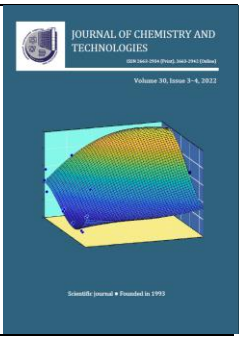
Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua



UDC 535.372:541.49:546.65

4f-LUMINESCENCE OF 3d-4f HETERONUCLEAR PORPHYRIN COMPLEXES

Nikolay N. Semenishyn*[1], Serhii S. Smola[1], Mariya Yu. Rusakova[2], Natalya V. Rusakova[1]
[1]A. V. Bogatsky Physico-Chemical Institute NAS of Ukraine, 86, Lustdorfs'ka doroga, 65080, Odessa, Ukraine
[2] I. I. Mechnikov Odessa National University, Dvoryans'ka 2, 65026, Odessa, Ukraine

Received 14 July 2022; accepted 5 October 2022; available online 31 October 2022

Abstract

Porphyrin compounds with Nd(III), Yb(III) and Cu(II), Zn(II), Pd(II) were obtained on the basis of ditopic porphyrins, the structure of which allowed obtaining various heterometallic complexes. Specified f-metals were chosen due to the fact that the infrared luminescence of these metal ions can be sensitized by porphyrins, on the other hand, the presented d-metal ions have a very different effects on the porphyrin chromophore. Photosensitized *4f*-luminescence in the near-infrared region and molecular fluorescence in the visible region of 3d-4f heteronuclear complexes are extremely sensitive to the nature of d- and f-metal ions. Thus, effective molecular fluorescence (quantum yield 4–11 %) is characteristic for the cases of free porphyrin cores and complexes with Zn(II). Moreover, these cases reveal three types of emission – fluorescence, phosphorescence and *4f*-luminescence at the same time. We found out that the molecular fluorescence effectiveness and the values of its band maxima did not depend on the nature of the peripheral chelate fragments. Fluorescence of copper and palladium complexes is almost completely quenched, but Pd(II)-porphyrin serves as *4f*-sensitizer in contrast to Cu(II)-porphyrin. The effect of oxygen on the luminescence of the complexes was considered. It was found that only Pd-Nd complexes are sensitive to its presence – deoxygenation led to 20 % enhancement of *4f*-luminescence effectiveness.

Keywords: lanthanides; porphyrins; *4f*-luminescence; sensitization; heteronuclear complexes

4f-ЛЮМІНЕСЦЕНЦІЯ В 3d-4f ГЕТЕРОЯДЕРНИХ КОМПЛЕКСАХ ПОРФІРИНІВ

Микола М. Семенішин[1], Сергій С. Смола[1], Марія Ю. Русакова[2], Наталія В. Русакова[1]
[1] Фізико-хімічний інститут НАН України, вул. Люстдорфська дорога, 86, м. Одеса, Україна
[2] Одеський національний університет ім. І. І. Мечникова, вул. Дворянська, 2, м. Одеса, 65026, Україна

Анотація

На основі дитопних порфіринів, структура яких дозволяє отримувати різноманітні гетерометалічні комплекси, отримано сполуки порфіринів з Nd(III), Yb(III) та Cu(II), Zn(II), Pd(II). Зазначені f-метали були обрані через те, що інфрачервона люмінесценція цих іонів металів може бути сенсибілізована порфіринами, а, з іншого боку, представлені іони d-металів мають різний вплив на порфіриновий хромофор. Фотосенсибілізована *4f*-люмінесценція в ближній інфрачервоній області та молекулярна флуоресценція у видимій області гетероядерних 3d-4f комплексів надзвичайно чутливі до природи іонів d- та f-металів. Так, у випадку вільних порфіринових ядер і комплексів з Zn(II) характерна ефективна молекулярна флуоресценція (квантовий вихід 4–11 %). Крім того, для цих цих сполук характерні три типи випромінювання одночасно – це флуоресценція, фосфоресценція та *4f*-люмінесценція і нами було встановлено, що ефективність всіх видів емісії та значення максимумів їх смуг не залежать від природи периферичних хелатних фрагментів. Флуоресценція комплексів купруму та паладію майже повністю погашена, але Pd(II)-порфірин виконує роль *4f*-сенсибілізатора на відміну від Cu(II)-порфірину. Розглянуто вплив кисню на люмінесценцію комплексів і виявлено, що лише комплекси Pd-Nd чутливі до його присутності – деоксигенація призводить до 20 % підвищення ефективності *4f*-люмінесценції.

