SPECTRAL MANIFESTATION OF THE AGGREGATION OF MOLECULES OF OCTACARBOXYPHTHALOCYANINE AND ITS ZINC COMPLEX IN A NANOPOROUS SILICATE GEL MATRIX

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The luminescent-spectral properties of molecules of 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine and its zinc complex embedded in nanoporous silicate gel matrices were studied. It was found that H-aggregates of the phthalocyanines are formed at the initial stage of formation of the silicate framework. It was discovered that the monomeric form of the zinc complex in the gel matrix is restored when the silicate material is dried. The reasons for destruction of the aggregates in the restricted volume of the matrix of nanoscale pores are discussed.

Keywords: octacarboxyphthalocyanine, zinc complex, sol-gel synthesis, silicate matrix, absorption and fluorescence spectra, monomeric and aggregated forms.

Introduction. The range of practical applications of phthalocyanines can be extended by changing their structure — by modifying the benzene fragments of the phthalocyanine ring with functional side substituents and/or by choosing an additional central metal atom that enters into coordination with the phthalocyanine macrocycle (the formation of metal complexes) and also by combining various axial ligands with the central atom. In [1-5] it was shown that the addition of eight COOH groups at the ortho positions of phthalocyanine (the formation of the free base 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine ($H_2(COOH)_8Pc$)) significantly increases the solubility of the compounds in water and other solvents. Investigations of octacarbonylphthalocyanines as potential photosensitizers for photodynamic therapy [6, 7] or as agents having high catalytic and photocatalytic activity [5, 8] were motivated by their intense absorption in the phototherapeutic window (600–800 nm) and also by the above-mentioned ability to form aqueous solutions as close as possible to physiological. At the same time an effect undesirable for such applications can arise in the solutions, i.e., the formation of aggregates of the phthalocyanines on account of noncovalent forces of attraction between two or more molecules of the monomer. Photoelectrochemical investigations [9, 10] showed that $M(COOH)_8Pc$ in the solid state, adsorbed on the surface of a thin porous film of ZnO, can fulfill the role of photosensitizers in photovoltaic cells. A thin composite film containing layers of Cu(COOH)₈Pc and an organic polymer exhibits third-order nonlinearity [11] and can be used in optoelectronics. Investigations of the luminescence spectral characteristics of Zn(COOH)₈Pc, deposited on a gold surface in the form of films [12] or covalently bonded to the surface of magnetic nanoparticles of Fe₃O₄ [13], and also the spectral manifestations of its interaction with amino acids and albumin [14] can also find useful practical applications. In the present work, the luminescence-spectral characteristics and structural changes of $H_2(COOH)_8Pc$ and $Zn(COOH)_8Pc$, inserted into bulk solid nanoporous silicate gel matrices, were investigated.

Subjects of Investigation and Experimental Procedure. The $H_2(COOH)_8Pc$ and its zinc complex $Zn(COOH)_8Pc$ were synthesized and purified at GNTs NIOPIK (Scientific–Research Institute of Organic Intermediates and Dyes, Moscow, Russia) with scientific cooperation by the methods described in [7, 15].

The volumetric silicate gel-matrices activated with octacarboxyphthalocyanines were obtained by the method in [16], i.e., by hydrolysis and condensation of tetraethoxysilane $Si(OCH_2CH_3)_4$ (TEOS) in a water–alcohol medium with the

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components of the reaction mixture in the molar ratio TEOS:ethanol:water:formamide = 1:5:55. Commercial TEOS (Sigma-Aldrich) was used without further purification. In order to accelerate the hydrolysis process ~0.1 mole of hydrochloric acid was added, and the mixture was stirred for 4 h until a uniform solution was obtained (the beginning of the hydrolysis stage). The prepared reaction mixture, which had an acid reaction (pH ~ 4), was poured into plastic cuvettes, and saturated solutions of $H_2(COOH)_8Pc$ and $Zn(COOH)_8Pc$ in dimethylformamide (DMFA) were added. The choice of DMFA was based on its high solubility in the water-alcohol medium. The cuvettes were tightly closed with an airtight Parafilm M film and left at room temperature in the dark. In five days a solid xerogel was formed (the polycondensation stage): a silicate framework, into the pores of which the phthalocyanine molecules were inserted, was formed. In order to remove the liquid components (water ethanol, DMFA) from the nanopores of the gel materials an opening with a diameter of ~1 mm was made in the covering film, and the gel matrices were kept at room temperature and atmospheric pressure for a long time (up to 60 days). The drying process led to an appreciable decrease in the volume of the gel, as a result of which the silicate matrices shrank to 50–70% of their original volume.

