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Indication and identification of hazardous substances

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Tetraphenylporphyrine based nanosized film elements for detection of Eu(III) cations in water by fluorescent method

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Abstract – Monomolecular layer of tetraphenylporphyrin mixed with stearic acid transferred onto modified quartz plates is shown to exhibit fluorescent properties sensitive to the presence of europium(III) cations in aqueous media. A principal possibility of producing a sensor element for quantitative determination of europium in water is proposed, and its performance parameters are determined.

Keywords: water analysis, europium, porphyrins, fluorescence, thin films.

Наноразмерные пленочные элементы на основе тетрафенилпорфирина для обнаружения катионов европия в воде флуоресцентным методом

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Аннотация – Показано, что мономолекулярный слой тетрафенилпорфирина в смеси со стеариновой кислотой, перенесенный на модифицированные кварцевые пластины, проявляет флуоресцентные свойства, чувствительные к присутствию катионов европия(III) в водных средах. Предложен сенсорный элемент для количественного определения европия в воде и определены его рабочие параметры.

Ключевые слова: анализ воды, европий, порфирины, флуоресценция, тонкие пленки.

INTRODUCTION

Macrocyclic tetrapyrrole compounds and their numerous metal complexes are widely used in a variety of applications related to ensuring chemical safety and environment protection issues. Thus, metal complexes of porphyrins and phthalocyanines are known to induce reactive oxygen species and can effectively deactivate pathogenic microorganisms due to the relevant catalytic [1–3] and photocatalytic [4] activity. In addition, intense absorption bands in the electronic spectra of porphyrins make it possible to use these compounds for sensitive analysis of various chemical and biological species [5]. Since fluorescent properties of tetrapyrroles are able to change significantly in the presence of specific compounds, they can be potentially used for developing sensor elements based on fluorescence based detection principle [6, 7].

It is well known that fluorescence of many dyes is quenched by rare-earth element (REE) ions, including ions of certain lanthanides, both in solutions and solid media [8]. In that regard, it would be interesting to find out the extent of sensitivity of fluorescence parameters of tetrapyrroles to the presence of various lanthanides ions.

It bears mentioning that toxicity issues of lanthanide compounds have not been adequately studied, although there are available literature data allowing us to classify REE compounds as low toxic substances [9–13]. Nevertheless, monitoring the circulation of lanthanides in the environment is of great importance, since the list of applications of these metals is rather long [14–17], it involves not only their use in technologies for manufacturing optical and luminescent items, but also developing materials applied as magnets, catalysts, alloys, components of medical devices, nanomaterials, etc.

In this work, we are considering an effect of quantitative response of lanthanide cations in aqueous solutions to the fluorescence of zinc complex of tetraphenylporphyrin immobilized in nanosized films on a solid surface with the aim of potential using this effect in sensor devices for control the content of lanthanide cations in an aqueous medium.

EXPERIMENTAL

The zinc complex of tetraphenylporphyrin (ZnTPP) of spectral purity was synthesized at Ivanovo State University of Chemical Technology. The structure of the complex is shown in Figure 1. The identity and purity of ZnTPP were additionally confirmed by MALDI mass spectrometry on a Thermo DSQ II instrument.

Nanosized films were obtained using a molecular layering unit (Joyce Loebl, UK) [18]. The preparation of the substrates was carried out using a procedure of modifying quartz plates 10 x 44 x 1 mm by applying monolayers of stearic acid (SA) formed on the surface of a subphase (bidistilled water containing 0.05 M KCl, pH 6.5). To obtain a monolayer of SA, 150 μl of the 1 mM SA solution in chloroform was applied with a microsyringe. The formed monolayers with a barrier velocity of 2.5 mm/s and a surface pressure of 30 mN/m were transferred onto the quartz plate by vertical lifting at a speed of 0.3 mm/s according to the Langmuir-Blodgett method. Polar or nonpolar substrates were obtained by transferring in this way 10 or 11 SA-monolayers, respectively.

A monolayer of ZnTPP was obtained by the procedure involving a dropwise addition of 150 μl of the 0.5 mM solution of ZnTPP in 1 mM SA in chloroform onto the surface of the same subphase. A monolayer was formed in the same conditions as in the case of the preparation of SA films. Next, one monolayer of the mixture of ZnTPP and SA was transferred by vertical lifting onto polar or nonpolar substrates, thereby obtaining a nonpolar or polar working surface of the sensor element, respectively. The subphase temperature was 22°C in all the experiments with the air humidity in the installation of 50 ± 5%.

