ANALYSIS OF THE STRUCTURE OF THIN FILMS OF Zn-PORPHYRINS BY THE KINETICS OF THE FLUORESCENCE ANISOTROPY[*]

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The structure of thin films of Zn-tetraoctylphenylporphyrin (ZnTOPP) obtained by the spinning method is investigated. The kinetics of the decay of the fluorescence anisotropy of the films is analyzed in the form of a sum of exponents and by simulating the orientation of ZnTOPP complexes on the substrate (quartz) surface with allowance for the processes of the electron excitation energy transfer. The ZnTOPP films have a lamellar structure where individual layers form ordered domains. Within a domain, linear nonintersecting stacks of molecules are formed. In each stack the planes of the molecules are collinear, oriented perpendicularly to the surface of the substrate base, and form an angle of 45° with the directing axis of a stack.

Keywords: *thin films, Zn-tetraoctylphenylporphyrin, decay of the fluorescence anisotropy, simulation, electron excitation energy transfer.*

Introduction. Time-dependent fluorescent analysis — a direct method of determining the reaction rate constants of molecules in excited electronic states — is advantageously used in investigating the processes of electron excitation energy and charge transfer and the kinetics of photochemical and photobiological processes and also for determining the spatial structure of various molecular complexes and their associates and aggregates [1, 2]. The currently available analytical models of fluorescence decay allow evaluation of the molecular ensemble-averaged characteristics and parameters of the investigated processes, which is efficient only for isotropic or highly ordered condensed media [3, 4]. If the systems are not isotropic but only fragmentarily ordered, where anisotropic transfer of the electron excitation energy can occur in various directions, the use of analytical models is found to be difficult [5, 6]. For such systems the most promising method for evaluating the parameters of the kinetic curves of decay is the simulation method [7, 8]. The use of this method has made it possible to investigate the properties of energy transfer and relaxation in ZnTOPP thin films (Fig. 1a) obtained by the spinning method [9, 10]. In [11], on the basis of investigation of optical spectra and the kinetic curves of the decay of fluorescence and its anisotropy, it is shown that ZnTOPP films (the evaluated thickness of a deposited layer is ~100 nm) have a lamellar structure (Fig. 1b) where an individual layer represents a combination of domains within which linear nonintersecting stacks of parallel ZnTOPP molecules are formed at a distance of 0.5–2.0 nm. The distance between the molecules in the stacks is 0.2–0.5 nm, and they are oriented in such a way that one of the two vectors of dipole moments of each molecule forms a normal to the base surface, while the second vector is in the plane parallel to the plane of the quartz substrate (Fig. 1c). In such films, the electron excitation energy can be transferred inside the layers, with the energy transfer between individual layers being negligible. An analysis of the kinetic curves of the fluorescence decay of ZnTOPP thin films with the use of the simulation method has allowed determination of the rate constants of energy transfer (1 psec^{-1} and 80 nsec^{-1} for intra- and
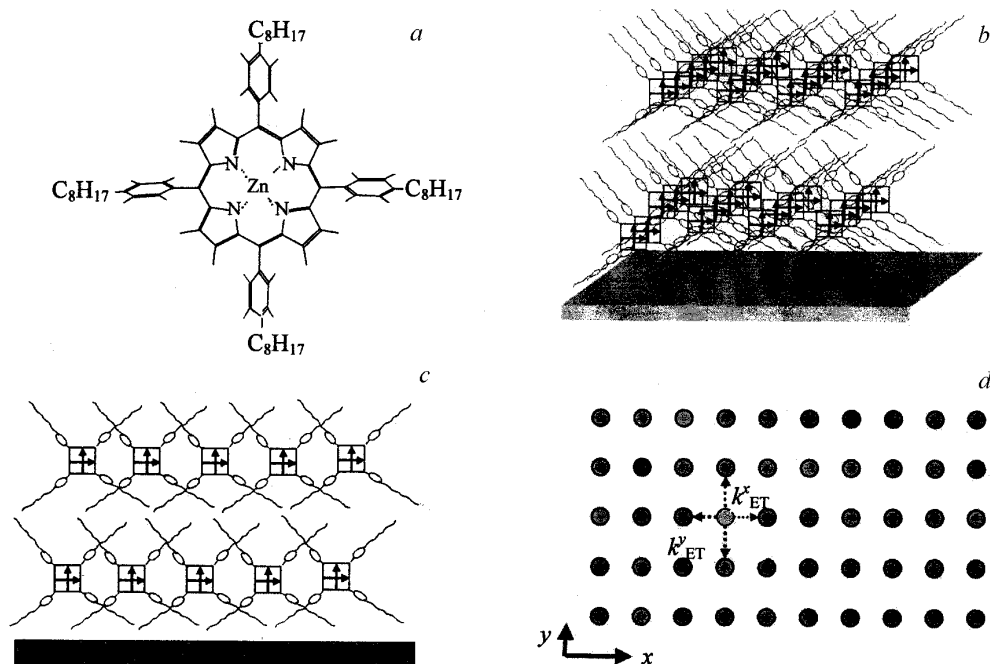