Ключові слова: лантаніди; порфірини; *4f*-люмінесценція; сенсибілізація; гетероядерні комплекси.

**Corresponding author: e-mail address: ssmbikola@yahoo.com*

doi: 10.15421/jchemtech.v30i3.261538

Introduction

Recently, porphyrins, as separate class of macrocyclic tetrapyrrole compounds, and their metal complexes are widely studied due to their catalytic properties [1], anticancer and antimicrobial activity [2–3], characteristic and intensive light absorption and emission [4]. The peculiarity of metalloporphyrins is determined not only by the macrocyclic effect of the ligand (*e.g.* [5]), but also by its structural rigidity. The latter is due to the planar structure of the large conjugated 18π aromatic ring of the ligand with a coordination center of four nitrogen atoms [6]. Porphyrin molecule imposes special requirements on the geometrical parameters of the metal ion in terms of complex formation due to its high rigidity. Thus, lanthanide-porphyrins (which are of high interest for medicine and technique due to their emission in near infrared region [7]) still remain relatively labile compounds because of formal discrepancy of porphyrin core and lanthanide ion [8]. Thereby, it was proposed to study stable periphery coordinated lanthanide-porphyrins instead of core-coordinated ones [9]. But in this case porphyrin core of lanthanide-porphyrin remains empty and can be coordinated by other metal ion.

The chemistry of heteronuclear lanthanide compounds based on tetrapyrrole macrocycles is a relatively new area of research. The effect of a heterometal ion on molecular fluorescence and *4f*-luminescence characteristics of their complexes have been elucidated only in several works [10–11]. Obviously, the luminescent properties of such compounds are determined by photophysical processes (quenching or, conversely, enhancement of the molecular fluorescence, sensitization of the *4f*-luminescence), which are significantly affected by nature of the heterometal ion.

3d-Transition metals ions (Cu^{2+}, Zn^{2+}, and Pd^{2+}) were chosen to form core-coordinated complexes. It should be noted that all mentioned 3d-elements have approximately the same size of ionic radii (about 80 pm) and easily form complexes with porphyrins, however they have drastically different influence on porphyrin molecule because of their electronic structure. It is known that the effective metal ion charges in copper-porphyrins are the lowest due to the highest electron density transfer from macrocycle nitrogen atoms to the metal ion and copper-porphyrins have almost fully quenched molecular fluorescence [12]. Similarly to Cu^{2+}, diamagnetic Pd^{2+} complexes lack fluorescence from the S_2 state, but Pd-porphyrins do not lack fluorescence from the S_1 state. The phosphorescent properties of Pd(II)- and Cu(II)-porphyrins are notably different, too: the latter have a level located below the T_1 state, which therefore quenches molecular phosphorescence, moreover intersystem crossing is very fast due to the presence of paramagnetic copper ion and radiative $T_1 \rightarrow S_0$ transfer become uncompetitive. It should be noted that Pd-porphyrins can generate singlet oxygen (which serve as a basis for photodynamic therapy [13]) and the additional photoexcitation energy pathway should be considered. The zinc ion is prone to covalent interaction, but it does not have vacant d-orbitals ($3d^{10}$ electronic structure of the outer shell). Zn(II)-porphyrins as diamagnetic complexes keep both molecular fluorescence and phosphorescence [14]. Only Nd(III), Er(III) and Yb(III) lanthanide ions luminescence can be sensitized by porphyrin chromofore [8], so Nd(III) and Yb(III) ions were chosen to form complexes excepting Er(III), since there are some instrumental difficulties with its emission at 1540 nm, in particular there are no standards for so far region in terms of relative quantum yield calculation. Thus, the present work describes the synthesis and properties of heteronuclear complexes M-tpp-edta-Ln and M-tpp-dtpa-Ln where M = Cu, Zn, Pd; Ln = Nd, Yb. H_2tpp – 5,10,15,20-tetraphenylporphyrin, H_4edta – H_4ethylenediamine-N,N,N',N'-tetraacetic acid, H_5dtpa – diethylenetriamine-N,N,N',N'',N''-pentaacetic acid.

