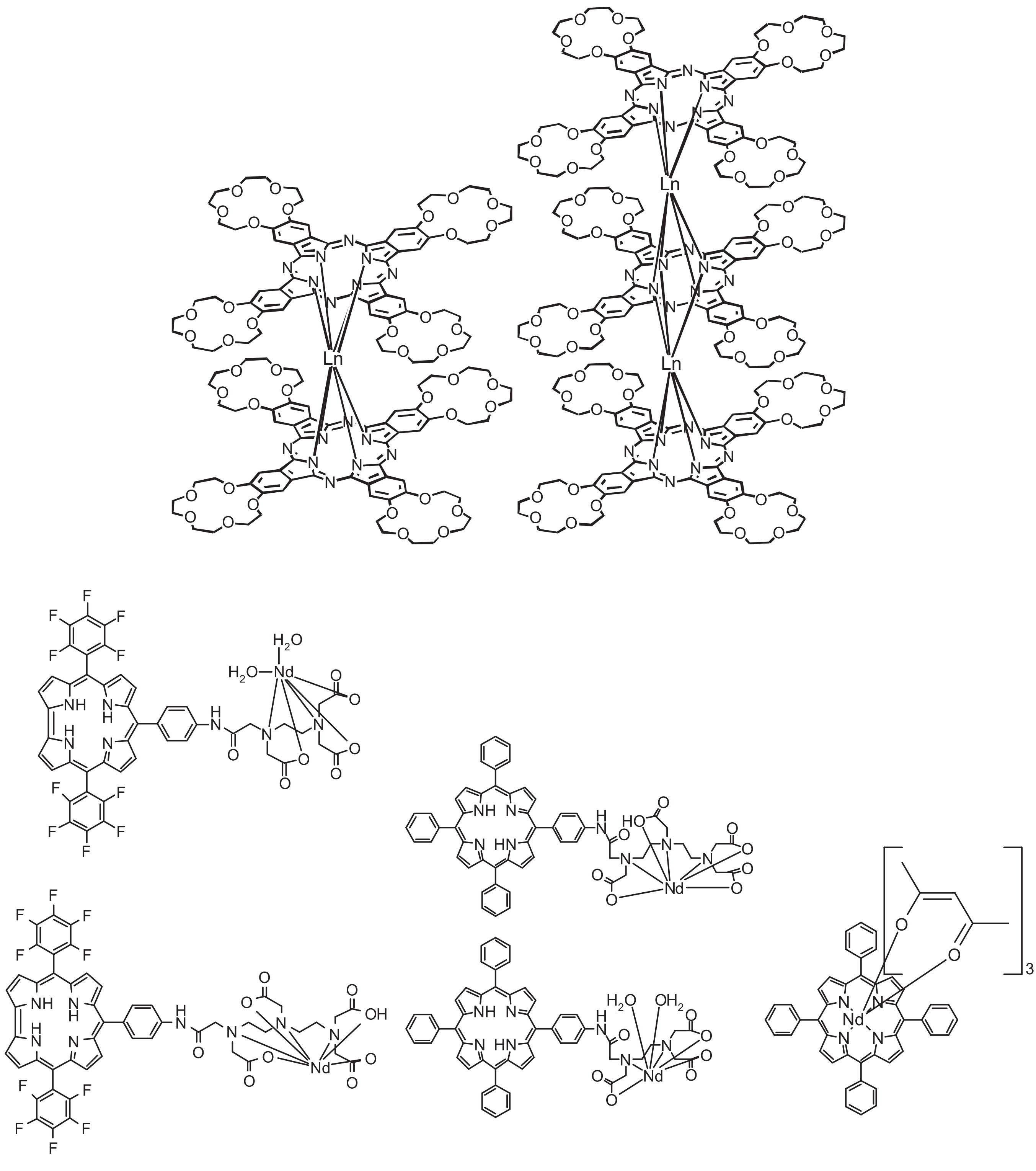

Figure 1. Structure of double-decker (Nd-Phthal$_2$) and triple-decker (Nd$_2$-Phthal$_3$) phthalocyaninates, peripheral complexes of corroles (Nd-edta-H$_3$dpfc·2H$_2$O and Nd-Hdtpa-H$_3$dpfc), peripheral complexes of porphyrins (Nd-edta-H$_2$atpp·2H$_2$O and Nd-Hdtpa-H$_2$atpp) and tpp-complex (from left to right respectively) of neodymium(III).

are able to sensitize the 4f-luminescence of neodymium (Figure 2).

Corroles

Absorption spectra of ditopic corroles metallated by the peripheral polydentate binding site with Nd(III) have near-UV Soret band maximum at 410 nm, and two *Q*-bands in the visual range with λ_{max}=568 and 615 nm. Note, that there are no any changes in absorption spectra of Nd-edta-H$_3$dpfc·2H$_2$O and Nd-Hdtpa-H$_3$dpfc in comparison with parental ditopic ligands H$_3$dpfc-H$_3$edta H$_3$dpfc-H$_4$dtpa.

