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Emission spectroscopic properties of water soluble porphyrins in hydrogen peroxide chemiluminescence system with *d*- and *f*-electron metals

Krzysztof Staninski, Małgorzata Kaczmarek, Stefan Lis, and Marian Elbanowski*

Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, Poznań 60-780, Poland

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Abstract

Two water-soluble porphyrins: 4,4′,4″,4‴-(porphine-5,10,15,20-tetrayl)-tetrakis (benzoic acid) ($TCPPH_2$) and 4,4′,4″,4‴-(porphine-5,10,15,20-tetrayl)-tetrakis (benzenesulfonic acid) ($TSPPH_2$) have been subjected to spectroscopic study in the presence of *d*-electron metals: Zn(II) and Cu(II) and *f*-electron metals: La(III), Eu(III), Gd (III) and Yb(III). Results of the spectrophotometric study have provided evidence proving the complexation of Cu(II) and Zn(II) cations by porphine in water solutions and the complexation of lanthanide ions exclusively by peripheral carboxyl and sulfonic groups. For the first time, chemiluminescence of the systems containing porphyrins has been measured without the use of strongly luminescent reagents such as TCPO or luminol. The emission spectra of the systems porphyrin/metal ion/H_2O_2 have been recorded and the quantum yield of their luminescence has been measured. The absorption spectra of the systems recorded before and after the reaction in the presence of hydrogen peroxide are identical, which means that the porphyrin ring does not undergo destruction. A significant similarity between the fluorescence and chemiluminescence spectra indicates a possibility of excitation of porphyrins and their complexes in the reaction with hydrogen peroxide.

Keywords: Chemiluminescence; Absorption; Porphyrins; Zn(II); Cu(II); Ln(III) ions

Introduction

Reactions based on the phenomenon of chemiluminescence (CL) with involvement of porphyrins have found wide applications, especially in analytical aspects, e.g., for routine analysis in clinical laboratories [1–3]. The use of porphyrins has been stimulated by their high sensitivity and selectivity to metal ions. The reactions were performed with such compounds as luminol (5 amino-2,3-dihydro-1,4 phthalazinedione) or bis(2,4,6 trichlorophenyl oxalate) (TCPO), in a basic environment in the presence of hydrogen peroxide. The observed changes in the CL intensity were a result of the interaction between the excited products of oxidation and the complex formed by the porphyrin and the metal.

This paper presents the effect of hydrogen peroxide on porphyrins and their complexes without the use of strongly luminescent components (luminol or TCPO) studied in order to test the possibility of porphyrins excitation as a result of the chemical reaction. Spectrophotometric studies of the complexation of Cu(II) and Zn(II) as well as lanthanide(III) cations by porphyrins in water solution are evidenced.

Experimental

The study was performed on two porphyrins: 4,4′,4″,4‴-(porphine-5,10,15,20-tetrayl)-tetrakis(benzenesulfonic acid) tetrasodium salt ($TSPPH_2$) and 4,4′,4″,4‴-(porphine-5,10,15,20-tetrayl)-tetrakis(benzoic acid) ($TCPPH_2$), 98% FLUKA; Zn(II) and Cu(II) chlorides, extra-pure, FLUKA and hydrogen peroxide H_2O_2 35% pure for analysis FLUKA.

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*Corresponding author.

E-mail address: elbabmar@amu.edu.pl (M. Elbanowski).

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The lanthanide chlorides of La(III), Eu(III), Gd(III) and Yb(III) were obtained in the reaction of their oxides (99.9%, made in the Department of Rare Earth, Faculty of Chemistry, Adam Mickiewicz University) with HCl (pure for analysis FLUKA). The solutions were made with doubly distilled water.

The CL was measured for the water solutions of porphyrins and metal ions adding, on constant stirring, hydrogen peroxide in excess. The porphyrins were used in the concentrations 10^{-7}–10^{-6} mol/L. The spectra were recorded in the optimum conditions for M:L = 10:1, which ensured the formation of porphyrin–metal complexes. The intensity of CL and CL emission spectra were measured by the single-photon counting system described in [4]. The fluorescence spectra were measured by a modified Perkin–Elmer LS-50B spectrofluorimeter. The measurements of absorbance were made on a Shimadzu UV 2401 PC spectrophotometer.