Experiment and discussion of the results

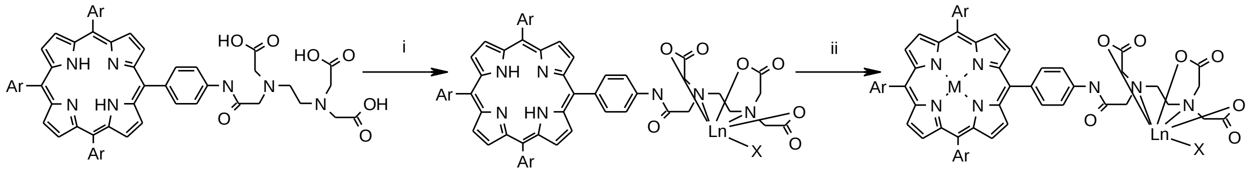
Luminescence excitation and emission spectra were recorded on a spectrofluorimeter "Fluorolog FL 3-22" ("Horiba Jobin Yvon") using 450 W Xe-lamp. Integral intensity of luminescence was measured using the software of the device. The relative quantum yield of molecular fluorescence (φ_{ML}) was determined using solution of Zn-tpp in ethanol as a primary standard. Determination of the φ_{ML} (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_0 and φ_x – luminescence quantum yield of the standard and of the sample respectively,

A_0 and A_x – absorption at the wavelength 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. Luminescence lifetime (τ) was measured under excitation at the Soret band.

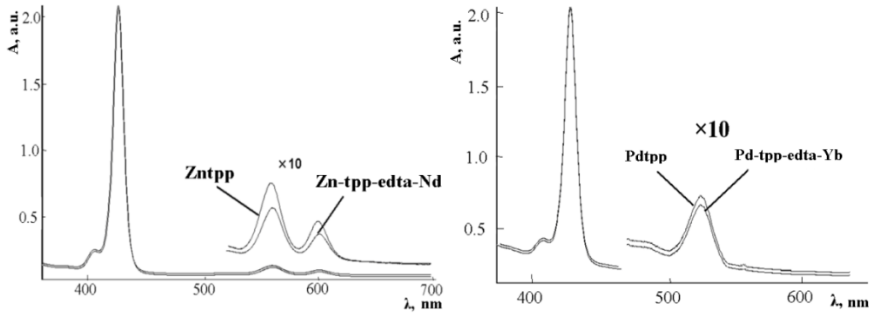
The synthesis of heteronuclear complexes was carried out sequentially, as it was performed previously [9]: a mononuclear complex of lanthanide was obtained at the first stage (Scheme 1),



Scheme 1. Synthesis of heteronuclear f-d complexes. i) DMF, $LnCl_3 \cdot 6H_2O$, 50°C, 98% yield; ii) DMF, refluxing, $MAcO_3$aq.

then the formation of heteronuclear compounds occurred by refluxing a mononuclear complex in DMF solution with chloride (acetate) of 3d-metal at the second stage. Obtaining all heteronuclear complexes did not face any difficulties, because the formation of 3d- and 4f-porphyrinates takes place under significantly different conditions. In this case, the substitution of the lanthanide ion by the 3d-metal ion is impossible due to notably different lgK of 3d-edta and 4f-edta complexes. For example, lgK(Zn-edta) = 16.44 and lgK(Lu-edta) = 19.80 [15].

