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## Fluorescence line narrowing study of cyclopentaneporphyrin chemical dimers at 4.2 K

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### Abstract

The monomers of Zn-cyclopentanoporphyrins (ZnOEP-cycle and ZnOEP-cycle=CH<sub>2</sub>) and their chemical dimers covalently linked via isocycles (Zn-cyclodimers) have been studied by the method of fluorescence line narrowing (FLN) in tetrahydrofurane-toluene (3:1) glassy matrixes at 4.2 K. Well-resolved fluorescence spectra upon laser excitation into the S<sub>0</sub>→S<sub>1</sub> absorption band have been observed. In contrast to this, it has been shown that the excitation into the region of S<sub>0</sub>→S<sub>2</sub> absorption band leads to FLN disappearance for individual monomers. On the basis of this effect positions of the S<sub>0</sub>→S<sub>2</sub> electronic transitions in the energy scale have been determined. The normal coordinate treatment of FLN spectra of ZnOEP-cycle=CH<sub>2</sub> and those for the Zn-cyclodimers permitted us to determine the normal modes which are connected with the formation of the dimeric species. The weak interaction of Q-transitions of donor (**D**, ZnOEP-cycle) and acceptor (**A**, ZnOEP-cycle=CH<sub>2</sub>) subunits in Zn-cyclodimers manifests itself in the strong fluorescence quenching of **D**. Under excitation into the S<sub>0</sub>→S<sub>1</sub> transition of **D** the FLN spectra of the dimers (belonging to their **A** subunits) were not observed. These facts are connected with the effective non-radiative singlet-singlet energy transfer in conditions of essential spectra inhomogeneity.

### 1. Introduction

In the recent years, it has been shown that covalently-linked porphyrin dimers are suitable objects for the study of various aspects of molecular spectroscopy [1–5]. They also serve as a good model for the investigation of the energy and charge transfer processes in photosynthetic systems in vivo [6–10]. The investigations of such systems have been fulfilled in a temperature range of 77–300 K mainly where the applicability of various theoretical models describing energy transfer processes in chemically bonded chromophores has been analyzed in some cases [8, 10].

The methods of low-temperature site-selection spectroscopy such as fluorescence line narrowing (FLN) and spectral hole burning (SHB) open additional possibilities for the study of structural properties and photophysical processes in chemical dimers. It is well known that these methods have been used fruitfully for the investigation of monomeric molecules of tetrapyrrolic compounds [11–13]. Besides, on the basis of this approach, the dynamics of primary photoprocesses in native photosynthetic systems have been investigated [14, 15] as well as spectral properties of chlorophyll in detergents [16] and pigment aggregated forms in solutions [17] have been cleared up. However, the complexity and ambiguity of the chemical structure of the investigated systems

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leads to considerable difficulties in the synonymous interpretation of the data being obtained.

Covalently linked dimers of tetrapyrrolic compounds with known structural parameters occupy an intermediate position between monomeric chromophores and aggregated complexes *in vivo* and *in vitro*. Recently, we have studied FLN and SHB of the symmetrical ethane-bisporphyrins [18]. It has been shown that in the temperature range of 1.8–51 K, non-radiative energy transfer (ET) takes place with probability  $F=10^{11} \text{ s}^{-1}$ . The ET rate calculated within the Förster model is considerably lower than the experimental one. This fact indicates the inapplicability of Förster formalism for the singlet–singlet ET under conditions of substantial inhomogeneous spectral broadening of the interacting chromophores at 4.2 K.

In the present work, the fluorescence spectra of Zn-cyclopentaneporphyrin chemical dimers upon selective laser excitation have been studied at 4.2 K. On the basis of the comparison of these spectra with those of monomeric precursors, the effects of dimer formation on the FLN spectra of the subunits as well as the peculiarities of ET processes in conditions of essential inhomogeneous spectral broadening have been identified.

A choice of metalloporphyrins with isocyclic substitution and their chemical dimers as objects for the investigation was not accidental. Firstly, it is well known [19] that the isocyclic ring as an element of the chlorophyll structure plays the essential role in the formation of natural light-harvesting antenna complexes, responsible for absorption and ET to photosynthetic reaction centers [9]. Secondly, reaction centers themselves contain a chlorophyll or bacteriochlorophyll dimer (so-called “photosynthetic special pair”) which takes part in the conversion of light energy into the chemical energy of separated charges [9]. Therefore site-selective spectroscopy of chemical dimers covalently bonded via the isocyclic ring represents a convenient background to study specific spectral effects and interchromophoric interaction processes taking place in the native photosynthetic complexes.

## 2. Experimental

The structure of the monomers and chemical dimers, their principal spectral and kinetic parameters

at 77–293 K have been obtained in our laboratory previously [20, 21]. The Zn-cyclodimers consist of one molecule of Zn-3<sup>1</sup>,5<sup>1</sup>-cyclo-3<sup>1</sup>-methyl-2,7,8,12,13,17,18-heptaethylporphyrin (ZnOEP-cycle or donor of excitation energy, **D**) and Zn-3<sup>1</sup>,5<sup>1</sup>-cyclo-3<sup>1</sup>-exomethylen-2,7,8,12,13,17,18-heptaethyl-22H, 24H-porphyrin (ZnOEP-cycle=CH<sub>2</sub> or acceptor of excitation energy, **A**) molecule covalently linked through relatively rigid methine bridge. Chemical dimers, Zn-3<sup>1</sup>,5<sup>1</sup>-cyclodimer and Zn-3<sup>1</sup>,3<sup>1</sup>-cyclodimer, having one molecule of the ZnOEP-cycle and one molecule of the ZnOEP-cycle=CH<sub>2</sub>, are distinguished by the position of the spacer relative to the isocycle of ZnOEP-cycle (see Fig. 1).

A tetrahydrofuran-toluene mixture (3:1) was used as a host glassy matrix. The measurements were performed on samples immersed into liquid helium in the optical cryostat.

