

SPECTRAL-LUMINESCENT PROPERTIES OF ALKOXYSILANE–METALLOPHthalOCYANINE CONJUGATES COVALENTLY BONDED TO THE POLYMERIC CHAINS OF SILICATE GEL MATERIALS

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Conjugates of metal hydroxyl phthalocyanines ($M(OH)_nPc$; $M = Si, Ge, Al, Ga$) with 3-aminopropyltriethoxysilane (APTEOS) are synthesized. By means of the sol-gel method, polymeric silicate gel materials doped with the $(APTEOS)_n-M(OH)_nPc$ conjugates are prepared: the latter form structural links in the composition of the copolymer with the siloxane fragments of the polymeric chains (in the case of $n = 2$) or are "grafted" to such chains in the form of side substituents ($n = 1$). It is shown by spectral-luminescent and kinetic spectroscopy methods that the $(APTEOS)_n-M(OH)_nPc$ conjugates, on the introduction into a silicate gel material, retain their molecular structure and the photophysical characteristics of MPc in the monomeric form. The obtained macromolecular substances are promising as monomeric dopants in new functional materials for optics and quantum electronics.

Keywords: metallophthalocyanines, sol-gel synthesis, nanoporous silicate matrices, electronic absorption spectra, fluorescence spectra, monomeric and aggregated forms, fluorescence lifetime.

Introduction. Materials doped with metallophthalocyanines (MPc) find a variety of applications in the industry (lightfast dyes and pigments, gas sensors, catalysts, etc.), optics and optoelectronics (nonlinear optical materials, electrochromic devices, photoconductors, components of organic solar cells, etc.), biomedicine (early diagnosis and treatment of oncological diseases by photodynamic therapy) and other areas [1]. The use of MPc is due in large part to the specificity of the optical spectra of their monomeric forms consisting of an intense narrow absorption (and fluorescence) band adjacent to the near-IR region around 670 nm, called the *Q*-band, and a wide band in the UV region near ~340 nm, called the *B*-band. These two bands of the absorption spectra of MPc are separated by an optical interval, practically transparent in the visible region. At the same time, the majority of MPc show a stable tendency to aggregation in different media as a result of intermolecular π - π -interaction between conjugated systems of molecules [2] — a phenomenon that increases with increasing concentration of MPc. The presence of peripheral substituents and axial ligands, anionic and additional (extraligands), can increase the distance between the planes of the MPc macrocycle and thereby hinder the process of their aggregation. It should be noted that in acidic solutions, dihydroxy silicon phthalocyanines are able to form siloxane –Si–O–Si– bonds by polycondensation with the participation of the central silicon atoms SiPc and thus form polymers with the "face-to-face" phthalocyanine structure $(-PcSi-O-SiPs-)_n$ -polymers [3, 4], considered to be one-dimensional organic conductors [5]. Any type of aggregation of MPc sharply reduces the value of their specific applications, since aggregation leads, on the one hand, to significant changes in photophysical properties, primarily to partial or complete quenching of luminescent radiation as a consequence of preferential radiationless relaxation of excitation energy, on the other hand, to a change in spectral properties, since in most cases aggregation of MPc causes a hypsochrome shift of the *Q*-absorption band relative to the monomer absorption band (cases of a bathochromic shift of the *Q*-band are possible), its splitting and/or broadening.

Potential possible uses of MPc for optical applications can be fully realized only in the composition of functional materials. The most important for practical and commercial use are nanoporous silicate materials doped with organic dyes and obtained by the sol-gel method from alkoxy silanes — materials in the form of bulk matrices and thin films [6].

