

Optical and physico-chemical properties of tetrapyrrole molecules in nanoporous silicate gel matrices

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Dedicated to Professor Evgeny Luk'yanets on the occasion of his 75th birthday

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ABSTRACT: In this mini-review, we present the main results of our works on the spectroscopy of the molecules of tetrapyrrole pigments incorporated into nanoporous gel matrices. Xerogels activated by organic dyes are promising materials for applications in various fields of technology. The influence of the technique of embedment of the activator molecules on their physico-chemical properties has been analyzed. The specificity of the action of a silicate matrix as external medium, as compared to liquid and solid solutions, is shown.

KEYWORDS: sol-gel synthesis, silica gel matrices doped with tetrapyrrole molecules, chemical grafting, cation forms of porphyrins, aggregation, UV-vis absorption spectra, fluorescence, fluorescence line narrowing, persistent spectral hole burning, sensor.

INTRODUCTION

Development of modern technologies requires creation of various miniature optical devices operating in wide spectral region and usable in engineering, medicine, ecology, *etc.* — for continuous and nondestructive monitoring of the efficiency and security of human life-activity and for realization of production processes. The most convenient for practical use are the optical devices elaborated on the basis of bulky or thin-film solid-state materials. Very promising, in this respect, are materials activated by organic molecules [1, 2]. As a scientific basis for the development of specific optical devices, a systematic study of the correlation between the spectral properties of a molecular optical center and its structure is necessary, the notion of optical center including an organic compound and local environment in a solid-state matrix. Among the matrices that are currently used in the search for practical applications, special attention is given to silicate matrices that are synthesized by the sol-gel method from silicium alkoxides [3]. Such nanoporous

matrices are obtained at room temperature and possess several advantages: transparency in a wide spectral region (from UV to NIR); high optical homogeneity; increased mechanical strength which allows withstanding sharp temperature differences; high threshold of optical damage — gel matrices endure incident radiation intensities of hundreds MW/cm² without destruction; the possibility to control the porosity of the obtained xerogels; strongly pronounced capillary effect, *etc.* [4]. These properties determined considerable interest on gel materials as new nanostructured functional materials promising for use in nano-, opto-, and microelectronics. Specific conditions of sol-gel synthesis of these materials may be widely varied (the choice of chemical structure of initial metal alkoxides; alteration of reaction components concentration, varying pH by using a set of acid-base catalysts, varying reaction temperature and conditions of gel drying, *etc.*) which makes it possible to modify the final physico-chemical characteristics of gel systems. The field of virtual practical applications of inorganic gel materials is essentially expanded due to the fact that they may be activated by polyatomic organic molecules which is feasible because the sol-gel synthesis is carried out at temperatures that are close to ambient conditions. At the

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same time, there are certain difficulties in the embedment of organic molecules into gel matrices. For instance, the solubility of many organic dyes in the reaction medium is usually low, and this requires special choice of the components of sol-gel synthesis. Also, association effects take place in the matrix due to small volume of the pores — the local concentration is high. In both cases, chemical modification of the chromophore is needed — either for solubilization, or to hinder aggregation. It is necessary to note that, in the process of sol-gel synthesis, reactive hydroxyl groups appear in high concentration on the surface of pores of the end gel material; these groups can essentially influence the optical and physico-chemical properties of the embedded molecules.

For the last two decades, the authors participated in experimental studies of the optical and physico-chemical properties of various classes of organic compounds introduced in silicate gel matrices and gel films, among them — laser dyes [5–7], hypericin-like compounds [8–10], lanthanide chelates [11, 12], fullerenes [13]. In this mini-review, we consider the results of spectroscopic investigation of tetrapyrrole molecules (porphyrins and metal phthalocyanines) embedded in silicate gel matrices.

SUBJECTS OF INQUIRY AND METHODS

In the course of investigations, the following tetrapyrroles were used for dyeing silicate gel matrices: porphine (H_2P), *meso*-tetraphenylporphine (H_2TPP) and its pentafluorophenyl analog (H_2TPP-F_{20}), octaethylporphine (H_2OEP), *meso*-tetrapropylporphine (H_2TPrP), two stereoisomers of a substituted tetraazabacteriochlorin (*cis*-TABC' and *trans*-TABC'), metal complexes of phthalocyanine and its derivatives: magnesium complex of tetracarboxyphthalocyanine ($MgPc(COOH)_4$), ytterbium complexes of phthalocyanine ($YbClPc$) and 1,2-naphthalocyanine ($Ybaa-1,2-Nc$; $Ybaa-1,2-Nc$, aa — acetylacetonate), zinc complex of 1,2-naphthalocyanine ($Zn-1,2-Nc$).

Sol-gel synthesis of inorganic and organic-inorganic (hybrid) xerogels was performed on the basis of silicium alkoxides $Si(OR)_4$ ($R=Alkyl$), mainly TEOS ($R=Ethyl$). Si alkoxides are easily hydrolyzed on the addition of water and some organic solvents and form, in the process of sol-gel synthesis, nanoporous solid-state silica gel material. To obtain hybrid matrices vinyl triethoxysilane (VTEOS) was added to the reaction mixture. The following molar proportions of components were used for the preparation of the inorganic TEOS and organic-inorganic TEOS+VTEOS matrices, respectively — TEOS:ethanol:water = 1:5:5 and TEOS:VTEOS:ethanol:water = 0.7:0.3:6:6. To promote the hydrolysis process, *ca.* 0.1 mole of HCl was added to the reaction mixtures. The reaction mixtures were stirred for 2–3 h of until homogeneous solutions were formed (the hydrolysis step). The formation of solid xerogels

(the polycondensation step) occurred during several weeks at *ca.* 60 °C and atmospheric pressure.

The embedment of tetrapyrrole molecules into gel matrices was carried out using three methods. Two of them were used systematically while the third one requires chemical modification of the pigment and was realized only once. In the first method, that of direct synthesis, a solution of the dye is added to the starting reaction mixture; dimethylsulfoxide (DMSO) was mainly used as a solvent, about 6–9% by volume (0.2–0.3 mL). This method was used for all tetrapyrroles studied. The disadvantages of the method are: limited choice of solvents and low-temperature treatment.

The second method consists in the impregnation of the previously synthesized and heated gel matrix with the pigment solution. After the gel formation, densification was achieved by drying the gel under ambient conditions, which was followed by heat treatment, with slow (~10 °C per hour) raising of temperature up to 600 °C. Doping was performed by impregnation with a solution of the studied pigment, in DMSO or $CHCl_3$, with subsequent drying of the sample at room temperature.

The third method of inorganic xerogels dyeing is the method of chemical “grafting” of the pigment molecules to the xerogel nanopores surface [14, 15]. To realize this method, the pigment molecules should be chemically modified, so that they carry side-substituents with trialkoxysilane end groups that can participate in the hydrolysis-condensation reactions and form covalent bonds between the activator molecule and silicate framework. The method of chemical grafting removes a number of undesirable effects taking place when using the two above-mentioned traditional methods.

MAIN RESULTS OF EXPERIMENTAL STUDIES

The room temperatures of sol-gel synthesis in combination with the soft chemical conditions under which hydrolysis and condensation of monomeric alkoxides are carried out enable one, at the stage of polymeric skeleton formation, to embed organic molecules in their porous structure and obtain dyed silicate materials (gel matrices and films). However, in most cases, the use of the first method of dyeing leads to noticeable changes in the spectral properties of impurity molecules. The whole set of experimental data obtained can be interpreted argumentatively in terms of additional protonation of tetrapyrrole molecule center in the TEOS gel matrix.