The FLN method of molecules in isotropic media applied in our experiments is based on simultaneous use of selective laser excitation within the absorption band of the 0→0 electronic transition of the compounds under investigation and liquid helium temperature. Under such conditions the fluorescence spectra consist of narrow zero-phonon lines (ZPL), and the difference in frequencies between a ZPL and the excitation line is equal to the frequency of the corresponding vibration in the ground state [22].

The FLN spectra were measured with DFS-24 spectrometer (0.8 m). A pulsed tunable dye laser (repetition rate 20 Hz, half width of the generation band <0.1 nm, turning region of 540–650 nm) pumped by an ILGI-504 N<sub>2</sub>-laser was used for excitation of the fluorescence. Data were acquired by a “box-car” integrator coupled with a PC. A more detailed description of this experimental setup is given elsewhere [23].

## 3. Results and discussion

### 3.1. Localization of Zn-cyclopentaneporphyrin electronic transitions in energy scale

According to the four-orbital model of Gouterman [24] the asymmetry caused by the existence of the isocycle in the ZnOEP-cycle or the ZnOEP-cycle=CH<sub>2</sub> molecules leads to a breakdown of the S-excited states degeneracy characteristic for metalloporphyrins with symmetry D<sub>4h</sub>. As a result, absorption bands

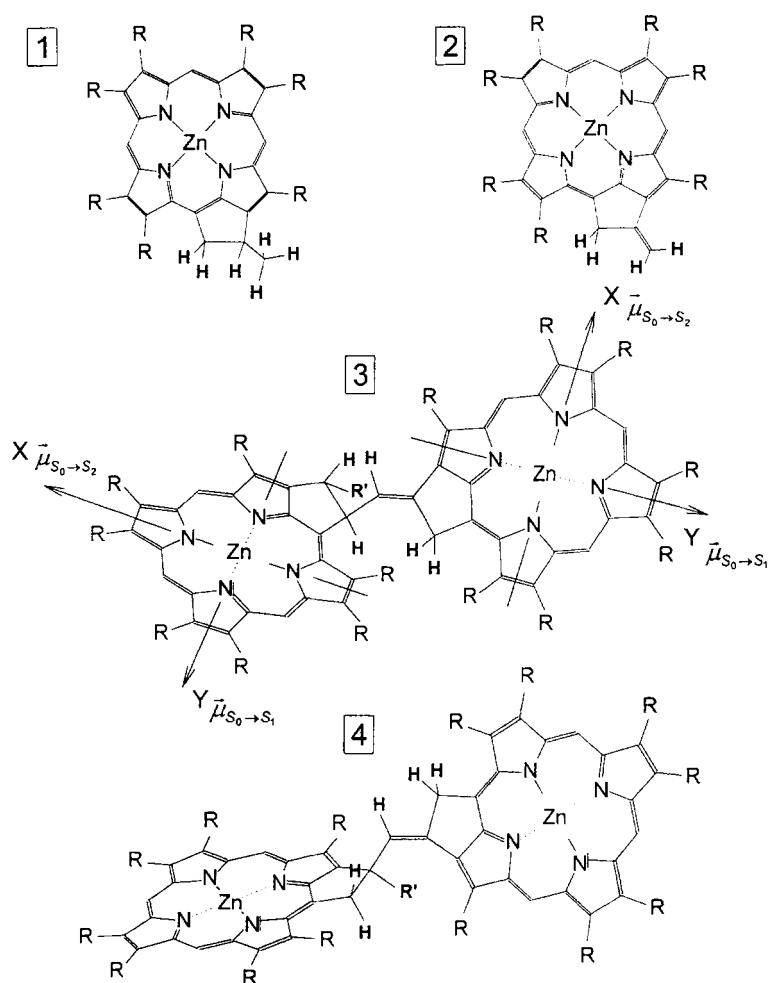


Fig. 1. Structure of the ZnOEP-cycle (1) and the ZnOEP-cycle=CH<sub>2</sub> (2), the Zn-3<sup>1</sup>,5<sup>1</sup>-cyclodimer (3) and Zn-3<sup>1</sup>,3<sup>1</sup>-cyclodimer (4). R: C<sub>2</sub>H<sub>5</sub>; R': CH<sub>3</sub>. The arrows show the orientation of the dipole moments of the S<sub>0</sub>→S<sub>1</sub> and S<sub>0</sub>→S<sub>2</sub> electronic transitions in the dimer components.

of the S<sub>0</sub>→S<sub>1</sub> and S<sub>0</sub>→S<sub>2</sub> electronic transitions are expected to be resolved. Fig. 2 shows absorption electronic spectra of Zn-cyclopentane porphyrins and their chemical dimers measured earlier at 77 K [25]. As seen from the figure the totality of data on absorption and polarized fluorescence excitation spectra in the region of the long-wave Q-bands both for the ZnOEP-cycle and the ZnOEP-cycle=CH<sub>2</sub> does not provide real arguments for the synonymous determination of the localization of the S<sub>0</sub>→S<sub>1</sub> and the S<sub>0</sub>→S<sub>2</sub> electronic transitions in energy scale.

The existence of such transitions for Zn-complexes and free bases of isocycle substituted octaethylporphyrins at 77 K was discussed in [26]. On the basis of studying electronic absorption and polarized fluorescence data for various compounds the relatively intense Q<sub>x</sub> (0,0) band peaked at λ<sub>max</sub> = 573 nm in the ZnOEP-cycle absorption spectrum has been attributed to the S<sub>0</sub>→S<sub>1</sub> transition. However, it should be noted that the value of the fluorescence polarization degree (*P*) for this band is equal to +38% and does not change upon going to the more short wavelength Q<sub>y</sub> (0,0) transition. This situation is not typical in the

