

STUDY OF THE Zn-PORPHYRIN STRUCTURE BY FLUORESCENCE SPECTROSCOPY METHODS^{**}

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Results of investigation of the optical properties of zinc complexes of mesotetraphenylporphyrin and monopyridyltriphenylporphyrin in impurity-free organic solvent are presented. Analyses of absorption and emission spectra and fluorescence decay kinetics in terms of both a sum of exponentials and using simulation of energy-transformation processes in a tetramer-type Zn-porphyrin complex compound are carried out.

Key words: *coordination porphyrin compounds, tetramer-type structure, depolarization, energy transfer, simulation.*

Introduction. Investigation of the optical properties of porphyrin compounds has gained wide acceptance during the last decade, mostly because of their potential applications in photovoltaic cells. In addition, the possibilities of producing solid-state solar cells by synthesis of semiconductors with porphyrin compounds have been intensely explored [1].

A relatively large splitting or shift in the region of the Soret absorption band is frequently observed in the optical absorption spectrum of ordered porphyrin films. The magnitude of the shift or splitting of the Soret band contains information on the relative distance and orientation of molecules in the compound [2]. For dimers with a known structure in solution, the first (point dipole) approximation of magnitudes of the shift and splitting of the Soret band is known from Kasha's theory [3]. For ordered films, this theory is not valid. Due to this, the synthesis and investigation of the organic system of well-structured aggregates, being an intermediate link between dimers on the one hand and ordered films on the other hand, are of considerable interest.

In the present work, we make an attempt at investigating an intermediate system of this type using the zinc complex of 5-(4-pyridyl)-10,15,20-triphenylporphyrin as an example of the system. Measurements of absorption and luminescence spectra, and fluorescence intensity and anisotropy decay kinetics of the above porphyrins are carried out. Possible forms and compounds of porphyrin aggregates in solutions are investigated. Simulation methods [4, 5] were used for the analysis of fluorescence decay kinetics.

Chemicals. Porphyrins and their zinc complexes were synthesized according to the previously described methods [6, 7]. Samples were prepared by dissolving Zn-porphyrin in toluene distilled over metallic sodium (A, 10^{-5} M Zn-meso-tetraphenylporphyrin (ZnTPP); B, 10^{-5} M ZnTPP with 10^{-5} M pyridine (Py) added; C, 10^{-5} M Zn-5-(4-pyridyl)-10,15,20-triphenylporphyrin (ZnMPyTrPP)).

Experimental. Optical spectra of the samples A, B, and C were recorded within the temperature range of 278-328 K (Cary SE spectrometer and Perkin-Elmer spectroluminometer).

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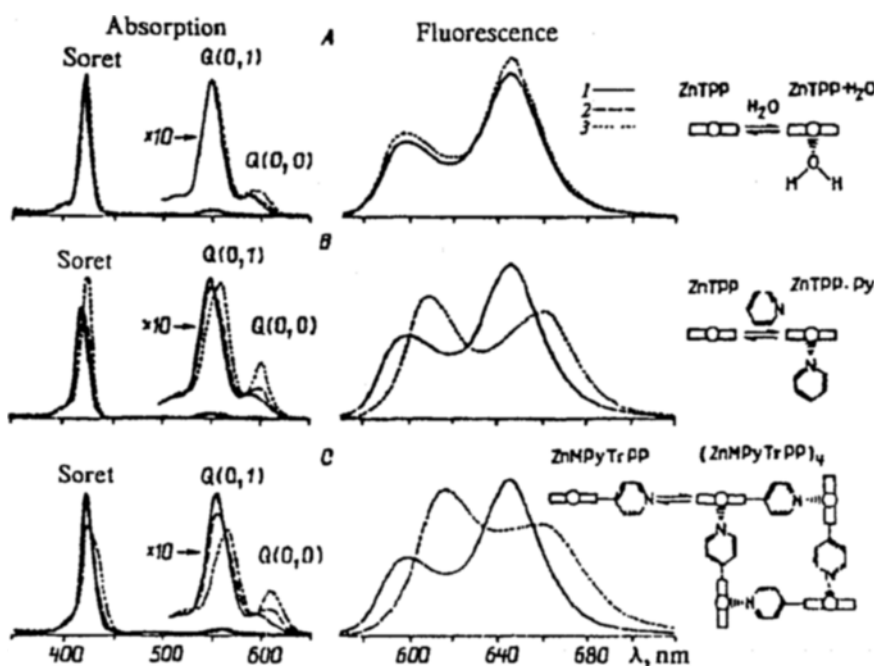