In contrast to mononuclear complexes, the last stage of the synthesis of heteronuclear compounds can be controlled by UV-Vis absorption spectra: the formation of 3d-porphyrinate was accompanied by a change in the position of the Soret band and the degeneracy of four *Q*-bands in only two *Q*-bands in the visible part of the spectrum.



a b

Fig. 1. Absorption spectra of (a) Zn and (b) Pd porphyrinates and their heteronuclear complexes with lanthanides. C =10^{-6} M; DMF; 298 K.

The absorption spectra (Fig. 1, Table 1) of heteronuclear lanthanide complexes depend on the nature of the 3d-metal ion coordinated to the central nitrogen atoms of the porphyrin, since its orbitals participate in the formation of molecular orbitals due to coplanarity with the ligand chromophore, in contrast to the lanthanide ion at the periphery. This is confirmed by the coincidence of the absorption spectra of 3d-4f-heteronuclear complexes and spectra of corresponding 3d-monoporphyrinates coordinated by the central nitrogen atoms.

The complex formation of porphyrins with metal ions with unfilled d(f) shells leads to a complication of the system of excited energy levels. It is known that the formation of states of high multiplicity, as well as mixing of metall-ligand states, are possible for complexes of porphyrins with these metals, as a result of the exchange interaction of d(f)- and π-electrons. Thus, the fluorescence spectra of all heteronuclear lanthanide-containing complexes under excitation at the absorption bands maxima at 298 K contain two *Q*-bands with different intensity distributions: (0-0) in the region of 600–605 nm and (0-1) – 648–652 nm. The bands become more narrow in frozen solutions and shift hypsochromically by 2–8 nm.

Note the differences in the fluorescence spectra associated with the nature of the 3d-metal. For example, a maximum appears around 633 nm (which is absent in liquid solutions) additionally to hypsochromically shifted maxima in fluorescence spectra of Zn(II) complexes solutions at 77 K (Table 1). Perhaps this is a result of the appearance of an additional excited vibrational S_n sublevel upon the binding of the edta (or dtpa)-Ln fragment due to a change in the symmetry of the complex. In the Zn-tpp complex, as well as in other metal complexes, this effect is absent.

Table 1

Photophysical data of studied compounds (DMF, RT, C=10^{-5}M.)

#	λ_{abs}, nm	λ_{ML}, nm		E_{S1}, cm^{-1}	φ_{ML} ×10^{2*}		λ_p,nm	E_{T1},cm^{-1}	φ_{4f}×10^{3*}	
		298K	77K		298K	77K			aerated	oxygen free
H_2tpp-H_4edta	419.514,551,593,648	654,715	650,716	15290	11	12	829	12060	-	-
H_2tpp-H_5dtpa	418,515,552,591,650	655,716	650,716	15270	11	12	822	12170	-	-
Zn-tpp-edta-Yb	422,560,600	609,661	599,634,654	16420	4	7	789	12790	0.39	0.39
Zn-tpp-dtpa-Yb	421,562,600	608,661	599,633,655	16440	4.1	9	790	12800	0.55	0.55
Zn-tpp-edta-Nd	423,568,615	609,661	599,634,654	16420	4	7	789	12790	0.40	0.40
Zn-tpp-dtpa-Nd	422,568,615	608,661	599,633,655	16440	4.2	9	790	12800	0.51	0.51
Cu-tpp-edta-Yb	416,541,574	-	610,650	16400	-	0.2	-	-	-	-
Cu-tpp-dtpa-Yb	417,540,575	-	610,650	16400	-	0.3	-	-	-	-
Cu-tpp-edta-Nd	416,539,574	-	610,650	16400	-	0.2	-	-	-	-
Cu-tpp-dtpa-Nd	417,541,574	-	610,650	16400	-	0.3	-	-	-	-
Pd-tpp-edta-Yb	415,519	567,611	-	17640	0.01	-	685	14600	0.21	0.21
Pd-tpp-dtpa-Yb	416,519	566,611	-	17670	0.01	-	686	14580	0.24	0.24
Pd-tpp-edta-Nd	416,517	566,609	-	17670	0.01	-	685	14600	0.32	0.38
Pd-tpp-dtpa-Nd	417,519	567,609	-	17640	0.01	-	686	14580	0.42	0.44
Zn-tpp**	425	604,659	-	16560	2.2	-	-	-	-	-

* ± 10 %; ** Data from [16]

Fluorescence quantum yields of heteronuclear Zn(II) compounds at 298 K are 1.4 times higher than Zn-tpp complexes. These characteristics increase by 2–5 times at 77 K. In this case the fluorescence intensity and bands maxima values do not depend on the nature of peripheral chelate fragments.