Results and discussion

The absorption spectra of the porphyrins $TCPPH_2$ and $TSPPH_2$ in water solutions and the solutions containing one of the porphyrins and each of the metal cations studied were measured. The absorption spectrum of $TCPPH_2$ solution is shown in Fig. 1.

The introduction of Cu(II) or Zn(II) ions brought about characteristic changes in the *Q* band in the range 500–650 nm, indicating the metallation of the porphyrin ring. Very similar changes were observed for the solutions of $TSPPH_2$ with the ions Cu(II) or Zn(II). Analysis of the spectra of $TCPPH_2$ and $TSPPH_2$ solutions with the lanthanide ions added (in the Q band) proved that these ions were not complexed in the porphyrin ring cavity. It is supposed that the porphyrins studied can form complexes with lanthanide ions only through peripheral polar carboxylic or sulfonic groups, analogously to the situation in similar systems in methanol solutions [3].

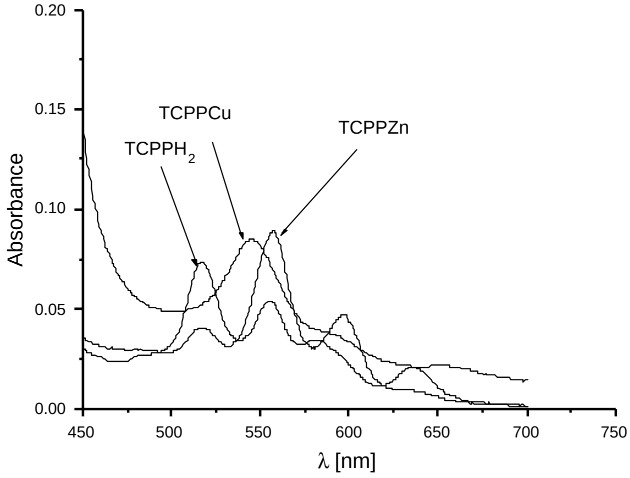

Fig. 1. The absorption spectra of $TCPPH_2$ and the TCPPCu and TCPPZn complexes for the porphine concentration 5×10^{-6} mol/L and the M:L ratio of 10:1.

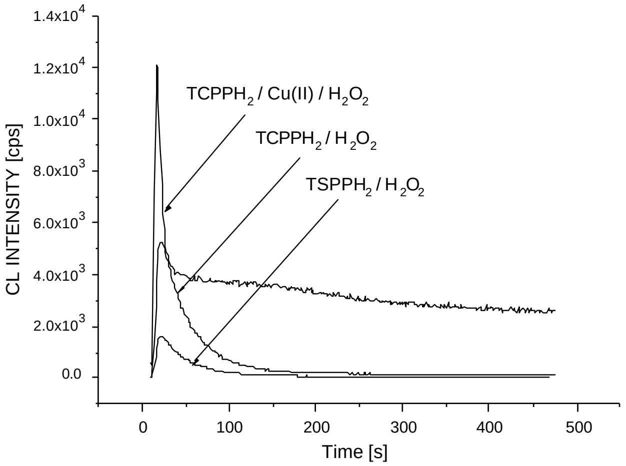

Fig. 2. The kinetic curves of CL in the systems $TCPPH_2/H_2O_2$ $TSPPH_2/H_2O_2$ and $TCPPCu/H_2O_2$ for the M:L ratio of 10:1 in solutions of pH 10.5.

The reaction of CL was initiated by addition of hydrogen peroxide to a solution containing $TCPPH_2$ or $TSPPH_2$ and individual types of the metal ions studied. The maximum intensity of emission was noted in the solutions of pH 10.5–11.0. Directly after the addition of hydrogen peroxide, the emission intensity rapidly increased and reached a maximum within a few seconds (Fig. 2). From that moment, the intensity of CL exponentially decreases, reaching the noise level in a few minutes.

