Spectroscopy of interchromophoric interactions in self-organized porphyrin and chlorin complexes

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Spectral-luminescent properties of multimolecular complexes (triads and pentads, complexation constants range from $5 \cdot 10^6$ to $5 \cdot 10^7$ M^{-1}) formed by two-fold coordination of di-pyridyl and tetra-pyridyl substituted porphyrin or related molecules with Zn-porphyrin and Zn-chlorin dimers having various spacers between macrocycles (-CH$_2$-CH$_2$- or phenyl ring) have been studied in methylcyclohexane solutions in a temperature range from 140 to 360 K. The red shift of Zn-dimer electronic Q- and B-bands ($\Delta v \leq 550$ cm^{-1}) upon complexation with pyridyl containing ligands is explained in terms of extra-ligation which influences the relative position for HOMO's a_{1u} and a_{2u} according to the four-orbital model. The splitting of Zn-dimer B-bands ($\Delta E \geq 600$ cm^{-1}) as well as the significant transformation of these bands in trimeric and pentameric complexes (redistribution of the absorption band intensities in Soret region and appearance of complicated splitted spectral manifolds $\Delta v \leq 1900$ cm^{-1}) is connected with excitonic interactions of strong B-transitions of π-conjugated macrocycles included in the complex. Observed experimental splittings are compared with theoretical values calculated using the point dipole approximation and a computer-simulated geometry of the complexes under investigation. It has been observed that mutual influence of π-electronic macrocycles in the complexes leads to the red shift of porphyrin extra-ligand free base Q-bands ($\Delta v \approx 120$ cm^{-1}) and is accompanied by quenching a fluorescence of certain components.

1. INTRODUCTION

The creation and investigation of supramolecular systems of tetrapyrrolic macrocycles based on the chemical synthesis as well as self-organization phenomena are perspective to mimic the primary photoprocesses of photosynthesis such as excitation energy transfer and electron transport. Up-to-date these phenomena have been investigated presumably for dimeric porphyrin assemblies [1,2] and for the ones with covalently linked electron donors or acceptors [3-5]. More complex arrays have been studied to a less extent [6-8].
    Recently we have described some photophysical and thermodynamic properties of trimeric and pentameric porphyrin and chlorin complexes [9]. In order to interpret in details the

photophysics of such systems it is necessary to analyze their spectral parameters taking into account a possible geometry of the systems and to compare experimental data with theoretical calculations using nowadays approaches. In this paper we discuss the influence of interchromophoric interactions of different types on spectral parameters of the complexes.

2. EXPERIMENTAL

Zn(II)1,4-bis[5-(10,15,20-tri-p-hexylphenylporphyrinyl)]benzene, (ZnHTPP)₂, with phenyl ring as a spacer is used as a main dimeric component of triads and pentads under investigation. Complexes with dimers of different origin, 1,2-bis{γ-[zinc(II) octaethylchlorinyl]}ethane - (ZnOECh)₂, and (ZnOEP)₂ with -CH₂-CH₂- spacer were studied as well. Porphyrin, chlorin and tetrahydroporhpyrin monomers (free bases and Cu-complexes) with 2 or 4 of pyridyl substituents in mesopositions having the nitrogen atom either in the meta- or para-position of pyridyl ring have been used as bi- or tetrafunctional ligands. Chemical structures of the components used to form the arrays are given in [9,10]. Synthesis, purification and identification of all monomeric and dimeric compounds as well as the procedure of calculation of thermodynamic parameters of the complexes (complexation constants, activation energy) will be published elsewhere [9,10]. All measurements were performed for the methylcyclohexane solutions (concentration ranged from $5 \cdot 10^{-7}$ to $8 \cdot 10^{-6}$ M) in the temperature range from 140 K to 360 K. When necessary small amounts (<10 % by volume) of dichloromethane were added to the stock solutions to dissolve some ligands.

Steady-state fluorescent and absorbance measurements were performed using Shimadzu UV-3101 PC and Beckman 5270 spectrophotometers, Shimadzu RF-5001 PC and SLM-4800 spectrofluorimeters. Fluorescence lifetimes and time-resolved spectra were measured using photon-counting spectrofluorometer PRA 3000 and a laser fluorescent picosecond setup (the response time is down to 30 ps) [9].

Values of excitonic interaction energy, V_{12}, in the complexes of interest and the corresponding splitting, ΔE, were estimated on the base of an approach developed in [11,12].

$$\Delta E = 2V_{12} \cdot \left[1 + \frac{\lambda_{dim}^2}{4\varepsilon_{int}^2 - 1} \right],$$ (1)

$$V_{12} = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \vec{R}_{12}) \cdot (\vec{\mu}_2 \cdot \vec{R}_{12})}{R^3} = \frac{e^2 \cdot M^2 \cdot K}{h \cdot c \cdot n^2 \cdot R^3},$$ (2)

where $K = \cos\alpha - 3 \cdot \cos\beta \cdot \cos\theta$ is an orientation factor of dipole-dipole interaction; h is the Plank constant; c is the speed of light; n is a refractive index; R is a distance between centers of interacting dipoles; $\lambda_{dim} = \sqrt{\left[\frac{B(0,1)}{B(0,0)} \right]_{mon}}$ is a parameter of vibronic displacement (B(0,0) and B(0,1) are intensities of pure electronic and vibronic bands in Soret region for the monomeric component, correspondingly); $\varepsilon_{int} = \frac{V_{12}}{h\nu}$ is a parameter of excitonic coupling (hv

is an energy of average vibrational quantum); $M = \sqrt{\dfrac{\varepsilon_{max}}{2500 \cdot G} \cdot \dfrac{\Delta\lambda}{\lambda}}$ is a length of the interacting dipoles (Å), G is a transition degeneracy, $\dfrac{\Delta\lambda}{\lambda}$ is a ratio of the band halfwidth to the wavelength of its maximum, ε_{max} is a value of decimal extinction coefficient at the band maximum ($l \cdot cm^{-1} \cdot mole^{-1}$).

