ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2023, Vol. 97, No. 6, pp. 1195–1201. © Pleiades Publishing, Ltd., 2023.
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PHYSICAL CHEMISTRY OF NANOCLUSTERS, SUPRAMOLECULAR STRUCTURES, AND NANOMATERIALS

Evolution of the Impurity Sites and Electronic Spectra of Aluminum Phthalocyanine in a Silicate Nanoreactor

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Received September 8, 2022; revised November 21, 2022; accepted November 27, 2022

Abstract—The evolution of the electronic absorption spectra of substituted aluminum phthalocyanine incorporated into a nanoporous silicate gel matrix has been studied. The decomposition of the contour of the long-wavelength *Q*-absorption band of molecules into Voigt components reveals the dependence of the formation of various types of impurity sites in the matrix nanopores, which act as a solid-state nanoreactor, on the drying time of the matrix. Possible mechanisms of the effect of the internal structure of the synthesized silicate material during the transition from a sol state to a dried xerogel state on the spectral properties of phthalocyanine impurity molecules are discussed. Models of the interaction of the impurity molecules with the surface of the matrix nanopores during drying are considered; the features of the evolution of the resulting impurity sites are elucidated.

Keywords: metal phthalocyanine, sol–gel matrix, nanoreactor, impurity site, electronic absorption spectra, Voigt band components

DOI: 10.1134/S003602442306002X

Silicate matrices formed by sol–gel synthesis [1], i.e., by the hydrolysis and polycondensation of tetraethoxysilane (TEOS), are solid-state materials with a developed system of nanopores. Owing to the filling of nanosized cavities with solutions of organic molecules, the interaction of impurity molecules with the surface of nanopores strengthens in a limited volume and thereby leads to significant changes in their chemical and physical properties compared with those of a homogeneous solution. It was shown [2] that an aluminum complex of phenylthio-substituted phthalocyanine (hydroxyaluminum tetra-(3-phenylthio)-phthalocyanine $(PhS)_4$-PcAlOH) incorporated into a silicate matrix by direct sol–gel synthesis undergoes a significant hypsochromic shift of the *Q*-band during the drying of the matrix, while the fluorescent monomeric form is preserved. We note that, earlier, $(PhS)_4$-PcAlOH was studied as part of a solar cell, namely, as a component adsorbed on a nanocrystalline TiO_2 film electrode providing sensitization of photoinduced electron transfer in the near-infrared region [3]; it was used as a component of multijunction polymer solar cells [4] and studied in a polyvinyl alcohol film [5, 6]. The prospects of practical applications of solid-state materials colored with monomeric species of $(PhS)_4$-PcAlOH have stimulated spectral studies of the evolution of a doped colloidal silicate TEOS system during the transition of it from a sol state to a transparent solid xerogel matrix and further drying. The use of molecular spectroscopy and numerical calculations has made it possible to study the evolution of the formation of various types of impurity sites in nanopores of a silicate matrix, which act as a solid-state nanoreactor.

EXPERIMENTAL

Phenylthio-substituted aluminum phthalocyanine (Aldrich Chemical Company) as tetra-(3-phenylthio)-phthalocyanine aluminum chloride ($(PhS)_4$-PcAlCl) was used without further purification. It was shown [7] that at the stage of synthesis and purification of metal phthalocyanines and during the preparation of working solutions, i.e., in the case of using nondried solvents, the phthalocyanines undergo hydrolysis, which leads to the substitution of an OH group for the anionic Cl^- ligand of the central metal ion. It could be assumed that the aluminum ion of the metal phthalocyanine undergoes a similar "religanding" process; therefore, the studied phthalocyanine is designated in this work as $(PhS)_4$-PcAlOH. The molecular structure of $(PhS)_4$-PcAlOH is shown in the inset of Fig. 1a.

