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SPECTRAL AND AGGREGATION PROPERTIES OF PHENYLTHIO-SUBSTITUTED Al-PHTHALOCYANINE MOLECULES IN NANOPOROUS SILICATE MATRICES

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The absorption, fluorescence, and fluorescence excitation spectra of phenylthio-substituted Al-phthalocyanine in solutions, polyvinyl butyral films, and silicate gel matrices at room temperature were studied. It was found that monomeric fluorescent forms of impurity molecules are formed not only in ethanol and polyvinyl butyral but also in inorganic and organic-inorganic silicate matrices colored by the direct sol–gel synthesis method. It was shown that nonfluorescent aggregates, presumably of the H-type, are formed when the tetraethoxysilane matrix is stained by the impregnation method. The obtained solid silicate matrices can be used as multipurpose luminescent materials for the near-IR region.

Keywords: *phenylthio-substituted Al-phthalocyanine, absorption and fluorescence spectra, organic polymer, silicate matrices, aggregates.*

Introduction. Phthalocyanines (Pcs) are synthetic dyes that are close to porphyrins in their luminescence spectral characteristics. Having high thermal, chemical, and photochemical stability Pcs are not only used as traditional light-resistant pigments and dyes but are used widely in many contemporary and technological applications such as medicine, electronics, solar energy, nonlinear optics, etc. [1, 2].

Extension of the practical applications of Pcs depends on their ability to form complexes with metals and also on the presence of peripheral bulky substituents that increase their solubility in many solvents. One such Pc derivative is the aluminum complex of phenylthio-substituted phthalocyanine, hydroxyaluminum tetra(3-phenylthio)phthalocyanine ($(PhS)_4$-PcAlOH), the synthesis of which was described in [3]. Having a high quantum yield of triplet formation ($\varphi_T \approx 70\%$ in DMSO), the compound shows promise for use as photosensitizer for photodynamic therapy (PDT) and diagnosis of oncological diseases [4]. Since $(PhS)_4$-PcAlOH is highly hydrophobic its liposomal form based on lipids (Tiosens) was developed for the formation of its solutions close to physiological with the possibility of intravenous administration of this IR photosensitizer [5]. It was shown that the liposomal drug form of Tiosens has a fairly high level and selectivity of accumulation in tumors and can be used effectively in PDT [6, 7]. The absorption and fluorescence in the near infrared region (700–850 nm), where the natural absorption of biological tissues is minimal, opens up the possibility of using $(PhS)_4$-PcAlOH for fluorescent diagnosis of oncological diseases [8]. The compound is used with similar aims for visualization of the distribution of a tumor by surface-enhanced Raman scattering (SERS) and photothermal heating [9]. According to [10] $(PhS)_4$-PcAlOH can at the same time be used in therapy and diagnostics (theranostics) , i.e., can be regarded as a light-sensitive theranostic substance.

In addition, the phthalocyanine complex was investigated in a solar cell as a component adsorbed on a TiO_2-nanocrystalline film electrode that secured sensitization of photoinduced electron transfer in the near IR region [11] and has also been used as a component of multijunction polymer solar cells [12]. We note that solid-state materials doped with the monomeric forms of metal phthalocyanines are used in many practical fields (optics, optoelectronics, etc.). Spectral

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investigations of $(PhS)_4$-PcAlOH molecules only in ordinary [13] and stretched [14] polyvinyl alcohol have been reported in the literature. This has prompted the search for new solid-state matrices capable of retaining the monomeric (fluorescent) form of $(PhS)_4$-PcAlOH and also calls for study of the structure and properties of macroheterocyclic molecule–environment systems.

Subjects of Investigation and Experimental Procedure. The phenylthio-substituted Al-phthalocyanine was supplied by the Aldrich Chemical Company as tetra-(3-phenylthio)phthalocyanine aluminum chloride ($(PhS)_4$-PcAlCl) and was used without further purification. As shown in [15], effective substitution of the anionic Cl ligands of the central metal ion by OH groups occurs at the stages of synthesis and purification of the metal phthalocyanines and also during purification of the working solutions, i.e., hydrolysis occurs when the undried solvents are used. We assume that the analogous process of "religandization" at the central aluminum ion occurs in the case under investigation, and the Pc used in the present investigation was therefore designated as $(PhS)_4$-PcAlOH.