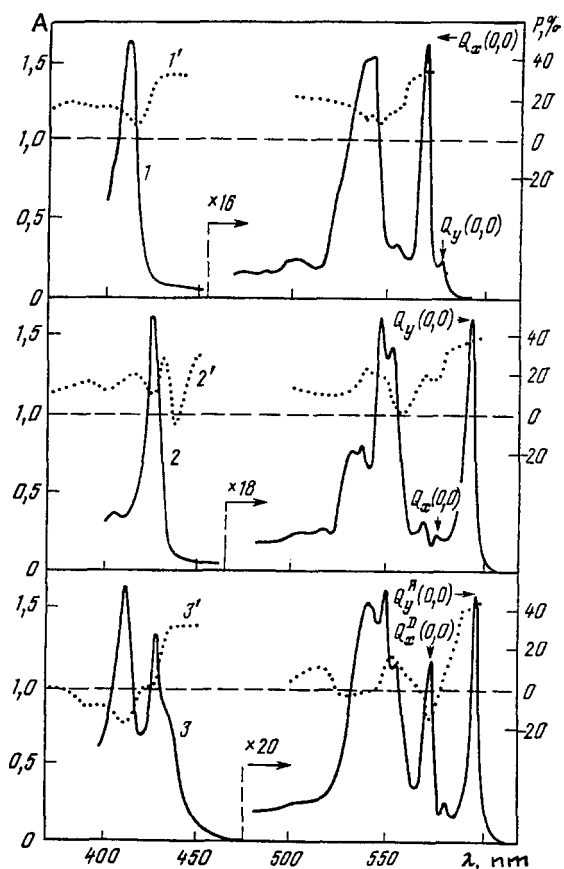


Fig. 2. Absorption (1–3) and polarized fluorescence ( $1^1$ – $3^1$ ) spectra of the ZnOEP cycle (1,  $1^1$ ), the ZnOEP-cycle=CH<sub>2</sub> (2,  $2^1$ ) and the Zn-3<sup>1</sup>,3<sup>1</sup>-cyclodimer (3,  $3^1$ ) in an EPA mixture (diethyl ether–petroleum ether–isopropanol 5:5:2) at 77 K.  $\lambda_{\text{rec}} = 580$  ( $1^1$ ) and 605 nm ( $2^1, 3^1$ ). The  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  transitions are shown on the basis of the FLN spectroscopy data.

case of non-symmetrical metalloporphyrins [19], for which the  $S_0 \rightarrow S_2$  transition is characterized by negative values of  $P$ , mainly, ( $P = -10 - 20\%$ ), i.e. the oscillator of the  $S_0 \rightarrow S_2$  transition is normally oriented with respect to the oscillator of the  $S_0 \rightarrow S_1$  transition. Additional data on the energy of the  $S_0 \rightarrow S_1$  and the  $S_0 \rightarrow S_2$  electronic transitions for Zn-complexes of porphyrins with isocycle and their chemical dimers have been obtained from analysis of linear dichroism spectra of stretched polymeric films activated by the ZnOEP-cycle, the ZnOEP-cycle=CH<sub>2</sub> and Zn-cyclodimers [27]. The identification made in Ref.

[26] has been basically justified but for the ZnOEP-cycle=CH<sub>2</sub> (see Fig. 2(b)) the situation remained ambiguous yet because of the overlap of the low-intensive band of the electronic  $S_0 \rightarrow S_2$  transition with those of vibrational transitions of the intense  $S_0 \rightarrow S_1$  electronic transition.

It has been shown earlier for various non-symmetrical metalloporphyrins [28] that FLN method was effective and direct for the determination of the localization of electronic transitions into excited  $S_1$ - and  $S_2$ -states in energy scale. The principle of this method may be presented as follows (see Fig. 3). The optical absorption and fluorescence spectra of porphyrins at 4.2 K are characterized by the so-called inhomogeneous broadening ( $\sim 150 \text{ cm}^{-1}$ ) caused by the interaction of chromophores with the matrix. For the simplicity of the explanation of main spectroscopic features realized upon the laser excitation of molecules under investigation let us consider three types of centers (so-called “sites”) A, B, C from the whole set of sites forming spectral bands. According with the ideas cited in Ref. [22] upon excitation in the region of the  $S_0 \rightarrow S_1$  electronic transition of solvated molecules the fluorescence spectrum consists of a set of narrow ZPLs (see curves  $F_A, F_C$  on Fig. 3). It is connected with the sharp resonance between the excitation laser line and a narrow absorption band of one site and reflects the situation when limited number of chromophores from the whole inhomogeneous spectral distribution are excited. It should be mentioned that in real experiments several different sites are excited simultaneously upon laser excitation even.

When going to the excitation into the region of vibronic sub-levels of  $S_1$ -state the “multiplet” is observed within a pure electronic band of the fluorescence spectrum (see curve  $F_m$ ). As one can see from Fig. 3, this fact corresponds to the case when various sublevels of different sites (for example A and C) are excited simultaneously. In other words, under these conditions of excitation the differences between the positions of multiplet components and of the excitation line in the energy scale determine the frequencies of vibrations in the  $S_1$ -state. Below we shall discuss these spectral data for our objects.

In contrast to the situation mentioned above, for excitation within the  $S_0 \rightarrow S_2$  transition, absorption band leads to FLN disappearance [28]. Fig. 3 shows that, in this case, a number of sites get excited by a