A nanoporous silicate matrix was formed by the classical sol–gel synthesis method, which reduces to the formation of a sol from TEOS, that is, $(C_2H_5O)_4Si$, by subjecting it to hydrolysis and polycondensation [7, 8]. Commercial TEOS (Sigma-

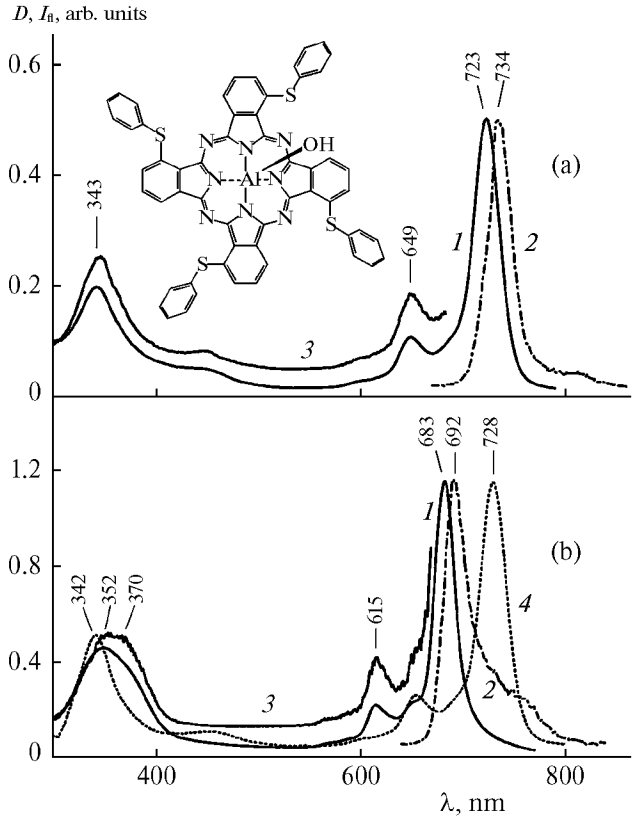

Fig. 1. (a) The absorption spectrum (*1*), fluorescence spectrum at λ_{exc} = 343 nm (*2*), and fluorescence excitation spectrum at λ_{rec} = 735 nm (*3*) of $(PhS)_4$-PcAlOH in DMF at 298 K and (b) absorption spectrum (*1*), fluorescence spectrum at λ_{exc} = 353 nm (*2*), and fluorescence excitation spectrum at λ_{rec} = 693 nm (*3*) of $(PhS)_4$-PcAlOH in a TEOS matrix at 298 K after 49 days of drying; (*4*) absorption spectrum of $(PhS)_4$-PcAlOH in an ethanol–water–formamide–hydrochloric acid mixture (molar ratio of 5 : 5 : 5 : 0.1). The inset shows the molecular structure of $(PhS)_4$-PcAlOH.

Aldrich) was used for the synthesis without further purification. The original reaction mixture was a mixture of components with a TEOS : ethanol : water : formamide molar ratio of 1 : 5 : 5 : 5. The introduction of formamide into the original mixture provided the formation of silicate matrices that did not undergo cracking during drying; in addition, formamide did not adversely affect the hydrolysis and polycondensation processes. To accelerate the hydrolysis process, ~0.1 mol of hydrochloric acid was added to the reaction mixtures. In this case, the TEOS molecules in the reaction medium undergo exchange interaction with water, where the $-OC_2H_5$ ethoxy groups are replaced by –OH hydroxyl groups. The complete hydrolysis of one TEOS molecule requires four water molecules; the reaction is described by the following equation:

$$(C_2H_5O)_4Si + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH.$$

The reaction mixture was stirred for 4 h until a highly dispersed colloidal solution was formed. The resulting sol, which was a two-phase solid–liquid system containing hydrated $Si(OH)_4$ particles, was poured into plastic cuvettes; a saturated $(PhS)_4$-PcAlOH solution in dimethylformamide (DMF) was then added at the following volumetric ratio of the components: 3 mL of the sol : 50 μL of a saturated phthalocyanine solution. The cuvettes were tightly closed with a Parafilm M sealing film and left to stand at room temperature in the dark. The transformation of the sol to a gel was provided by the polycondensation reaction (it occurred simultaneously with the hydrolysis process), where the resulting hydrated silicate tetrahedra interact with each other via ≡Si–OH silanol groups to give rise to ≡Si–O–Si≡ siloxane bridges:

$$\equiv Si{-}OH + HO{-}Si\equiv \rightarrow \equiv Si{-}O{-}Si\equiv + H_2O$$

and form a solid amorphous spatial network.