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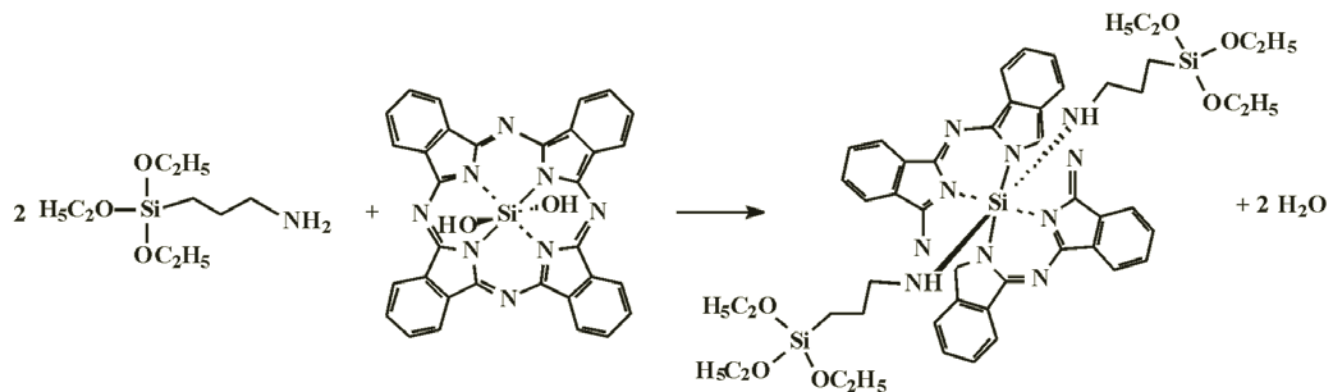
The advantage of silicate gel materials is their mechanical strength, heat resistance, high photostability, and absence of absorption in the visible spectral range. The research conducted by our group showed that the majority of MPC, when incorporated into solid nanoporous silicate gel materials by adding the appropriate MPC solutions to the reaction sol-gel medium, undergo an aggregation process both in inorganic (based on TEOS (tetraethoxysilane)) and in hybrid organo-inorganic (based on TEOS + VTEOS (vinyltriethoxysilane)) materials [7, 8]. It was shown in [9, 10] that in the sol-gel synthesis process, SiCl₂Pc can be included as separate units into linear polymer chains of the silicate framework, while exhibiting the spectral properties of the monomeric form.

The purpose of this work is to use MPC with metals of groups IIIA (Al and Ga) and IVA (Ge and Si) to investigate the possibility of forming covalent-type MPC bonds in the formation of structural units in the copolymer composition with siloxane chains of the matrix or in binding of MPC to siloxane chains in the form of lateral substituents, i.e., for the development and elucidation of the prospects for a new direction in the preparation of monomeric forms of MPC in silicate gel materials. The studies are based on a comparison of the spectral characteristics of phthalocyanine complexes containing central Al³⁺ and Ga³⁺ ions with one axial OH-ligand in their first coordination sphere (AlOHPc and GaOHPc) and phthalocyanine complexes with central Ge⁴⁺ and Si⁴⁺ ions with two axial OH ligands (Ge(OH)₂Pc and Si(OH)₂Pc). Axial anionic OH ligands can participate in polycondensation reactions. Due to this, individual MPC molecules are able to form a single frame with a polymeric silicate material (in the form of separate copolymer units or side substituents).

Research Objects and Experimental Methods. Metalmonohydroxophthalocyanines and dihydroxy metal phthalocyanines are produced from effective spontaneous hydrolysis by air moisture of the corresponding metal chloride phthalocyanines (AlClPc and GaClPc) and metal dichloride phthalocyanines (SiCl₂Pc and GeCl₂Pc) in the isolation and purification stage, i.e., by "re-liganding" ("migrating") the central metal ions [5, 8]. "Re-liganding" occurs due to the fact that kinetic stability of the ≡M–Cl bond to hydrolysis for the said MPC is extremely low; therefore, upon interaction with water, a ≡M–OH bond is formed (for example, SiCl₂Pc + 2OH⁻ = Si(OH)₂Pc + 2Cl⁻). Synthesis and purification of AlClPc, GaClPc, SiCl₂Pc, and GeCl₂Pc were performed by the methods described in [8].