The reaction TEOS sol-gel mixtures that have passed the stage of hydrolysis and partial condensation are liquid solutions containing ethyl alcohol (excess and formed at the stage of hydrolysis), water (excess and formed at the stage of condensation), and ethoxysilanols $Si(OC_2H_5)_{4-n}(OH)_n$ of high orders ($n = 3, 4$), which form, in the process of further condensation, silicate

polymeric three-dimensional porous structures with end groups mainly of the silanol $\equiv\text{Si}-\text{OH}$ type. Further, in the process of evaporation of solvents from the lattice pores, there occurs transformation of the sol into a solid silicate gel matrix. As the drying proceeds, when appreciable shrinkage of the lattice and compression of the gel are observed, the size of the pores covered with hydroxyl groups decreases. Under such conditions, the tetrapyrrole molecules left in the pores approach the surface of the silicate gel matrix. From an example of the molecules of free-base porphine (H_2P) [16] one can see that, on the formation of solid TEOS gel matrices, essential alteration of absorption spectra takes place (see Figs 1b and 1c) showing that the neutral molecules of H_2P interact with the surface of the pores *via* the formation of hydrogen bonds between the central atoms of nitrogen and the hydrogen atoms of the surface OH groups. As the result, all the neutral molecules of H_2P present in the sol-gel mixture, when in the matrix, are transformed into the dicationic form:



The surface hydroxyl $-\text{OH}$ groups strengthen the acidic character of the TEOS gel matrix which is initially specified by the HCl solution dopes.

The behavior of H_2P in the organo-inorganic VTEOS gel matrix corroborates the described mechanism. In this case spectral changes are not observed (see Fig. 1a), since

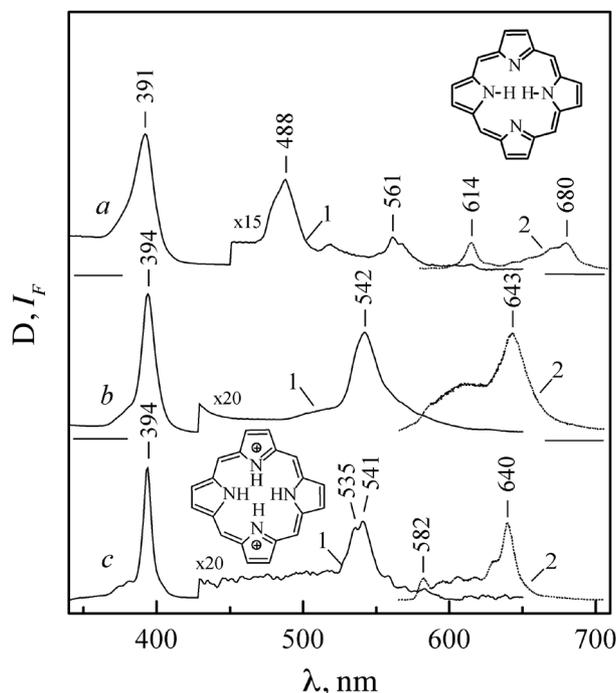
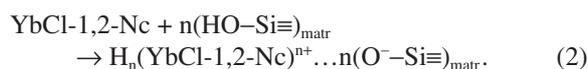


Fig. 1. Absorption (1) and fluorescence (2) spectra at excitation in the 350–410 nm range of H_2P in VTEOS at 300 K (a) and TEOS at 300 K (b) at 77 K (c) gel matrices

the hydroxyl groups located on the surfaces of the TEOS gel matrix pores are replaced in such a matrix by vinyl (C_2H_5) ones which, forming a peculiar “organic carpet” on the surface of the VTEOS gel matrix pores, inhibit strong interaction of the impurity with the silicate skeleton, on the one hand, and are incapable of additionally protonating the center of the H_2P molecules, on the other.

A considerable bathochromic shift (~ 20 nm) is observed for the spectra of YbCl-1,2-Nc in passing from the liquid sol to the solid gel matrix (Fig. 2) [17]. This indicates that this Yb complex undergoes protonation at the macrocycle periphery due to the formation of hydrogen bonds between the aza-bridge nitrogen atoms with the surface $-\text{OH}$ groups and subsequent proton transfer leading to the appearance of the $\text{H}_n(\text{YbCl-1,2-Nc})^{n+}$ cation:



The results of the temperature dependence investigations for the spectroscopic properties of the YbCl-1,2-Nc in TEOS gel matrix show that the ytterbium complex is thermally stable at temperatures up to 250–270 $^\circ\text{C}$, which opens a prospect for obtaining silicate gel-glasses dyed by pigments of this class.

The cation forms of porphyrins serve as useful models for studying the non-planarity of the porphyrin macrocycle. This nonplanarity may be biologically important. In this connection, of interest is investigation of vibronic spectra of protonated forms of porphyrins as sources of structural information. The method of quasi-line spectra was inefficient due to the substantial violation of the crystalline structure of *n*-alkane matrices by acidic additives. The results of the recording of the fine-structure fluorescence spectra of dications of a number of porphyrins by the method of selective monochromatic excitation at 4.2 K

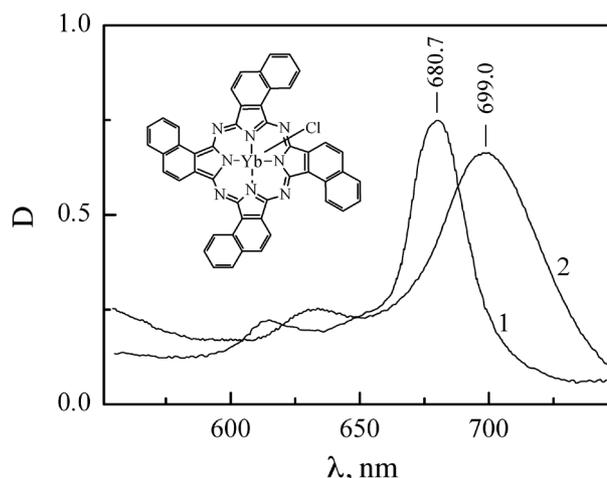


Fig. 2. Absorption spectra of YbCl-1,2-Nc in TEOS liquid sol mixture (1) and in TEOS solid gel matrix (2) at 293 K

(this method is usually termed FLN — fluorescence line narrowing) have not been further developed mainly due to the difficulties of obtaining information on polarization of zero-phonon lines because of the considerable scattering of light in the matrices used.

The above described fundamentally new approach to obtain cationic forms of porphyrins, based on the use of inorganic silicate gel materials, does not require addition of acids for protonation of embedded molecules and produces transparent dyed solid gel matrices in which the nanopores surface OH groups are the source of extra protons. In our first works on the application of FLN at 4.2 K to such systems for the dications of *meso*-tetraphenylporphine (H_4TPP)²⁺ and its pentafluorophenyl analog (H_2TPP-F_{20}) [18], as well as for H_4P^{2+} [19], embedded in including TEOS silicate gel matrices, we studied the effect of protonation and the influence of the matrix structure on frequencies and activity of the tetrapyrrole macrocycle normal modes including out-of-plane vibrations.

Specifically, it was shown that in the 150–950 cm⁻¹ frequency region of the FLN spectrum of H_4P^{2+} in TEOS gel matrix, apart from the frequencies correlating with those of ZnP and H_2P , additional frequencies emerge [19]. Their values fall into the “empty” gaps of the spectra of ZnP and H_2P . This can be explained by the activation of out-of-plane vibrations due to violation of the planarity of the macrocycle in the dication. The FLN spectrum of H_4P^{2+} in TEOS matrix was compared with the spectrum acquired for a frozen CF₃COOH solution [20]. The comparison showed that several vibrational frequencies of H_4P^{2+} change in passing from the frozen acid solution to TEOS matrix. This means that fine-structure vibronic spectra are sensitive to the nature of the interaction of embedded porphyrin cations with silicate gel matrix which imparts to them diagnostic importance.

In order to obtain deeper insight into the nature of the guest-host interaction in the case of porphyrins in gel matrices, systematic study of such systems is necessary. In reference 21 (see also reference 22) octaethylporphine (H_2OEP), which has useful spectroscopic features, was used as a dopant. H_2OEP is a typical octaalkylporphine substituted at the β-positions of the pyrrole rings. Its absorption and fluorescence spectra are very similar to those of porphyrins of biological origin (protoporphyrin, mesoporphyrin, *etc.*) having alkyl or pseudoalkyl groups at the pyrrole β-positions.