The synthetic polymer polyvinylbutyral (PVB) was chosen as solid-state matrix for incorporation of the $(PhS)_4$-PcAlOH. Samples based on PVB in the form of optically transparent thin films colored with the Pc were prepared by pouring an ethanol solution of the film-forming polymer onto a horizontal glass substrate followed by drying. The thickness of the films was controlled by the number of pouring operations (typically 3–4) and amounted to 100–500 μm.

The bulk inorganic (based on tetraethoxysilane (TEOS)) and mixed organic-inorganic (based on a mixture of TEOS and vinyltriethoxysilane (VTEOS)) gel-matrices were synthesized by the sol–gel method. The TEOS and VTEOS (Sigma–Aldrich) were not submitted to additional purification. The sol–gel method for the synthesis of silicate matrixes was described in [15].

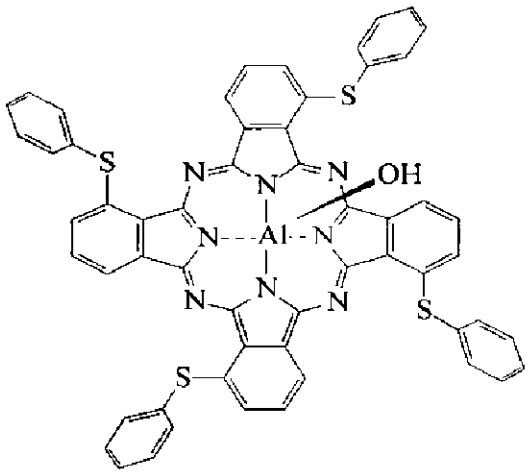
The silicate matrixes were activated by two methods — direct sol–gel synthesis of the matrix from a reaction solution containing the $(PhS)_4$-PcAlOH molecule and impregnation of the nanoporous silicate matrix with a solution of the Pc. During activation by the first method various volumes of a saturated solution of the $(PhS)_4$-PcAlOH in DMFA to produce samples with various concentrations of the impurity were added to the reaction mixture that had been poured into plastic cuvettes. The cuvettes were sealed hermetically with a film of Parafilm M and were kept in the dark at room temperature. After two days a silicate framework of xerogel with pores filled with the $(PhS)_4$-PcAlOH solution was formed (the polycondensation stage). In order to remove the liquid components (water, ethanol, DMFA) from the obtained gel materials a small opening was made in the film, and the colored TEOS and TEOS + VTEOS gel matrices were kept for a long time (~100 days) at room temperature and atmospheric pressure. The drying process led to an appreciable reduction in the volume of the gel, as a result of which the matrices shrank to ~35% of the initial volume. In the second method "clean" nanoporous gel matrices were synthesized and were then impregnated with the ethanol solution of $(PhS)_4$-PcAlOH and dried at room temperature to remove the ethanol from the nanopores.

The electronic absorption spectra were recorded on a RV 2201V spectrophotometer (Solar, Belarus), and the fluorescence and fluorescence excitation spectra were recorded on a SM2203 spectrofluorimeter (Solar, Belarus) at room temperature.

The semiempirical AM1 quantum-chemical method from the HyperChem chemical software package (Hypercube Inc.) was used for optimization of the geometrical structure of the $(PhS)_4$-PcAlOH molecule in the ground state. The geometry was considered optimized when the change in the total energy of the structure after successive computation steps was not greater than 0.01 kcal/mole.

Results and Discussion. Tetra(3-phenylthio)phthalocyanine contains an Al^{3+} ion in a pentacoordinated state: four coordination bonds are formed by the nitrogen atoms of the phthalocyanine macrocycle while the fifth bond is formed by the oxygen atom of the hydroxyl group located at the axial position outside the phthalocyanine ring. This is confirmed experimentally by the NMR data indicating the presence of an additional extracoordinated OH group in the structure of the phthalocyanine [16].

The optimized structure of the $(PhS)_4$-PcAlOH molecule



confirms the planar structure of the phthalocyanine macrocycle. The planarity of the macrocycle is not destroyed during coordination of the aluminum atom since the radius of the Al^{3+} ion is not greater than the distance from the coordinating nitrogen atom to the center of the "window." The four phenylthio substituents at the benzene rings do not lie in the plane of the macrocycle but are directed symmetrically along one side of the macrocycle, forming the steric *cis* isomer. The dihedral angle here between the plane of any phenyl ring and the plane of the macrocycle amounts to ~52°.