Fig. 1. Absorption and fluorescence spectra; $T = 328$ (1), 308 (2), and 283 K (3); $\lambda_{\text{exc}} = 512$ nm

Decay curves of vertically and horizontally polarized fluorescence components were recorded by the single-photon-counting method, described in detail in [8]. For detection of luminescence decay kinetics of the samples *A*, *B*, and *C*, emission wavelengths of nonliganded (597 nm), liganded (611 nm), and complexed tetramer forms (625 nm) were selectively chosen. Intensity decays were recorded at 283, 308, and 328 K. The number of detection channels was equal to 1024. The detection channel width was 11.11 ps.

Experimental data were analyzed using the Fluorescence Data Processor software developed at the System Analysis Department of the Belarusian State University. The multiexponential model [9] was used for approximation of fluorescence and fluorescence anisotropy decays.

Analysis of Absorption and Luminescence Spectra. As a result of cooling of the solution of sample *A*, a small increase in the concentration of liganded ZnTPP molecules is clearly observed in the absorption spectra (Fig. 1A) (absorption at ~ 605 nm manifesting itself as a stretched shoulder of the 585-nm band). Possible ligands are H_2O molecules (less than 1% in the solution). Very weak temperature effects are revealed in the luminescence spectra (Fig. 1A).

A decrease in the temperature from 328 to 278 K leads to shifts of the $Q(0, 0)$ and $Q(0, 1)$ maxima of the visible absorption bands and of the Soret band of the sample *B* from 589 to 601 nm, from 550 to 561 nm, and from 423 to 428 nm, respectively (Fig. 1B). These effects are due to coordination of pyridine molecules with the metal atom. As a result of dissociation of the ZnTPP·Py complex at relatively high temperatures, the luminescence spectra (Fig. 1B) are similar to those of sample *A*. At low temperatures, both luminescence bands of sample *B* are shifted to the long-wavelength range, which also does not contradict the shifts of the absorption bands.

Cooling of the sample *C* solution leads to formation of a coordination compound via the Zn-pyridine ligand, which follows from the shift of the Q -bands in the absorption spectrum (Fig. 1C) [10, 11]. The shifts from 550 to 560 nm and from 589 to 604 nm of the $Q(0,1)$ and $Q(0,0)$ bands, respectively, are similar to those of sample *B*. Therefore, these effects are due to an increase in the concentration of liganded molecules as a result of cooling of the solvent to 283 K. However, the Soret band is split into two components, one of which is shifted toward the red region (from 422 to 430 nm), and the other of which is virtually not shifted with respect to the monomer band (328 K, 423 nm). The splitting of the Soret band assumes the presence of only 50% of liganded forms, which is

substantiated by the dimer model proposed in [12], but contradicts conclusions based on the shifts of the Q -bands. By taking into account the shift of the absorption Q -bands, one can assume that the simplest structure explaining the behavior of the absorption spectra is a symmetric tetramer, schematically shown in Fig. 1C. Splitting of the tetramer Soret band is explained by an additional excitonic interaction in the S_2 state between two molecules whose planes are normal to each other. The dipole approximation for the excitonic interaction of associated molecules is known from Kasha's theory [3]. On its basis, the blue-shifted component is a result of an interaction between parallel transition dipole moments (both are oriented parallel to the mutual molecular axis), and the nonshifted component is a result of an interaction of mutually perpendicular transition dipole moments. The general effect of liganding manifests itself as the red-shifted component of the Soret band. The virtually nonshifted component is a result of the blue excitonic shift and the red liganding-induced shift. At a relatively high temperature, at which no liganded forms are present, the luminescence spectra (Fig. 1C) are similar to those of sample A, and upon cooling, they become similar to the spectra of sample B.

Analysis of the Fluorescence Intensity and Anisotropy Decay Kinetics of Zn-Porphyrins. Results of an analysis of experimental data in terms of multiexponential models for fluorescence intensity and anisotropy agree with the conclusions drawn in the investigation of the optical spectra. The fluorescence lifetimes of liganded forms differ insignificantly from those of nonliganded molecules.