In parallel with the above process, the interaction of the silanol groups with ethoxy groups can occur; the interaction leads to the formation of similar siloxane bonds, yet, with the release of alcohol:

$$\equiv Si{-}OC_2H_5 + HO{-}Si\equiv$$
$$\rightarrow \equiv Si{-}O{-}Si\equiv + C_2H_5OH.$$

Eventually, within 2 days, the low-temperature hydrolysis and polycondensation processes lead to the formation of a solid nanoporous silicate matrix, that is, a material of high optical quality, whose nanopores are filled with a multicomponent solution containing $(PhS)_4$-PcAlOH molecules. The silicate matrix is a nanoporous polymeric silicon–oxygen framework (silicon atoms linked by ≡Si–O–Si≡ siloxane bonds) with a bulk nanoporous structure and a large surface area covered with a large number of ≡Si–OH silanol groups. Based on the fact that the synthesized silicate material has a nanoporous structure, it is classified as a nanomaterial.

After the formation of a silicate gel matrix, the structure and properties of it continue to change over time: the system passes through the aging and drying stages. To remove liquid components (water, ethanol, formamide, and DMF) from the matrix nanopores, a hole with a diameter of ~1 mm was formed in the coating film, and the gel matrixes were held at room temperature and atmospheric pressure for a long time (up to 70 days). The drying process led to a substantial decrease in the gel volume, owing to which the silicate matrices underwent shrinkage to ~35% of their initial volume.

Electronic absorption spectra were measured on a PB2201B spectrophotometer (Solar, Belarus). Fluorescence and fluorescence excitation spectra were recorded on an CM2203 spectrofluorimeter (Solar, Belarus). All the measurements were conducted at room temperature. Conclusions about the formation

of new types of impurity sites of $(PhS)_4$-PcAlOH in a silicate nanoreactor were based on the results of analyzing the spectral position, profile, and half-width of the long-wavelength Q-absorption band, being the most sensitive to the state of the π-electron system of the macrocycle. The structure of the contour of the Q-band of $(PhS)_4$-PcAlOH at the different drying stages of the matrix was analyzed using numerical methods by the contour decomposition into Voigt components. For the assumed number of components (from three to six), their parameters (intensity, position of the maximum, and half-width) were determined using original scripts implemented in the languages of well-known mathematical packages [9, 10]. The scripts contained built-in procedures of the packages as well as literature approved ones [11–13], which are based on well-known gradient descent (Levenberg–Marquardt) and derivative-free (Nelder–Mead) optimization algorithms. To increase the probability of finding global optimum solutions, the calculations were repeated many times (typically, hundreds and thousands of times) with the randomization of all initial values of the parameters to be optimized. Further, the obtained results were estimated statistically.

RESULTS AND DISCUSSION

The absorption spectra of $(PhS)_4$-PcAlOH in DMF (Fig. 1a, spectrum *1*) and the TEOS silicate matrix dried for 49 days (Fig. 1b, spectrum *1*) have a shape characteristic of the absorption spectra of metal phthalocyanines. The absorption spectrum in DMF exhibits an intense $Q(0–0)$ band at 723 nm, which corresponds to transitions to a doubly degenerate electronic state. The weaker bands in the region of 600–700 nm are electronic–vibrational bands generic of the Q-band. The band in the near UV region at 343 nm (B-band), by analogy with metalloporphyrins, is referred to as the Soret band. The low-intensity band in the region of 400–480 nm corresponds to $n–\pi^*$ transitions oriented almost perpendicular to the macrocycle plane [14]. It is evident from Fig. 1b (spectrum *1*) that the absorption bands of $(PhS)_4$-PcAlOH in a dried nanoporous silicate matrix undergo significant spectral shifts (for example, the Q-band is hypsochromically shifted by 40 nm), while the general shape of the spectrum is preserved.

Upon excitation to the Soret band, intense fluorescence of $(PhS)_4$-PcAlOH is observed both in DMF (Fig. 1a, spectrum *2*) and in the TEOS matrix (Fig. 1b, spectrum *2*). The similarity of the fluorescence excitation spectra (Figs. 1a, 1b, spectra *3*) to the absorption spectra suggests that $(PhS)_4$-PcAlOH in solution and in the silicate matrix is in the monomeric form.