To obtain in the nanoporous gel material a high concentration of impurity MPC with the spectral properties of the monomeric form, MPC molecules were covalently bound to 3-aminopropyltriethoxysilane (NH₂(CH₂)₃Si(OC₂H₅)₃) (APTEOS), i.e., a molecular complex (conjugate) for subsequent participation in the process of inorganic polycondensation with the formation of a silicate gel material. Below, a two-step procedure for the preparation of such gel materials is exemplified by dihydroxy silicon phthalocyanine (Si(OH)₂Pc), based on the modification of the procedure [9, 10].

At the first stage of obtaining the gel material, a conjugate of Si(OH)₂Pc with APTEOS was synthesized. As a result of the interaction of two active OH-groups of phthalocyanine with the terminal amino groups of the two APTEOS molecules, new covalent bonds form, i.e., the APTEOS–SiPc–APTEOS conjugate is formed with the release of two water molecules, as shown in the general schematic of conjugate synthesis:



To this end, a mixture of Si(OH)₂Pc (0.575 mg, 0.001 mmol) and APTEOS (1.0 mL) was stirred in a flask under reflux at 120°C for 24 h until a dark blue solution formed. With increasing reaction time and/or temperature, the solution became green, which may be due to the thermal destruction of a small amount of interacting components with the formation of low-molecular compounds transforming the total absorption spectrum. To avoid humidifying the reaction mixture, anhydrous calcium chloride (CaCl₂) was installed at the inlet of the reflux condenser.

The GPTMOS additive is necessary to slow the rate of hydrolysis of APTEOS, the high value of which results in an inhomogeneous hydrolysis and polycondensation reaction to form a precipitate in the reaction medium. Further, the resulting mixture APTEOS–SiPc–APTEOS/GPTMOS was diluted with ethyl alcohol and placed in an open vessel.

In this state, two alkoxides (APTEOS and GPTMOS) react slowly with atmospheric water, participating in the hydrolysis and polycondensation process, forming a joint silicate framework in which APTEOS–SiPc–APTEOS conjugates are inserted through covalent bonds into the structure of siloxane chains of gel material as separate links (formation of an irregular copolymer). When the formed gel material reached a suitable viscosity, thin silicate films were obtained by irrigating it on the surface of the optical glass. Within a few days, the polycondensation stage was terminated and a solid silicate film stained with SiPc molecules having the spectral properties of the monomeric form was formed. The obtained gel material has a hybrid organo-inorganic structure, since the 3-glycidoxypropyl groups of GPTMOS and amino groups of APTEOS not combined in the conjugate cannot participate in the hydrolysis process and eventually end up on the surface of the nanopores of the inorganic framework of the gel material.

A similar two-stage method was used to synthesize gel materials doped with $\text{Ge}(\text{OH})_2\text{Pc}$, AlONPc, and GaOHPc molecules in the corresponding conjugates with APTEOS.

To compare the spectral data, the synthesized $\text{M}(\text{OH})_n\text{Pc}$ are embedded in hybrid organo-inorganic silicate gel matrices based on TEOS and VTEOS containing an organic vinyl group in the structure. In the joint hydrolysis and polycondensation of such raw silicon alkoxides, the active OH-groups of $\text{M}(\text{OH})_n\text{Pc}$ cannot participate in the formation of a conjugate with them similar to that described above. Organo-inorganic xerogels were obtained from a mixture of TEOS and VTEOS in a 70:30 mol.% ratio. The molar ratio of the additional components was (TEOS + VTEOS):water:ethanol:formamide = (0.7 + 0.3):5:5:5. After stirring for 30 min, a few drops of hydrochloric acid were added. In the polycondensation step, saturated solutions of $\text{M}(\text{OH})_n\text{Pc}$ in DMF were added to the reaction mixture. Details of the synthesis are described in detail in [8].

For the synthesis of gel materials, commercial TEOS, VTEOS, APTEOS and GPTMOS (Sigma-Aldrich) were used, which were not subjected to additional purification.

Samples of organic polymeric polyvinyl butyral (PVB) films stained with $\text{M}(\text{OH})_n\text{Pc}$ were obtained by watering from an ethanol solution of PVB and their subsequent drying in a limited volume with saturated solvent vapors. The thickness of the films was controlled by the number of repeated waterings, the number of which (3–4) depended on the viscosity of the ethanol solution of the polymer. The dried PVB films had a finite thickness in the range of 100–500 μm .