Fig. 1. Formalized structure of the Zn-porphyrin films: a) ZnTOPP molecule; b) three-dimensional representation of the lamellar-layer film structure; c) cross section of two layers; d) fragment of the domain with arranged ZnTOPP molecules; arrows point to the direction of energy transfer; the rate constants of energy transfer are $k_{ET}^{x} = 1$ psec^{-1} and $k_{ET}^{y} = 80$ nsec^{-1}.

interstack transfer, Fig. 1d). The fluorescence lifetime of an isolated ZnTOPP monomer was reported to be 1.8 nsec [9], and only qualitative assumptions were made regarding the possible intrastack molecular orientation.

In the present work, a quantitative analysis of the kinetic curves of the decay of the fluorescence anisotropy of ZnTOPP thin films has been carried out aimed at investigation of their intrastack molecular orientation. The experimental data were analyzed with the use of both exponential decomposition and simulation of intrastack orientation with account for the processes of the electron excitation energy transfer.

Materials and Methods. Porphyrins and their zinc complexes were synthesized using the procedures of [12]. Specimens of ZnTOPP thin films ($15 \times 15 \times 1$ mm) were prepared by the method of spinning, with deposition, onto quartz glasses, of solutions in toluene or trichloromethane ($CHCl_3$) distilled over sodium.

The decay curves of the vertically and horizontally polarized components of fluorescence were measured by the method of one-quantum recording described in detail in [13]. A scheme of the experiment involving excitation of a specimen followed by recording of the vertically and horizontally polarized fluorescence components is shown in Fig. 2a. It should be noted that a specific feature of the experiment is the positioning of the investigated specimen so that it makes an angle of $\alpha = 25^{\circ}$ with the direction of propagation of an optical excitation pulse. For the excitation and recording of the kinetics of the fluorescence decay, the 440-nm (near a maximum of the Soret band) and 650-nm (near a maximum of the emission band $Q(0, 0)$) wavelengths were chosen. The intensities of decay were recorded at room temperature. The number of recording channels was 4096, and the width of a recording channel was 2.85 psec.

An analysis of the experimental data with the use of the function of the sum of exponents was made with the aid of the Fluorescence Data Processor program developed at the Chair of System Analysis at the Belarusian State University [14]. For an analysis of the experimental data by the simulation method, the algorithms described in [13] were used.

Discussion of the Results of an Analysis of the Kinetics of the Decay of the Fluorescence Anisotropy of ZnTOPP Thin Films in the Form of a Sum of Exponents. The curves of decay of the fluorescence anisotropy of ZnTOPP films were approximated by a function of the sum of the exponents, $r(\beta_1, \beta_2, \phi_1, \phi_2, t) = \beta_1 \exp(-t/\phi_1) +$
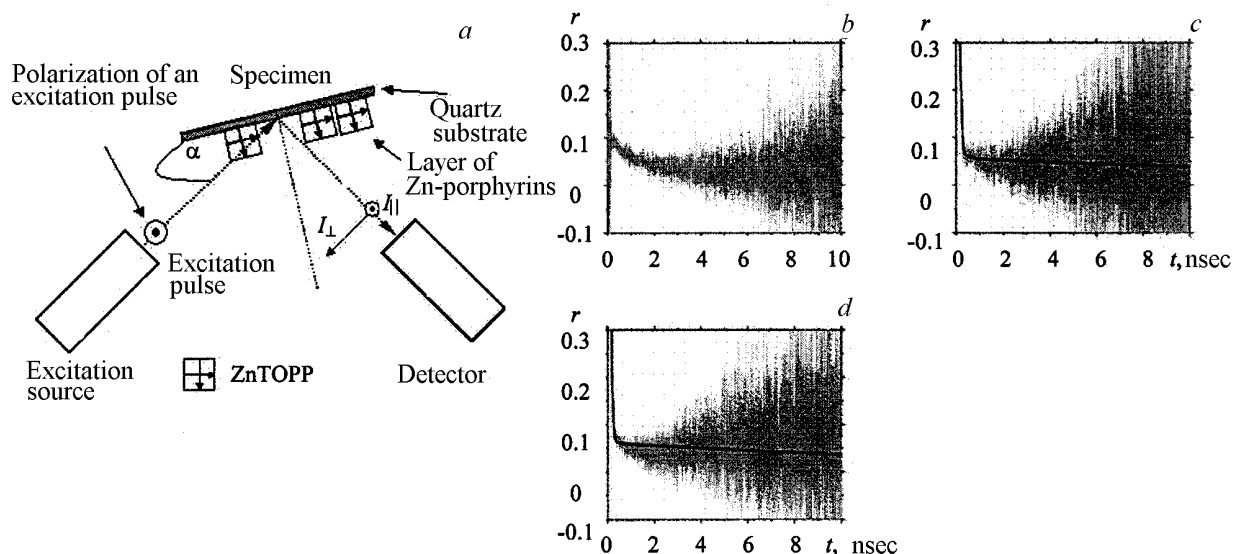
Fig. 2. Schematic of the experiment with time resolution (a); the intensity of the decay of the fluorescence anisotropy of the solution of ZnTOPP in toluene (b) and of the films obtained from the solutions ($2 \cdot 10^{-5}$ M) of ZnTOPP in toluene (c) and in $CHCl_3$ (d) (λ_{exc} = 440 nm; λ_{rec} = 650 nm); the solid line is a theoretical curve in the form of a sum of exponents with the parameters from Table 2.

