

## 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  $Fe_3O_4$  [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 = 1:5:5:5. 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  $\text{H}_2(\text{COOH})_8\text{Pc}$  and  $\text{Zn}(\text{COOH})_8\text{Pc}$  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,  $\lambda_{\text{exc}} = 405$  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  $\text{H}_2(\text{COOH})_8\text{Pc}$  and  $\text{Zn}(\text{COOH})_8\text{Pc}$  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  $\text{H}_2(\text{COOH})_8\text{Pc}$  and  $\text{Zn}(\text{COOH})_8\text{Pc}$  molecules have the planar structure of the phthalocyanine ring. Figure 1a shows the optimized geometry of the  $\text{H}_2(\text{COOH})_8\text{Pc}$ . The zinc atom in the  $\text{Zn}(\text{COOH})_8\text{Pc}$  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  $\text{H}_2(\text{COOH})_8\text{Pc}$  in which the inclination of the planes containing the carboxyl groups to the plane of the macrocycle adopts different but fixed values (from  $25^\circ$  to  $50^\circ$ ). It can be assumed that the experimental samples contain a mixture of such isomers, and one of the possible isomers of  $\text{H}_2(\text{COOH})_8\text{Pc}$  is shown in Fig. 1. As shown by the calculations, the total energies of the molecules of the possible rotational isomers of  $\text{H}_2(\text{COOH})_8\text{Pc}$  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 ( $\delta^+$ ) at the hydrogen atom, while an effective negative charge ( $\delta^-$ ) 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  $\pi$ -electronic conjugation system of the macrocycle. Figure 2 shows the long-wave region of the EAS of  $\text{H}_2(\text{COOH})_8\text{Pc}$  and  $\text{Zn}(\text{COOH})_8\text{Pc}$  in DMFA and TEOS gel–matrices after drying for 5, 30, and 60 days.

The electronic absorption spectra of the free base  $\text{H}_2(\text{COOH})_8\text{Pc}$  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  $\text{Zn}(\text{COOH})_8\text{Pc}$  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  $\text{H}_2(\text{COOH})_8\text{Pc}$  [2] and  $\text{Zn}(\text{COOH})_8\text{Pc}$  [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 ( $\text{ZnPc}$ ) [5] to 697 nm ( $\text{Zn}(\text{COOH})_8\text{Pc}$ )) is mainly explained by the appearance of a mesomeric effect — shift of the electron density of the  $\pi$ -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  $\text{H}_2(\text{COOH})_8\text{Pc}$

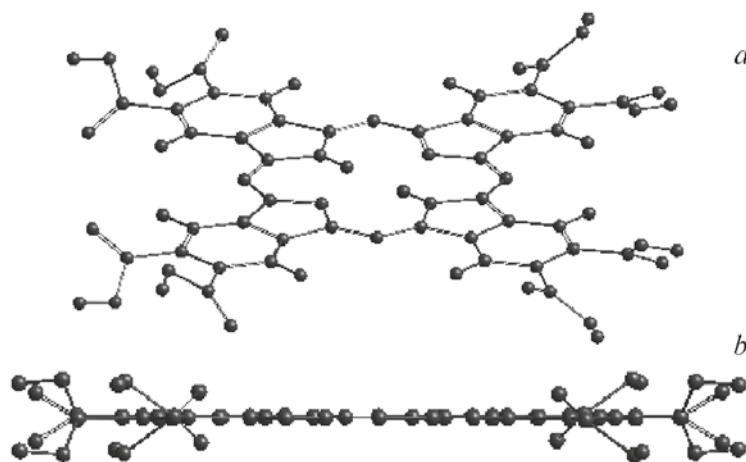


Fig. 1. Three-dimensional image of the optimized geometry of one of the stereoisomers of  $\text{H}_2(\text{COOH})_8\text{Pc}$  (a) and its projections onto a plane perpendicular to the macrocycle (b).