The steady-state absorption spectra were measured with a Cary-500 Scan UV-Vis-NIR spectrophotometer (Varian, USA, Australia). Fluorescence and fluorescence excitation spectra were obtained using a spectrofluorimeter (ZAO "Solar," Belarus). The fluorescence lifetime (τ_{fl}) was determined by analyzing the fluorescence decay kinetics measured on a PRA System-3000 pulse fluorometer (Photochemical Research Association, UK, Canada) operating in the time-correlated single-photon counting mode and modernized by using a pulsed LED PLS 380 with $\lambda_{\text{exit}} = 378 \text{ nm}$, $\Delta t \approx 800 \text{ ps}$, $f = 2.5 \text{ MHz}$ (PicoQuant, Germany) as a source of exciting radiation.

Spectral-luminescent and kinetic measurements were performed at ambient temperature.

Results and Discussion. *Spectral-luminescent properties of $\text{Si}(\text{OH})_2\text{Pc}$ and the APTEOS–SiPc–APTEOS conjugate.* Absorption spectra of $\text{Si}(\text{OH})_2\text{Pc}$ in pyridine and in the hybrid organo-inorganic TEOS + VTEOS gel matrix are presented in Fig. 1a along with the absorption spectrum of the APTEOS–SiPc–APTEOS conjugate copolymerized into linear siloxane chains of the gel-film. The absorption spectrum in pyridine (curve 1) corresponds to the monomeric form of MPc with an intense Q -band at 671 nm. With the introduction of $\text{Si}(\text{OH})_2\text{Pc}$ into the silicate TEOS + TEVOS gel-matrix, a complex broadened band appears with a maximum at 633 nm (curve 2) in the shortwave region relative to the monomeric absorption band, which corresponds to the absorption of H -dimers of MPc with the "face-to-face" structure. The main reason for the formation of aggregated forms in silicate matrices is the localization of $\text{Si}(\text{OH})_2\text{Pc}$ impurity molecules in the nanoscale pores of the matrix framework, the volume of which substantially decreases as the gel-matrices shrink as they dry, thereby increasing the local concentration of phthalocyanine inside the pores. It should be noted that the analogous "blue" shift of the spectra of $(-\text{PcSi}-\text{O}-\text{SiPc})_n$ -type polymers in comparison with the spectrum of the corresponding monomeric form was described by the authors of [3–5].

As can be seen from Fig. 1a (curve 3), the absorption spectrum of the APTEOS–SiPc–APTEOS conjugate as structural units of the non-regular copolymer with siloxane chains of the gel film corresponds to the monomeric form of $\text{Si}(\text{OH})_2\text{Pc}$. Taking into account the long-wave shift of the Q -band by $\sim 5 \text{ nm}$, the conjugate absorption spectrum completely coincides with the spectrum of $\text{Si}(\text{OH})_2\text{Pc}$ monomers in pyridine (curve 1). This similarity in the structure of the impurity centers is due to the copolycondensation of the APTEOS–SiPc–APTEOS conjugate with siloxane groups (sol-gel synthesis of the material based on the APTEOS–SiPc–APTEOS/GPTMOS mixture). As a result, long axial extraligands, such as aminopropyl groups in this case, increase the distance between the planes of copolymerized phthalocyanine macrocycles in polymer chains, reducing their interaction and excluding aggregation.