The quantum yields of 4f-emission (φ_{4f}) for the Nd-H$_3$dpfc-edta and Nd-H$_3$dpfc-dtpa were $2.8{\cdot}10^{-3}$ and $1.4{\cdot}10^{-3}$ in DMF, while methanol solutions provided φ_{4f}=$0.5{\cdot}10^{-3}$ and $0.7{\cdot}10^{-3}$, respectively. Note, that there is no any significant

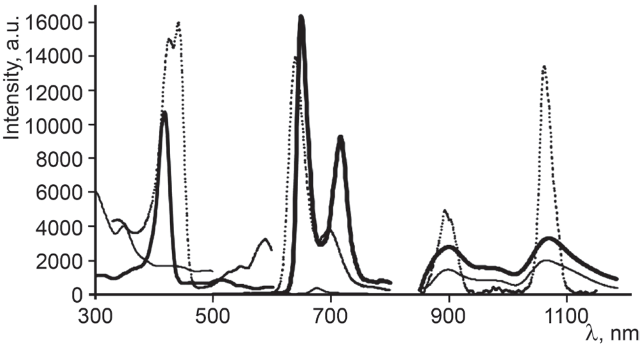

Figure 2. Excitation spectra (300–500 nm) of 4f-luminescence at 1060 nm, molecular fluorescence (600–750 nm) and 4f-luminescence (850–1150 nm) spectra (from left to right) of double-decker complex Nd-Phthal$_2$ (thin line —), peripheral complex Nd-edta-H$_2$atpp·2H$_2$O (thick line ━) and peripheral complex Nd-edta-H$_3$dpfc·2H$_2$O (dotted line ····).

effect of the paramagnetic ion on the molecular fluorescence (*vide infra*).

The molecular fluorescence lifetime measurement curves were monoexponential in all cases. There is also an effect of methanol *vs.* DMF solutions on fluorescence lifetimes and the quantum yields of both fluorescence and 4f-emission. The values in methanol solutions were consistently found to be smaller than in DMF (Table 1), which may be attributed to more effective vibrational accepting modes for nonradiative energy decay in methanol.

Porphyrins

The absorption spectra of Nd-edta-H$_2$atpp·2H$_2$O and Nd-Hdtpa-H$_3$dpfc in DMF are typical for metal-free porphyrins, and its bands are only slightly shifted to longer wavelengths with respect to parental H$_2$atpp, despite the bulky substituent in one of the phenyl cycles, which is coordinated with Nd(III) ion. Both complexes have the same spectra: near-UV Soret band maximum at 419 nm, and four *Q*-bands in the visual range with λ_{max}=515, 550, 591 and 647 nm.

As described earlier, quantum yield of 4f-luminescence depends on coordination number of lanthanide ion. In case of peripheral complexes Nd is coordinated by edta and dtpa. Coordination numbers of Nd in edta less than in dtpa. The latter results in the same values of quantum yield in all kind of dtpa-derivatives studied and more less values of the one in all kind of edta-derivatives (Table 1). It can be easily explained, as complexed lanthanide ion with low coordination number in solution has much inclination to form donor-acceptor bond with additional ligands (*e.g.* solvent molecules) than ion with greater coordination number. Additonal complexation on lanthanide ion can result in non-radiative photochemical processes, which decrease quantum yield value (see above).

Note, that almost all of studied peripheral complexes have two types of emission (like in case of ditopic corroles): porphyrin molecular luminescence with basic band λ_{max}≈650 nm and 4f-luminescence of neodymium with band λ_{max}≈890 and ≈1060 nm.

The complex Nd-tpp(Acac) doesn't fluoresce. In this case paramagnetic ion is coordinated directly to the chromophore macrocycle, which results in full molecular fluorescence quenching.

Phthalocyanines

Absorption spectrum of double-decker sandwich compound of neodymium tetra(15-crown-5)phthalocyaninate consists of Soret band with maximum at 368 nm (Table 1) in the near UV-range and intensive *Q*-band with maximum at 669 nm in the visible range. Less intensive absorption band with maximum at 480 nm is also observed, which is typical for electroneutral radical forms of the double-decker complexes of the structure [Phthal]$^{2-}$Ln^{3+}[Phthal•]$^{-}$.

The electronic absorption spectrum of triple-decker complex Nd$_2$-Phthal$_3$ reveals two *Q*-bands (intensive Q_1-band with maximum at 640 nm and less intensive Q_2-band with maximum at 707 nm), as well as Soret band at 362 nm.

The molecular fluorescence of the poly-decker neodymium-phthalocyaninates was observed at the noise level, so its quantum yield (φ_{ML}) is hard to be determined. The reason of the latter is the same as for the complex Nd-tpp(Acac).

Essential 4f-luminescent signal was fixed only in the double-decker Nd complexes, while triple-decker complex showed it at very low and undetectable value.