For the embedment of the H_2OEP molecules into TEOS gel matrix the second method was used. Doping was performed by impregnation with CHCl₃ solution.

Figure 3 presents data for the doped TEOS xerogel. From the general pattern of the absorption spectrum, it may be seen that it is formed by at least two forms of the pigment. The fluorescence spectrum acquired at room temperature under broadband excitation leads to the same conclusion. The shortest wavelength fluorescence band, at 577 nm, is evidently the 0–0 band of the first

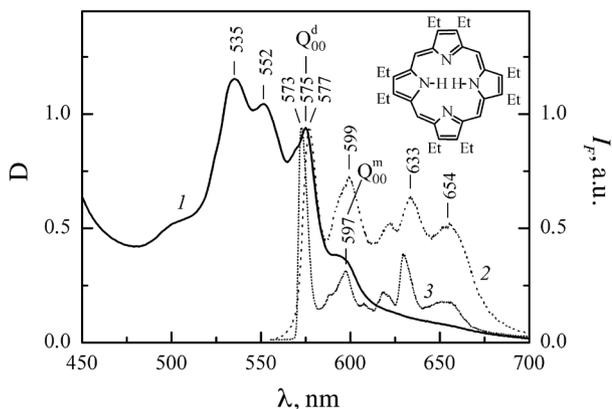


Fig. 3. Total absorption spectrum (1) and fluorescence spectra under broadband excitation (in the range 300–410 nm) (2,3) of octaethylporphine-doped TEOS xerogel at 300 K (1,2) and 4.2 K (3). Q_{00}^d denotes the $Q_{1,2}(0,0)$ band of the dicationic form, H_4OEP^{2+} ; Q_{00}^m denotes the $Q_1(0,0)$ band of the monocationic form, H_3OEP^+

form, corresponding to the 575-nm absorption band. The 599-nm fluorescence band may be (and actually is; see below) the 0–0 band of the second form. On lowering of the temperature down to 4.2 K, the fluorescence spectrum measured under broadband excitation does not change significantly: the bands become narrower and slightly shift to the blue (see Fig. 3, curves 2 and 3).

In order to determine the number of spectral forms in the system and their characteristics, we measured the fluorescence excitation spectra at selective monitoring and the fluorescence spectra under selective excitation. These experiments have shown that there are only two forms of octaethylporphine in the TEOS xerogel.

The fluorescence excitation spectrum measured at 77 K for the first form (Fig. 4, curve 1) shows that this form is a dication whose absorption spectrum is modified by interaction with the matrix. The excitation spectra at 77 K were measured at monitoring in the maximum of the main vibronic band of the corresponding fluorescence spectrum, which enabled recording of the 0–0 absorption band contour. Comparison of the fluorescence excitation spectrum of the first form with the absorption spectrum of H_4OEP^{2+} in solution, taking into account the influence of temperature (spectral shifts due to temperature changes are insignificant; cf. fluorescence spectra 2 and 3 in Fig. 3 in the 0–0 band range near 575 nm) shows the following: (1) The spectra are similar; *i.e.* the first form has the H_4OEP^{2+} structure. (2) The 0–0 band of H_4OEP^{2+} in the gel matrix is shifted to the blue by 22 nm (~650 cm⁻¹). (3) The 0–0 band intensity for H_4OEP^{2+} in the gel matrix, according to a qualitative estimate allowing for the band narrowing, is somewhat higher (approximately, by a factor of 1.1).

If the 22-nm hypsochromic shift were caused by the lowering of the $3a_{2u}$ MO energy, as in the series of metalloporphyrins, the $Q_{1,2}(0,0)$ band intensity would

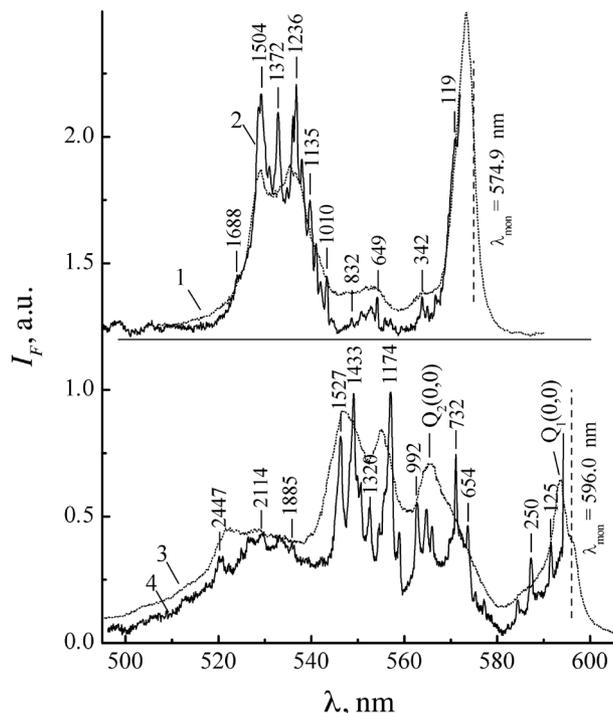


Fig. 4. Fluorescence excitation spectra of H_4OEP^{2+} (1,2) and of H_3OEP^+ (3,4) in the TEOS xerogel matrix at 77 K (1,3) and 4.2 K (2,4). $\lambda_{\text{mon}} = 630.8$ nm (1), 574.9 nm (2), 656.9 nm (3) and 596.0 nm (4)

be higher (see, e.g. [23]). For instance, for ZnOEP in solution, the $Q_{1,2}(0,0)$ band is at 569 nm ($\Delta\lambda$ relative to H_4OEP^{2+} is -28 nm), and its intensity (relative to the $Q_{1,2}(0,1)$ band) is higher than for H_4OEP^{2+} by a factor of 2. Therefore, one may infer that the geometry of the dication in the TEOS matrix is different from that in solution (the molecular core seems to contract).

Let us now turn to the consideration of the second, long-wavelength, form. Analogous comparison of its fluorescence excitation spectrum (Fig. 4, curve 3) with the absorption spectrum of the monocation, H_3OEP^+ , in solution [24] leads to a conclusion that, in the TEOS gel matrix, apart from the octaethylporphyrin dications, monocations are also formed. In solutions, porphyrin monocations exist in a narrow interval of pH, and their observation presents some difficulties (detected for the first time in reference 25, they were also investigated in reference 26). Specifically, on lowering the temperature, they turn into dications. On the contrary, in the matrix, they are quite stable, which made it possible to carry out low-temperature investigations. It may be mentioned that, in the case of a porphine-doped TEOS xerogel, we noted the formation of a species resembling a monocation during storage and suggested that deprotonation of dications took place [16].

The comparison of curve 3 of Fig. 4 with the absorption spectra of H_3OEP^+ in solution [24] shows the following distinctions. (1) The $Q_1(0,0)$ band in the gel matrix is shifted hypsochromically but less than for the dicationic

form (by only 5 nm). (2) The band at 566 nm in the fluorescence excitation spectrum (curve 3) does not find correspondence in the fluorescence spectrum or in the fine-structure fluorescence excitation spectrum (Fig. 4, curve 4; for more details, see below), which permits one to assume it to be the $Q_2(0,0)$ band, taking into account the fluorescence polarization spectrum [24]. The S_2-S_1 (Q_2-Q_1) interval is obtained as 830 cm^{-1} , i.e. less than in solution, where it amounts to $\sim 1000\text{ cm}^{-1}$, which results in the overlapping of the $Q_2(0,0)$ and $Q_1(0,1)$ bands. (3) The band at 528 nm in solution is more intense than its analog in the TEOS gel matrix. Presumably, a geometry change on the introduction into the matrix takes place for the monocation as well.