The evolution of a colloidal silicate system from a sol state to a transparent nanoporous solid silicate matrix is a complex process that includes the evaporation of the liquid components of the reaction mixture from nanopores, shrinkage, and an increase in the mechanical strength of the system. The experiment showed that these processes significantly affect the spectral properties of $(PhS)_4$-PcAlOH impurity molecules. Figure 2 (spectrum *1*) shows the long-wavelength absorption band of $(PhS)_4$-PcAlOH in a silicate gel matrix, which was recorded 4 days after the formation of a solid framework. With respect to the DMF solution, a slight bathochromic shift (~1 nm) of the Q-band (724 nm) due to the multicomponent composition of the liquid medium filling the nanopores is observed. During the drying of the matrix, the studied band undergoes both a hypsochromic spectral shift and a substantial transformation of the band contour (Fig. 2, spectra *1–4*). It is evident that after 49 days of drying (spectrum *4*) the hypsochromic shift of the band achieves a value of $\Delta\lambda \approx 41$ nm ($\Delta\nu \approx 820$ cm^{-1}). In addition, the shape of the absorption spectrum and the observed intense fluorescence suggest that the monomeric form of the impurity molecules is preserved; that is, the $(PhS)_4$-PcAlOH molecules do not interact with each other. Longer drying (for more than 50 days) does not affect the spectral position and shape of the bands.

The dependence of the position of the maximum of the Q-absorption band of $(PhS)_4$-PcAlOH on the drying time of the silicate matrix has a characteristic S-shape (Fig. 2, inset), which is an indicator of a change in the state of the system. In this case, the S-curve indicates the transition of the system from one spectral state to another; that is, it suggests that the impurity sites in the nanoporous silicate material undergo temporal structural rearrangements. Since the chemical transformations occur arbitrarily in nanosized cavities (nanopores), the cavities play the role of nanoreactors, where qualitatively new states of impurity molecules are formed.

It was found [15, 16] that Al(III) tetra-crown-phthalocyaninate can interact with OH^- and F^- anions in various organic media to form a six-coordinated complex with two axially bonded ions. These complexes exhibit a hypsochromic shift of the absorption spectra and have intense fluorescence. In this work, a test experiment was conducted to study the absorption spectrum of an ethanol–water–formamide–hydrochloric acid mixture (molar ratio of 5 : 5 : 5 : 0.1) with the addition of $(PhS)_4$-PcAlOH in DMF, i.e., a counterpart of the reaction mixture (TEOS-free) used to synthesize the silicate matrix. The solution was stored in the dark to exclude phototransformations at room temperature and showed the stability of the absorption spectrum for 20 days. The spectrum is shown in Fig. 1b (spectrum *4*); it is evident from the spectrum that the Q-band is bathochromically shifted (728 nm) relative to the band in DMF (723 nm). In the S-shaped curve, this position of the Q-band maximum corresponds to the "0" point, which is the