TABLE 1. Parameters Determined from the Kinetics of the Decay of the Fluorescence Anisotropy of the ZnTOPP Films in the Form of a Sum of Exponents

Solvent	β_1	ϕ_1, psec	β_2	ϕ_2, nsec	χ^2
Toluene	0.24	14	0.053	$+\infty$	1.01
	[0.12; 0.36]	[11; 17]	[0.051; 0.056]	[18, $+\infty$]	
$CHCl_3$	0.25	12	0.059	$+\infty$	1.07
	[0.15; 0.29]	[9; 15]	[0.055; 0.062]	[14, $+\infty$]	

Note. The films were obtained from solutions ($2 \cdot 10^{-5}$ M) of ZnTOPP in toluene and $CHCl_3$; an estimate of the 95% confidence interval is given in square brackets.

$\beta_2 \exp(-t/\phi_2)$, with the parameters β_1 and β_2 given in Table 1 (Fig. 2b, c, d). Two times of rotational correlation were recorded: a "short" time (ϕ_1 = 12–14 psec) and the unresolved, in the investigated range, component of "long" time with the evaluated left boundary of the confidence interval (ϕ_2 > 14–18 nsec). The value of the "short" component coincides with the rate constant of interstack energy transfer (k_{ET}^{y} = 80 $nsec^{-1}$) obtained as a result of simulation of the fluorescence decay [9]. The "long" time can be attributed to the influence of the energy transfer between neighboring domains.

The anisotropy of film fluorescence at the instant 0 (the so-called initial anisotropy $r_0 = \beta_1 + \beta_2$) is r_0^{f} = 0.29–0.31, which is much larger than the value r_0^{s} = 0.1 typical of the metalloporphyrin monomers in an aqueous solution (Fig. 2b, c, d) [15]. Its 95% confidence interval is sufficiently broad ([0.12; 0.36]), which is related to the experimental error introduced into the evaluation of the parameter β_1. At the same time, the value of the parameter β_2 is determined sufficiently exactly (Table 1) and has a narrower 95% confidence interval ([0.051; 0.062]). The high initial anisotropy is the result of grouping of porphyrins on the substrate plane. Obviously, the parameters β_1 and β_2 characterize the position and orientation of the molecular stacks. For instance, the parameter β_2 describes the orienta-
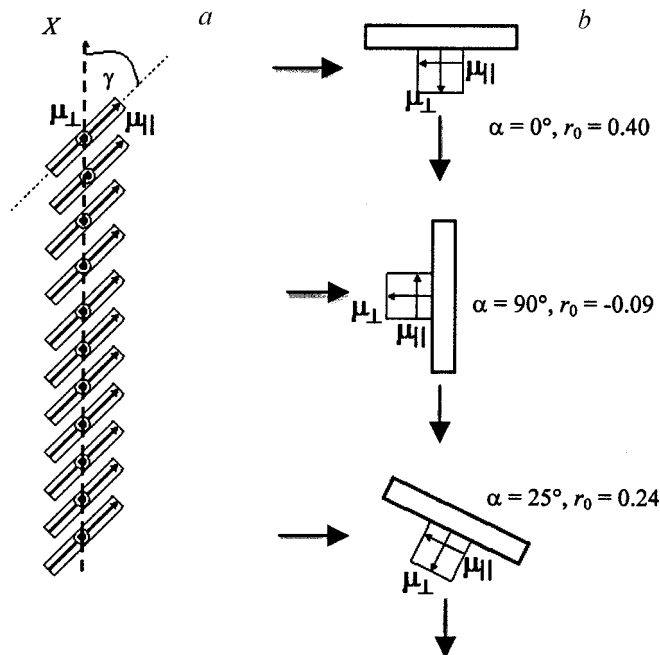
Fig. 3. Schematic and results of simulation of the films of Zn-porphyrins: a) interpretation of the parameter γ used in the procedure of simulation; b) values of the initial anisotropy at different angles of inclination of the film specimen toward the direction of propagation of the pulse of optical excitation ($\rightarrow$).