Measurements of the electronic absorption spectra (EAS) were made on a Cary-500 Scan spectrophotometer (Varian, USA). The fluorescence spectra were obtained with excitation by pulsed radiation from a semiconductor laser diode (analog of SANYO DL4146-101S, $\lambda_{exc} = 405$ nm) and detection of radiation using a photoelectronic amplifier (PM943-02, Hamamatsu, Japan). The luminescence spectral measurements were done at room temperature.

The semiempirical quantum-chemical AM-1 method from the HyperChem chemical software package (Hypercube, Inc.) was used to optimize the geometric structure of the $H_2(COOH)_8Pc$ and $Zn(COOH)_8Pc$ molecules in the S_0 ground state. The geometry was considered optimized when the change of total energy after successive computation steps was not greater than 0.01 kcal/mole.

Results and Discussion. The optimized structures of the H₂(COOH)₈Pc and Zn(COOH)₈Pc molecules have the planar structure of the phthalocyanine ring. Figure 1a shows the optimized geometry of the H₂(COOH)₈Pc. The zinc atom in the Zn(COOH)₈Pc molecule lies practically in the plane of the macrocycle and, as shown in [14], can come out of the plane if an axial ligand is added. As mentioned in [5, 14], the planes of the eight carboxyl substituents at the periphery of the four benzene rings lie at an angle to the plane of the macrocycle (the noncoplanar structure, Fig. 1b). By virtue of the asymmetry of the structure of the COOH group the carboxyl substituents can be arranged in different ways in relation to each other (of the same or different types), leading to the formation of a number of rotational isomers (conformers) of H₂(COOH)₈Pc in which the inclination of the planes containing the carboxyl groups to the plane of the macrocycle adopts different but fixed values (from 25° to 50°). It can be assumed that the experimental samples contain a mixture of such isomers, and one of the possible rotational isomers of H₂(COOH)₈Pc is shown in Fig. 1. As shown by the calculations, the total energies of the molecules of the possible rotational isomers of H₂(COOH)₈Pc hardly differ at all ($E_i = -9993.15 \pm 0.40$ kcal/mole). It is known that the polarity of the O–H bond of the carbonyl group in the molecules of carboxylic acids, which octacarboxyphthalocyanines are, rises thereby increasing the effective positive charge (δ^+) at the hydrogen atom, while an effective negative charge (δ^-) is formed at the oxygen atom of the C=O bond. This enables the formation of both intra- and intermolecular hydrogen bonds with the COOH groups and has a significant effect on the luminescence-spectral characteristics of the octacarboxyphthalocyanines.

The intermolecular interaction processes of octacarboxyphthalocyanines in silicate TEOS gel-matrices (the formation of aggregates) were investigated by analysis of the spectral position of the long-wave absorption bands (Q bands), their intensities, and their half-widths as parameters most sensitive to the state of the π -electronic conjugation system of the macrocycle. Figure 2 shows the long-wave region of the EAS of H₂(COOH)₈Pc and Zn(COOH)₈Pc in DMFA and TEOS gel-matrices after drying for 5, 30, and 60 days.

The electronic absorption spectra of the free base H₂(COOH)₈Pc in DMFA (Fig. 2a, curve 1) has two closely situated strong bands at 741 and 691 nm (with a shoulder at 683 nm), which correspond to two electronic transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ (Q_x and Q_y components, symmetry of the conjugated system D_{2h}). The Zn(COOH)₈Pc in DMFA (Fig. 2b, curve 1) has one strong band at 697 nm, which indicates an increase of the symmetry of the conjugated system to D_{4h} and degeneracy of the S_1 and S_2 states. On the short-wave side from these bands there are much weaker vibronic bands (in the region of 610–670 nm). These data agree with published data for H₂(COOH)₈Pc[2] and Zn(COOH)₈Pc [3, 12] in DMFA. A bathochromic shift of the long-wave bands in relation to the bands of the corresponding unsubstituted phthalocyanines (e.g., in DMFA from 670 nm (ZnPc) [5] to 697 nm (Zn(COOH)₈Pc)) is mainly explained by the appearance of a mesomeric effect — shift of the electron density of the π -conjugation chain of the macrocycle onto the electronegative COOH groups. The possible effect of indirect conjugation of the nonplanar carboxyl substituents with the macrocycle is weak, and it can be stated that it plays a secondary role in the bathochromic shift of the bands. We note that the half-width of the Q_x band of H₂(COOH)₈Pc