Molecular fluorescence spectra of copper complexes at 298 K contain two bands shifted hypsochromically (5–7 nm) compared to zinc compounds. There is also a noticeable decrease of fluorescence quantum yields at ambient temperature.

All complexes have the most intense 0-0 phosphorescence band at 775–820 nm at 77 K (λ_{ex} = 555 nm). It was found that emission spectra of the studied compounds at 77 K were in the millisecond range and had low-intensity bands, the maxima of which coincided with the fluorescence bands (in addition to the phosphorescence bands). The measurements of the decay kinetics at different emission wavelengths (λ_{max} = 600 and 650 nm) previously [17] showed that the observed emission had a lifetime approximately two times shorter than phosphorescence with a maximum at 780 nm, which allowed us to attribute short-wavelength bands to delayed fluorescence.

As was shown previously [18], the binding of the Ln^{3+} ion to the center of the porphyrin macroring could significantly increase the phosphorescence yield due to the enhancement of the intersystem crossing without causing delayed fluorescence. In our case, its binding to the complexone also increases the phosphorescence yield and significantly expands the region of long-lived radiation due to the delayed fluorescence. Phosphorescence of Zn(II) complexes is observed not only in frozen solutions, but also at room temperature in degassed solutions. Phosphorescence is quenched in the presence of oxygen in liquid solutions.

4f-Luminescence is absent in all studied heteronuclear complexes of porphyrins with Cu(II). It is explained by the fact that the $T_1 \rightarrow S_0$ intersystem crossing in Cu-porphyrinates has a very high probability about 10^{12} s^{-1} [19], and the probability of transitions $T_1 \rightarrow {}^2F_{5/2}$ (for Yb^{3+}) and $T_1 \rightarrow {}^4F_{3/2}$ (for Nd^{3+}) is about 10^8 s^{-1} – 10^{10} s^{-1} [20-

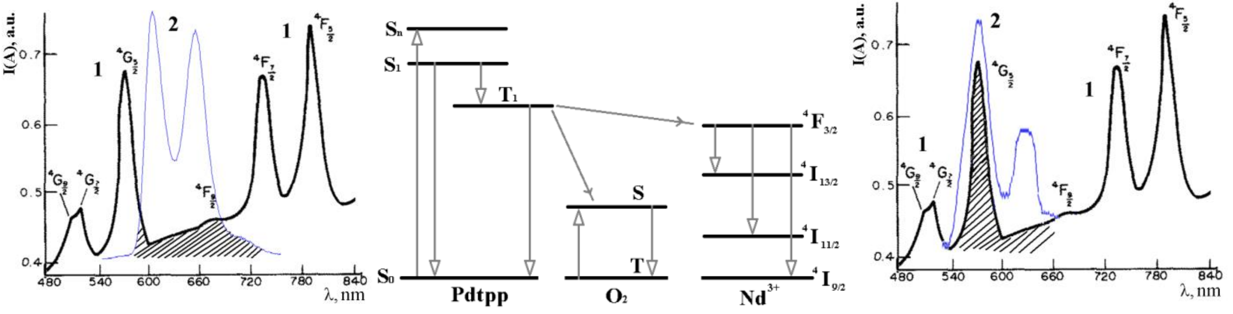
21]. Thus, the process of luminescence sensitization turns out to be uncompetitive: its probability is 2–4 orders of magnitude less than the probability of the $T_1 \to S_0$ intersystem crossing.