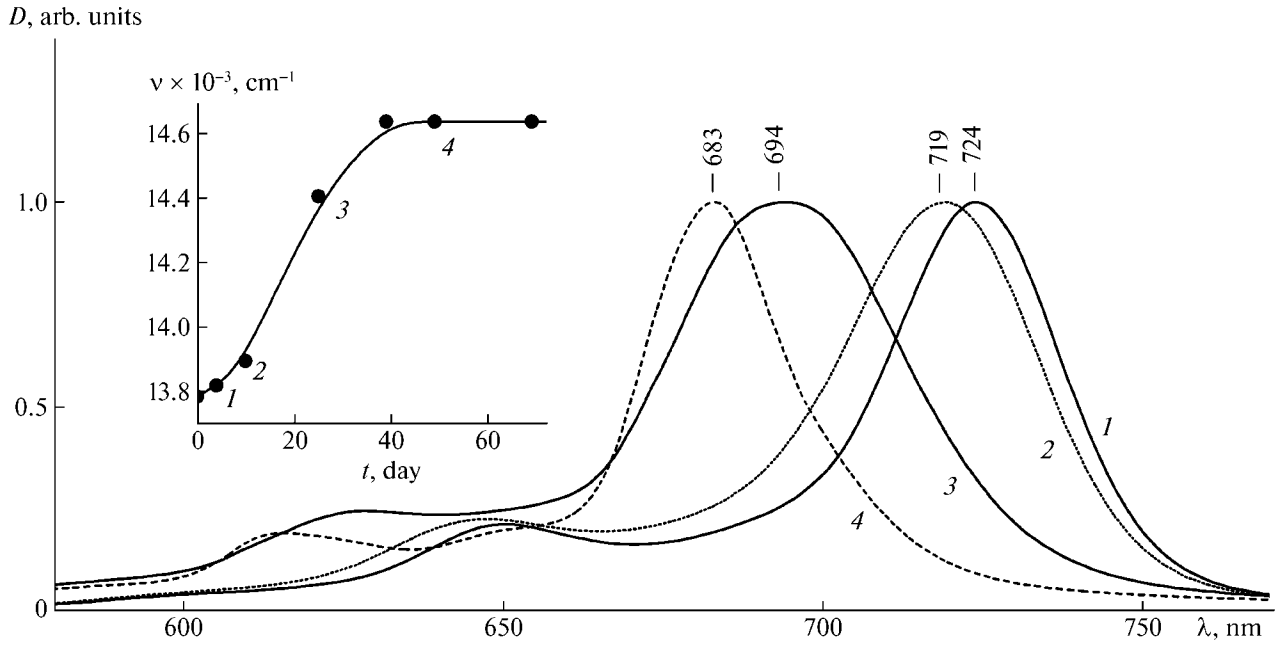

Fig. 2. The long-wavelength region of the absorption spectrum of $(PhS)_4$-PcAlOH in a TEOS matrix after (*1*) 4, (*2*) 10, (*3*) 25, and (*4*) 49 days of drying of the xerogel. The inset shows the dependence of the position of the maximum of the *Q*-absorption band of $(PhS)_4$-PcAlOH on the drying time of the xerogel.

Q-band maximum in the first hours after the formation of the silicate framework of the gel matrix.

To reveal the relationship between the temporal hypsochromic spectral shift of the *Q*-absorption band maximum, as well as changes in the shape of the band contour, and the mechanisms and evolution of the interconversions of impurity sites that form this band, the contour was decomposed into Voigt components and their parameters for the different drying stages were determined. The decomposition results are shown in Fig. 3.

At the initial stage of the drying process (up to 10 days), the shift of the maximum of the long-wavelength absorption band is negligible (Fig. 2). Presumably, the shift is caused by the compaction of the gel structure and the partial displacement of the liquid components from the matrix nanopores. In the case of drying for up to 20–25 days, the hypsochromic shift of the *Q*-band achieves ~30 nm; this fact can be attributed to the intensive evaporation of solvents (water, ethanol, formamide, DMF) from the matrix nanopores and, as a consequence, the destruction of the original solvation shell of the $(PhS)_4$-PcAlOH molecules. In this case, according to the contour decomposition results, a new spectral form hypsochromically shifted to $\lambda_{max} \approx 699$ nm arises (Figs. 3a–3d, curves *3*); the maximum content of it is observed after 25 days of drying (Fig. 3c). It can be assumed that this spectral form corresponds to $(PhS)_4$-PcAlOH molecules in a relatively free state (similar to the gaseous phase), because the matrix pores are already almost completely free of the liquid components (presumably, except for formamide, the boiling point of which is fairly high) and the nanopore surface effectively exhibits sorption properties. This assumption is supported by the disappearance of the initial spectral form (Figs. 3a–3d, curves *2*) due to the destruction of the original solvation environment in the matrix nanopores. A similar spectral behavior is observed, for example, for molecules of the free base of phthalocyanine, whose *Q*-absorption band is located at 698 nm in liquid quinoline and 1-chloronaphthalene [17], whereas in the steady-state gas phase and in a supersonic free jet it is shifted to 686 [18] and 661 nm [19], respectively. The removal of the solvation layer, which is provided (formed) by weak physical van der Waals interactions between the impurity and solvent molecules, does not change the chemical structure of $(PhS)_4$-PcAlOH.