We applied the FLN method to the cationic forms under study. The emission spectra acquired under monochromatic excitation at 4.2 K are shown in Fig. 5. Under selective monitoring in the 0-0 fluorescence band range and scanning λ_{exc} , the fine-structure fluorescence excitation spectra of both cationic forms were obtained (Fig. 4, curves 2 and 4). The comparison of the excitation and emission spectra shows that, in the low-frequency range (up to 1000 cm^{-1} for the dication and up to 700 cm^{-1} for the monocation), approximate mirror symmetry of the spectra is observed. In the higher frequency range, the correspondence worsens due to the lowering of frequencies of vibronic transitions in absorption.

Note that, in the monocation fine-structure fluorescence excitation spectrum, there are no lines that might correspond to the band that we have assigned to the $S_2 \leftarrow S_0$ ($Q_2 \leftarrow G$) transition, separated from the $Q_1(0,0)$ band by 830 cm^{-1} . As mentioned, it confirms the proposed assignment. The matter is that there exists the effect of

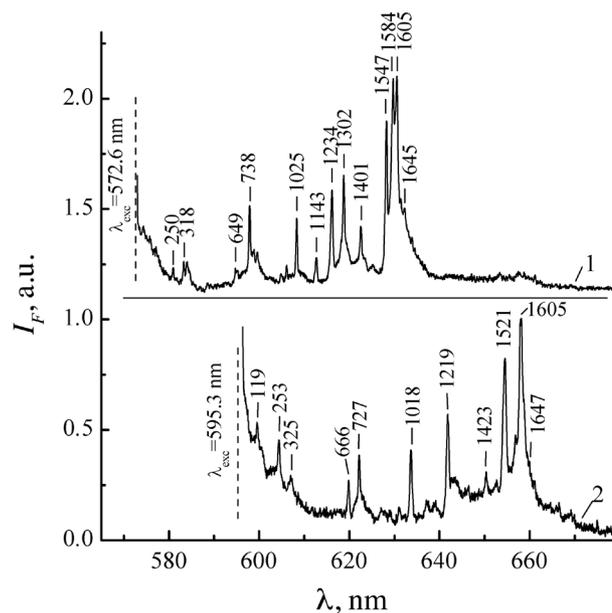


Fig. 5. Fluorescence line narrowing spectrum of H_4OEP^{2+} (1) at $\lambda_{\text{exc}} = 572.6$ nm and of H_3OEP^+ (2) at $\lambda_{\text{exc}} = 595.3$ nm in the TEOS xerogel matrix at 4.2 K

so-called non-correlation, *i.e.* distinction in the S_2 – S_1 interval values for different impurity centers. As a result of noncorrelation, the fine structure of the fluorescence spectra disappears under excitation in the range of the S_2 – S_0 transition [27] and, in the corresponding part of the fine-structure fluorescence excitation spectrum, a diffuse band arises [20]. Thus, in our case, the diffuse $Q_2(0,0)$ band is masked by the vibrational structure of the first electronic transition.

The results of the vibrational analysis of the FLN spectra of both cationic forms are presented in references 21 and 22. On the whole, the acquired experimental data allow one to state that the vibrational frequencies of H_4OEP^{2+} and H_3OEP^+ correlate with the frequencies of CuOEP and H_2OEP rather well, which enables a discussion of the obtained material from the common points.

It is important to note that the monocationic forms have been observed in solutions and studied for only β -alkyl derivatives of porphyrins: in references 24 and 25, the OEP monocation; in reference 26, the etioporphyrin monocation. In this case, such monocations exist only in specially selected solvent mixtures, in a narrow pH interval, and their observation presents some difficulties because, as the temperature is lowered, they convert to dications. Study of porphyrins with four alkyl-substituted carbon bridges (*meso* substitution within the tetraalkylporphine series from ethyl to *n*-octyl) showed that in acid solutions, they only form the dicationic forms [28].

In reference 29, the possibility of existence of monocationic form is shown for *meso*-alkylsubstituted free-base porphine, H_2TPrP (*meso*-tetrakis(*n*-propyl)porphine), in nanoporous TEOS gel matrix. The H_2TPrP molecules were incorporated into the TEOS gel matrix by impregnation with an *n*-octane solution.

On the basis of investigation and analysis of the fluorescence and fluorescence excitation spectra (at 300, 77 and 4.2 K) of silicate gel matrices dyed with H_2TPrP , as well as based on the comparison of these spectra with the absorption spectra of acidified solutions and on the analysis of low-temperature FLN vibronic spectra, it was shown that, similarly to the case of H_2OEP , the formation of two cationic form of H_2TPrP takes place in the TEOS gel matrix: the short-wavelength form has the dication structure (H_4TPrP^{2+}), whereas the long-wavelength form — the monocation structure (H_3TPrP^+).

The fine-structure spectra obtained for H_4TPrP^{2+} show that in the pores of a silicate gel matrix, for some of the molecules (dications), the homogeneous broadening is less than in the case of the H_4TPrP^{2+} — frozen *n*-octane matrix system (for H_4TPrP^{2+} in frozen *n*-octane solution, selective monochromatic excitation does not produce fine structure fluorescence spectrum). Most likely, in the nanoporous gel matrix, the C_3H_7 groups are more weakly bound to the silicate framework, and the interaction of the framework

with the tetrapyrrole cations is realized by participation of hydrogen bonds between the central nitrogen atoms and the hydrogen atoms of the hydroxyl groups of the porous xerogel.

To summarize, the experiments with monochromatic excitation and monitoring showed that for H_2OEP and H_2TPrP unique conditions are created in a nanoporous gel matrix for the existence of the monocationic form. This is favored by a low surface density of hydroxyl groups (after heat treatment of the original gel sample), as compared with the volume density of H^+ in an acidified *n*-octane solution.

Another branch of low-temperature fine-structure spectroscopy, based on the phenomenon of persistent spectral hole burning (PSHB), was also applied to tetrapyrrole molecules in gel matrices [30].

One of the applications of the phenomenon of PSHB is holographic processing of ultrashort laser pulses. Pulse shaping can be achieved with the use of PSHB materials, which behave as spectrally selective photographic plates used to engrave a suitable frequency-domain pattern [31, 32]. Of special interest in this respect is the optical processing of ultrashort pulses generated by titanium-sapphire lasers [33–35]. This necessitates the search for effective broadband materials exhibiting PSHB in the corresponding spectral region — about 800 nm.

Recently, following the synthesis of unsubstituted tetraazachlorin by Prof. E.A. Luk'yanets and co-authors [36] more stable derivatives were synthesized that contain fragments attached to the reduced pyrrole ring which prevent its dehydrogenation. In particular, one of these fragments is dibenzobarrelene carrying two *tert*-butyl groups [37]. In reference 37 an analogs derivative of tetraazabacteriochlorin was obtained in addition (its structure is shown in Fig. 6). Two stereoisomers of this compound were separated, differing in the position of the dibenzobarrelene fragments relative to the macrocycle plane (denoted *cis*-TABC' and *trans*-TABC'). Data on spectral, photophysical, and other properties of reduced derivatives of tetraazaporphine (porphyrazine) preceding reference 30 were published [38–43], including results of

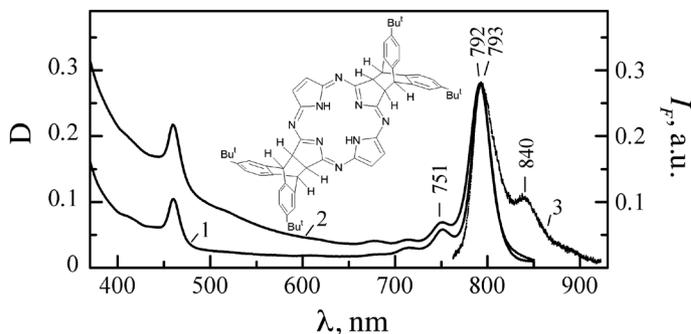


Fig. 6. Absorption spectra (1,2) and fluorescence spectra at $\lambda_{exc} = 789.2$ nm (3) of *cis*-TABC'/PVB (1,3) and *cis*-TABC'/TEOS (2) at 300 K. The values of λ_{max} for the PVB host at 300 K are indicated on the figure

quantum-chemical calculations [39, 41] (for unsubstituted compounds); quantum-chemical calculations for unsubstituted tetraazabacteriochlorin had been carried out earlier [42]. Newer references were listed in reference 42 (see also [43]).