3. RESULTS AND DISCUSSION

When titration of Zn-dimer bulk solution by pyridyl substituted tetrapyrrole macrocycle and study the transformation of absorption and fluorescence spectra of mixtures it has been established that the two-point interaction of pyridyl nitrogens with Zn-ions of the dimers leads to the formation of trimeric complexes for bipyridyl ligands and pentameric assemblies for tetrapyridyl ones. Computer simulated structures of some complexes under investigation are presented below.
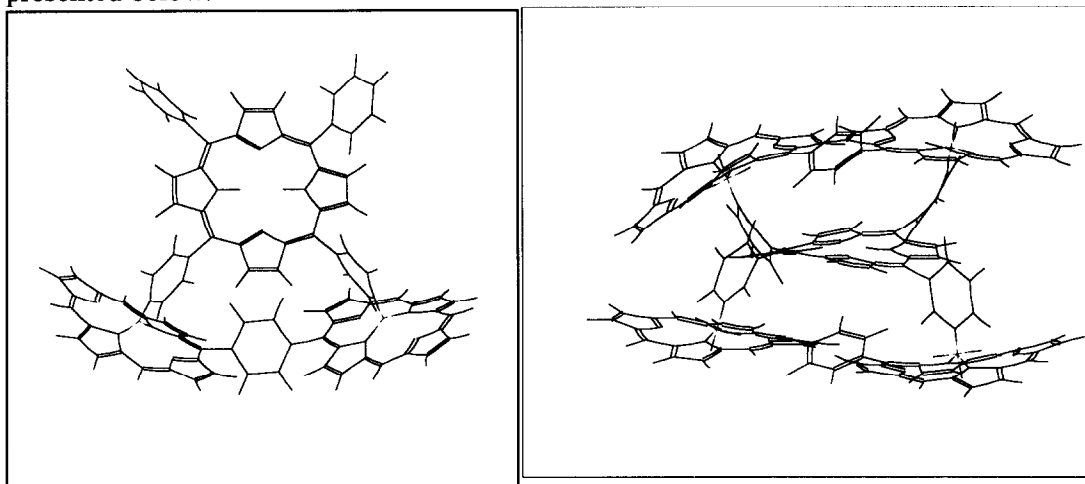
The formation of self-organized multimolecular assemblies of various types and composition manifests itself in some common and specific transformations of optical spectra of interacting components:

- for triads and pentads the red shift of Zn-dimer electronic Q- and B-bands ($\Delta v \leq 550$ cm^{-1}) is characteristic and is accompanied by changes of the relative intensities of Zn-dimers Q(0,0) and Q(0,1) bands in absorption and fluorescence spectra; such effects are typical with those when pyridine is used as an extra-ligand;
- the appearance of triads in titration experiments is accompanied by the existence of isobestic points in absorption and fluorescence spectra (under excitation at isobestic point); for pentads such isobestic point in emission spectra are not found; in the most of cases the strong Zn-dimer fluorescence quenching is observed ($\tau_s \leq 10$ ps according with picosecond time-resolved fluorescent measurements);
- strong B-transitions of the ligands can not take part in excitonic coupling within the complexes because of lack of resonant conditions with ligated components of the dimers involved into the complexes; hence variation of Soret band shape upon two-fold

coordination of Zn-dimers can be connected with variation of resonant conditions within a ligated dimer or appearance of charge-transfer bands; $(ZnHTPP)_2+H_2P-(p^\wedge Pyr)_2$ triad shows clearly a redistribution of relative intensities of Soret band components caused by a variation of dimer geometry upon two-fold coordination; on the other hand $(ZnHTPP)_2+H_2P-(m-Pyr)_2$ triad absorption spectrum contains shoulder at 407 nm which can be connected with formation of a charge transfer state within the complex;

- $2(ZnHTPP)_2+H_2P-(m-Pyr)_4$ pentad absorption spectra demonstrates a complicated splitting (at least 8 components with $\Delta v \leq 1900$ cm^{-1}) which can be connected with excitonic coupling of components of two dimers linked in a specific "meta-opposite" geometry (see right part of the Figure above); other geometries of the pentads prevent excitonic interactions between two linked dimers which results in their "triad-like" spectra;

- upon complexation the red shift (from 2 to 11 nm depending on the nature of components and complex structure) and broadening $Q(0,0)$ bands of extra-ligand are detected; for all pentads and in some cases for triads the noticeable quenching of extra-ligand fluorescence have been revealed.

4. ACKNOWLEDGMENTS

5. REFERENCES

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