Simultaneously with the removal of liquid hydrolysis products from the nanopores, the structure of the nanoporous matrix undergoes compaction, which leads to a significant decrease in the pore sizes. In this case, free $(PhS)_4$-PcAlOH molecules approach the nanopore surface and interact with it; the interaction gives rise to the formation of new types of impurity sites. According to the *Q*-absorption band decomposition results, as early as the 25th day of drying (Fig. 3c), the complex contour of the band exhibits two detectable components at 685 and 673 nm (curves *4* and *5*, respectively). The further drying of the matrix, which leads to the formation of a xerogel, shows that these

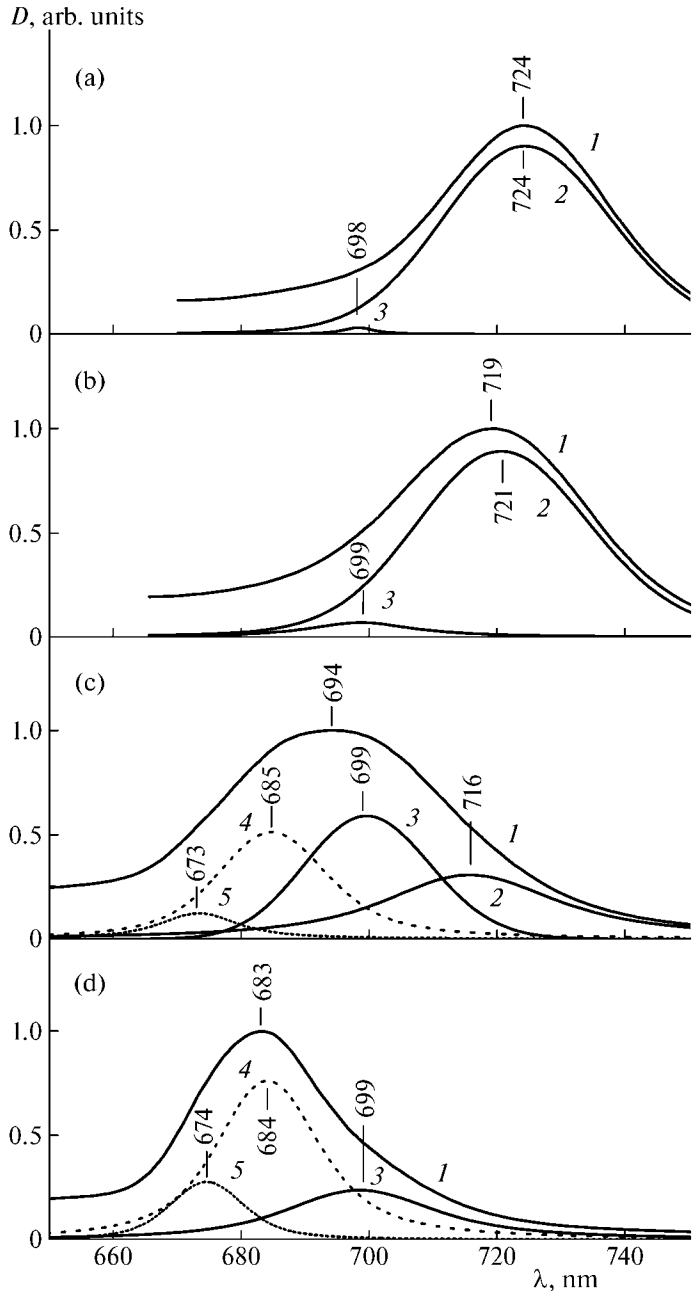

Fig. 3. Decomposition of the long-wavelength absorption band of $(PhS)_4$-PcAlOH in a silicate xerogel (*1*) into Voigt components (*2–5*) after (a) 4, (b) 10, (c) 25, and (d) 49 days of drying of the material.

components are enhanced with the simultaneous weakening of component *3* (Fig. 3d). The formation, accumulation, and stabilization of new spectral forms at 684 and 674 nm (Fig. 3d, curves *4*, *5*) can be associated with the chemical interaction of $(PhS)_4$-PcAlOH molecules with the reaction sites on the surface of the silicate matrix nanopores. With the filling of these reaction sites, the rate of the spectral shift of the experimental multicomponent *Q*-band slows; after 40 days of drying, the S-shaped curve achieves a steady state (see the inset in Fig. 2).