PSHB experiments were carried out with the mentioned stereoisomers. Two kinds of matrices were used: organic, polyvinylbutyral (PVB), and inorganic, a silicate xerogel. The main result of this study was to have established the capability of substituted tetraazabacteriochlorin isomers to exhibit PSHB. The difference absorption spectra in the spectral hole region for all four systems studied are compared in Fig. 7. The obtained results give unambiguous evidence that the phototransformation process is more effective and the holes are deeper for the TABC' isomers embedded in inorganic TEOS gel matrix. In both types of matrices used, these characteristics are better for the *cis*-isomer of TABC' than for the *trans*-isomer.

Thus, it was found that for the TEOS xerogel and PVB matrices doped with *cis*-TABC' and *trans*-TABC',

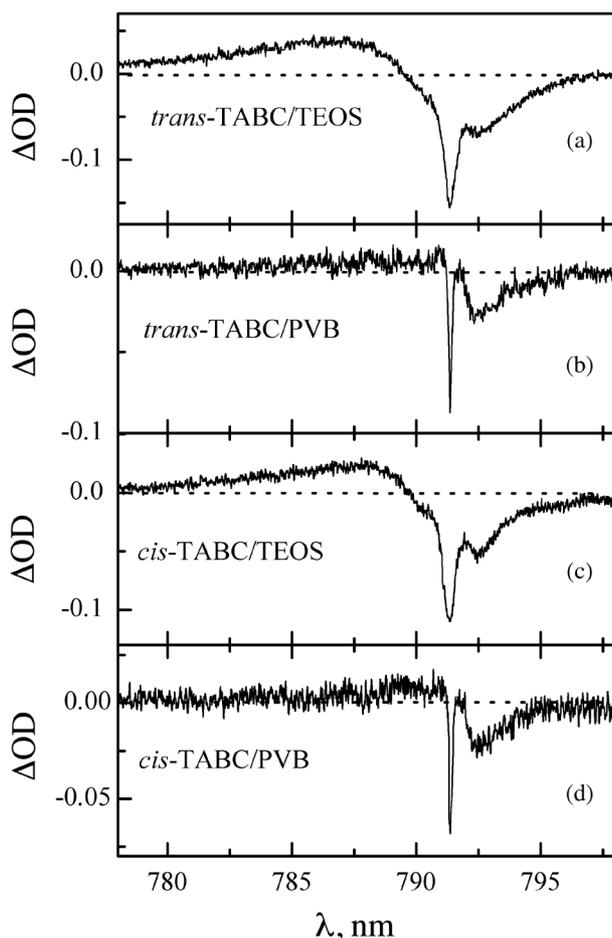


Fig. 7. Profiles of persistent spectral holes in the $Q_1(0,0)$ band of *trans*-TABC' (a,b) and *cis*-TABC' (c,d) in the PVB matrix (b,d) and TEOS xerogel (a,c) burned by laser radiation at 5 K ($\lambda = 791.3$ nm, $P = 40$ mW.cm⁻², burning time 120 s (a,c) and 180 s (b,d))

especially selected tetrapyrrole pigments which have an intense $Q_1(0,0)$ band in the 800 nm range, effective PSHB takes place at laser diode excitation wavelength and 5 K. The experimental data make it possible to reject, in this case, the mechanism of PSHB based on the NH phototautomerization that is typical for free-base porphine derivatives. The absorption band of the photoproduct is close to the $Q_1(0,0)$ band and shifted to the blue. For the inorganic matrix the efficiency of hole burning is higher, but the relative depth of the hole and its width are larger. These facts were explained by the formation of labile intermolecular hydrogen bonds between the surface hydroxyl groups of the matrix pores and the nitrogen atoms of the embedded molecules in the TABC'-xerogel system.

From the point of view of possible practical applications, higher efficiency is the advantage of TEOS xerogel systems and narrower ZPH is the advantage of PVB systems.

In reference 45, we performed a series of comparative investigations on the influence of the technique of embedment of 1,2-naphthalocyanine metal complexes (Yb and Zn) into nanoporous silicate xerogels (method of direct synthesis vs. xerogel impregnation method), as well as the effect of the nature of extra ligand (acidoligand Cl⁻ vs. acetylacetonate, aa) on the spectral properties and structure of molecular impurity centers.

Figure 8 shows the Q band region of the absorption spectra of 1,2-Nc metal complexes in TEOS materials dyed by the direct synthesis method that were recorded after two formation stages of solid xerogels, *i.e.* after hydrolysis (liquid sols) and after polycondensation (solid gels). The experiment showed that changing the starting reaction medium during hydrolysis has practically no effect on the spectral properties of the Yb complexes (an insignificant hypsochromic shift of the Q band is observed). The absorption spectra remain monomeric in shape. In contrast with this, the absorption spectrum of Zn-1,2-Nc reveals the formation of aggregates in liquid TEOS sol. It is known [46] that the appearance of a broad and strong band in the range ~635 nm, for metallophthalocyanines and their derivatives, with simultaneous broadening and a bathochromic shift of the $Q(0,0)$ band is a result of aggregation of phthalocyanine pigments. Aggregation proceeds especially effectively in a medium containing water, the molecules of which aggregate pigment molecules *via* intermolecular H-bonds with the bridge N atoms of phthalocyanine to form sandwich-like H- or J-aggregates [46, 47]. The presence of bulky axial ligands or anionic ligands that displace metal ions from the N4 plane causes steric hindrance to the contact of phthalocyanine macrocycles, *i.e.* hinders the aggregation. This occurs for YbCl-1,2-Nc and Ybaa-1,2-Nc in liquid TEOS sols (Fig. 2, curve 1 and Fig. 8a, solid line).

The formation of the solid gel framework affects the embedded 1,2-Nc metal complexes in different ways

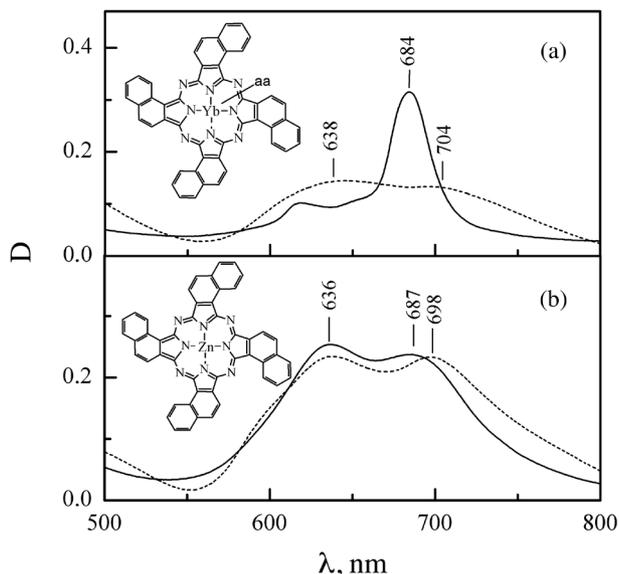


Fig. 8. Absorption spectra of Ybaa-1,2-Nc (a) and Zn-1,2-Nc (b) in TEOS liquid sol mixture (solid lines) and in TEOS solid gel matrix (dotted lines) at 293 K (direct synthesis method)