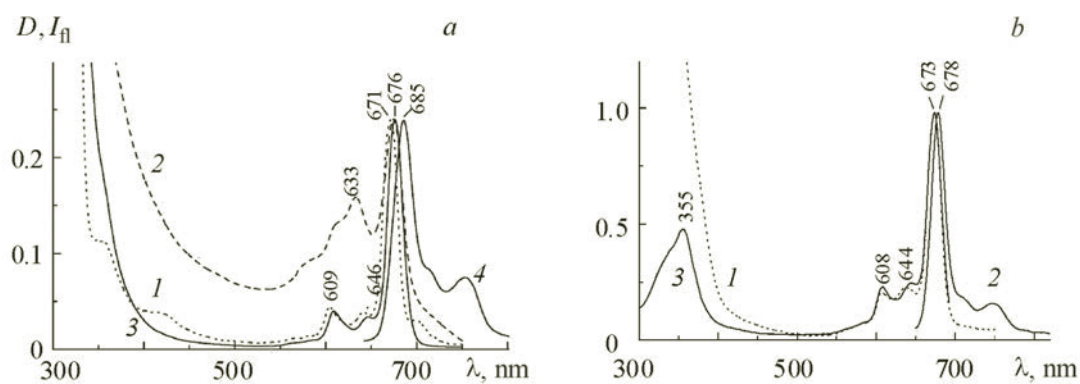


Fig. 1. Spectra: a — absorption of $\text{Si(OH)}_2\text{Pc}$ in pyridine (1) and in a TEOS + VTEOS (2) gel-matrix, absorption (3), and fluorescence ($\lambda_{\text{ex}} = 355 \text{ nm}$) (4) of the APTEOS–SiPc–APTEOS conjugate in the composition of a copolymer; b — absorption (1), fluorescence ($\lambda_{\text{ex}} = 355 \text{ nm}$) (2), and fluorescence excitation ($\lambda_{\text{reg}} = 730 \text{ nm}$) (3) of $\text{Si(OH)}_2\text{Pc}$ in the PVB film.

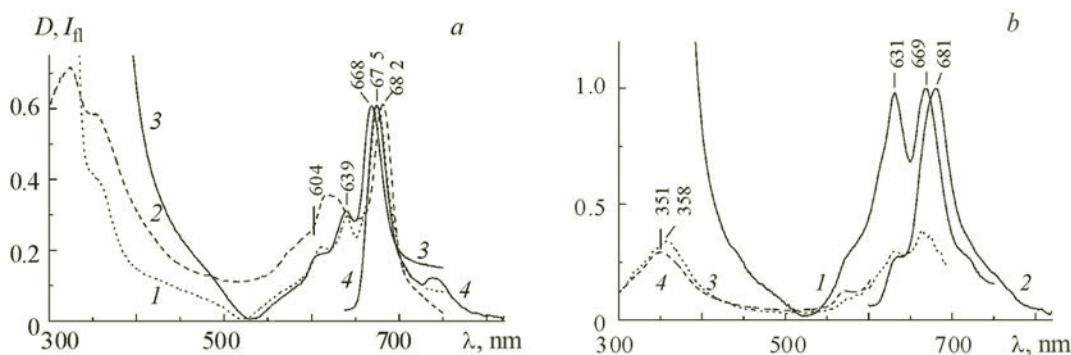


Fig. 2. Spectra: a — absorption of $\text{Ge(OH)}_2\text{Pc}$ in pyridine (1) and in the TEOS + TEVOS (2) gel-matrix, absorption (3), and fluorescence ($\lambda_{\text{ex}} = 355 \text{ nm}$) (4) of the APTEOS–GePs–APTEOS conjugate within the composition of a copolymer; b — absorption (1), fluorescence ($\lambda_{\text{ex}} = 355 \text{ nm}$) (2), and fluorescence excitation [$\lambda_{\text{reg}} = 730$ (3) and 630 nm (4)] of $\text{Ge(OH)}_2\text{Pc}$ in the PVB film.

It is of interest to compare the spectral-luminescent properties of monomeric forms of $\text{Si(OH)}_2\text{Pc}$ in an organic polymer and the APTEOS–SiPc–APTEOS conjugate within the composition of a silicate copolymer. Figure 1b shows the absorption, fluorescence, and fluorescence excitation spectra of $\text{Si(OH)}_2\text{Pc}$ in the PVB film, and Fig. 1a — absorption (curve 3) and fluorescence spectra (curve 4) of the APTEOS–SiPc–APTEOS conjugate within the composition of the silicate gel-film linear chain copolymer. The totality of the presented spectra and their characteristic form suggest that in both matrices the SiPc macrocycles are in monomeric form. The large Stokes shift of the fluorescence band at 685 nm (Fig. 1a, curve 4) of the APTEOS–SiPc–APTEOS conjugate is related to the reabsorption effect due to the relatively high optical density of the gel-film.