In contrast to the copper complexes, heteronuclear compounds of zinc and palladium reveal *4f*-luminescence in the region of 880-890 nm (transition $^4F_{3/2} \to {}^4I_{9/2}$), 1055-1065 nm (transition $^4F_{3/2} \to {}^4I_{11/2}$) and 1340-1350 nm (transition $^4F_{3/2} \to {}^4I_{13/2}$) for the Nd^{3+} ion and in the region of 975–985 nm (transition $^2F_{5/2} \to {}^2F_{7/2}$) for the Yb^{3+} ion.

Compared to the corresponding mononuclear Yb complexes, the luminescence quantum yield in all 3d-4f-heteronuclear Yb complexes decreases by 3–4 times in zinc complexes and by 5–8 times in palladium complexes. This somewhat unexpected fact is probably caused by high phosphorescence quantum yields (φ_P up to 100 % and φ_T up to 100 %) of palladium complexes due to the high probability of the $T_1 \to S_0$ transition ($\approx 10^4$ s^{-1}) (Table 1) [11]. Thus, the $T_1 \to S_0$ radiative transition almost does not compete with the $T_1 \to {}^2F_{7/2}$ transition in regular Ln-porphyrins. For the latter the typical probabilities of the $T_1 \to {}^2F_{7/2}$ transition are about 10^8–10^{10} s^{-1} and if the lanthanide is outside the porphyrin chromophore, these values are expected to decrease due to the difficulties of the interaction between the lower triplet state of the porphyrin and the resonant level of the lanthanide ion. Therefore, despite the difference by 4–6 orders of magnitude, we can assume a more noticeable competition, since estimated energy transfer rate constants are around 10^4-10^5 s^{-1} [11].

In contrast to ytterbium complexes, coordination of zinc somewhat increases the IR luminescence intensity of the Nd^{3+} ion in heteronuclear neodymium complexes (Table 1). Perhaps this is due to the fact that the porphyrin emission spectrum undergoes a significant hypsochromic shift in heteronuclear complexes (about 50 nm). As a result, the molecular fluorescence bands partially overlap with three neodymium ion absorption ($^4I_{9/2} \to {}^4F_{9/2}$, $^4I_{9/2} \to {}^4F_{7/2}$ and $^4I_{9/2} \to {}^4G_{5/2}$ transitions, Fig. 2a), while in mononuclear complexes with only two bands ($^4I_{9/2} \to {}^4F_{9/2}$ and $^4I_{9/2} \to {}^4F_{7/2}$ transitions).

In almost all cases, palladium-neodymium complexes have somewhat less efficient *4f*-luminescence than corresponding mononuclear complexes. It is probably due to the overlapping of the emission bands of palladium porphyrinate with only one f-f absorption band of the neodymium ion (transition $^4I_{9/2} \to {}^4G_{5/2}$, Fig. 2c). The same effect (decrease of the *4f*-luminescence intensity) is observed in the corresponding Pd-Yb complexes.



a b c

Fig. 2. Overlapping of f-f absorption spectrum of the Nd^{3+} ion (1) with the molecular fluorescence spectra (2) of Zn-tpp-dtpa-Nd (a) and Zn-tpp-dtpa-Nd (c). Photophysical processes in heteronuclear Pd-Nd complexes (b).

It is known that oxygen is an efficient quencher of triplet states of palladium and platinum porphyrinates [11]. This is due to the high rate of the $T_1 \to S_0$ transition, which is $\approx 10^7$ s^{-1} (S_0 is the level of singlet oxygen $^1O_2$). This intermolecular energy transfer can significantly compete with the intramolecular transition $T_1 \to {}^4F_{3/2}$, since speeds of the latter are in the range 10^8–10^{10} s^{-1}.

Luminescent measurements of degassed solutions of heteronuclear Pd-Nd complexes were carried out in this work and it was shown that in the absence of oxygen, the quantum yield of *4f*-luminescence φ_{4f} increased up to almost 20 % in comparison to aerated solutions. So, by eliminating the quenching of the triplet state by oxygen (Fig. 2b), it is possible to increase the efficiency of the *4f*-luminescence of the neodymium ion in heteronuclear complexes of palladium and neodymium.