(Fig. 2, curve 2 and Fig. 8, dotted lines). For YbCl-1,2-Nc, the $Q(0,0)$ absorption band broadens and undergoes a bathochromic shift of ~ 13 nm. The absorption spectrum of Ybaa-1,2-Nc in solid TEOS matrix changes drastically. Instead of the strong $Q(0,0)$ band, two broad ones appear. Changes in the spectrum of Zn-1,2-Nc after formation of the solid xerogel are less noticeable. The longest wavelength band undergoes a bathochromic shift of ~ 11 nm whereas the general shape of the spectrum and the position of the band at 636 nm are retained. The spectral properties of the investigated impurity molecules change because of the influence of hydroxyls of the silanol groups $(\text{HO}-\text{Si}\equiv)_{\text{mat}}$ on the surface of the silicate framework pores the surface concentration of which increases greatly during the fresh gel-xerogel transition, *i.e.* during drying of the matrix, because of a ~ 6 – 10 -fold decrease in the volume of the xerogel and, therefore, the surface area of the matrix pores. According to the literature [48], their average concentration reaches 4.5 OH groups per nm^2 of surface pores. Gradual evaporation of residual solvents from the xerogel cavities increases the concentration of impurity molecules on the pore surface that is covered with reactive OH groups. This is equivalent to increased acidity of the surface layer. For YbCl-1,2-Nc, the activity of the silanols appears in the formation of cationic pigment species *via* protonation of bridge N atoms according to the scheme proposed in reference 17 (see Equation 2). This leads to the broadening of the longest wavelength absorption band and its bathochromic shift (Fig. 2). It is important that the anionic ligand Cl^- interacts with the central metal atom of YbCl-1,2-Nc and hinders aggregation of cationic forms of naphthalocyanine (see above). Conversely,

acetylacetonate bonded to Yb in Ybaa-1,2-Nc can be cleaved in acidic medium. This favors simultaneous occurrence of two processes, protonation and aggregation of pigments. Two broad bands characteristic of aggregates appear in the absorption spectrum of Ybaa-1,2-Nc in solid xerogel (Fig. 8a). The bathochromic shift of ~ 11 nm of the long-wavelength absorption band of Zn-1,2-Nc on going from TEOS sol to TEOS gel (Fig. 8b) is due to the protonation of its aggregated form.

Unique sorption properties are one of the features of xerogels with a well-developed nanoporous structure. Considering that the average pore diameter of the silicate xerogel reaches ~ 10 nm (estimated using the literature data [49] for sol-gel synthesis conditions analogous to ours), *i.e.* is much greater than the linear size of 1,2-Nc molecules (~ 1.7 nm), nanoporous xerogels can be dyed by impregnation with liquid solutions of these pigments. It is noteworthy that the impregnation method can be used only for heat-treated matrices that have increased mechanical strength. The solvent and the dissolved compound together jointly penetrate into the inner cavities of the xerogels. Experiments showed that the metal complexes of 1,2-naphthalocyanine under study exhibit different degree of their penetration into the inner cavities of xerogels. The impregnation coefficient (K), the ratio of the optical density of impregnated (but not dried) TEOS matrix at a certain wavelength (in our instance, for the maximum of the $Q(0,0)$ absorption band) to the optical density of the DMSO solution (external solution) impregnating it, at this same wavelength, ($K = D_{\text{TEOS}}/D_{\text{DMSO}}$), was used for quantitative analysis of the xerogel impregnation. The concentration of impurity molecules in the external solution was held practically constant during the impregnation ($\sim 5 \times 10^{-6}$ M for all 1,2-naphthalocyanine metal complexes). Coefficient K was determined taking into account the thickness of the TEOS gel matrix (calculated per cm of thickness). Figure 9 shows K as a function of time for the three

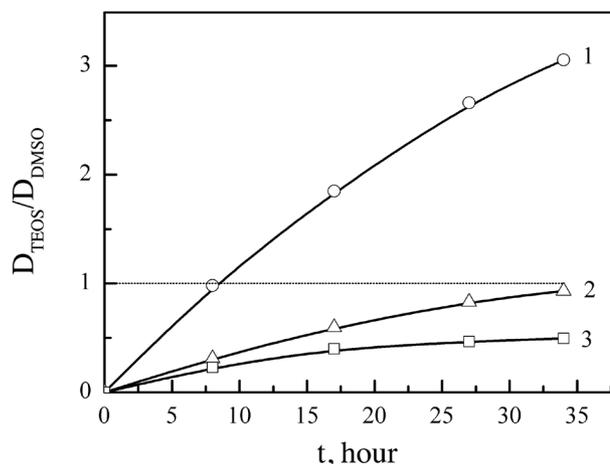


Fig. 9. Impregnation coefficients of gel matrix by DMSO solutions of 1,2-naphthalocyanine derivatives as functions of time: YbCl-1,2-Nc (1), Ybaa-1,2-Nc (2), Zn-1,2-Nc (3)

1,2-naphthalocyanine metal complexes. It can be seen that the effectiveness of the pigments penetration into the matrix pores depends substantially on their chemical structure. The concentration of YbCl-1,2-Nc in the TEOS matrix after only 8 h impregnation is equal to the concentration of the external solution whereas it is three times greater than the latter after 34 h (Fig. 9, curve 1). The concentration of Ybaa-1,2-Nc in the matrix reaches the concentration of the external solution only after 34 h impregnation (curve 2). At the same time, the concentration of Zn-1,2-Nc in the TEOS matrix is one half that of the external solution (Fig. 9, curve 3). The accumulation of one dye or another in the xerogel pores must be explained using concepts related to the nature of the movement of dissolved molecules in a limited volume and their interaction with the surface of the matrix nanopores. The heat treatment (up to 600 °C) of the gel matrices used in the work causes a sharp decrease in the surface concentration of OH groups (by ~15–20 times) [48]. The surface is dehydroxylated during heat treatment as a result of polycondensation of adjacent hydroxyls to form water molecules that are removed from the matrix as water vapor. Such “thermopolycondensation” creates less reactive $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ siloxane bridges with the O atom on the nanopore surface. The high impregnation coefficient for the YbCl-1,2-Nc molecules is apparently due to quasi-chemical interaction of pigment with dehydroxylated nanopores surface and attachment (adsorption) to it of the pigment molecules, as a result of which the concentration of the pigment solution in the pore cavity (inner solution concentration) is always less than the concentration of the outer impregnating solution, which creates conditions for their equilibration, *i.e.* for constant entry of a new portion of dissolved compound into the nanopores. The bulky organic extraligand at the Ybaa-1,2-Nc molecule most probably prevents such effective adsorption of these molecules on the pore surface. Their concentration in the TEOS matrix, which is determined by the rate of pigment penetration into the nanopores, gradually equilibrates to the concentration of the outer solution. Poor penetration of Zn-1,2-Nc from the outer solution into the gel-matrix can be explained by the existence of repulsive forces between the surface of the nanopores and the dissolved pigment, the nature and mechanism of action of which are still unstudied. It is important that evidence of pigment aggregation was not observed in all experiments with the Yb complexes (even for the maximum *K* for YbCl-1,2-Nc) in the absorption spectra of impregnated (but not dried) gel matrices. This indicates that they interact with the surface of the xerogels and not with each other.

Spectral investigations of TEOS gel matrix dyed by impregnation and subjected to prolonged drying to remove DMSO from the nanopores confirmed that interaction with hydroxyls plays a decisive role in changing the spectral properties of the studied 1,2-naphthalocyanines in silicate xerogels. It was shown that impregnation

of heat-treated gel matrices with DMSO solutions of 1,2-naphthalocyanine Yb complexes, with subsequent drying, has practically no effect on the spectral properties of the pigments. This is due to the exceedingly small surface concentration of OH groups. Spectra of impregnated Yb complexes retain their monomeric shape with an insignificant hypsochromic shift of the $Q(0,0)$ band by 3–5 nm relative to the DMSO solutions. Under analogous conditions Zn-1,2-Nc molecules exhibit signs of aggregation (a strong band appears at 637 nm). This is the result of increased local concentration of molecules in the surface layer.

At the same time, in reference 45 it was shown that xerogels dyed with metal complexes of 1,2-naphthalocyanine can be used in devices for attenuation of the power density of pulse laser radiation of nanosecond duration (optical radiation limiters), weakly absorbing light in the green region of the visible spectrum (*e.g.* 2nd harmonic radiations of Nd:YAG laser) that have high threshold of optical and temperature damage.