Comparison of the fluorescent and 4f-luminescent properties

Molecular fluorescence of the studied compounds has strong dependence on the type of Nd(III) coordination. Thus, porphyrin and phthalocyanine complexes Nd-Phthal$_2$,

Table 1. Absorption and luminescent data.

Complex	UV-VIS absorption, λ, nm	$\lambda_{ML(4f)}$, nm	λ_{4f}, nm	τ_{ML}, ns^a	$\varphi_{ML}\cdot10^{2\,b}$	$\varphi_{4f}\cdot10^{3\,b}$
Nd-edta-H$_2$atpp·2H$_2$O	419, 514, 550, 590, 646	654, 715	886, 1055	12.8	11	0.15
Nd-Hdtpa-H$_2$atpp	419, 515, 550, 591, 647	655, 716	885, 1056	13.5	11	0.2
Nd-edta-H$_3$dpfc·2H$_2$O	410, 567, 615	639, 695	891,1061	3.4(3.2^c)	7.6(4.7^c)	2.8(0.5^c)
Nd-Hdtpa-H$_3$dpfc	410, 568, 615	639,696	894,1065	3.3(3.0^c)	8.2(3.8^c)	1.4(0.7^c)
Nd-Phthal$_2$	291, 368, 480, 605, 669	675, 744	893, 1060	–	<0.01	0.1
Nd$_2$-Phthal$_3$	293, 362, 640, 707	679, 748	896, 1062	–	<0.01	<0.01
Nd-tpp(Acac)	425, 558, 593	–	885, 1055	–	<0.01	2.4

RT, DMF, $\lambda_{exc.}$=Soret band, C=10^{-5} M.
^{a} ±0.02ns; ^{b} 10 %; ^{c} methanol solution.

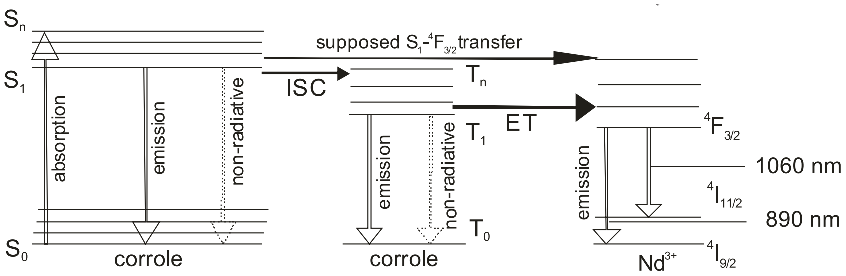

Figure 3. Photophysical processes in complexes of corroles with neodymium.

Nd_2-$Phthal_3$ and Nd-tpp(Acac) have a very low quantum yields of molecular fluorescence. On the other hand, all peripheral complexes have relatively good value of the φ_{ML}. Note, that due to extreme instability of the directly coordinated lanthanide-corroles, we can not provide their photophysical data.[7]

All the results presented so far indicate that the peripheral complexes are dual-range emitters: tetrapyrrole-based molecular fluorescence in visual range and 4f-luminescence in the NIR range. Thus, dual emission observed at RT in aerated solutions, while all macrocyclic tetrapyrroles exhibit NIR emission as phosphorescence only at deoxygenated conditions and usually in frozen solutions.[12] The distance between the paramagnetic ion and the chromophore is so large that there is no perturbing effect of the former on the photophysical properties of the latter. This is very different from the case of metallation of tetrapyrrole rings with paramagnetic lanthanide ions, where energy transfer from the excited chromophore to the lanthanide is quantitative and no residual fluorescence is obtained.[13]

4f-Luminescence is observed in almost all studied Nd-complexes as a result of intramolecular transition of excitation energy. Low quantum yield of 4f-luminescence (φ_{4f}) in case of triple-decker sandwich compound of neodymium can be explained with self-quenching in pair lanthanide-lanthanide (because of energy exchange between Nd ions),[14] since they are located very close to each other.

Low 4f-luminescence efficiency of the peripheral atpp-complexes is based on low interaction of donor (chromophore) and acceptor (Nd(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.

Spectral-luminescent data of the corrole-based Nd-compounds are unusual. Thus, φ_{4f} of peripheral complex Nd-edta-H_3dpfc·$2H_2O$ is comparable and even a little bit more than for Nd-tpp(Acac). The main assumption for this phenomenon deals with sensitization mechanism (Figure 3). The energy of the lower triplet state of the studied corrole (which is traditionally donor level for the resonant level of Ln ion) is undetectable, since free corroles do not phosphoresce.

So, the mechanism of sensitization probably has another or additional pathway through the lower singlet state.

Conclusions

4f-Luminescence of the neodymium(III) complexes with different tetrapyrrole macrocycles (porphyrins, phthalocyanines and corroles) was compared for the first time. It was proposed that binding type plays a key role in formation of energy relaxation pathways in the molecule. Corroles have unusual behaviour in terms of Nd sensitization and it requires more deeper analysis.

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