By analogy with the silica surface [20, 21], it can be assumed that the surface of the silicate matrix nanopores has two types of impurity chemical adsorption sites, namely, coordinatively unsaturated Si atoms of the ≡Si–O–Si≡ siloxane groups and hydroxyls of the ≡Si–OH silanol groups. The author of [20, 21] assumed that coordinatively unsaturated surface metal atoms are chemical adsorption sites. In particular, silicon atoms have free 3*d* orbitals, which can accept (be involved in the formation of a donor–acceptor bond) a lone pair of *p*-electrons of the outer electron shell

($3s^2 3p^4$) of the sulfur atom of the $(PhS)_4$-PcAlOH impurity molecule. In this manner, a new type of impurity sites of $(PhS)_4$-PcAlOH molecules is formed during their interaction with the silicon–oxygen framework of the matrix. In this case, it can be argued that the nanosized porous structure of the sol–gel matrix acts as a nanoreactor, in which new chemical bonds with impurity monomeric molecules are formed.

With an increase in the $(PhS)_4$-PcAlOH molecule concentration near the nanopore surface (during the drying of the matrix), the axial anionic OH ligands of metal phthalocyanine can be involved in the formation of impurity sites of other types. Axial OH ligands of impurity molecules are capable of undergoing a condensation reaction with isolated surface $H-O-Si\equiv_{matr}$ silanol groups, while binding via an oxygen bridge to the surface of the silicate framework nanopores and releasing H_2O molecules:

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

These mechanisms of interaction with the surface are of a chemical nature, because a new chemical bond between the impurity and the matrix is formed. In this case, structural changes do not lead to the aggregation of the impurity molecules.

It was reported [2] that individual $(PhS)_4$-PcAlOH molecules can also be involved in the alkoxysilane polycondensation reaction at the initial stage of the formation of a three-dimensional silicate network, when hydrated silicate tetrahedra interact with the axial OH ligand of the molecule; as a consequence, aluminum phthalocyanine forms a single a framework with the polymeric silicate material and is localized on the nanopore surface in the form of a side substituent.

It can be assumed that the quantitative population of impurity sites of the different types on the nanopore surface depends on the surface dehydration during drying as well; the dehydration occurs via the condensation of closely adjacent silanol groups to form a new strong siloxane bond and release water:

$$_{matr}\equiv Si-OH + H-O-Si\equiv_{matr} \rightarrow \equiv Si-O-Si\equiv + H_2O$$

and leads to an increase in the number of chemical adsorption sites of the first type and a decrease in the number of sites of the second type.

Analysis of the half-widths of the Voigt components indirectly confirms the proposed mechanism for the transformation of $(PhS)_4$-PcAlOH impurity molecules in a silicate nanoreactor. Thus, the half-width of the long-wavelength Voigt component of the *Q*-band (Figs. 3a–3d, curves *2*) has a value of $\Delta\nu \approx 600\ cm^{-1}$, which is characteristic of the inhomogeneous broadening of the spectral bands of molecules in a liquid solution. During the destruction of the solvation shell (drying of the matrix), the $\Delta\nu$ value decreases to $\sim 500\ cm^{-1}$: the molecules localized in the bulk of the nanopores transit into a free vapor state (Figs. 3a–3d, curves *3*). The interaction of $(PhS)_4$-PcAlOH molecules with the nanopore surface leads to the formation of short-wavelength impurity sites; the inhomogeneous broadening of their bands decreases to ~400 and $\sim 300\ cm^{-1}$ (Figs. 3a–3d, curves *4* and *5*, respectively). A decrease in the $\Delta\nu$ value for the short-wavelength Voigt components can be attributed to the fact that any active site of the nanopore surface (silanol and siloxane groups) can interact with a single $(PhS)_4$-PcAlOH molecule; as a consequence, the surface is covered with a single layer of impurity molecules. Since the size of nanopores in a silicate matrix varies in a certain range (in this sense, their surface is inhomogeneous), the active sites are not absolutely independent of each other. The result is that the inhomogeneous broadening of the spectral bands of molecules adsorbed on the surface is not completely eliminated.

CONCLUSIONS

The evolution of the electronic absorption spectra of aluminum phthalocyanine molecules incorporated into a nanoporous silicate gel matrix has been studied. The spectral position of the maximum of the *Q*-absorption band as a function of the drying time of the matrix is described by an S-shaped curve, which represents the evolutionary transition from the state of impurity molecules in the bulk of the nanopores to their interaction with the silicate framework. The decomposition of the *Q*-band contour into Voigt components has shown the time dependence of the formation of the different types of impurity sites in the matrix nanopores, which act as a solid-state nanoreactor. The long-wavelength region of the S-curve represents the destruction of the solvation shell of phthalocyanine impurity molecules; the short-wavelength region represents the interaction of the molecules with the nanopore surface, which leads to the formation of spectral forms that are stable over time. Possible mechanisms of interaction of $(PhS)_4$-PcAlOH impurity molecules with the surface of nanopores of an inorganic silicate framework during transition from a sol state to a dried xerogel state and the nature of the resulting impurity sites have been discussed.