The influence of the method of embedment and the nature of gel matrix on spectral-luminescent properties of incorporated molecules of magnesium complex of tetracarboxyphthalocyanine ($\text{MgPc}(\text{COOH})_4$) was investigated in reference 50.

As shown by experiment, all the gel matrices used have a substantial effect on the spectral-luminescent properties of impurity $\text{MgPc}(\text{COOH})_4$ molecules introduced by the direct synthesis method. Thus, the absorption spectrum of $\text{MgPc}(\text{COOH})_4$ in DMSO having an intense $Q_{1,2}(0,0)$ band at 680 nm, changes appreciably in purely inorganic TEOS and the hybrid organic/inorganic TEOS+VTEOS gel matrices: an intense absorption band appears in the 620–640 nm region, the intensity of the band in the 690–700 nm region decreases, and the absorption bands themselves are broadened. As noted above, spectral changes of this kind are connected with effective association of the pigment and formation of a sandwich-type aggregated form. Obviously, the presence of an aqueous alcoholic component in the original sol-gel reaction medium promotes this process. Furthermore, for xerogels dyed by the direct synthesis method, typically there is no fluorescence from impurity $\text{MgPc}(\text{COOH})_4$ molecules at broadband (370–470 nm) photoexcitation, which also is evidence in favor of formation of an associated, nonfluorescent spectral form of $\text{MgPc}(\text{COOH})_4$. An additional reason for the formation of aggregates may be the increase in the local concentration of the pigment on the surface of the pores of the matrix in the process of drying.

Retention of the original spectral form of $\text{MgPc}(\text{COOH})_4$ in the porous xerogels is nevertheless possible if the impregnation method is used to dye them or for a different composition of the initial sol-gel reaction mixture, such as TEOS+TEOT (TEOT signifies tetraethoxytitanate), with the direct synthesis dyeing method. A distinguishing feature of sol-gel synthesis of

an inorganic mixed TEOS+TEOT gel matrix is that there is no water or acid additive in the initial reaction mixture. In these cases, conversely, the most intense band in the absorption spectra is the longest-wavelength band in the 690–700 nm region. Also, photoexcitation in the 370–470 nm region causes appreciable fluorescence, the main band of which has a substantial Stokes shift for both matrices. These facts suggest that in such matrices, at least two spectral forms of $\text{MgPc}(\text{COOH})_4$ are formed: associates similar to those observed in DMSO (fluorescent), and nonfluorescent associates (possibly π dimers). Retention of the fluorescent forms in both cases is favored by the fact that, during impregnation of a solid TEOS gel matrix with a DMSO solution and during synthesis of the inorganic mixed TEOS+TEOT gel matrix, water is not present as a chemical component. Under such conditions for dyeing the xerogels, a substantial portion of the $\text{MgPc}(\text{COOH})_4$ molecules remains in the original form, which is the reason of fluorescent capability.

The authors of reference 51 proceeded from the idea that chemical “grafting” of $\text{MgPc}(\text{COOH})_4$ molecules to an inorganic gel framework (the third method of activating) should increase their concentration in the gel matrix and partially eliminate formation of aggregates. For the formation of covalent bonds between the pigment molecules and the silicate framework it is necessary to chemically modify the pigment molecules, so that the end groups of its side-substituents could-participate in the polycondensation reaction equally with the TEOS molecules. Trialkoxysilane groups are the best choice for this purpose.

To obtain a xerogel dyed by the new method, first, $\text{MgPc}(\text{COOH})_4$ was chemically modified by 3-aminopropyltrimethoxysilane ($\text{NH}_2-(\text{CH}_2)_3-\text{Si}(\text{CH}_3\text{O})_3$, APTMOS). The amination reaction was carried out similarly to that described for protoporphyrin IX [52]. As a result, the compound $\text{MgPc}[\text{CO}-\text{NH}-(\text{CH}_2)_3-\text{Si}(\text{CH}_3\text{O})_3]_4$ was obtained with four trimethoxysilane groups on the periphery of the phthalocyanine macrocycle. The structure of this Mg phthalocyaninosilicate is shown in Chart 1. We see that the APTMOS substituents in this compound fulfill two functions: on the one hand, they contain reactive $-\text{Si}(\text{CH}_3\text{O})_3$ groups, ensuring its participation in the sol-gel synthesis; and on the other hand, they are flexible organic bridges (“spacers”) binding the phthalocyanine macrocycle to the silicate gel framework formed as a result of the synthesis. The immobilization of Mg phthalocyanine molecules on the surface of the pores of the silicate gel matrix was realized by copolymerization of the monomer obtained with pure TEOS monomer. In the following the copolymer is denoted MgPc-TEOS .

Experiments showed that the absorption band of MgPc-TEOS has a complex contour (see Fig. 10). On the background of a broadened band, we see several inflection points suggesting that the nature of the interaction of modified molecules of $\text{MgPc}[\text{CO}-\text{NH}-(\text{CH}_2)_3-\text{Si}(\text{CH}_3\text{O})_3]_4$ both

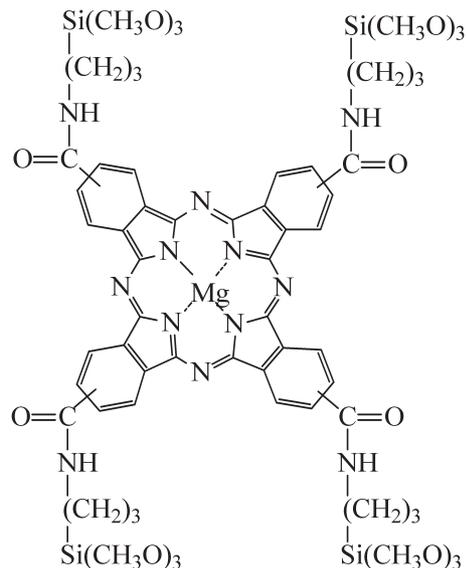


Chart 1. Structural formula of Mg phthalocyaninosilicate

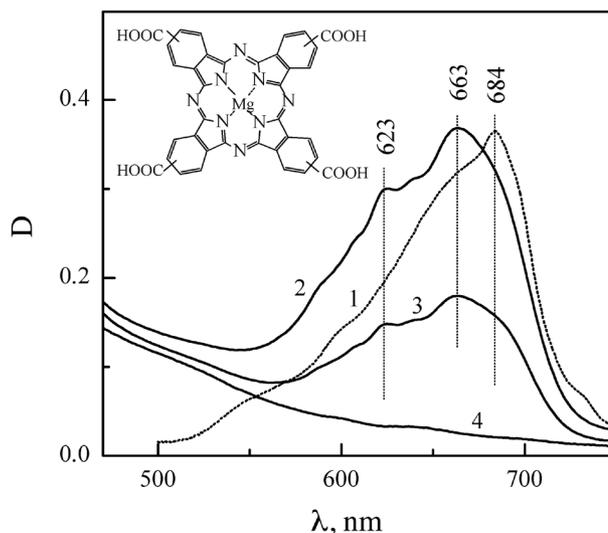


Fig. 10. Absorption spectra of MgPc-TEOS copolymer after sol-gel synthesis (1), subsequent heat treatment at 70°C for 6 h (2), and holding in a normal atmosphere for 0.5 h (3) and 3 h (4)

with each other and with the structural elements of the silicate framework is complicated, *i.e.* several structurally different spectral species are formed. Since heat treatment makes it possible to remove water molecules from the pores of the gel framework, modified molecules, being chemically immobilized on the surface of the pores, appear mainly as the spectral form with an intense Q band at 684 nm, indicating that the energy of the Q state is not changed relative to that of $\text{MgPc}(\text{COOH})_4$ in DMSO solution. Such will be the case if the macrocycle of the Mg-phthalocyanine silicate is copolymerized with the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ framework *via* one or two spacers. Obviously, in this situation, analogously to biopolymers,

the rigid polymer $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ framework separates the copolymerized pigment molecules by significant distances, considerably impeding or entirely preventing formation of higher order associates.