Substrates with polar and nonpolar ZnTPP monolayers were immersed in 8 ml of aqueous solutions of the $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$, $EuCl_3$, $GdCl_3$, $TbCl_3$, $DyCl_3$, $HoCl_3$, $ErCl_3$, $TmCl_3$, $YbCl_3$, or $LuCl_3$ salts solutions (provided by colleagues from Russian Technological University MIREA) with the concentrations in the range of 10^{-8}–10^{-4} M in such a manner that the size of the monolayer area contacting with the solution was 26 x 10 mm. The temperature of the solution was maintained at 25°C. After 10 min, the plates were removed from the solutions, washed with bidistilled water, and dried in the air. After that, fluorescence spectra were recorded for the samples in the range of 600–750 nm upon excitation at a wavelength of 430 nm, which corresponds to the maximum absorption of ZnTPP.

Fluorescence spectra were recorded on a Shimadzu RF 5000 spectrofluorimeter (Japan) using a ZhS-16 yellow filter with cutting off scattered light. Quartz plates with the monolayers were placed at an angle of 45° in the path of the incident light. The spectra were processed using the Origin 6.1 computer program with measuring the integrated intensity (S) as the area under the spectrum curve.

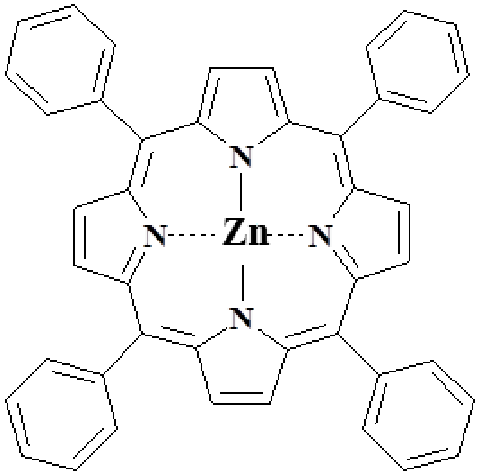

Fig. 1. Structure of zinc complex of tetraphenylporphyrin (ZnTPP).

RESULTS AND DISCUSSION

The molecular layering procedure applied in this study provides obtaining multilayers in which the external molecular layer is polar or nonpolar depending on the orientation of the stearic acid (SA) molecule. The thickness of the films obtained by this procedure was determined by the number of the monolayers and varied in the range of 20–25 nm (this evaluation is relied on the fact the length of the SA molecule is about 2 nm).

ZnTPP molecules immobilized in the films containing SA, retain their inherent fluorescence with a maximum of ~660 nm. At the same time, the fluorescence spectra are independent of the orientation of the SA molecules. ZnTPP fluorescence spectra were not affected by soaking the films of polar and nonpolar structure in water.

When polar films were maintained in $EuCl_3$ solutions, an effect of quenching ZnTPP fluorescence was observed (Figure 2). Furthermore, we revealed that the quenching became noticeable at the $EuCl_3$ concentration of $1 \cdot 10^{-8}$ M with its intensification up to the $EuCl_3$ concentration of $1 \cdot 10^{-4}$ M. The quenching coefficient was estimated as S_0/S ratio, where S_0 and S are the integrated intensities in the absence and in the presence of lanthanide ions, respectively, and was found to be 2.4 (extrapolation error ± 0.2). At higher concentrations of europium chloride, no more quenching of ZnTPP fluorescence was observed.