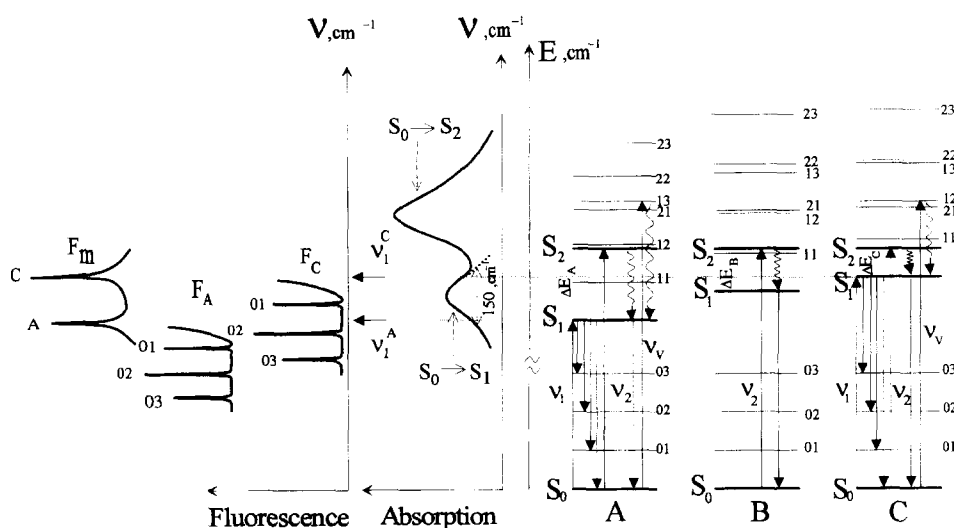


Fig. 3. Schematic presentation of FLN spectra formation for molecules under conditions of an inhomogeneous spectral broadening at 4.2 K in isotropic matrices. Energy level diagram corresponds to three sites (A, B and C) and is typical for metallocomplexes of porphyrins with isocyclic substitution. Vibrational sublevels of every electronic state are indicated by two numbers. Frequencies  $\nu_1$ ,  $\nu_2$  and  $\nu_V$  correspond to excitation into the electronic  $S_1$ -state,  $S_2$ -state and the vibrational sublevel manifold of the  $S_1$ -state.

spectrally narrow laser line. The interaction of these sites with the matrix at 4.2 K manifests itself in the difference of the energy gap  $\Delta E$  ( $S_1 - S_2$ ) for every site (see, for example, such situation for A, B, and C sites on Fig. 3). As a result, after a non-radiative conversion  $S_2 \rightarrow S_1$ , emission from  $S_1$ -state centers is substantially inhomogeneously broadened. So, the effect of FLN disappearance upon the selective laser excitation may be used as a method for the determination of the position of  $S_2$  and higher electronic levels in energy scale. Possibilities of a given approach have been demonstrated on the identification of absorption bands of the chlorophyll *a* mono- and bi-solvates [29].

Figs. 4 and 5 show fluorescence spectra of the ZnOEP-cycle and the ZnOEP-cycle=CH<sub>2</sub> monomers at various excitation conditions. It is seen from Fig. 4 (spectrum b) that at  $\lambda_{\text{exc}} = 579$  nm the ZnOEP-cycle fluorescence spectrum consists of a set of ZPLs with FWHM  $\sim 0.3$ – $0.5$  nm characteristic of FLN spectra. At the same time the transition to  $\lambda_{\text{exc}} = 572$  nm leads to a full FLN disappearance in spectrum (Fig. 4, spectrum a). In the last case the fluorescence spectrum is analogous to that measured under broadband excitation in the region of Soret band. This fact indicates unambiguously that the absorption band peaked at  $\lambda_{\text{max}} = 572$  nm corresponds to the  $S_0 \rightarrow S_2$

electronic transition in the ZnOEP-cycle molecules. This conclusion agrees with the above mentioned interpretation reported in Ref. [26].

In the case of ZnOEP-cycle=CH<sub>2</sub> the real position of the  $S_0 \rightarrow S_2$  transition in energy scale is not so apparent because of the existence of an additional vibronic structure of the  $S_0 \rightarrow S_1$  transition in the spectral range of interest. To solve this question we carried out measurements at different excitation wavelengths. Really, under excitation within the intense long-wavelength band peaked at 594 nm FNL is observed which proves that this band belongs to the  $S_0 \rightarrow S_1$  electronic transition (see Fig. 5, spectrum c). On transition to  $\lambda_{\text{exc}} = 576$  nm, this spectrum becomes structureless (see Fig. 5, spectrum a). Further shift of the laser excitation line to  $\lambda_{\text{exc}} = 569$  nm leads again to FNL effect (see Fig. 5, spectrum b). The data obtained may be interpreted in the following way. The band with  $\lambda_{\text{max}} = 594$  nm in absorption spectra of the ZnOEP-cycle=CH<sub>2</sub> belongs to the  $S_0 \rightarrow S_1$  electronic transition whereas the band with  $\lambda_{\text{max}} = 576$  nm is formed by the  $S_0 \rightarrow S_2$  electronic transition. A "multiplet" observed in the range of the 0–0 fluorescence band of the ZnOEP-cycle=CH<sub>2</sub> (see Fig. 5, spectrum b) belongs to the vibronic sublevels of the  $S_1$  electronic state. Therefore, the band with  $\lambda_{\text{max}} = 569$  nm

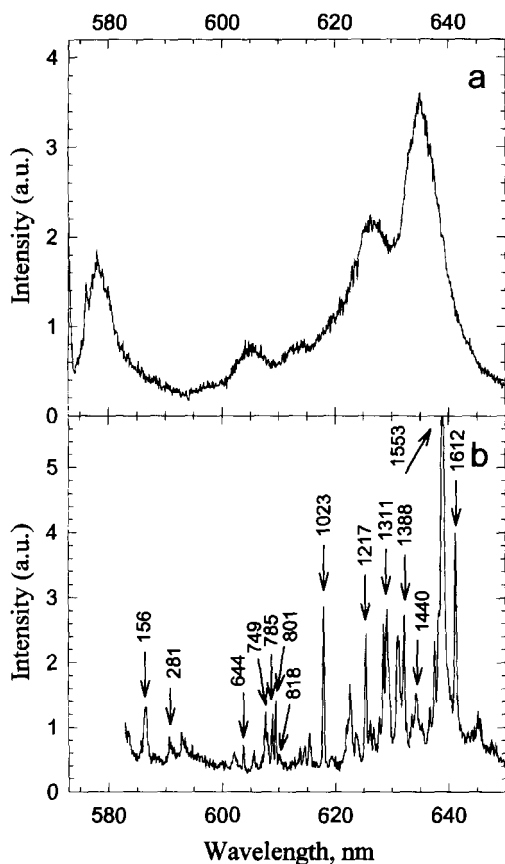


Fig. 4. Fluorescence spectra of the ZnOEP-cycle in tetrahydrofuran-toluene mixture (3:1) at 4.2 K under selective excitation. Excitation wavelength:  $\lambda_{\text{exc}} = 572$  nm (a) and 579 nm (b). Frequencies of the normal modes are indicated only for certain ZPLs.

in the ZnOEP-cycle=CH<sub>2</sub> absorption spectrum would not be identified with S<sub>0</sub>→S<sub>2</sub> transition for these compounds.