Spectral-luminescent properties of $\text{Ge(OH)}_2\text{Pc}$ and the APTEOS–GePc–APTEOS conjugate. The obtained spectral-luminescent properties of the APTEOS–GePc–APTEOS conjugate are similar to those of the APTEOS–SiPc–APTEOS conjugate described above. Figure 2a shows the absorption spectra of $\text{Ge(OH)}_2\text{Pc}$ in pyridine and in the hybrid organo-inorganic TEOS + VTEOS gel-matrix. Comparing the spectrum of $\text{Ge(OH)}_2\text{Pc}$ in the gel-matrix with the pyridine solution spectrum, it can be seen that the Q-band of the monomeric form is located at 682 and 675 nm, respectively, and the bands of the aggregated form in the gel material are in the 610–640-nm region. It was shown in [11] that the replacement of the phthalocyanine axial Cl^- ligands with the OH-group in the germanium complex reduces its stability — the complex partially undergoes dissociation, which leads to the absence of shielding of the central atom by the axial ligands and, consequently, to the formation of aggregated forms.

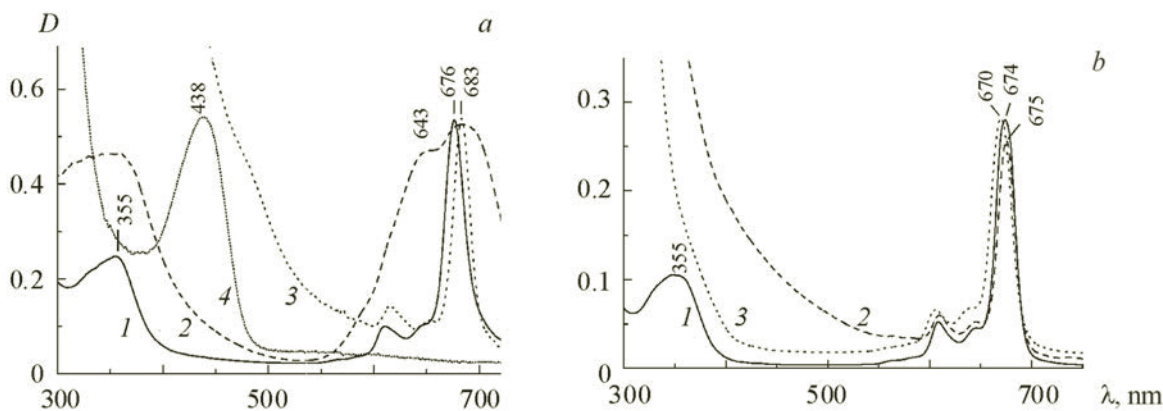


Fig. 3. Absorption spectra: a — GaOHPc in DMF (1) and in the TEOS + VTEOS (2) gel-matrix, the APTEOS–GaPc conjugate covalently "grafted" to polymer chains of the silicate gel-film after drying for 2 (3) and 17 days (4); b — AlOHPc in DMF (1) and in the TEOS + VTEOS (2) gel-matrix, the APTEOS–AlPc conjugate covalently "grafted" to polymer chains of the silicate gel-film after drying for 2 days (3).