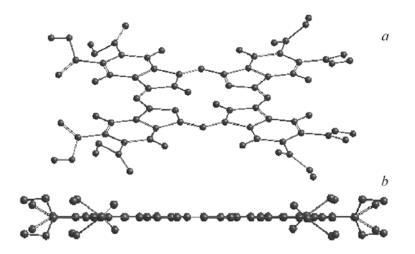


Fig. 1. Three-dimensional image of the optimized geometry of one of the stereoisomers of $H_2(COOH)_8Pc$ (a) and its projections onto a plane perpendicular to the macrocycle (b).

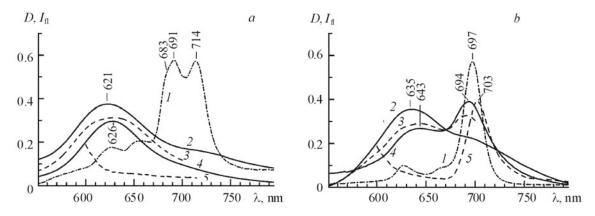


Fig. 2. Electronic absorption spectra of $H_2(COOH)_8Pc$ (a) and $Zn(COOH)_8Pc$ (b) in DMFA (1) and in the TEOS gel-matrix after drying for 5 (2), 30 (3), and 60 (4) days; 5) fluorescence spectrum ($\lambda_{exc} = 405 \text{ nm}$) of $H_2(COOH)_8Pc$ (a) and $Zn(COOH)_8Pc$ (b) in TEOS gel-matrix after drying for 60 days.

 $(\Delta v_{714} \approx 430 \text{ cm}^{-1})$ is close to the half-width of the *Q* band of Zn(COOH)₈Pc ($\Delta v_{697} \approx 440 \text{ cm}^{-1}$). The spectral characteristics of H₂(COOH)₈Pc and Zn(COOH)₈Pc are indicators of a molecular (monomeric) state for the substances in DMFA solutions. In [17] it was concluded that DMFA, which has high permittivity, enables reversible dissociation of the COOH groups (-COOH \leftrightarrow -COO⁻ + H⁺), electrostatic repulsion of which predominates over chromophore–chromophore π - π interaction, and this is the reason why carboxy-substituted phthalocyanines exist in monomeric form in DMFA.

With the introduction of $H_2(COOH)_8Pc$ and $Zn(COOH)_8Pc$ into the TEOS gel-matrix after drying for 5 days their electronic absorption spectrum undergo substantial changes (Fig. 2, curve 2); the spectral bands have a hypsochromic shift in relation to the bands of the monomeric forms and become significantly broader with decrease of the absorption intensity. The hypsochromic shift of the spectrum of $H_2(COOH)_8Pc$ (from 714 nm in DMFA to 621 nm in TEOS) and $Zn(COOH)_8Pc$ (from 697 in DMFA to 635 nm in TEOS) is accompanied by broadening of the bands to $\Delta v_{621} \approx 2000 \text{ cm}^{-1}$ and $\Delta v_{635} \approx 2100 \text{ cm}^{-1}$. (The appearance of a contribution from nonuniform broadening of the absorption bands is possible.) At this stage of drying of the TEOS weak bands for the residual amount of the original monomeric form appear in the EAS in the region of 700 nm.