As shown in Fig. 2, the kinetics of CL decay in the system $TCPPH_2/Cu(II)/H_2O_2$ is different from those of the other systems. The high and long-lasting intensity of emission recorded for this system suggests the occurrence of side processes related with catalytic decomposition of hydrogen peroxide and recombination of radicals formed as a result of this decomposition [5,6]. In this system, the exponential emission decay is probably disturbed by formation of dimols of singlet oxygen, whose weak emission in the range 540–630 nm was recorded simultaneously with that of the porphyrin complex.

The highest intensity of CL was noted for the system $TCPPH_2/Zn(II)/H_2O_2$. The character of CL emission decay was similar to those recorded for the systems $TCPPH_2/H_2O_2$ and $TSPPH_2/H_2O_2$, but its intensity was much higher, on average by 1.5 order of magnitude.

The quantum yield of CL, relative to that of a standard system (luminol/hemina/H_2O_2, pH 11.0), was in the range 10^{-9}–5×10^{-11} and reached a maximum for the system $TCPPH_2/Zn(II)/H_2O_2$. The intensities of CL in particular systems are presented in Table 1.

Table 1
Intensity of CL of the systems porphine/metal ion/H_2O_2 in arbitrary units, for the metal:ligand molar ratio 10:1 in solutions of pH 10.5

CL system	I_{CL} (a.u.)
$\mathrm{TCPPH_2\backslash H_2O_2}$	100
$\mathrm{TCPPH_2\backslash La(III)\backslash H_2O_2}$	86
$\mathrm{TCPPH_2\backslash Eu(III)\backslash H_2O_2}$	73
$\mathrm{TCPPH_2\backslash Gd(III)\backslash H_2O_2}$	80
$\mathrm{TCPPH_2\backslash Yb(III)\backslash H_2O_2}$	76
$\mathrm{TSPPH_2\backslash H_2O_2}$	27
$\mathrm{TSPPH_2\backslash La(III)\backslash H_2O_2}$	24
$\mathrm{TSPPH_2\backslash Eu(III)\backslash H_2O_2}$	25
$\mathrm{TSPPH_2\backslash Gd(III)\backslash H_2O_2}$	21
$\mathrm{TSPPH_2\backslash Yb(III)\backslash H_2O_2}$	26
$\mathrm{ZnTCPP\backslash H_2O_2}$	1450
$\mathrm{ZnTCPP\backslash La(III)\backslash H_2O_2}$	1210
$\mathrm{ZnTCPP\backslash Eu(III)\backslash H_2O_2}$	980
$\mathrm{ZnTCPP\backslash Gd(III)\backslash H_2O_2}$	950
$\mathrm{ZnTCPP\backslash Yb(III)\backslash H_2O_2}$	890
$\mathrm{ZnTSPP\backslash H_2O_2}$	210
$\mathrm{ZnTSPP\backslash La(III)\backslash H_2O_2}$	208
$\mathrm{ZnTSPP\backslash Eu(III)\backslash H_2O_2}$	206
$\mathrm{ZnTSPP\backslash Gd(III)\backslash H_2O_2}$	209
$\mathrm{ZnTSPP\backslash Yb(III)\backslash H_2O_2}$	211

The relative error of the CL intensity values is 13%.

The intensities of CL of the systems containing $TCPPH_2$ are higher than those containing $TSPPH_2$. The presence of Zn(II) cations causes a significant increase of the CL intensity, whereas the presence of all lanthanide cations causes its small decrease. This decrease is stronger in the systems containing $TCPPH_2$ than in those with $TSPPH_2$, in which it is practically non-existent taking into regard the accuracy of the measurements.

In order to check the influence of *Ln*(III) ions on the CL of the systems, porphyrin/Zn(II), CL was also measured in the systems, of a solution of TCPPZn or TSPPZn complexes and lanthanide ions (Table 1). For the system with TCPPZn complexes, the CL emission was also decreased by the *Ln*(III) ions.

The CL emission spectra were studied using the cut-off filters method.