tion of the stacks within the limits of a domain. For the purpose of a more detailed study of the kinetics of the decay of the fluorescence anisotropy of ZnTOPP films, in the present work the simulation method is used, making it possible to determine, with a high accuracy, the location and orientation of molecules and at the same time to reproduce the processes of electron excitation energy transfer in self-organized aggregates.

Discussion of the Results of Simulation of the Kinetics of the Decay of the Fluorescence Anisotropy of ZnTOPP Thin Films. An analysis of the structure of ZnTOPP films by the method of simulation consists of the approximation of experimental curves of the decay of the fluorescence anisotropy by a set of data obtained by a simulated model [8]. A formally logical description of the algorithm for simulating the processes of energy transfer is given in [8, 10], and a formalized description of the investigated molecular system of ZnTOPP films is given in [9, 10]. Below, we briefly describe some conditions that influence the kinetics of the decay of the anisotropy of ZnTOPP films.

1. An individual molecular domain consisting of linear nonintersecting stacks of ZnTOPP parallel molecules (1000 × 200) is considered.

2. The planes of the ZnTOPP molecules in the stacks are oriented in such a way that one of the two vectors of dipole moments forms a normal to the base surface, while the other is in the plane parallel to the plane of the quartz substrate.

3. The planes of a ZnTOPP molecule in the stacks are collinear.

With regard for the foregoing, the system under consideration can formally be represented by two vectors of dipole moments, one of which forms a normal to the base surface of the film ($\mu_\perp$), while the other is distributed with equal probability in the plane parallel to the plane of the substrate base ($\mu_\parallel$) due to the difference in the orientation of the domains. A formally logical description of the algorithms of modeling of the processes of energy transfer in the system of Zn-porphyrins is given in [9]. In simulation of the optical processes influencing the decay of the fluorescence anisotropy, it is necessary to additionally take into account the orientation of molecular dipole moments [8]. For

TABLE 2. Parameters Determined from the Kinetics of the Decay of the Fluorescence Anisotropy of the ZnTOPP Films with Use of the Simulation Method[*]

Solvent	τ, nsec	k_{ET}^y, nsec^{-1}	γ, deg	χ^2
Toluene	1.82 [1.80; 1.84]	75 [68; 82]	45 [44.5; 45.5]	1.03
CHCl$_3$	1.80 [1.78; 1.82]	71 [62; 79]	45 [44.5; 45.5]	1.09

Note. The films are obtained from solutions ($2 \cdot 10^{-5}$ M) of ZhTOPP in toluene and CHCl$_3$; an estimate of the 95% confidence interval is given in square brackets.

