9510 *J. Phys. Chem. A* **2004,** *108,* 9510−9515

Persistent Spectral Hole Burning in Substituted Tetraazabacteriochlorin in Organic Polymer and Inorganic Silicate Xerogel[†]

Jean-Pierre Galaup,*,[‡] Serguei M. Arabei,[§] Konstantin N. Solovyov,[§] Tatiana A. Pavich,[§] and Elena A. Makarova[||]

Laboratoire Aimé Cotton, Bât. 505, Centre d'Orsay, 91405 Orsay Cedex, France,
Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus, 70 F. Skaryna Ave.,
220072 Minsk, Belarus, and Organic Intermediates and Dyes Institute, 1/4 B. Sadovaya Str.,
103787 Moscow, Russia

Received: February 4, 2004; In Final Form: July 14, 2004

The ability to exhibit persistent spectral hole burning has been established for the stereoisomers of dibenzobarrelene-substituted tetraazabacteriochlorin (*cis*-TABC and *trans*-TABC) incorporated in inorganic silicate xerogel and organic polymer (polyvinylbutyral) matrices. Hole burning properties of these molecules absorbing light at ∼790 nm have been studied. For the inorganic matrix, the efficiency of hole burning is higher and the relative depth of the hole and its width are larger than for the organic matrix polymer. These facts are 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.

Introduction

One of the applications of the phenomenon of persistent spectral hole burning (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.[1,2] Of special interest in this respect is the optical processing of ultrashort pulses generated by titanium-sapphire lasers.[3−5] This necessitates the search for effective broadband materials exhibiting PSHB in the corresponding spectral region − about 800 nm.

Free-base and metallo-naphthalocyanine derivatives in polymer hosts are examples of such materials.[6−8] Studies of PSHB in silicon-naphthalocyanine-doped polyvinylbutyral (PVB) with different additions showed that, in 2-color experiments, the hole-burning efficiency can be increased, especially in the case of fullerene C_{70} additive.[7,8]

Recently, following the synthesis of unsubstituted tetraazachlorin,[9] 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.[10] In ref 10 an analogous derivative of tetraazabacteriochlorin was obtained in addition (its structure is shown in Figure 1). Two stereoisomers of this compound were separated, differing in the position of the dibenzobarrelene fragments relative to the macrocycle plane (in this paper we denote them *cis*-TABC and *trans*-TABC). Data on spectral, photophysical, and other properties of reduced derivatives of tetraazaporphine (porphyrazine) are published,[11−15] including results of quantum-chemical calculations[12,14] (for unsubstituted compounds); quantum-chemical calculations for unsubstituted tetraazabacteriochlorin had been carried out earlier.[15]

The distinctive feature of the TABC absorption spectra (very similar for the two isomers) is the intense long wavelength band at ca. 790 nm. In this communication we report on PSHB experiments with these substances.

Two kinds of matrices were used: organic, PVB, and inorganic, a silicate xerogel. The latter is a promising system for practical applications due to its chemical stability. The sol−gel route allows us to prepare dense inorganic materials in which dopant molecules can permanently be trapped in nanometric pores. By using tetraethoxysilane (TEOS) molecules as precursors, a glass-like pure silicate xerogel can be synthesized, in which the surface of the pores will be favorably covered with hydroxyl groups.

It should be noted that methods of low-temperature fine-structure spectroscopy were used previously for the investigation of unsubstituted bacteriochlorin.[16−20]

Experimental Details

Substituted tetraazabacteriochlorin was synthesized by the Diels−Alder reaction from unsubstituted tetraazaporphine with 2,6-di(*tert*-butyl)anthracene in the presence of $AlCl_3$, as described in ref 10. The two isomers were separated by column chromatography on silica. With the help of NMR it was established[10] that one fraction corresponds to the trans configuration, i.e., the dibenzobarrelene fragments are disposed on different sides of the plane of the macrocycle ("chair"), while the other corresponds to the cis configuration ("bath").

For the preparation of organic polymeric samples (films) doped with TABC isomers, monodisperse PVB powder was dissolved in ethanol and an ethanol solution of the pigment was added. By repeated casting of the mixed solution with subsequent drying in the dark at room temperature, solid polymeric films of *cis*-TABC/PVB and *trans*-TABC/PVB were obtained.