Thus, the spectral data obtained for the individual monomeric ZnOEP-cycle and ZnOEP-cycle=CH<sub>2</sub> provide a background for analysis of the spectral properties of the dimers.

### 3.2. Vibronic structure treatment

We have shown previously [25] that in the dimers under consideration, the Zn-3<sup>1</sup>,5<sup>1</sup>-cyclodimer or the Zn-3<sup>1</sup>,3<sup>1</sup>-cyclodimer, the ZnOEP-cycle subunit is the electronic excitation energy donor (**D**) whereas the ZnOEP-cycle=CH<sub>2</sub> subunit plays the acceptor role

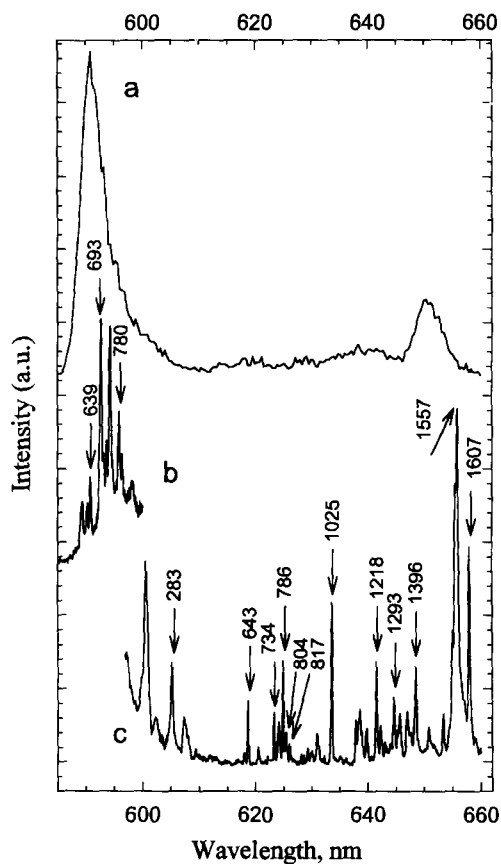


Fig. 5. Fluorescence spectra of the ZnOEP-cycle=CH<sub>2</sub> in tetrahydrofuran-toluene mixture (3:1) at 4.2 K under selective excitation.  $\lambda_{\text{exc}} = 576$  nm (a), 569 nm (b) and 594 nm (c).

(**A**). Accordingly, the usual broad-band fluorescence spectra of both dimers contain emission bands of **A** only in the temperature range 4.2–300 K. In this respect the method of a laser selective excitation at 4.2 K permits us to elucidate experimentally the mutual influence of  $\pi$ -conjugated macrocycles on vibrational states of **A** subunit in the dimer.

Taking into account this possibility, it is of interest to compare frequencies of normal modes for individual ZnOEP-cycle=CH<sub>2</sub> indicated in Fig. 5 (see spectrum c) with corresponding frequencies for the same subunit in the Zn-3<sup>1</sup>,5<sup>1</sup>-cyclodimer indicated in Fig. 6 (see spectrum c) as well as in the Zn-3<sup>1</sup>,3<sup>1</sup>-cyclodimer indicated in Fig. 7 (see spectrum c). As one would expect, most of the normal vibrations active in fluorescence spectra of monomeric

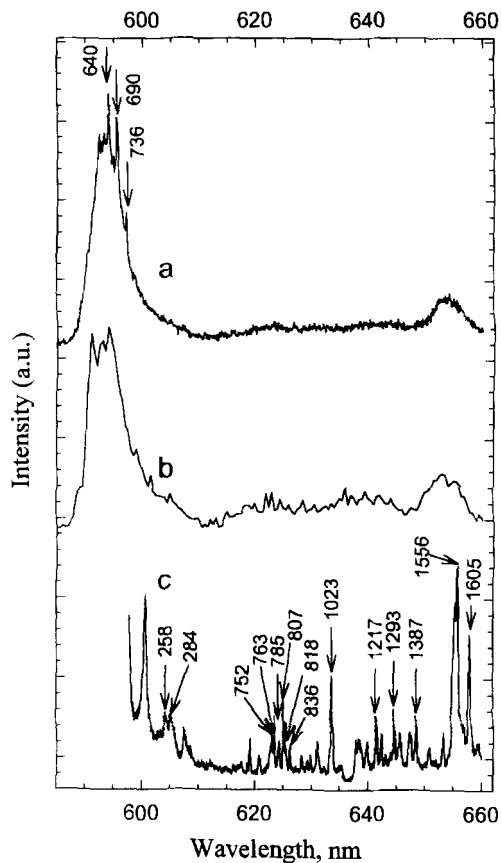


Fig. 6. Fluorescence spectra of the Zn-3<sup>1</sup>,3<sup>1</sup>-cyclodimer in a tetrahydrofuran–toluene mixture (3:1) at 4.2 K under selective excitation.  $\lambda_{\text{exc}} = 572$  nm (a), 579 nm (b) and 594 nm (c).