Support for the formation of covalent bonds between the molecules of Mg phthalocyaninosilicate and the surface of the nanopores in the silicate xerogel comes from experiments on leaching (extraction) of MgPc molecules from the interior volume to the surface of the different types of xerogels using a liquid extraction agent, DMSO. In order to estimate the efficiency of the process of leaching of the MgPc molecules, we used the time dependence of the ratio of the optical density of the liquid DMSO extraction agent (D_{extr}) to the initial optical density of the solid gel matrix (D_0) at the maximum of the longest-wavelength Q absorption band. As is seen from Fig. 11, extraction of molecules of MgPc(COOH)₄ from nanopores in the hybrid TEOS+APTMOs xerogel, dyed by the direct synthesis method, *i.e.* without chemical modification, readily occurs into the volume of the external DMSO solution (curve 2). In contrast to this, no leaching of MgPc molecules from the MgPc-TEOS copolymer is observed over a lengthy time period (up to 7 days) (curve 1). The insolubility of the copolymerized molecules in the DMSO extraction agent, penetrating into the pores of the xerogel, is evidence of formation of covalent chemical bonds between MgPc-[CO-NH-(CH₂)₃-Si(CH₃O)₃]₄ and the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ framework, which also blocks the process of its leaching from the nanoporous material into the external solution. Thus, the leaching experiments confirmed the chemical structure of MgPc-[CO-NH-(CH₂)₃-Si(CH₃O)₃]₄. Moreover, the correctness of the conclusions about the chemical structure of the synthesized compounds in silicate xerogels was supported by the IR Fourier spectroscopy data that are discussed in detail in reference 51.

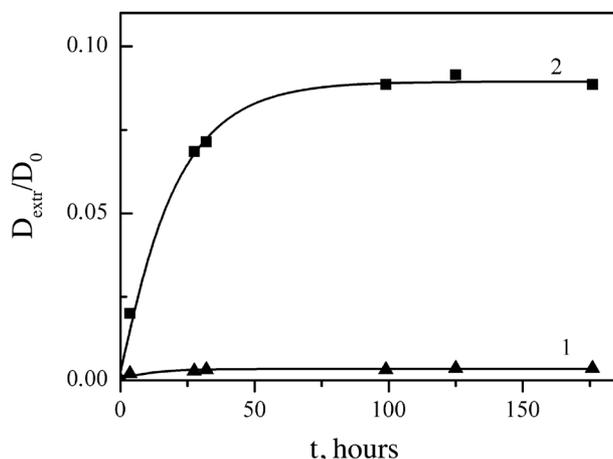


Fig. 11. Ratio of the optical density of the liquid DMSO extraction agent (D_{extr}) to the initial optical density of the solid gel matrix (D_0) vs. leaching time for the MgPc-TEOS copolymer (1) and the xerogel TEOS+APTMOs (2), dyed with MgPc(COOH)₄ by the direct synthesis method

It was established that when a nanoporous MgPc-TEOS gel copolymer (the initial absorption spectrum is shown in Fig. 10, curve 2) is under ambient atmospheric conditions, its blue-green color slowly changes to a light orange. In the electronic absorption spectrum, the observed changes are detected primarily by the disappearance of the broad absorption band in the 550–750 nm region. Thus after 0.5 h, the intensity of the indicated band appreciably decreases (curve 3), while after 3 h it disappears completely (curve 4). It was found that the bleaching process is reversible: subsequent heat treatment of the orange gel MgPc-TEOS copolymer at 70 °C for a few hours leads to recovery of its blue-green color and accordingly its initial absorption spectrum (curve 2), thus proving that no degradation of Mg phthalocyanine occurs. The observed phenomenon can be explained based on analysis of the structure of the silicate gel MgPc-TEOS copolymer. A characteristic feature of nanoporous xerogels is that they have unique sorption characteristics. In fact, a xerogel, having a large number of internal nanosized cavities (pores), under the action of external pressure or as a result of the capillary effect can trap molecules with various structures from the outside and retain them inside its volume. Most likely water molecules penetrate efficiently into the pores of the studied gel MgPc-TEOS copolymer under ambient atmospheric conditions, and these water molecules also interact with the pigment molecules copolymerized with the silicate framework. We may hypothesize that in such covalent grafting of Pc, the central magnesium atom does not participate in formation of a bond with the surface of the xerogel pore. In this situation, Mg phthalocyanine can easily add one water molecule to the central Mg²⁺ ion (as an extra ligand), and this water determines the direction and mechanism of association of the molecules. In this case, the absorption spectrum of molecular microcrystals formed may change radically, which is in fact observed in the experiment. The IR spectrum of the MgPc-TEOS copolymer undergoes substantial changes after being held for 3 h in the atmosphere, the monosubstituted amide band (shoulder at 1650 cm⁻¹ of the 1629 cm⁻¹ band) becoming appreciably weaker and the band of the dimer form of grafted MgPc-[CO-NH-(CH₂)₃-Si(CH₃O)₃]₄ disappearing completely (1300–1500 cm⁻¹ region). Note that such associates/dimers are not stable and mild heat treatment of the gel MgPc-TEOS copolymer easily breaks them down, in this case removing water molecules from the xerogel pores.

At the same time, complete disappearance of the absorption bands in the 500–700 nm region which is not characteristic of phthalocyanine dyes aggregates allows one to propose, as a hypothesis, another interpretation of the observed effect. It is known that for many organic dyes there exist *leuco*-forms that are generated (usually reversibly) as a result of transfer of, first, an electron and, second, a proton ($e + \text{H}^+$, *i.e.* the H atom in totality). It

may be assumed that, in the case under consideration, reversible reduction of the pigment molecules takes place involving the addition of the hydrogen atoms to the bridge N atoms and leading to the interruption of the conjugation chain in the macrocycle. The water molecules may be the source of H⁺ as well as the hydroxyls of the nanopores surface whereas the free radicals of the end groups, that have not found a partner in the process of copolymerization, may be the source of e. The solution of this problem will require additional investigations.

Our studies revealed the uniqueness of xerogel materials, in which organic molecules grafted to the surface of nanopores display new spectral and structural properties, and the nanometer-sized pores themselves fulfill the function of a nanoreactor with respect to the change in these properties, which can substantially enhance the effectiveness of practical use of dyed nanostructured gel materials. The results obtained can be the basis for designing sensor devices based on nanostructured xerogels with dyes (metal phthalocyanines, in particular) immobilized on the nanopore surface for analysis of impurity content of water and other components, especially in gaseous atmospheres. Moreover, as shown by the experiments, the absence of extraction (leaching) of the phthalocyanine pigment from deep inside the nanopores of the gel copolymer to its surface and then into the volume of the solvent extraction agent makes it possible to use the new material as a sensor for analysis of liquid media for content of impurity components.

CONCLUSION

The performed studies of electronic spectra of absorption and fluorescence, as well as those of some other characteristics of tetrapyrrole molecules incorporated into silicate gel matrices have shown that under certain conditions their properties can be close to the corresponding properties in liquid and solid solutions. At the same time the specificity of the action of a silicate matrix as external medium, as compared to liquid and solid solutions, has been revealed. The data of low-temperature fine-structure spectroscopy display that both inhomogeneous and homogeneous broadening of zero-phonon lines is larger for gel materials, but the application to them of the PSHB method is possible. More complicated phenomena take place in cases when the hydroxyls of the nanopores surface interact with the N atoms of tetrapyrroles, either central or bridge ones, which can lead to the macrocycle protonation. The aggregation of molecules in nanopores brings in essential complications. The comparison of two methods of xerogel activation — those of direct synthesis and impregnation — showed that both methods have advantages and disadvantages, so that individual approach is necessary in every concrete case. An attempt of application of the method of chemical grafting proved to be rather successful. Sensor properties

of the obtained gel material have been discovered. The results acquired can be used for controlling the spectral-luminescent and structural properties of novel molecular materials that may be created on the basis of gel matrices activated by tetrapyrroles.

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