The absorption spectra of solutions of $(PhS)_4$-PcAlOH in ethanol, DMSO, and DMFA have identical structure with insignificant shift of the bands (by up to 10 nm). Figure 1a (curve 1) shows the absorption spectrum in ethanol, which has the form characteristic of metal phthalocyanines. The strong $Q(0–0)$ band at 726 nm ($\Delta\nu \approx 520$ cm ^{1}) corresponds to transitions to a doubly degenerate electronic state. The weaker bands in the region of 600–700 nm are its genetically electronic-vibrational bands. The band in the near UV region at 341 nm ($B(0–0)$ band) is called by analogy with metal porphyrins a Soret band. The absorption in the region of 400–500 nm corresponds to $n–\pi^*$ transitions, directed almost perpendicular to the plane of the macrocycle [17], with bands of very low intensity. The fluorescence spectrum in ethanol (curve 2) during monochromatic excitation to the Soret band (λ_{exc} = 342 nm) has a strong 0–0 band with a maximum at 739 nm ($\Delta\nu \approx 500$ cm^{-1}) and a weak electronic-vibrational band in the region of ~817 nm. Such distribution of the intensity in the fluorescence spectrum leads to destruction of the mirror symmetry with the absorption spectrum in the region of the $S_1 \leftarrow S_0$ transition, which may indicate rearrangement of the molecule in the S_1 state. The unsymmetrical contour of the 0–0 fluorescence band indicates insignificant reabsorption in the solution with $D \approx 0.4$ at 726 nm. The purity of the phthalocyanine is confirmed by the similarity of the absorption spectrum and the fluorescence excitation spectrum (curve 3). Analysis of the spectra of the solutions of $(PhS)_4$-PcAlOH in ethanol confirms that the molecule has symmetry close to D_{4h} despite the fact that the optimized geometry relates to a point group of lower symmetry. The luminescence-spectral characteristics of the $(PhS)_4$-PcAlOH in ethanol correlate qualitatively with its characteristics in DMSO and in biological tissue [8].

The symmetrical addition of four phenylthio substituents to the phthalocyanine macrocycle results in a shift of the long-wave absorption band into the region adjacent to the near IR region. For example, the $Q(0–0)$ band is shifted from 670 nm for PcAlCl [18] to 726 nm for $(PhS)_4$-PcAlOH in ethanol, from 672 nm [19] to 719 nm in DMFA, and from 683 nm [20] to 737 nm in DMSO. As seen, the bathochromic shift of the $Q(0–0)$ band of $(PhS)_4$-PcAlOH in the various solvents amounts on the average to ~50 nm (~1000 cm ^{1}).

Change from the liquid solutions to the solid organic polymeric film of PVB colored with $(PhS)_4$-PcAlOH does not change the form of the absorption spectrum (Fig. 1b, curve 1). The bathochromic shift of the $Q(0–0)$ band in PVB by ~12 nm in comparison with the ethanol solution agrees with the bathochromic shift of the band in a film of polyvinyl alcohol (~729 nm) [13, 14]. We note that introduction of the dye into a rigid matrix of polyvinyl alcohol changes the form of the absorption spectrum, indicating the formation of an appreciable amount of aggregates [13], although the aggregation in an extended elastic film of this polymer is insignificant [14]. In PVB the half-width of the 0–0 absorption band is ~570 cm^{-1} while the half-width of the fluorescence band is 600 cm^{-1}, which is significantly greater than in the ethanol solution. This is due to the formation of at least two impurity sites in the PVB, which is confirmed by the fluorescence excitation spectra (curves 3 and 4) and by the fluorescence spectra with monochromatic excitation (Fig. 1b, inset).