The absorption spectrum of the APTEOS–GePc–APTEOS conjugate incorporated by structural links into the polymer chains of the silicate framework (Fig. 2a, curve 3) is similar in structure to the spectrum of the pyridine solution. The main contributor to both spectra is the monomeric form of MPc — the absorption *Q*-band in the APTEOS–GePc–APTEOS conjugate with a maximum at 668 nm. At the same time, the band at 639 nm indicates the existence of a small admixture of aggregates in the samples. The predominance of the monomeric form of the APTEOS–GePc–APTEOS conjugate incorporated in the polymer chains of the silicate gel-film is confirmed by its fluorescence excitation spectrum at $\lambda_{\text{reg}} = 730$ nm (not shown), in which there are no signs of aggregated forms in the region of 580–700 nm. As in the case of SiPc, in the case of copolycondensation of the macromolecules of APTEOS–GePc–APTEOS conjugate with siloxane units in the chains of the silicate framework, their aggregation is effectively inhibited, and the concentration of the monomeric form is significantly increased.

Analysis of the spectral-luminescent properties of Ge(OH)₂Pc in the PVB film (Fig. 2b) revealed the features of the formation of the spectral forms of this MPc in the polymer. The absorption spectrum (curve 1) has two broadened intense bands at 631 and 669 nm, and a typical absorption band of monomers appears to be redirected with an intense band at 669 nm. Absorption spectra with similar shapes were obtained in [12], according to which *Q*-bands for monomeric and dimeric forms of GePc have maxima at 668 and 631 nm. The fluorescence spectrum (curve 2) shows that, in addition to associates in PVB, there is a monomeric form that has an intense fluorescence band at 681 nm. A weak emission band at 632 nm and a more intense broadened band at 670 nm (in the form of an inflection of the intense band at 681 nm) can be attributed to the associates.

Spectral-luminescent properties of GaOHPc and the APTEOS–GaPc conjugate. The complex contour of the electronic absorption spectrum of GaOHPc in the TEOS + VTEOS gel-matrix (Fig. 3a, curve 2), which indicates the formation of aggregates of different structures in the silicate material, takes the form of a monomeric spectrum for macromolecules of the APTEOS–GaPc conjugate covalently "grafted" as side substituents to the polymer chains of the silicate gel-film (curve 3) after two days of drying. However, an increase in the drying time of the gel-film to 17 days leads to a sharp change in the spectrum (curve 4) — it consists of one absorption band at 438 nm, and the sample exhibits a visually conspicuous blue-green fluorescence.

Since GaOHPc has one axial ligand (one OH-group), interaction with APTEOS results in the formation of the APTEOS–GaPc conjugate, which is not copolycondensed by separate fragments into polymeric silicate chains, but can be covalently "grafted" to the nanopore surface of the gel-material, that is, it will be a lateral substituent of the polymeric siloxane chain. Moreover, the conjugate is surrounded by aminopropyl groups not bound to the central Ga³⁺ ion, partly overlapping the nanopore surface, which interferes with the aggregation of APTEOS–GaPc conjugates. It can be assumed that as the gel material dries, the monomeric molecules of the APTEOS–GaPc conjugate approaching the surface OH-groups undergo degradation with the formation of benzene-derivative-type *meso*-aza-dipyrromethene products. As shown in [8], AlOHPc in the TEOS gel-matrix also does not form aggregated forms, which is most likely the cause of its destruction to form similar fluorescent benzene-derivative *meso*-aza-dipyrromethenes.

TABLE 1. Fluorescence Lifetimes of $M(OH)_2Pc$ in Solid-State Matrices at 298 K and $\lambda_{ex} = 378$ nm

Compound	Matrix	λ_{reg} , nm	τ_{1fl} , ns	τ_{2fl} , ns
Si(OH) ₂ Pc	PVB	680	5.0	—
APTEOS–SiPc–APTEOS conjugate	Silicate copolymer	680	5.7	—
Ge(OH) ₂ Pc	PVB	680	5.0 (26%)	2.0 (74%)
		630	1.6 (37%)	3.6 (63%)
APTEOS–GePc–APTEOS conjugate	Silicate copolymer	680	5.9	—

Spectral-luminescent properties of AIOHPs and the APTEOS–AlPc conjugate. As in the case of the introduction of AIOHPc into the TEOS + VTEOS gel-matrix, the absorption spectrum of the APTEOS–AlPc conjugate "grafted" in the form of side substituents to the polymer chains of the silicate gel-film after drying for two days has the form of the absorption spectrum of MPc in monomeric form (Fig. 3b, curves 2 and 3).