At the same time, the effect of deoxygenation of the medium is almost absent in the corresponding heteronuclear Yb complexes, and this is due to the fact that the deactivation of triplet states of ytterbium porphyrins by oxygen does not compete with the process of excitation energy transfer.

Conclusions

Lanthanide containing heteronuclear complexes with 3d-metals revealed photosensitized *4f*-luminescence in near infrared region. It was found that *4f*-luminescence parameters depend on the nature of 4f- and 3d-metals and emission of some complexes depend on the presence of oxygen. Complexes of Zn^{2+} and core-free porphyrin complexes reveal three types of emission – effective molecular fluorescence, phosphorescence and *4f*-luminescence at the same time, and it was found that fluorescence intensity and bands maxima values do not depend on the nature of peripheral chelate fragments. Pd^{2+} ion can act as a *4f*-luminescence sensitizer but its efficiency depends on the presence of oxygen. At the absence of the latter *4f*-luminescence quantum yield increases up to almost 20 %. Pd^{2+} ion is a quencher of molecular fluorescence due to the high rate of intersystem crossing as well as Cu^{2+} ion, but the last one is a strong paramagnetic quencher of molecular fluorescence and also totally quenches *4f*-luminescence.

References

[1] Piccirillo, G., Maldonado-Carmona, N., Marques, D. L., Villandier, N., Calliste, C. A., Leroy-Lhez, S., Eusébio, M. E. S., Calvete, M. J. F., Pereira, M. M. (2022). Porphyrin@Lignin nanoparticles: Reusable photocatalysts for effective aqueous degradation of antibiotics. *Catal. Today*, In press. https://doi.org/10.1016/j.cattod.2022.09.009

[2] Batinic-Haberle, I., Tovmasyan, A., Huang, Z., Duan, W., Du, L., Siamakpour-Reihani, S., Cao, Zh., Sheng, H., Spasojevic, I., Alvarez Secord, A. (2021). H_2O_2-Driven Anticancer Activity of Mn Porphyrins and the Underlying Molecular Pathways. *Oxid. Med. Cell. Longev.*, 6653790. https://doi.org/10.1155/2021/6653790

[3] Sen, P., Soy, R, Mgidlana, S., Mack, J., Nyokong, T. (2022). Light-driven antimicrobial therapy of palladium porphyrins and their chitosan immobilization derivatives and their photophysical-chemical properties. *Dyes Pigments*, 203, 110313. https://doi.org/10.1016/j.dyepig.2022.110313

[4] Teixeira, R., Vaz Serra, V., Botequim, D., Paulo, P. M. R., Andrade, S. M., Costa, S. M. B. (2021). Fluorescence Spectroscopy of Porphyrins and Phthalocyanines: Some Insights into Supramolecular Self-Assembly, Microencapsulation, and Imaging Microscopy. *Molecules*, *26*(14), 4264. https://doi.org/10.3390/molecules26144264

[5] Hirohiko, H., Sung-Kil, L., Nagawa, Y., Hiratani, K. (2001). A Macrocyclic Effect on the Reduction of p-Quinones. *Supramol. Chem.*, *13*(6), 683–692. https://doi.org/10.1080/10610270108027498

[6] Kingsbury, C. J., Senge, M. O. (2021). The shape of porphyrins. *Coordin. Chem. Rev.*, 431, 213760. https://doi.org/10.1016/j.ccr.2020.213760

[7] Bulach, V., Sguerra, F., Hosseini, M. W. (2012). Porphyrin lanthanide complexes for NIR emission. *Coordin. Chem. Rev.*, *256*(15–16), 1468–1478. https://doi.org/10.1016/j.ccr.2012.02.027

[8] Chan Wai-Lun, Xie Chen, Lo Wai-Sum, Bünzli, J.-C. G., Wong Wai-Kwok, Wong Ka-Leung (2021). Lanthanide–tetrapyrrole complexes: synthesis, redox chemistry, photophysical properties, and photonic applications. *Chem. Soc. Rev.*, *50*(21), 12189–12257. https://doi.org/10.1039/c9cs00828d