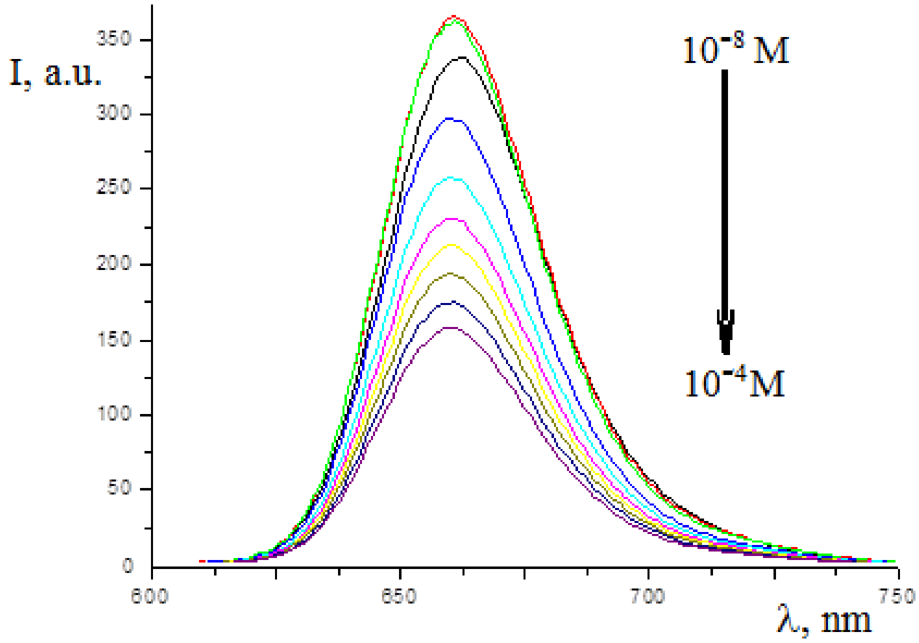

Fig. 2. Fluorescence spectra of ZnTPP in polar films mixed with stearic acid on quartz plates after contact with water (red line) and with $EuCl_3$ solutions with the concentration of $1 \cdot 10^{-8}$, $5 \cdot 10^{-8}$, $1 \cdot 10^{-7}$, $5 \cdot 10^{-7}$, $1 \cdot 10^{-6}$, $5 \cdot 10^{-6}$, $1 \cdot 10^{-5}$, $5 \cdot 10^{-5}$, $1 \cdot 10^{-4}$, and $1 \cdot 10^{-4}$ M (the color of lines changes from green to purple).

It is noteworthy that the fluorescence intensity demonstrated only a slight decrease after contacting ZnTPP films with the aqueous solutions of the salts of other metals of the lanthanide series. Moreover, fluorescence intensity even remained unchanged in the cases of the solutions of cerium and dysprosium chlorides. The data for the ZnTPP fluorescence quenching coefficients in polar films for the cases of their interaction with chloride solutions of various lanthanides studied are shown in Table 1 for the concentration of $1 \cdot 10^{-4}$ M.

Table 1. Fluorescence quenching coefficients of ZnTPP in polar films upon contact with lanthanide chloride solutions with the concentration of $1 \cdot 10^{-4}$ M for 10 min

REE	La^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
S_0/S	1.2	1.1	1.4	1.1	2.4	1.1	1.1	1.1	1.1	1.2	1.4	1.1

Examples of the relatively high quenching ability of europium(III) cations (compared to the related lanthanide metals) with respect to the luminescence of a number of fluorophores (Flu), such as anthracene, phenanthrene, and phenosafranin, are described in the literature [8]. In [19], it was proposed that the reason for the relatively high degree of quenching of fluorescence of aromatic compounds by Eu^{3+} ions is the reversible electron transfer in accordance with the following mechanism:

$$\text{Flu}^* + \text{Eu}^{3+} \rightarrow \text{Flu}^{+} + \text{Eu}^{2+},$$

where Flu* and Flu^{+} are fluorophore excited state and its radical cation, respectively. We suppose that the selective ability of Eu^{3+} of quenching fluorescence of dyes is due to the fact that the Eu^{3+} cation has the highest electron affinity compared to that for other ions of REEs, thus, it can be relatively easily reduced to Eu^{2+}. In the studied cases of ZnTPP fluorescence, the europium chloride solution turned out to be the only example among the considered systems which exhibited the significant quenching ability. Therefore, we can conclude that it is possible to use the investigated systems for selective determination of Eu^{3+} cations in aqueous media. This statement is consistent with the experimental data obtained for the aqueous solutions containing mixtures of two to four lanthanides of different nature. In contrast to the $EuCl_3$ solution, the effect of quenching of fluorescence of ZnTPP changed insignificantly in these systems (Table 2).

Table 2. Fluorescence quenching coefficients of ZnTPP in polar films upon contact with the mixtures of lanthanide chloride solutions with the concentration of $1 \cdot 10^{-4}$ M for 10 min

REE	$Eu^{3+} + Sm^{3+}$	$Eu^{3+} + Dy^{3+}$	$Eu^{3+} + Tb^{3+} + Gd^{3+}$	$Eu^{3+} + Sm^{3+} + Yb^{3+} + Nd^{3+}$
S_0/S	2.2	2.3	2.0	2.2

As far as nonpolar films are concerned, their contact with the solutions of lanthanide salts produced no changes in the ZnTPP fluorescence spectrum even at high salt concentrations, which allows us to conclude that diffusion of the cations into the nonpolar film is not observed. In the case of polar surfaces, one can assume an active involvement of the surface carboxyl groups of SA into the binding of metal cations.

Thus, the detection of europium (III) salts can be performed by fluorescence method. The data obtained in this study are of interest for the development of portable devices for monitoring the content of europium (III) cation presence in natural and waste waters. Sources of europium emissions into the environment come from various industrial sectors, such as metallurgy, hydrogen and nuclear energy industries, manufacturing of laser and luminescent materials, medical industry, etc. [20].

CONCLUSION

In summary, applying the molecular layering procedure makes it is possible to obtain a miniature element on quartz plates that is found to be sensitive to the presence of europium(III) cations in water. Thus, a principle possibility is demonstrated to create a polar contact layer containing a fluorescent dye. The sensitivity of the obtained sensor element is $1 \cdot 10^{-8}$ M, the detection time is 10 min. The time for recording the fluorescence spectrum does not exceed 1 min. The advantages of the element are its high selectivity towards the analyte, the relative ease of its preparation, a possibility of its serial production, and availability of the required components. Further research can be focused at studying the effect of water quality by this analytical procedure.

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