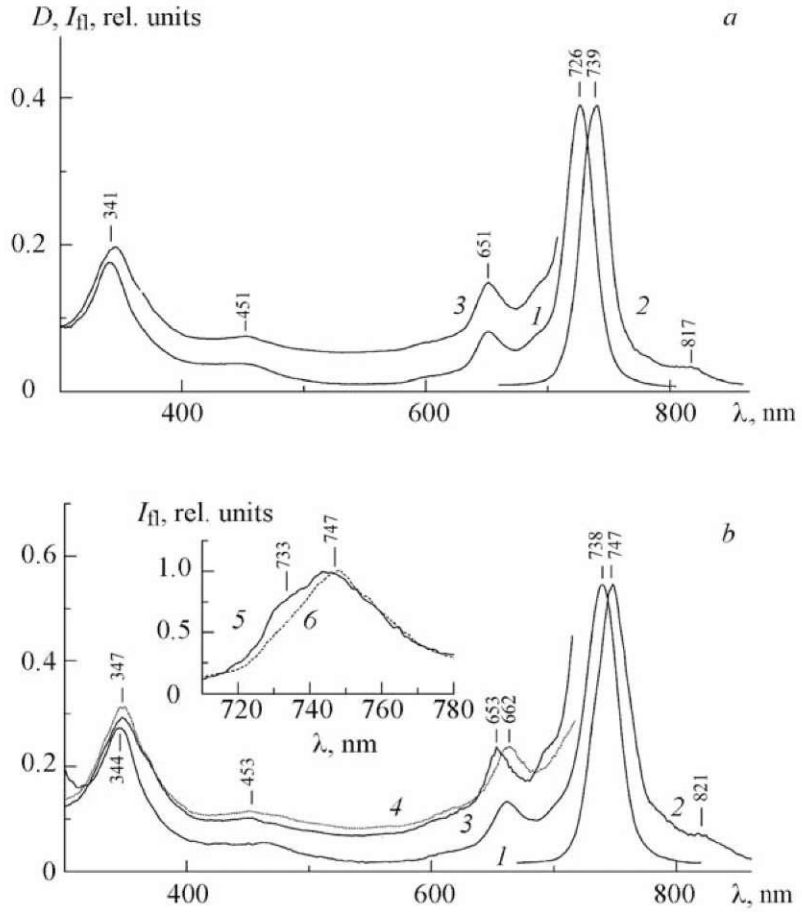


Fig. 1. The absorption (1), fluorescence [λ_{exc} = 342 (2a), 345 (2b), 653 (5b), and 662 nm (6b)], and fluorescence excitation [λ_{rec} = 732 (3a), 735 (3b), and 750 nm (4b)] spectra of $(PhS)_4$-PcAlOH in ethanol (a) and PVB (b) at 298 K.

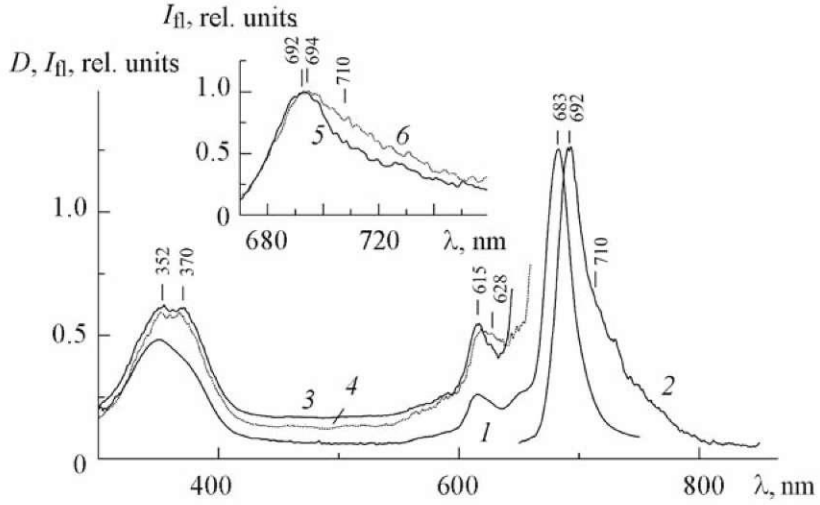


Fig. 2. Absorption (1), fluorescence (at λ_{exc} = 352 nm) (2), and fluorescence excitation [at λ_{rec} = 692 nm (3) and 712 nm (4)] spectra of $(PhS)_4$-PcAlOH in the TEOS gel matrix (direct synthesis) at 298 K; inset, the 0–0 fluorescence band at λ_{exc} = 615 (5) and 628 nm (6).

