

Near Infrared Luminescence of Lanthanides in Complexes with Organic Dyes

Yurii Korovin^{1,2} and Natalia Rusakova¹

Received March 18, 2002

Spectral-luminescence characteristics of Yb³⁺ and Nd³⁺ ions in water solutions of their complexes with some organic dyes of sulfophenylphthaloxones group have been considered. Complexes can be efficiently excited with visible light ($\lambda_{\text{exc}} = 532 \text{ nm}$). 4f-Luminescence as a result of energy transfer from the dye moiety to the lanthanide ion was shown. Complexation of new polydentate ligand L of sulfophenylphthaloxones type increases the luminescence lifetimes because of the reduced solvation of the ion by water. They were determined as 12.60 μs for complex Yb-L and 1.45 μs for Nd-L.

KEY WORDS: Ytterbium and neodymium complexes; organic dyes; luminescence.

INTRODUCTION

4f-Luminescence observed in complexes with organic dyes is shown only by some of lanthanides ions Ln³⁺, first of all, Yb³⁺ ($\lambda_{\text{max}} = 980 \text{ nm}$) and Nd³⁺ ($\lambda_{\text{max}} = 880, 1060, \text{ and } 1340 \text{ nm}$). This is caused by the long-life triplet levels (T) of the latter having higher energy than radiative levels of the mentioned ions (i.e., intramolecular transfer of excitation energy is possible). However, the low-located radiative levels of these ions are especially affected by quenching of O-H and C-H oscillators of solvents and ligands molecules [1]. Hence, the characteristics of 4f-luminescence is relatively low. But this defect can be reduced through the search for ligands minimizing non-radiative losses of exciting energy. Taking into account the literature about luminescence of ions Ln³⁺ in the near IR spectral region, the main requirements can be formulated to the ligands, in complexes in which the high efficiency of these luminescence can be weighed: high denticity (N- and O-donor atoms; corresponding

value of T-levels [no more than 13500–14000 cm^{-1}]; presence of chromophoric groups (“photoantenna”); and possibility of functionalization.

EXPERIMENTAL

Ytterbium and neodymium chlorides, D₂O (99.9%), were purchased from Aldrich (Gillingham, Dorset). All other chemicals were of reagent grade and were used without further purification. The preparation of Yb(Nd) complexes with sulfophenylphthaloxones has been described elsewhere [2]. Ligand L was obtained by Mannich reaction at the interaction of phenol red (0.02 M) with excess (0.06 M) of 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (DO3A) and formaldehyde (0.06 M) at the 50°C during 30 h. Synthesis has been described in more detail previously [3]. Ligand L was obtained as a dark-orange solid in 84% yield. The purity of the prepared compound was controlled by ¹H NMR, mass spectroscopy, and TLC [3]. The preparation of the water-soluble Yb(Nd)-L complexes was as it has analogously been described for lanthanide complexes DO3A [4]. Data of elemental analysis prove that complexes with the ratio

¹ A. V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, 65080 Odessa, Ukraine.

² To whom correspondence should be addressed. E-mail: physchem@paco.net

Yb(Nd):L = 2:1 are formed (this ratio is 1:1 for the rest of the considered sulfophenylphthaloxones).

Luminescence spectra were obtained with a SDL-2 spectrofluorimeter with a photon counting system and a device for phosphorescence measurements (Leningrad Optic-Mechanical Association, St. Petersburg, Russia), Nd:YAG laser ($\lambda_{\text{exc}} = 532 \text{ nm}$) was used as an excitation source. The quantum yields for Yb³⁺ and Nd³⁺ ions in complexes (φ) were calculated by relative method using Zn-tetraphenylporphyrin as a standard, the quantum yield of which is 0.0315 [5]. The luminescence lifetimes (τ) were determined with a LGI-21 nitrogen laser, with pulse duration of 8–10 ns at a wavelength of 337 nm and analyzed by iterative reconvolution and non-linear least-squares method [6]. The radiation was detected by a liquid-nitrogen cooled Ge-detector (North Coast EO-817P) coupled to a C8-13 fast digital oscilloscope.

RESULTS AND DISCUSSION

A similarity between the absorption spectra and spectra of 4f-luminescence of the complexes indicate that ligand-to-lanthanide ion energy transfer takes place. Thus, the ligand absorbs the radiation and delivers the energy to the coordinated lanthanide ion. It has been previously established [7,8] that, for Yb³⁺ and Nd³⁺ ions, enough efficient 4f-luminescence is realized in water solutions of the complexes with some sulfophenylphthaloxones; the most important spectral-luminescent characteristics are given in more detail in Table I. In complexes with phthaloxone S, these characteristics are higher. It must be noted that the luminescence lifetimes for Nd

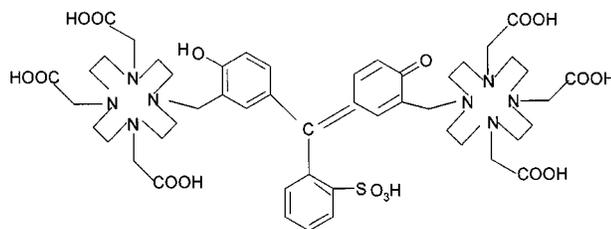


Fig. 1. Structure of the macrocyclic derivative of phthaloxone S (Ligand L).