ZnOEP-cycle=CH<sub>2</sub> and in the emission spectra of this compound within the dimers practically, coincide with each other. Certain distinctions are observed only in the low frequency ranges of 200–300 cm<sup>-1</sup> and 600–850 cm<sup>-1</sup>. According to the theoretical normal mode analysis made in Ref. [30] vibrations with participation of the isocycle CH<sub>3</sub>-group (position 3<sup>1</sup>) provide the main contribution in the region of 200–300 cm<sup>-1</sup> and stretching vibrations with participation of the isocycle manifest themselves dominantly in the region of 600–850 cm<sup>-1</sup>. In the case of Zn-3<sup>1</sup>,3<sup>1</sup>-cyclodimer two ZPLs of nearly the same intensity are detected at 258 cm<sup>-1</sup> and 284 cm<sup>-1</sup> (see Fig. 6, spectrum c), whereas for the Zn-3<sup>1</sup>,5<sup>1</sup>-cyclodimer the intensity of the peak at 250 cm<sup>-1</sup> is relatively small (see Fig. 7, spectrum c). At the

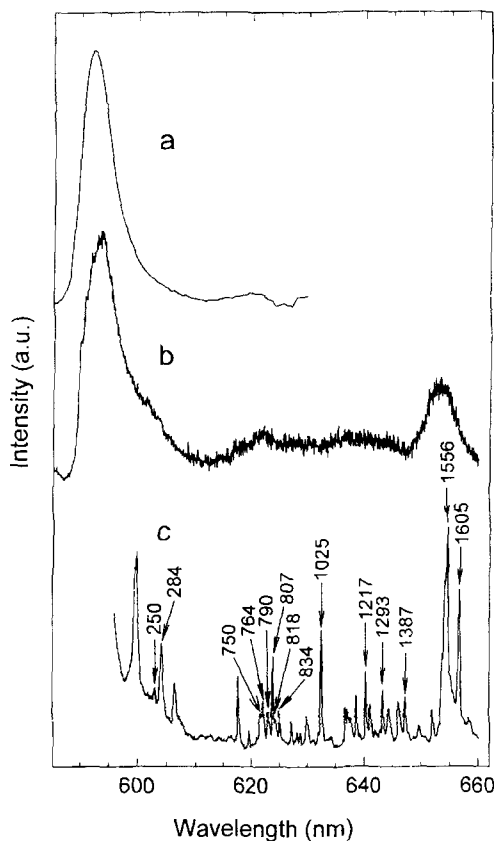


Fig. 7. Fluorescence spectra of the Zn-3<sup>1</sup>,5<sup>1</sup>-cyclodimer in a tetrahydrofuran–toluene mixture (3:1) at 4.2 K.  $\lambda_{\text{exc}} = 337$  nm (broad-band excitation) (a), 579 nm (b) and 594 nm (c).

same time, under similar excitation conditions, the only ZPL at 283 cm<sup>-1</sup> is detected for the ZnOEP-cycle=CH<sub>2</sub> in the range of 200–300 cm<sup>-1</sup> (see Fig. 5, spectrum c).

Taking into account the structure of the Zn-3<sup>1</sup>,3<sup>1</sup>-cyclodimer (see Fig. 1) justified by NMR <sup>1</sup>H [20] one can conclude that the appearance of new ZPL at 258 cm<sup>-1</sup> in the dimer spectrum is due to the interaction of the isocycle CH<sub>3</sub>-group with the dimer spacer (methyne bridge). Indeed, when transition to the Zn-3<sup>1</sup>,5<sup>1</sup>-cyclodimer where the covalent bond between the subunits occurs at different position of the isocycle in the ZnOEP-cycle (see Fig. 1) the essential weakening the intensity of this ZPL is observed. The low intensity of the ZPL at 250 cm<sup>-1</sup> in the last case may be connected with the weakening of the interaction of the

CH<sub>3</sub>-group with the spacer owing to the relative removal of this group from the spacer with respect to the situation in the Zn-3<sup>1</sup>,3<sup>1</sup>-cyclodimer.

The comparison of the vibronic structure in the spectral range of 700–850 cm<sup>-1</sup> for the ZnOEP-cycle=CH<sub>2</sub> and both dimers show that the number and relative intensities of ZPLs are practically the same, but the frequencies of all dimer ZPLs are higher by 10–20 cm<sup>-1</sup> (compare spectra c on Figs. 5–7). So, the ZnOEP-cycle=CH<sub>2</sub> has the following series of ZPLs: 734, 749, 764, 786, 804 and 817 cm<sup>-1</sup>, whereas the set of lines corresponding to the relative intensities in the spectra of the dimers is as follows: 752, 763, 785, 807, 818 and 836 cm<sup>-1</sup>. It should be stressed that these differences in frequencies are characteristic for the dimers only and are not observed for an equimolecular mixture of the ZnOEP-cycle and the ZnOEP-cycle=CH<sub>2</sub>.

One should note that the range of 700–850 cm<sup>-1</sup> is practically unique where the interaction of **D** and **A** subunits manifests itself in FLN spectra. The above mentioned normal mode analysis [30] leads to the conclusion that there are parallel contributions of the alkyl substituents and the stretching vibrations of the isocycle in this spectral range. As this takes place it is difficult to assume that all six vibrations shift their frequencies in the dimers. It may be assumed that few ZPLs of **A** subunit do not change their frequencies in the dimers with respect to monomeric ZnOEP-cycle=CH<sub>2</sub>, and some new ZPLs appear in FLN spectra of the dimers (for instance, ZPL at 836 cm<sup>-1</sup>). But this assumption does not explain the conservation of relative intensities for all ZPLs in this range. We guess that these spectral transformations may be explained by the influence of an additional mass of both spacer itself and the **D** subunit. Such an influence is bound to result in small changes of geometrical parameters of the isocycle and the nearest fragments of porphyrin macrocycle and, correspondingly, in frequency changes of the normal modes. A certain support to this conclusion may be given by the following experimental fact. In FLN spectra of the ZnOEP-cycle with various substituents at the isocycle, the ZPLs shift to higher frequencies is observed in the range of 700–850 cm<sup>-1</sup> upon increasing the substituent mass [31]. For instance, the substitution of the hydrogen atom by an OH-group leads to a shift of ZPLs from 785 and 818 cm<sup>-1</sup> to 794 and 824 cm<sup>-1</sup>, respectively.

Thus, the FNL method offers the additional independent information confirming not only the formation of chemical dimers, but the existence of specific intermolecular interactions of  $\pi$ -conjugated macrocycles in the ground state.