Increase of the drying time of the activated gel-matrices right up to 60 days has various effects on the EAS. Thus, with increase of the drying time of the TEOS sample (Fig. 2a, curves 3 and 4) $H_2(COOH)_8Pc$ retains the one-pole form with

an insignificant bathochromic shift of the maximum (by ~5 nm) to 626 nm and narrowing of the half-width of the band to $\Delta v_{626} \approx 1800 \text{ cm}^{-1}$. With increase of drying time the EAS of Zn(COOH)₈Pc exhibits fundamentally different behavior: in the spectral region of the monomeric form the band at 694 nm with $\Delta v_{694} \approx 1000 \text{ cm}^{-1}$ becomes stronger while the intensity of the short-wave band decreases with shift of the maximum to 643 nm (Fig. 2b, curves 3 and 4). The transformation of the EAS of Zn(COOH)₈Pc is characterized by the presence of isobestic points, indicating the presence of two spectral forms in the TEOS matrix. Excitation of the phthalocyanines in TEOS matrices that have been subjected to drying for 60 h by radiation with $\lambda_{exc} = 405 \text{ nm}$ shows that there is no fluorescent emission in H₂(COOH)₈Pc (Fig. 2a, curve 5) whereas Zn(COOH)₈Pc has a strong fluorescence band with a maximum at 703 nm and $\Delta v_{703} \approx 550 \text{ cm}^{-1}$ (Fig. 2b, curve 5). Since fluorescence of the employed laser its absence for H₂(COOH)₈Pc in the TEOS matrix with the presence of strong emission from the matrix itself at $\lambda < 620 \text{ cm}^{-1}$ indicates absence of the monomeric form in contrast to Zn(COOH)₈Pc in the TEOS matrix, where the fluorescence of its monomers and strong emission from the silicate matrix are observed.

By analyzing the luminescence spectral characteristics of the phthalocyanines in the TEOS gel-matrices it was possible to reach a series of conclusions about the reasons for their different behavior for $H_2(COOH)_8Pc$ and $Zn(COOH)_8Pc$.

At the early stages of the low-temperature hydrolysis and polycondensation of TEPS a three-dimensional polymeric framework (nanoporous material) is formed as a result of the connection of the silicon atoms by siloxane bonds (\equiv Si–O–Si \equiv). As a result of incomplete polycondensation of the molecular units of TEOS the surface of the nanopores can contain a number of silanol groups (\equiv Si–OH) attached to the framework. Part of the silanol groups can undergo dissociation (elimination of a proton H⁺), and centers of negative charge (\equiv Si–O⁻) on the surface of nanopores.

The H₂(COOH)₈Pc molecules, situated in the nanopores of the TEOS gel–matrix filled with the acid water–alcohol medium, are in a state of aggregation, as shown by the presence of a broad absorption band at 621 nm (Fig. 2a, curve 2) with a bathochromic shift in relation to the absorption of the "traces" of monomer (700–730 nm). Analogous spectral and structural changes were observed for H₂(COOH)₈Pc in water when the pH was reduced to 2–5 [4, 15] and indicated the formation of H aggregates (with a face-to-face structure) of two or more molecules. Such a type of aggregation is also confirmed by the absence of fluorescence from H₂(COOH)₈Pc in a silicate matrix (Fig. 2a, curve 5). The mechanism of H-type aggregation in carboxyphthalocyanines is closely linked to π - π interaction of adjacent macrocycles. For H₂(COOH)₈Pc in acidic aqueous media (even at low H⁺ concentrations) H aggregation is initiated by shift of the equilibrium toward neutralization of the charge of the dissociated –COO⁻ groups [17] and, consequently, by an additional process involving hydrogen bond formation between the out-of-plane COOH groups of adjacent molecules [18], leading to the formation of "pole-like" ("column-like") aggregated structures.

Other processes may also be responsible for the aggregation of $H_2(COOH)_8Pc$ in silicate gel-matrices. As seen from Fig. 2a (curve 3), the absorption band of the H aggregate becomes broader when the drying time is increased to 30 days. This is due to the formation not only of such dimers but also of more complex aggregates as a result of decrease in the volume of nanopores in the matrix and increase of the local concentration of the phthalocyanine. Further evaporation of the solvents and shrinkage of the gel (drying up to 60 days) lead to effective contact between the $H_2(COOH)_8Pc$ molecules and the silicate framework. As a result a hydrogen bond can be formed between the carbonyl oxygen atom of the carboxyl group and the surface silanol groups of the nanopores (C=O...HO–Si≡) and/or between the hydroxyl of the carboxyl group and the surface centers of negative charge (C=OH...¯O–Si≡), which enables the adsorption of fluorophores on the surface of the nanopores, stabilization, and retention of the state of aggregation. The slight bathochromic shift of the maximum of the absorption band of the aggregate and its narrowing (Fig. 2a, curve 4) indicate a change in the local environment of the impurity molecules in the nanopores of the matrix with the drying time of the material, i.e., possible decrease of the nonuniform broadening.