The spectra of CL and fluorescence of the porphyrins and their complexes were found very similar (Fig. 3). As in the basic environment used in our study, the reactions of autocatalytic decomposition of H_2O_2 leading to formation of singlet oxygen can occur, it is reasonable to conclude that the process of CL may involve excitation of the porphyrins studied and their complexes [4,5,7]. This excitation can occur as a result of the transfer of energy released during the decomposition of hydrogen peroxide and recombination of the radicals to a molecule of the porphine complex. Similar processes of excitation of lanthanide complexes have already been noted in the systems containing aminopolycarboxylic acids [8] and cryptands [9] as ligands. In order to verify the effects of H_2O_2 addition to the solutions studied, their UV/VIS spectra were taken before initiation of CL and after the reaction. In the spectral range analyzed (300–700 nm), these spectra were identical, which means that during the process of CL the pirol ring in the porphines and their complexes is not destroyed.

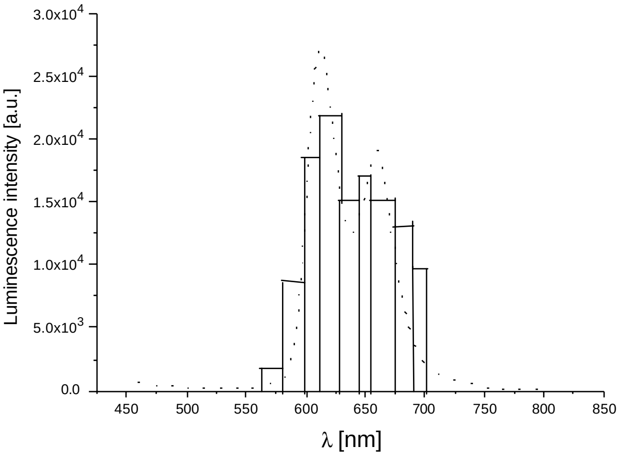

Fig. 3. The spectrum of CL of TCPPZn(II)/H_2O_2 and luminescence of TCPPZn (broken line) in a solution of pH 10.5 for the M:L ratio of 10:1. The concentrations of TSPPZn and H_2O_2 are 5×10^{-6} and 10^{-2} mol/L, respectively.

The phenomenon of increased emission in the systems containing, e.g., zinc ions has been observed earlier and has been interpreted as related to the diamagnetic character of Zn(II) cation [10,11], whereas no such effect has been noted for the paramagnetic cations like, e.g., Cu(II) [12]. This difference stems from the existence of trip-multiplet states due to the mixing of the spin multiplicity of the paramagnetic metal center and the porphyrin ring itself. It is important to note that the resultant multiplicity of the trip-multiplet state at higher energy ($^2T_1$) has formally got the same spin multiplicity as the ground-state molecule ($^2S_0$) thus a spin-allowed transition is enabled for relaxation this way [12].

As follows from the hitherto studies on the influence of Cu(II) ions on the emission of porphines, these ions showing paramagnetic character are effective quenchers of this emission [3,12,13]. According to our results, the intensity of CL in the systems TSPPCu(II)/H_2O_2 and TCPPCu(II)/H_2O_2 increases probably as a result of the side radical processes, manifested as the additional emission bands of singlet oxygen dimols appearing in the range 520–600 nm [5,10,14].

The suppression of the porphyrin emission by the paramagnetic lanthanide ions could be interpreted as the effect of the heavy atom enhancing the spin–orbit coupling leading to deactivation of the excited level through the intersystem crossing [15,16]. Moreover, it has been shown that an important role in the quenching process can play the electron transfer from the excited porphyrin/Zn complex to the *Ln*(III) ion [16].

Conclusions

The CL of the systems of porphyrin/metal ion/hydrogen peroxide has been studied for the first time without the use of strongly luminescent reagents (luminol, TCPO). The results have proved the possibility of porphyrin excitation in a chemical reaction involving hydrogen peroxide and processes of its decomposition in an alkaline environment. The metals complexing in the porphine molecule cavity that is Cu(II) and Zn(II) cause an effective increase in CL intensity, while the lanthanide ions *Ln*(III) cause a small quenching of the CL. In the systems with Zn(II), the observed increase in I_{CL} is a result of the additional involvement of singlet oxygen in the reaction.

This phenomenon has been hitherto observed only for the porphines with the carboxyl groups as peripheral groups [15]. The phenomenon of CL suppression by *Ln*(III) ions in the system TCPPZn\H_2O_2, in which the cavity is blocked by Zn(II) ions, confirms the fact that it is directly related to the lanthanides complexation by the carboxyl groups.

Acknowledgments

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