### 3.3. Spectral manifestation of energy transfer

In the dimers of interest, excitonic interactions of strong B-transitions forming the Soret region of absorption spectra do not lead to the change of probabilities of electronic excitation energy deactivation in dimer subunits [25]. The comparison of absorption spectra of the dimers and corresponding monomers shows that in the visible region **D** and **A** subunits conserve their spectral individual character (see Fig. 2 spectra 1, 2 and 3). At the same time, the weak dipole–dipole interaction of Q-transitions of the dimer components (interaction energy  $V_{12} < 3–5$  cm<sup>-1</sup> at distance  $R = 1.23$  nm between macrocycle centers) manifests itself in the effective non-radiative singlet–singlet energy transfer (ET) with the probability of  $F^{ss} = 1.1 \times 10^{10}$  s<sup>-1</sup> and efficiency of  $\Phi = 0.95$  at 77 K. As a result, the fluorescence spectrum of both dimers is depicted only by emission bands of **A** subunit exclusively, e.g. of the ZnOEP-cycle=CH<sub>2</sub> [25]. This situation is conserved upon transition to 4.2 K. Under broad-band excitation into any region of the dimer absorption spectrum the emission is represented by bands of **A**, the ZnOEP-cycle=CH<sub>2</sub>, with FWHM of 5 nm for 0→0 electronic transition (see Fig. 7 spectrum a), i.e. **A** fluorescence bands exhibit temperature narrowing at liquid helium temperatures.

As mentioned above (see Section 3.2) under selective excitation within the long-wave absorption band of the dimers ( $\lambda_{exc} = 594$  nm) an FLN spectrum of the **A** subunit is observed (see Figs. 6, 7 spectra c). In contrast to this, upon excitation at  $\lambda_{exc} = 579$  nm FLN spectra of the dimers are absent practically (see Figs. 6, 7 spectra b). It should be noted that the excitation line of 579 nm falls within the absorption range of the **A** S<sub>0</sub>→S<sub>2</sub> transition and the **D** S<sub>0</sub>→S<sub>1</sub> transition simultaneously. If one takes into account that at this excitation wavelength the main part in absorption belongs to the **D** S<sub>0</sub>→S<sub>1</sub> transition (the molar extinction coefficients ratio is  $\epsilon_D/\epsilon_A \approx 10$ , see absorption spectra of individual **D** and **A** molecules



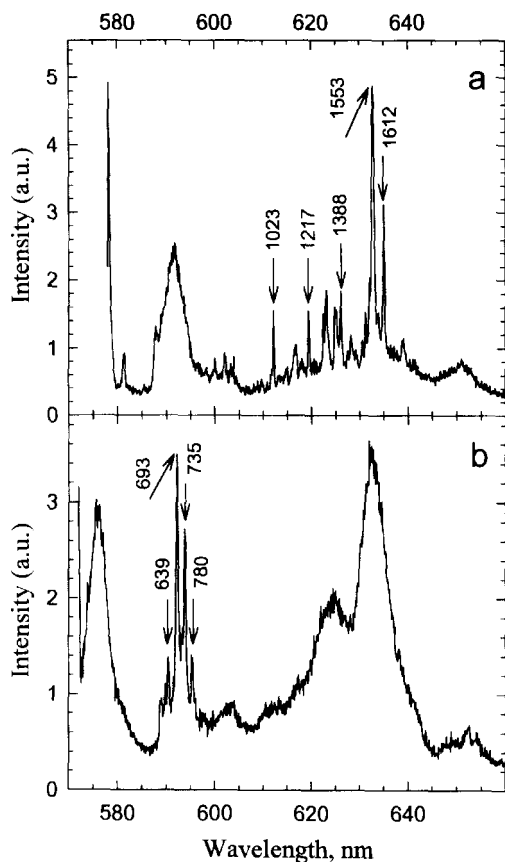


Fig. 8. Fluorescence spectra of an equimolecular mixture (ZnOEP-cycle + ZnOEP-cycle=CH<sub>2</sub>) in a tetrahydrofuran–toluene mixture (3 : 1) at 4.2 K and under selective excitation.  $\lambda_{\text{exc}} = 576$  nm (a) and 569 nm (b).

presented in Fig. 2), the disappearance of FLN spectra in this case may be attributed to an effective ET from the **D** subunit to the **A** one within both dimers.

Really, upon the same excitation ( $\lambda_{\text{exc}} = 576$  or 579 nm) of an equimolecular mixture of the ZnOEP-cycle and the ZnOEP-cycle=CH<sub>2</sub> (a total concentration  $C_{\Sigma} \leq 10^{-5} \text{ M}^{-1}$ ), superposition of two types of emission is observed in fluorescence spectra (see Fig. 8 spectrum a). In this case, the singlet–singlet ET is excluded fully because of large spatial separation of the solutes. Correspondingly, the ZPLs belong to the ZnOEP-cycle in an equimolecular mixture as far as their frequencies are coincident with the ZPLs' frequencies of the individual ZnOEP-cycle under se-

lective excitation within its  $S_0 \rightarrow S_1$  transition absorption band (see Fig. 4 spectrum b). Simultaneously, with that the structureless spectrum of the ZnOEP-cycle=CH<sub>2</sub> is observed upon excitation into its  $S_0 \rightarrow S_2$  transition. The shape and the position of bands in this structureless spectrum are consistent totally with those obtained for individual ZnOEP-cycle=CH<sub>2</sub> at the same excitation (see Fig. 5 spectrum a). To put it differently, in an equimolecular mixture the structureless emission of the ZnOEP-cycle=CH<sub>2</sub> forms a pedestal in the spectral range where the ZnOEP-cycle ZPLs manifest themselves.