[9] Semenishyn, N. N., Smola, S. S., Efryushina, N. P., Rusakova, N. V. (2015). Spectral and Luminescence Properties of Lanthanide(III) Complexes with Porphyrins and Corroles with Varied Structure. *Theor Exp Chem*, *51*(4), 224–229. https://doi.org/10.1007/s11237-015-9420-z

[10] Beeby, A., Dickins, R. S., Fitzgerald, S., Govenlock, L. J., Maupin, C. L., Parker, D., Riehl, J. P., Siligardi, G., Williams, J. A. G. (2000). Porphyrin sensitization of circularly polarised near-IR lanthanide luminescence: enhanced emission with nucleic acid binding. *Chem. Commun.*, (13), 1183–1184. https://doi.org/10.1039/b002452j

[11] Min-Kook Nah, Jae Buem Oh, Hwan Kyu Kim, Kyong-Hoon Choi, Yong-Rok Kim, Jun-Gill Kang (2007). Photophysical Properties and Energy Transfer Pathway of Er(III) Complexes with Pt–Porphyrin and Terpyridine Ligands. *J. Phys. Chem. A*, *111*(28), 6157–6164. 10.1021/jp0688512

[12] Huimin Ren, Chao Liu, Wei Yang, Jianzhuang Jiang (2022). Sensitive and selective sensor based on porphyrin porous organic cage fluorescence towards copper ion. *Dyes Pigments*, 200, 110117. https://doi.org/10.1016/j.dyepig.2022.110117

[13] Tisoco, I., Donatoni, M. C., Henrique Fernandes Vieira, V., De Toledo, J. R., Krambrock, K., Chaves, O. A., De Oliveira, K. T., Iglesias, B. A. (2022). Photophysical, photooxidation, and biomolecule-interaction of meso-tetra(thienyl)porphyrins containing peripheral Pt(ii) and Pd(ii) complexes. Insights for photodynamic therapy applications. *Dalton Trans.*, *51*(4), 1646–1657. https://doi.org/10.1039/d1dt03565g

[14] Chahal, M. K., Liyanage, A., Alsaleh, A. Z., Karr, P. A., Hill, J. P., D'souza, F. (2021). Anion-enhanced excited state charge separation in a spiro-locked N-heterocycle-fused push-pull zinc

porphyrin. *Chem. Sci.*, *12*(13), 4925–4930. https://doi.org/10.1039/d1sc00038a

[15] Cotton, S. (2006). *Lanthanide and Actinide Chemistry*. Uppingham, John Wiley & Sons,Ltd.

[16] Stel'makh, G. F., Tsvirko, M. P. (1983). Influence of the aggregated state and temperature on the spectral-fluorescent properties of Zn-tetraphenylporphin. *J. Appl. Spectrosc.*, *39*(3), 1041–1046. https://doi.org/10.1007/bf00659041

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

[18] Kuznetsova, R. T., Ermolina, E. G., Gadirov, R. M., Mayer, G. V., Semenishin, N. N., Zhuravlev, S. A., Rusakova, N. V., Korovin, Yu. V. (2009). Luminescent characteristics of tetraphenylporphyrin and its derivatives with lutetium. *Opt. Spectrosc.*, *106*(5), 672–676. https://doi.org/10.1134/s0030400x09050087

[19] Harriman, A. (1981). Luminescence of porphyrins and metalloporphyrins. Part 2.—Copper(II), chromium(III), manganese(III), iron(II) and iron(III) porphyrins. *J. Chem. Soc. Farad. T. 1*, *77*(2), 369–377. https://doi.org/10.1039/f19817700369

[20] Venchikov, V., Tsvirko, M. (2000). Determination of intramolecular energy-transfer efficiency in ytterbium chelates. *J. Appl. Spectrosc.*, *67*(4), 745–750. https://doi.org/10.1007/bf02681315

[21] Bhaumik M. L., El Sayed M. A. (1965). Mechanism and Rate of the Intramolecular Energy Transfer Process in Rare Earth Chelates. *J. Chem. Phys.*, *42*(2), 787–788. https://doi.org/10.1063/1.1696007