POLARIZED FLUORESCENCE OF MONOANIONS OF Zn-OCTAETHYLPHLORIN

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We investigate the luminescent properties (radiation spectrum, polarized spectrum) of the monoanions of Zn-octaethylphlorin, which is an intermediate product of the reduction reaction of porphyrins. An oscillator model is presented that includes three electronic oscillators, with a long-wave one being oriented perpendicularly to the remaining two. The lifetime of the excited singlet state $\tau = 30 \pm 13$ nsec is estimated.

Key words: porphyrin anions, luminescence spectrum, polarized spectrum, lifetime of excited state, oscillator model.

Investigation of the spectral properties of tetrapyrrole compounds on their redox transformations gives insight into the change in the structure of molecules in the course of reactions. Using mainly spectroscopic methods, it has been proven that the reaction of reducing porphyrin molecules proceeds through some intermediate stages with the formation of radical-anions, dianions, and of their protonated forms [1, 2]. At the present time the structure of all the intermediate and final products of the reaction is determined reliably, but the spectroscopic properties have not been investigated in detail for all of the intermediates. In particular, there is not enough information on the luminescence of anions of the phlorins that are intermediate products of the reduction process. There are no data altogether on the anisotropy of light emission by these molecules that are of use for interpreting absorption spectra.

In the present communication we give the results of an investigation of the luminescence properties (radiation spectrum, polarized spectrum, lifetime of the excited state) of monoanions of Zn-octaethylphlorin ([$\text{ZnOEPN}^-$]):

Due to an excess electronic charge, these objects have a high reactivity. Their participation in the reduction process has been proven by pulsed photolysis [3, 4]. But it is difficult to investigate the properties of the monoanions of phlorins directly in the course of a reduction reaction due to their short lifetime. One succeeds in obtaining stable phlorin-anions under model conditions when protonating the dianions of porphyrins (P):

Fig. 1. Absorption spectra of a solution of [ZnOEPN]⁻ in THF at a room temperature (1), in THF + diethyl ether in a ratio of 1:1 at 77 K, the concentration is increased (2); the luminescence spectrum at 77 K, λ_exc = 450 nm (3); the polarized spectrum at 77 K, λ_reg = 890 nm (4).

For the first time phlorin-anions were obtained by this technique in [5]. An investigation of the spectral properties of the anions of phlorins is presented in [6]; their luminescence is described in [7]. It should be noted, however, that in [7] fluorescence spectra are given in a limited spectral interval, and our data differ slightly from the results given there.

The technique for obtaining [ZnOEPN]⁻ corresponds in the main to that described above [1] and consists in the following. A solution of Zn-octaethylporphin (ZnOEP) in carefully purified tetrahydrofuran (THF) was brought into contact with a sodium mirror under vacuum. This caused a sequential transformation of the initial Zn-octaethylporphin into anion-radicals and dianions. The reduction process was controlled by absorption spectra. At the stage of the formation of dianions, a portion of methanol vapors was distilled into a frozen solution of [ZnOEPN]²⁻ under vacuum. The product formed was [ZnOEPN]⁻. We found that [ZnOEPN]⁻ in tetrahydrofuran with traces of methanol was insufficiently stable: a gradual reduction of the absorption bands of [ZnOEPN]⁻ and an increase in the absorption bands of the initial porphyrin were observed for some hours at room temperature. But if we evaporate the solvent, keep the precipitate for one hour in a vacuum, and distil the dried tetrahydrofuran, we will not observe changes in the absorption spectrum with time. To obtain a vitrifying mixture, which was necessary for polarization measurements, we distilled dried tetrahydrofuran and diethyl ether in a volume ratio of 1:1. The absorption spectra were recorded on SF-10 and Beckman UV 5270 spectrophotometers. Fluorescent measurements were conducted on a setup described in [8].

The absorption and luminescence spectra of [ZnOEPN]⁻ are presented in Fig. 1. The absorption spectrum at room temperature is characterized by a wide band with a maximum in the 800 nm region and an intense band at 456 nm and corresponds to the spectrum described in [5-7]. At 77 K (curve 2) the maxima in the absorption bands are displayed at 815 and 450 nm, respectively. The maximum in the luminescence spectrum at 77 K lies at 885 nm. The absorption bands with the maxima at 574, 538, and 408 nm belong to regenerated ZnOEP. It should be noted that it is virtually impossible to carry out a reaction with a 100-percent yield of anion-phlorins. Our observations and the data of [6] show that on addition of methanol to a solution of dianions, one always observes in the absorption spectra bands of the initial porphyrin or of higher-charged protonated forms, as impurities. This seems to be due to the fact that, in addition to dianions, the solution always contains small amounts of anion-...