[*]τ is the lifetime of the excited singlet state of the isolated ZnTOPP monomer; γ, angular deviation of the vectors $\mu_\parallel$ from the longitudinal x axis of a stack.
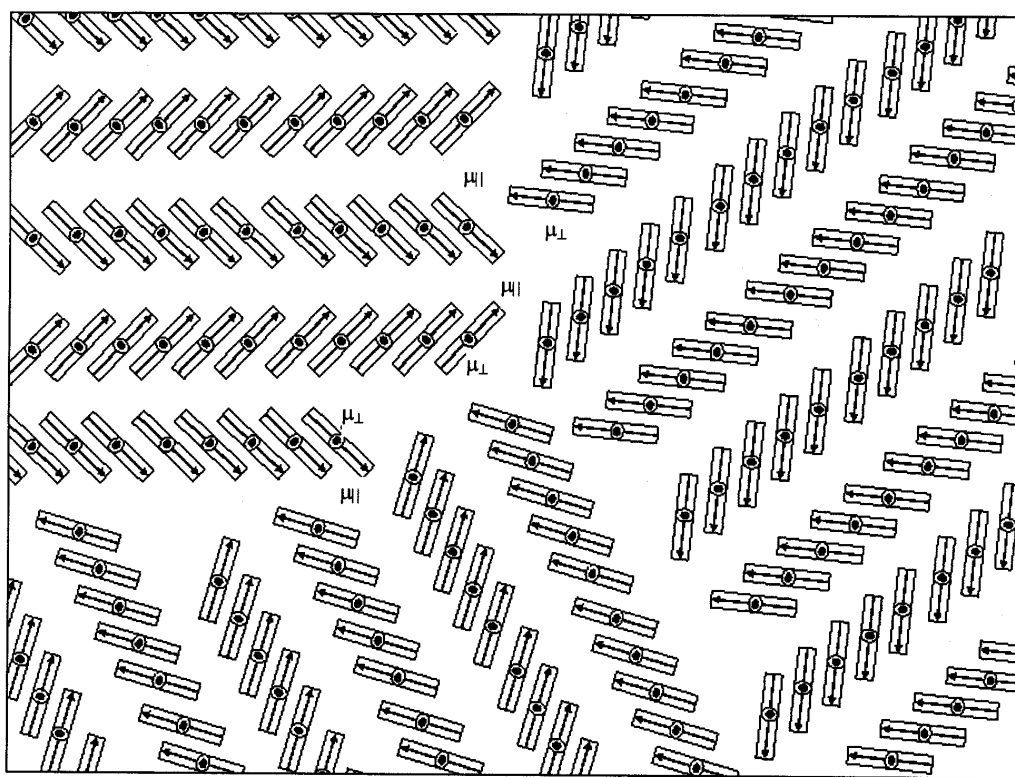

Fig. 4. Schematic structure of the layer of Zn-porphyrins determined as a result of simulation of the decay of the fluorescence anisotropy.

the determination of the position of the vectors of dipole moments $\mu_\parallel$ in the stacks, the angular parameter γ is introduced, which characterizes the angular deviation of the vectors $\mu_\parallel$ from the longitudinal x axis of a stack (Fig. 3a).

To simulate the instrumental function, the algorithm proposed in [16] was chosen. The parameters of the simulation model were evaluated by the method of Nelder and Mead [17], and the 95% confidence interval of the restored parameters, by the method described in [18]. The graphs of the weight residues and of the autocorrelation function and the criterion χ^2 were used to check the quality of the simulation and approximation of the experimental curves representing the decay of the fluorescence anisotropy. The number of start-ups of the simulation model varied from 10^7 to 10^9. All computations were carried out on an IBM-compatible personal computer with an Intel PIII 350-MHz processor.

According to the results obtained in analyzing the curves of the decay of the fluorescence anisotropy of ZnTOPP films with the use of the simulation method presented in Table 2, the initial anisotropy is $r_0^f = 0.24$ at $\alpha = 25^o$, while for the cases of $\alpha = 0$ and 90° the limiting values of the initial anisotropy are 0.40 and 0.09, respectively (see Fig. 3b). Thus, the relatively high initial anisotropy r_0^f is attributed to grouping of the ZnTOPP molecules: the planes of the molecules are perpendicular to the substrate base and collinear inside the stacks. This result confirms the conclusions of [11].

The rate constant for the interstack transfer of the electron excitation energy (75–71 $nsec^{-1}$) and the lifetime of the fluorescence of an isolated ZnTOPP monomer (1.80–1.82 nsec) evaluated in the present work do not contradict those obtained previously [9].

The angular deviation of the vectors $\mu_\parallel$ from the longitudinal x axis of a stack is $\gamma = 45^o$, which corresponds to the case of perpendicular planes of the molecules of the neighboring stacks (see Fig. 4). Indeed, with such an intrastack arrangement of molecules the anisotropy of fluorescence, with account for the electron excitation energy transfer, must be equal to 1/4 of its initial value, i.e., $0.24 \times 1/4 = 0.06$, which agrees well with the results of the analysis of experimental data with the use of the sum of exponents ($\beta \approx 0.06$, see Table 1). Our pattern of the interstack arrangement of ZnTOPP molecules partially resembles a crystalline one, and from the physical viewpoint it corresponds to the position of the energy minimum for molecules of the ZnTOPP type.

Conclusions. With the use of the simulation method for an analysis of the kinetic curves that represent the decay of the fluorescence anisotropy of ZnTOPP films the intrastack arrangement of the ZnTOPP monomers is determined. In each stack the molecular planes are collinear, are oriented perpendicularly to the base surface of the substrate, and form an angle of 45° with the guiding axis of a stack.

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