ACKNOWLEDGMENTS

The authors thank Prof. Claudine Crepin-Gilbert (Institut des Sciences Moléculaires d'Orsay, France) for providing aluminum phthalocyanine and fruitful discussion of the results.

FUNDING

This work was supported in part by the Belarusian Republican Foundation for Basic Research (agreement no. F21MS-017).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. L. L. Hench and J. K. West, Chem. Rev. **90**, 33 (1990). https://doi.org/10.1021/cr00099a003
2. S. M. Arabei, T. A. Pavich, I. V. Stanishevskii, and C. Crepin, J. Appl. Spectrosc. **89**, 201 (2022). https://doi.org/10.1007/s10812-022-01344-2
3. T. Komori and Y. Amao, J. Porphyr. Phthalocyan. **7**, 131 (2003). https://doi.org/10.1142/S1088424603000185
4. A. Anctil, B. J. Landi, and R. P. Raffaelle, in *Proceedings of the 34th IEEE Photovoltaic Specialists Conference PVSC 2009, Philadelphia, Pennsylvania, USA, June 7–12, 2009* (2009), p. 1344.
5. D. Frackowiak, K. Wiktorowicz, A. Planner, et al., Int. J. Photoenergy **4**, 51 (2002). https://doi.org/10.1155/S1110662X02000090
6. D. Frackowiak, R.-M. Ion, and A. Waszkowiak, J. Phys. Chem. B **106**, 13154 (2002). https://doi.org/10.1021/jp0212592
7. T. A. Pavich, S. M. Arabei, and K. N. Solovyev, J. Appl. Spectrosc. **85**, 1 (2018).
8. T. A. Pavich, I. V. Stanishevskii, D. T. Kozhich, et al., J. Appl. Spectrosc. **87**, 668 (2020).
9. Matlab. https://en.wikipedia.org/wiki/Matlab.
10. Scilab. https://en.wikipedia.org/wiki/Scilab.
11. S. M. Abrarov and B. M. Quine, Appl. Math. Comput. **218**, 1894 (2011). https://doi.org/10.1016/j.amc.2011.06.072
12. S. M. Abrarov and B. M. Quine, arXiv: 1205.1768v1 [math.NA] (2012). https://doi.org/10.48550/arXiv.1205.1768
13. F. Gao and L. Han, Comput. Optim. Appl. **51**, 259 (2012). https://doi.org/10.1007/s10589-010-9329-3
14. A. Waszkowiak, D. Frackowiak, K. Wiktorowicz, and J. Miyake, Acta Biochim. Pol. **49**, 633 (2002). https://doi.org/10.18388/abp.2002_3772
15. L. A. Lapkina, N. Yu. Konstantinov, V. E. Larchenko, et al., J. Porphyr. Phthalocyan. **13**, 859 (2009). https://doi.org/10.1142/S108842460900005X
16. L. A. Lapkina, G. A. Kirakosyan, V. E. Larchenko, A. Yu. Tsivadze, and Yu. G. Gorbunova, Russ. J. Inorg. Chem. **65**, 176 (2020). https://doi.org/10.1134/S0036023620020072
17. A. B. P. Lever, Adv. Inorg. Chem. Radiochem. **7**, 27 (1965). https://doi.org/10.1016/S0065-2792(08)60314-3
18. D. Eastwood, L. Edwards, M. Gouterman, and J. Steinfeld, J. Mol. Spectrosc. **20**, 381 (1966). https://doi.org/10.1016/0022-2852(66)90009-9
19. P. S. H. Fitch, C. A. Haynam, and D. H. Levy, J. Chem. Phys. **73**, 1064 (1980). https://doi.org/10.1063/1.440278
20. V. F. Kiselev, *Surface Phenomena in Semiconductors and Dielectrics* (Nauka, Moscow, 1970) [in Russian].
21. V. F. Kiselev, Dokl. Akad. Nauk SSSR **176**, 124 (1967).

Translated by M. Timoshinina