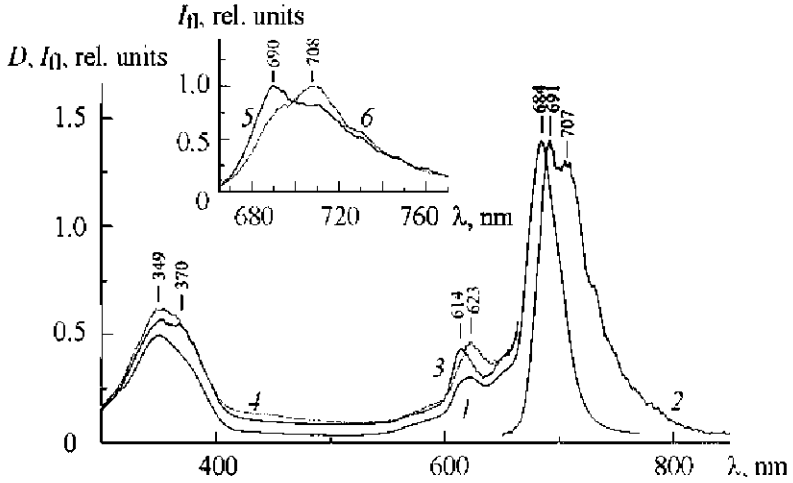


Fig. 3. Absorption (1), fluorescence (at λ_{exc} = 349 nm) (2), and fluorescence excitation [at λ_{rec} = 691 (3) and 707 nm (4)] spectra of $(PhS)_4$-PcAlOH in TEOS + VTEOS gel matrix (direct synthesis) at 298 K; inset, the 0–0 fluorescence band at λ_{exc} = 614 (5) and 623 nm (6).

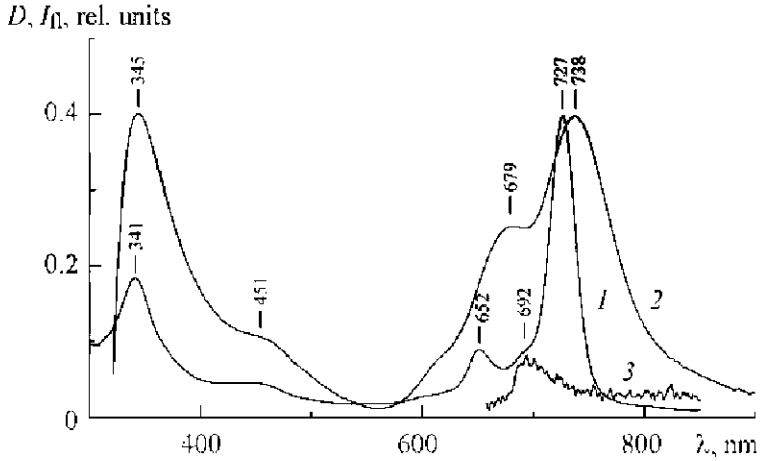


Fig. 4. Absorption (1, 2) and fluorescence (3) spectra at λ_{exc} = 345 nm for $(PhS)_4$-PcAlOH in ethanol (1) and the TEOS gel matrix (impregnation) (2, 3) at 290 K.

The $(PhS)_4$-PcAlOH molecules, introduced into the silicate matrix by direct synthesis, have an absorption spectrum (Fig. 2, curve 1) reminiscent of the absorption spectrum in ethanol and PVB in band structure and half-width (Fig. 1a and b). Here there is a substantial hypsochromic shift of the $Q(0–0)$ band as the matrix dries, which after drying of the matrix for 100 days is localized at 683 nm with $\Delta\nu \approx 540$ cm $^{-1}$. The Soret band conversely undergoes a bathochromic shift at ~10 nm with the appearance of a long-wave shoulder, while the activity of the $n–\pi^*$ transitions in the region of 400–500 nm gradually disappears. In addition strong fluorescence is observed (curve 2) during photoexcitation in the region of the Soret band.

In the mixed TEOS + VTEOS gel-matrix the long-wave absorption band of the $(PhS)_4$-PcAlOH at 684 nm has an unsymmetrical contour with $\Delta\nu \approx 740$ cm $^{-1}$ (Fig. 3, curve 1). At λ_{exc} = 349 nm the 0–0 fluorescence band is split into components at 691 and 707 nm (curve 2), indicating the formation of two types of impurity sites in the mixed silicate matrix.