Two rotational correlation times were detected at the wavelength of 597 nm: a short time (~ 0.05 - 0.10 nsec) with a relative contribution of $\sim 96\%$ and a long time (~ 10 nsec) with a relative contribution of $\sim 4\%$. It can easily be assumed that the 96% contribution is due to the monomer emission and the 4% contribution is due to luminescence of relatively large aggregates. This notion makes it possible to assume that nonliganded monomer molecules form small aggregates of unknown structure in solution. The presence of a single short rotational correlation time detected for all samples at $\lambda = 611$ and 625 nm is explained by the 100% contribution of the monomer forms.

Fluorescence of ZnMPyTrPP porphyrin at $\lambda_{\text{rec}} = 625$ nm at all temperatures is initially substantially depolarized ($r_0 \approx 0.08$ - 0.10). The temperature invariance of the depolarization bears witness to the fact that this effect is not due to reorientation of absorption and emission dipole moments, but rather takes place as a result of other depolarizing effects, in particular, energy transfer in the tetramer compound under investigation. In this case, the exponential model is not adequate for a description of fluorescence intensity and anisotropy decays. To investigate the fluorescence-intensity decay kinetics in more detail, we employed simulation methods making it possible to reproduce in detail energy-relaxation processes in tetramer-type porphyrin assemblies.

Investigation of Fluorescence Decay Kinetics of Porphyrins by Simulation Methods. The analysis consists of approximating experimental data by a theoretical function obtained in simulations [13]. Three optophysical processes – fluorescence, energy transfer, and nonradiative transitions given by exponential distribution laws – are simulated by the Monte Carlo method [14] for each tetramer compound molecule (sample C). In addition, the existence of exponentially fluorescing free ZnMPyTrPP molecules is taken into account.

Most universal search methods for parameter recovery such as the Nelder–Mead algorithm and its modifications employing the simulated annealing method [15] were used for estimation of the parameters of the simulation model.

Discussion. To provide a comprehensive study of the porphyrin systems, the simulation model developed was used for an analysis of fluorescence decay curves for all experimental data sets. In what follows, we review the main results of the analysis of fluorescence decay kinetics in terms of the simulation model.

Results of the analysis of fluorescence of samples A, B, and C detected at $\lambda = 597$ nm suggest that more than 95% of luminescence originates from free monomer, and less than 5% is emitted by more complex compounds. These results do not contradict conclusions drawn based on an analysis of the anisotropy decay in terms of a sum of exponentials. Thus, luminescence of compounds with an unknown structure (possibly, monomer assemblies) is detected at $\lambda = 597$ nm.

A certain increase (~ 13 - 19%) in the relative contribution of associated porphyrin molecules has been found for the samples A and B whose luminescence intensity was detected at $\lambda = 611$ nm. Under these conditions, luminescence of liganded forms is predominantly detected, which is also substantiated by the results of

investigations of the optical spectra. However, the simulation model taking into account tetramer-type compounds does not provide an adequate description of fluorescence from liganded forms of ZnTPP.

As has been pointed out earlier, fluorescence of the sample C detected at $\lambda = 625$ nm is originally depolarized. One of the possible reasons for the depolarization is the energy transfer in the tetramer-type structure formed. This assumption was corroborated by investigation of the fluorescence decay kinetics of sample C, which has shown that at a relatively low temperature (278 K) the contribution of complex tetramer porphyrin compounds to the total luminescence is relatively high (~43% found). For high temperatures, a decrease in the relative content (~30-35% found) of complex porphyrin molecules was detected. A certain increase in the relative content of the coordination structures with possible energy transfer (~30-43% within the temperature range investigated) explains the temperature invariance of the depolarization. It should be pointed out that this behavior of the system under consideration is also substantiated by results of investigation of the optical spectra.

The results of the simulation-based analysis of the fluorescence decay curves of porphyrins substantiate the conclusions drawn upon investigating the optical absorption and luminescence spectra of porphyrins. It should also be added that the hypothesis on the existence of the tetramer-type structure in an impurity-free solution of ZnMPyTrPP is also substantiated and does not contradict the results of the simulation-based analysis. To draw a more rigorous conclusion, the full set of possible structures in this system (trimers, fast dissociation reactions, etc.) should be considered.

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