complexes are shorter than for analogous Yb complexes, but the influence of solvent deuteration for Nd complexes is highest. The reason for this is the Yb³⁺ ions' less efficient overlap between the ²F_{5/2} excited state (10200 cm⁻¹) and the higher harmonics of the O-H oscillators (~3400 cm⁻¹). At the same time, it is evident that they can be improved in case coordination center will contain less number of water molecules (the inner coordination sphere of Ln-phthaloxone S contains 4–5 molecules of water, depending on lanthanide [3]). Therefore, encapsulation of a lanthanide ion in the macrocyclic cavity of a polydensity ligand containing also the chromophore moiety that plays the role of energy accumulator (“photoantenna”) is favorable [9]. We have established that complexes with ligand L (Fig. 1), where each of two lanthanide ions is coordinated by four nitrogen atoms of azacycle and three oxygen atoms of carboxylic groups contains two innersphere waters. Data for Yb and Nd-L complexes are given in Table II. Values of quantum yields and luminescence lifetimes are higher for these complexes (Table II) compared with those of phthaloxone S, other sulfophenylphthaloxone dyes, fluorescein derivatives [10], and some macrocyclic ligands (e.g., with porphyrins, calix[4]arenes, azamacrocycles) [11]. Nevertheless, increase of the luminescence lifetime in complexes with ligand L at the replacement of H₂O on D₂O is insignificant compared with sulfophenylphthaloxone complexes. Undoubtedly, it is the result of better protection of lanthanide ion in complex with ligand L from the quenching

Table I. Some Spectral-Luminescence Characteristics of Yb and Nd Complexes with Sulfophenylphthaloxones

Complex ^a	Position of T-levels, $E(\text{cm}^{-1})$	$\varphi \times 10^3$ (in D ₂ O)	$\tau(\mu\text{s})^b$	
			H ₂ O	D ₂ O
Yb-Phthaloxone S	14110	4.11	0.70	3.15
Yb-Xylenol orange	14030	4.96	0.60	2.70
Yb-Methylthymol blue	13870	1.90	0.40	1.60
Yb-Chrome azurol S	14250	1.06	0.25	1.35
Yb-Glycinthymol blue	13905	0.36	0.20	1.15
Yb-Glycincresol red	14015	0.20	0.15	0.80
Yb-Eriochrome cyanine R	14320	0.08	0.10	0.55
Nd-Phthaloxone S	14060	0.25	0.07	0.35
Nd-Xylenol orange	13950	0.21	0.06	0.30
Nd-Methylthymol blue	13750	0.08	0.05	0.25

^a All ligands were used as their sodium salts.

^b Errors are $\pm 10\%$.

Table II. Some Spectral-Luminescence Characteristics of Yb and Nd Complexes with Macrocyclic Derivative of Phthaloxone S (Ligand L)

Complex ^a	Position of T-levels $E(\text{cm}^{-1})$	$\varphi \times 10^3$ (in D ₂ O)	$\tau(\mu\text{s})^b$	
			H ₂ O	D ₂ O
Yb-L	14205	14.51	6.80	12.60
Nd-L	14220	2.34	0.75	1.45

^a The Ligand L was used as its sodium salt.

^b Errors are $\pm 10\%$.

affect of the higher harmonics of the O-H oscillators. It is envisaged that results of investigation of complexation of Yb³⁺ and Nd³⁺ ions with the ligand L in some organic solvents media will be published soon.

CONCLUSIONS

It has been proved that the high luminescent characteristics of complexes Yb³⁺ and Nd³⁺ with ligand L, excitation of 4f-luminescence by visible light, possibility to functionalize ligands by specific group (e.g., isothiocyanate) for further protein conjugation, allow these complexes (first of all, Yb³⁺) be considered as perspective luminescent labels.

ACKNOWLEDGMENTS

The National Academy of Sciences of Ukraine is acknowledged for financial support.

REFERENCES

1. Y. Haas and G. Stein (1971) *J. Phys. Chem.* **75**, 3677.
2. S. P. Sangal and A. K. Dey (1967) *Mikrochem. J.* **12**, 168.
3. N. Rusakova (1989) Ph.D. Thesis, A. V. Bogatsky Physico-Chemical Institute (Odessa).
4. D. D. Dischino, E. L. Delaney, J. E. Emswiler, G. T. Gaughan, J. S. Prasad, S. K. Srivastava, and M. F. Tweedle (1991) *Inorg. Chem.* **30**, 1265.
5. M. P. Tsvirko, G. F. Stelmakh, V. E. Pyatosin, K. N. Solovijov, T. F. Kachura, A. S. Piskarskas, and R. A. Gadonas (1986) *Chem. Phys.* **106**, 467.
6. D. V. O'Connor and D. Phillips (1984) *Time Correlated Single Photon Counting*, Academic Press, London.
7. N. S. Poluektov, S. B. Meshkova, and Yu. V. Korovin (1983) *Dokl. Akad. Nauk SSSR* **273**, 1422.
8. N. V. Rusakova, S. B. Meshkova, and N. S. Poluektov (1984) *Dokl. Akad. Nauk SSSR* **279**, 404.
9. N. Sabbatini and M. Guardigli (1993) *Coord. Chem. Rev.* **123**, 201.
10. M. H. V. Werts, R. H. Woudenberg, P. G. Emmerink, R. van Gassel, J. W. Hofstraat, and J. W. Verhoeven (2000) *Angew. Chem. Int. Educ.* **39**, 4542.
11. Yu. Korovin and N. Rusakova (2001) *Rev. Inorg. Chem.* **21**, 299.