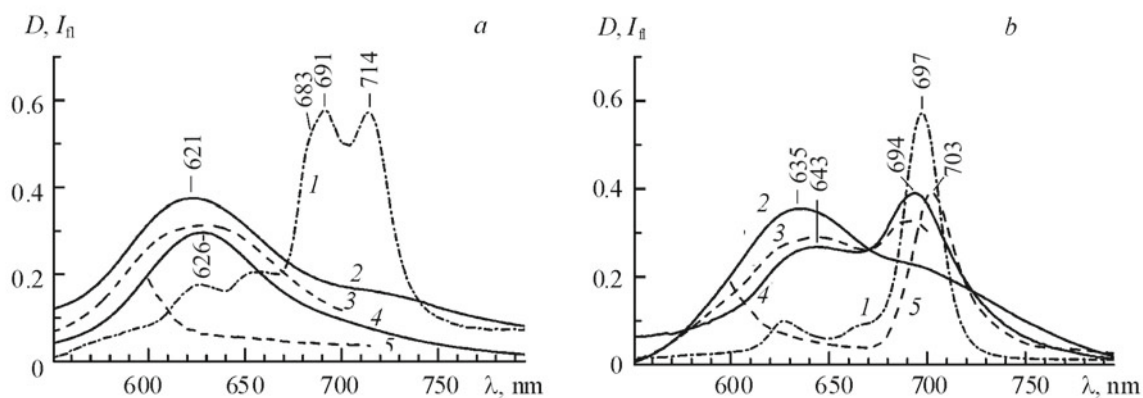


Fig. 2. Electronic absorption spectra of  $\text{H}_2(\text{COOH})_8\text{Pc}$  (a) and  $\text{Zn}(\text{COOH})_8\text{Pc}$  (b) in DMFA (1) and in the TEOS gel-matrix after drying for 5 (2), 30 (3), and 60 (4) days; 5) fluorescence spectrum ( $\lambda_{\text{exc}} = 405 \text{ nm}$ ) of  $\text{H}_2(\text{COOH})_8\text{Pc}$  (a) and  $\text{Zn}(\text{COOH})_8\text{Pc}$  (b) in TEOS gel-matrix after drying for 60 days.

( $\Delta\nu_{714} \approx 430 \text{ cm}^{-1}$ ) is close to the half-width of the  $Q$  band of  $\text{Zn}(\text{COOH})_8\text{Pc}$  ( $\Delta\nu_{697} \approx 440 \text{ cm}^{-1}$ ). The spectral characteristics of  $\text{H}_2(\text{COOH})_8\text{Pc}$  and  $\text{Zn}(\text{COOH})_8\text{Pc}$  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 ( $-\text{COOH} \leftrightarrow -\text{COO}^- + \text{H}^+$ ), electrostatic repulsion of which predominates over chromophore–chromophore  $\pi$ – $\pi$  interaction, and this is the reason why carboxy-substituted phthalocyanines exist in monomeric form in DMFA.

With the introduction of  $\text{H}_2(\text{COOH})_8\text{Pc}$  and  $\text{Zn}(\text{COOH})_8\text{Pc}$  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  $\text{H}_2(\text{COOH})_8\text{Pc}$  (from 714 nm in DMFA to 621 nm in TEOS) and  $\text{Zn}(\text{COOH})_8\text{Pc}$  (from 697 in DMFA to 635 nm in TEOS) is accompanied by broadening of the bands to  $\Delta\nu_{621} \approx 2000 \text{ cm}^{-1}$  and  $\Delta\nu_{635} \approx 2100 \text{ cm}^{-1}$ . (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)  $\text{H}_2(\text{COOH})_8\text{Pc}$  retains the one-pole form with



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  $\text{Zn}(\text{COOH})_8\text{Pc}$  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 monomeric fluorescent form. We note that restoration of the monomeric form of  $\text{Zn}(\text{COOH})_8\text{Pc}$  in the drying process 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  $\text{Zn}(\text{COOH})_8\text{Pc}$  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 solid-state 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  $\text{Zn}(\text{COOH})_8\text{Pc}$  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  $\text{Zn}(\text{COOH})_8\text{Pc}$  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  $\text{H}_2(\text{COOH})_8\text{Pc}$  molecules is preserved during drying, resulting in stronger  $\pi$ – $\pi$  interaction between the closely located adjacent planar macrocycles.

The highly transparent and luminescent silicate gel–matrices activated with  $\text{Zn}(\text{COOH})_8\text{Pc}$  can be used as promising materials in optical devices at wavelengths adjacent to the near IR region.

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