With the introduction of $(PhS)_4$-PcAlOH into the TEOS gel matrix by the impregnation method a fundamentally different form of absorption spectrum is observed (Fig. 4, curve 2). The absorption spectrum of the ethanol solution of

$(PhS)_4$-PcAlOH used to impregnate the matrix (curve 1) shows a bathochromic shift and broadening of all the absorption bands: $\lambda_{Q(0-0)}$ = 726 nm and $\Delta\nu_{Q(0-0)} \approx 520$ cm^{-1} in ethanol; $\lambda_{Q(0-0)}$ = 738 nm and $\Delta\nu_{Q(0-0)} \approx 1300$ cm^{-1} in the TEOS gel matrix. The absorption band at 679 nm also has increased relative intensity compared with the electronic-vibrational $Q(0-1)$ band (at 651 nm) in ethanol, indicating the formation of a new form of $(PhS)_4$-PcAlOH impurity molecules in the silicate matrix. At λ_{exc} = 345 nm there is an extremely weak fluorescence band with a maximum at 692 nm (curve 3), which probably corresponds emission from the initial monomeric form of the impurity molecules (cf. Fig. 2, curve 2) that are present in the sample in small amounts.

The changes in the absorption spectra of $(PhS)_4$-PcAlOH in the various media (ethanol, PVB. TEOS (direct synthesis) and TEOS + VTEOS gel matrices) amount only to retention of the general characteristic form of the spectra (Figs. 1–3). From this it follows that the molecular form, which gives rise to absorption, does not change in the transition from one medium to the other. Dilution of the ethanol solution of $(PhS)_4$-PcAlOH in the range of $D_{726} \approx 1.5$–0.2 does not change the general form of the spectrum. which indicates the absence of or a very small degree of aggregation of the $(PhS)_4$PcAlOH. Evidence for this is provided by the presence of narrow electronic-vibrational bands in the region of 600–700 nm in the spectra of all the employed solvents. In addition, the similarity in the absorption and excitation spectra of the investigated solutions indicates that the systems contain impurity sites that can be identified with the $(PhS)_4$-PcAlOH monomers. The solvation process is facilitated by the presence of thiophenyl substituents at the periphery of the $(PhS)_4$-PcAlOH macrocycle, which increases the distance between the adjacent molecules on the one hand and prevents aggregation on the other. The hypsochromic shift of the $Q(0-0)$ absorption band of $(PhS)_4$-PcAlOH in silicate gel matrixes in relation to their drying time is due to evaporation of the solvent molecules from the nanopores and to weakening of the intermolecular interaction with the impurity molecules, which gives rise to a "blue" shift of the long-wave absorption band (analogous with the gas phase). Such spectral behavior agrees, for example, with the behavior for molecules of the free Pc base, the $Q(0-0)$ absorption band of which in quinoline and in 1-chloronaphthalene lies at 698 nm [18], whereas in the static gas phase it is at 686 nm [21] and in the supersonic free stream it is at 661 nm [22].

Activation of the silicate TEOS matrices by various methods leads supposedly to the formation of various types of impurity sites. This is based on the results from analysis of the behavior of the spectral position and the half-width of the long-wave absorption band and the 00 fluorescence bands corresponding to the $S_1 \leftrightarrow S_0$ transitions as the most sensitive to the state of the π-electron system of the macrocycle.

The axial anionic OH ligands of the metal phthalocyanine can participate in polycondensation reactions of alkoxysilanes. As a result of this individual molecules of $(PhS)_4$-PcAlOH are capable of forming a single framework with a polymeric silicate material in the form of side substituents. As the silicate polymeric porous structure with terminal groups predominantly of the H–O–Si$\equiv_{matr}$ type is formed and the liquid reaction components evaporate the $(PhS)_4$-PcAlOH molecules lose the solvate shell, and their concentration at the surface of the pores increases. In this case the axial OH ligands of the impurity molecules enter into condensation with the surface silanol groups of the TEOS matrix, bonding through an oxygen bridge with the surface of the nanopores of the silicate framework and releasing molecules of H_2O:

$$(PhS)_4\text{-PcAl–O–H} + \text{H–O–Si}\equiv_{matr} \rightarrow (PhS)_4\text{-PcAl–O–Si}\equiv_{matr} + H_2O\ .$$

Such interaction with the surface hydroxyl OH groups results in preservation of the monomeric form of the impurity molecules (Fig. 2).