As in the case of $H_2(COOH)_8Pc$, the hypsochromic shift in the EAS of $Zn(COOH)_8Pc$ after drying for 5 days (Fig. 2b, curve 2) indicates the formation of H-type aggregates. In [19] it was established that the carboxyl groups of $Zn(COOH)_8Pc$ shift the electron density from the central nitrogen atoms of the phthalocyanine macrocycle, thereby weakening the $Zn^{2+} \leftarrow N$ bond and increasing the coordinating ability of the central metal ion. In this situation the polar aprotic DMFA molecules, added to the sol–gel reaction mixture as solvent for the phthalocyanine metal complex, solvate the Zn the phthalprotic DMFA mols the central metal atom. o 30 daysabsnb²⁺ cation, fulfilling the role of axial ligand (the result of coordination of the Zn²⁺ cations with the carbonyl oxygen atom of DMFA). The bulky axial ligand here increases the distance between the adjacent planes of the aggregated macrocycles, thereby weakening the intermolecular π - π interaction.

It can be stated that the bond of the H-type aggregates of $Zn(COOH)_8Pc$ with the surface of the nanopores of the TEOS gel-matrix explains the change of their spectral characteristics with increase of the drying time (Fig. 2b, curves 3

and 4). Evaporation of the molecules of the solvent, including DMFA, from the pores of the matrix leads to destruction of the aggregates with the structure of the axial extraligand and to the formation of monomeric forms attached to the surface of the nanopores at some distance from each other. As a result, we assume that the DMFA molecules play a dual role in the observed phenomenon: they enable first the formation of aggregates and then their destruction. Such a mechanism is confirmed, on the one hand, by the presence of isobestic points in the electronic absorption spectra (Fig. 2b) during transition of the Zn(COOH)₈Pc complex from the aggregated to the monomeric state during drying of the TEOS gel–matrix and, on the other, the fact that the appearance of a fluorescence effect after disaggregation of the phthalocyanine (Fig. 2b, curve 5) is a consequence of the formation of the nanoporous silicate gel–matrix occurs in the restricted volume of the nanosized pores of the matrix, i.e., in a chemical nanoreactor where the processes of formation of hydrogen bonds between the framework and the impurity molecules are induced. The disaggregation process proposed above differs fundamentally from the mechanism in [20], where the disaggregation of Zn(COOH)₈Pc results from change of pH in the aqueous buffer solutions.

Conclusions. The aim of the investigations was to seek possibilities of using phthalocyanines as functional solidstate materials in optical applications. As a rule, the molecules of this type of compound inserted into solid-state activated media exhibit a steady tendency for aggregation, leading to strong quenching of fluorescence and blurring of the spectrum, which has an unfavorable effect on the properties of these compounds and greatly restricts their practical applications.

The luminescence spectral characteristics of the molecules of octacarboxyphthalocyanine and its zinc complex, inserted into silicate gel-matrices, were investigated. It was found that H-aggregation of the phthalocyanines occurs at the initial stage of formation of the silicate framework, as indicated by the hypsochromic shift of the long-wave absorption bands and by the absence of fluorescence in the aggregates. It was shown that for $Zn(COOH)_8Pc$ in a TEOS gel-matrix the monomeric form is restored when the material is dried at room temperature. The reasons for destruction of the initially formed $Zn(COOH)_8Pc$ aggregates are interaction between the carboxyl groups of the phthalocyanine and the surface of the nanopores in the silicate framework and subsequent removal of the axial DMFA ligands in the drying process, leading to restoration of the monomeric molecules attached to the surface of the nanopores at some distance from each other. The aggregate H form for the ligand-free H₂(COOH)₈Pc molecules is preserved during drying, resulting in stronger π - π interaction between the closely located adjacent planar macrocycles.

The highly transparent and luminescent silicate gel-matrices activated with Zn(COOH)₈Pc can be used as promising materials in optical devices at wavelengths adjacent to the near IR region.

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