AIOHPc molecules, introduced in fundamentally different ways into the silicate organo-inorganic gel-materials, remain stable in monomeric form. The absence of degradation of monomers with the formation of benzene-derivative *meso*-aza-dipyrromethenes (unlike in the case of GaOHPc) indicates the protective effect of surface organic groups of silicate nanopores on AIOHPc molecules. The stability of the monomeric form of AIOHPc in matrices of different nature requires additional studies to assess the feasibility of practical applications of such materials.

Photophysical characteristics of $M(OH)_2Pc$ in solid-state matrices. To confirm the conclusions drawn from the spectral-luminescent data, the fluorescence lifetimes of the spectral forms of $M(OH)_2Pc$ in PVB films and APTEOS–MPc–APTEOS conjugates in copolymers with siloxane fragments of polymer chains of gel-films have been measured (Table 1). Analysis of the obtained data showed that in the transition from Si ($Z = 14$) to Ge ($Z = 32$), fluorescence lifetime of the monomeric form of MPc in PVB (τ_{1fl} at $\lambda_{reg} = 680$ nm) does not change. For Si(OH)₂Pc and Ge(OH)₂Pc, $\tau_{1fl} = 5.0$ ns. In the case of copolycondensation of the APTEOS–SiPc–APTEOS and APTEOS–GePc–APTEOS conjugates with siloxane links of the silicate framework, fluorescence lifetimes increase to 5.7 and 5.9 ns, respectively, which confirms the monomeric structure of the MPc chromophores. The increase in the fluorescence lifetime τ_{1fl} in the silicate gel-matrix can be related to the elimination of deformation of the MPc macrocycle when it is inserted as a separate link into linear chains of the inorganic polymer and/or the rigidity of the molecular system surrounding it. The obtained τ_{1fl} data indicate that the fluorescence quantum yield is quite high. For the aggregated forms of Ge(OH)₂Pc in PVB, fluorescence lifetime is shortened to ~ 2 –3 ns. It should be emphasized that the two-exponential nature of fluorescence decay of Ge(OH)₂Pc in PVB confirms the presence in this medium of two spectrally different forms of the dopant.

It should be noted that for *tert*-butyl-substituted Si(OH)₂Pc in toluene $\tau_{fl} = 6.8$ ns [13]. The obtained values of τ_{1fl} can be compared with the data on τ_{fl} and the fluorescence quantum yield ϕ_{fl} for solutions of MgPc ($Z = 12$) and ZnPc ($Z = 30$) in propanol [14]: 7.2 ns and 0.76 for MgPc, 3.8 ns and 0.45 for ZnPc. The comparison points to the intensification of nonradiative deactivation of the S_1 -state in SiPc in solid-state matrices and its weakening in GePc. This may be due to differences in the covalent radii of metal atoms. As noted in [11], the Ge atom has a covalent radius of 1.22 Å, which "fits well" into the "window" of the phthalocyanine molecule. In contrast, the Si atom has a covalent radius of 1.11 Å, and in Mg and Zn it is larger than the "window" radius of 1.30 and 1.31 Å [15]. Therefore, SiPc macrocycles in solid-state matrices can undergo deformation, and the Zn atom can exert a stronger influence than the Ge atom on fluorescence — intramolecular effect of a heavy atom.

Conclusions. It is shown that the methods of optical molecular spectroscopy make it possible to obtain useful information on the molecular structure and properties of excited electronic states of the spectral forms of the MPc. It was found that APTEOS–MPc–APTEOS conjugates copolycondensed with siloxane units in polymer chains of a silicate gel-film exhibit spectral properties of the monomeric forms. The development of new solid-state silicate materials doped with MPc conjugates by the method of covalent linking will expand the use of metallophthalocyanines as monomeric dopants, which will create scientific bases for the development of new functional materials in which practically useful systems for optics, quantum electronics and other areas will function using structural, spectral and physicochemical properties of the monomeric forms of these compounds.

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