So, the data obtained permit us to argue that upon selective excitation of the dimers within the  $S_0 \rightarrow S_1$  transition band of the **D** subunit the ET occurs to the **A** components whose absorption spectra are inhomogeneously broadened at 4.2 K in the frozen matrix used. Assuming that ET between **D** and **A** in the dimers, under the conditions of essential spectral inhomogeneity of **D–A** interacting pairs, may be resonant by nature (i.e. Förster mechanism is valid [32]) it is reasonable to note the following at least. As one can see from Figs. 2 and 4 the **D** fluorescence spectrum overlaps with the **A** absorption bands belonging to the  $S_0 \rightarrow S_1$  and the  $S_0 \rightarrow S_2$  transitions. Therefore, the situation is not excluded when singlet–singlet ET takes place from  $S_1$  level of the **D** subunit to both  $S_1$  and  $S_2$  levels of the **A** one. A detailed analysis of this situation together with direct measurements of the transfer rates and additional spectral data for the dimers of interest will be presented in a forthcoming paper. Nevertheless, we guess that in the conditions of dipole–dipole interactions there is no exact correlation between the energies of electronic transitions of **D** and **A** subunits in the dimers, e.g. the **D–A** energy gaps are not constant. As a result, we observe the loss of selectivity followed by the disappearance of the fine structure in dimer fluorescence spectra. In its spectral manifestation the effect being found resembles the situation characteristic of excitation into the  $S_0 \rightarrow S_2$  transition band of monomeric Zn-complexes of porphyrins with the isocycle. But the physical nature of the processes leading to the absence of correlation of excited states in the dimers is an alternative and is caused by the singlet–singlet ET under the conditions of essential inhomogeneous spectral broadening. The same process, the non-radiative ET with the probability  $F = 10^{11} \text{ s}^{-1}$ , has been found to cause a decrease

of the burning efficiency and the broadening of holes half-widths in SHB experiments for the symmetrical ethane-bisporphyrins at 1.8–51 K [18].

The important role of ET in lowering excitation selectivity has been justified theoretically in Ref. [32]. In this case, it is reasoned that the non-resonant transfer caused by the overlapping of phonon wings of a **D** emission spectrum with phonon wings of an **A** absorption leads to the ZPL disappearance. But it is well documented [18] that various porphyrins as well as their chemical dimers in a wide set of matrixes are characterized by values of the Debye–Waller factor no less than 0.7. Correspondingly, the strengths of electron–phonon interactions are weak in our case. Therefore, the contribution of non-resonant interactions by means of the overlap of phonon wings cannot play the essential role in ET processes in the dimers considered at 4.2 K.

In a given case, one would assume several alternative mechanisms of the ET with high rate constants. For instance, the full or partial resonance between ZPLs of a **D** emission and ZPLs of an **A** absorption may be realized in the dimers. For the elucidation of the role of narrow resonances between ZPLs in ET processes it is necessary to know, not only frequency distributions of ZPLs for **D** and **A** but the role of the inhomogeneous distribution of sites for the system under investigation. In that way, it would be possible to estimate, at least the mean transfer probability from selectively excited **D** to chemically bonded **A** in the dimer for all **D**–**A** pairs of the inhomogeneously broadened ensemble. It must be stressed that these questions have not been solved yet both in theoretical and experimental aspects and are a subject of much current interest.

On the other hand, such resonance conditions are not excluded for the corresponding overlap of ZPLs and weak phonon wings. At last, it should be noted that phonons with  $n = 1$  [33] not manifesting themselves as phonon wings and occupying a wide spectral region in absorption and fluorescence spectra upon selective excitation at 4.2 K (the so-called “non-structural” pedestal) may provide the resonance overlap of a **D** fluorescence and an **A** absorption which is necessary for the ET realization. This assumption may be the most probable one for the systems of interest.

Finally, a further experimental fact observed in the dimers’ emission spectra should be noted. For instance, upon excitation of the Zn-3<sup>1</sup>5<sup>1</sup>-cyclodimer at  $\lambda_{\text{exc}} = 572$  nm, the fine structure is observed in the range of the **A** fluorescence structureless 0–0 band (see Fig. 6, spectrum a). The same “multiplet” of ZPLs is present in the fluorescence spectrum of individual ZnOEP-cycle=CH<sub>2</sub> (see Fig. 5, spectrum b) and is characteristic also for emission spectra of **D** and **A** equimolecular mixture at the same excitation conditions (see Fig. 8, spectrum b). The nature of this “multiplet” has been discussed above (see Section 3.1). As seen from Figs. 6 and 8 the principal distinctions are found for the dimer and the equimolecular mixture. The dimer emission spectrum consists of the **A** fluorescence structureless part and the set of weak ZPLs. In contrast, for the **D** and **A** equimolecular mixture, fluorescence is represented by the **D** structureless spectrum and clearly pronounced structural “multiplet” of **A** exclusively. It should be mentioned that the conditions for excitation of the dimer and the mixture are the same:  $\lambda_{\text{exc}} = 572$  nm falls within the range of the **D** absorption  $S_0 \rightarrow S_2$  transition band and that of vibrational sublevels of the **A** absorption  $S_0 \rightarrow S_1$  transition simultaneously. Thus, it means that in the dimer the direct excitation of the **A** subunit is possible not only within its long-wavelength  $S_0 \rightarrow S_1$  transition but in the range of the **D** and **A** absorption bands overlap. Nevertheless, in the latter case, the **A** direct excitation is of lower efficiency in comparison with that via the ET. It is essential to note that such information cannot be obtained upon broad-band excitation even at liquid helium temperatures.

#### 4. Summary

The results presented herein have demonstrated the unique power of the method of FLN spectroscopy at 4.2 K. Upon studying the spectral features in complex artificial systems the nature of various interchromophoric interactions may be elucidated. By using this method the existence of specific interactions of  $\pi$ -conjugated macrocycles in Zn-porphyrin chemical dimers have been revealed. Furthermore, spectral manifestations of non-radiative singlet–singlet energy transfer in the dimers under the conditions of substantial spectral inhomogeneity of interacting

D–A pairs have been found. Several mechanisms of the observed effects are discussed. The obtained results may be used for an interpretation of site-selection experiments on photosynthetic systems *in vivo* and for a theoretical interpretation of the energy transfer process under the conditions of substantial spectral inhomogeneous broadening at low temperatures.

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