In [15] it was shown that the aluminum complex of Pc (AlOHPc) in the silicate TEOS matrix is destroyed as a result of interaction with the silicate framework, but this is not observed in the $(PhS)_4$-PcAlOH molecules. It probably indicates protective action from the phenylthio substituents.

In the organic-inorganic TEOS + VTEOS gel matrix most of the hydroxyl groups situated on the surface of the pores are substituted by vinyl groups (C_2H_5), which do not participate in the hydrolysis process and are bonded to the inorganic lattice on the surface of the nanopores of the matrix, forming a unique "organic cover." This leads to the result that there are two main types of impurity sites in the TEOS + VTEOS matrix. This shows up in the asymmetry of the long-wave absorption band and the splitting of the 0–0 fluorescence band into two components (Fig. 3). The existence of at least two types is confirmed by the fluorescence excitation spectra (curves 3 and 4) and fluorescence spectra with monochromatic excitation in the region of the vibronic absorption band (curves 5 and 6).

As seen from Fig. 4 (curve 2), the absorption bands of $(PhS)_4$-PcAlOH in the impregnated TEOS matrix undergo a bathochromatic shift and are substantially broadened. A long-wave shift of the bands is characteristic of J aggregates. However. in view of the complete absence of fluorescence in this case it can be asserted that aggregates of the H type are

presumably formed. In structure the *H* aggregates have a salt-like orientation of the molecules, while in the limiting case they have a face-to-face configuration, i.e., when the angle between the line passing along the dipole of the monomer and the line connecting the centers of the dipoles is close to 90°. If this angle approaches the critical value (54.7°) the absorption band of the aggregate remains spectrally unchanged or has a slight bathochromic shift. Such behavior of the long-wave band in the spectra of the *H* aggregates of certain derivatives of Pc was described in [23, 24] and was explained by increase in the packing density of the monomeric macrocycles in the aggregate, i.e., by transition to a state close to crystalline. In the TEOS-xerogels the internal cavities (nanopores) have a multitude of surface silanol groups (H–O–Si≡$_{matr}$) which at the drying stage condense effectively with each other with the formation of water molecules and the appearance of less reactive siloxane bridges (≡Si–O–Si≡) with the O atom on the surface of the nanopores. The surface of the nanopores modified in this way rules out the possibility of formation of a covalent bond between the impurity molecule and the silicate framework. In the matrix penetration process the liquid solvent together with dissolved material pass into the nanoporous material as a result of a capillary effect. Subsequent evaporation of the solvent leads to loss of the solvate shell and, as a result, to close contact of the molecules with each other (the formation of *H* aggregates) but not with the surface of the nanopores on account of the absence of silanol groups. With the elimination of solvation the formation of *H* aggregates is also promoted by the presence in the $(PhS)_4$-PcAlOH structure of sulfur atoms that are capable of bonding with the nonmetal atoms of another molecule or of forming a hydrogen bond with the axial OH ligand of the central Al atom.

Conclusions. On the basis of luminescence spectral data it is possible to suggest possible mechanisms for the interaction of $(PhS)_4$-PcAlOH impurity molecules with the surface of nanopores in inorganic and organic-inorganic silicate xerogels as well as in an organic polyvinylbutyral film. It was established that the spectral characteristics and structural changes in the impurity molecules depend on the method of coloring the silicate matrices. Monomeric forms of the molecules are formed during coloring by the direct synthesis method while aggregated forms presumably of the *H* type are formed in the impregnation method. It was found that the aggregated forms do not have fluorescence, whereas the monomeric molecules have strong fluorescence. The latter opens up prospects for the use of solid-state silicate materials doped with $(PhS)_4$-PcAlOH in the development of multipurpose luminescent materials for the near-IR region. The preferred material here is the inorganic TEOS material colored by direct sol–gel synthesis as a material that not only has enhanced mechanical and optical characteristics compared with the TEOS + VTEOS organic-inorganic material but is also characterized by the absence of absorption in the region of 300–1000 nm.

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