[†] Originally submitted for the "Gerald Small Festschrift", published as the July 22, 2004 issue of *The Journal of Physical Chemistry B* (Vol. 108, No. 29).

* To whom correspondence should be addressed. Tel.: +33-(0)1-6935-2059; Fax.: +33-(0)1-6935-2100; E-mail: jean-pierre.galaup@lac.u-psud.fr

[‡] Laboratoire Aimé Cotton, Centre d'Orsay.

[§] National Academy of Sciences of Belarus.

[||] Organic Intermediates and Dyes Institute.

10.1021/jp040095h CCC: $27.50

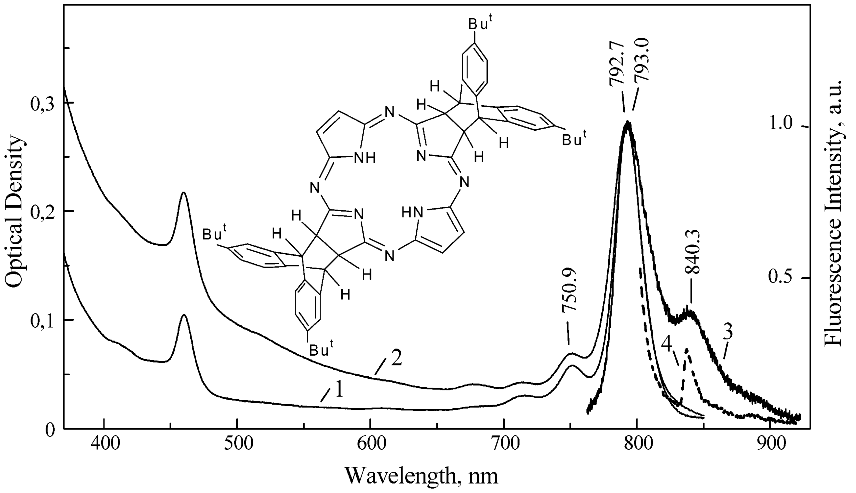

Figure 1. Absorption spectra (1,2) and fluorescence spectra at $\lambda_{exc} = 789.2$ nm (3,4) of *cis*-TABC/PVB (1,3,4) and *cis*-TABC/TEOS (2) at 300 K (1,2,3) and 5 K (4). The values of λ_{max} for the PVB host at 300 K are indicated on the figure.

The tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$) precursor was used to prepare the inorganic silicate host. Liquid TEOS was added to a water−ethanol mixture in the molar proportion TEOS−ethanol−water 1:5:5. Subsequently the reaction mixture was subjected to the well-known procedure of sol−gel synthesis, a two-step inorganic polymerization route (hydrolysis, then condensation).[21,22] After the gel formation, densification was achieved by drying the gel at ambient conditions, followed by a heat treatment at 600 °C. Doping was achieved by impregnating the corresponding pigment in an ethanolic solution and subsequently drying the *cis*-TABC/TEOS and *trans*-TABC/TEOS samples at room temperature.

The concentration of tetraazabacteriochlorins in the PVB and TEOS matrices was about 10^{-4} ml^{-1}. The sample thickness was within the limits of 0.5 mm and 1.0 mm. Room-temperature absorption spectra were measured using a Cary 400 scan spectrophotometer from Varian. Optical density (OD) at the maximum of the longest wavelength absorption band was in the range 0.25−0.45.

Hole-burning was carried out at liquid-helium temperature (most of the measurements were performed at a fixed temperature around 5 K), the samples being positioned in an optical liquid-helium bath cryostat (SMC-L'Air Liquide). A 792 nm diode laser ($\Delta\nu \approx 0.1$ cm^{-1}), with temperature and current stabilization modules, was used. Typical total irradiation power (for luminescence excitation and hole-burning experiments) was in the range 1−10 mW, whereas typical burning power densities ranged from 4 to 40 mW cm^{-2}. The wavelength was accurately monitored with a Burleigh WA1100 wavemeter. Spectral holes were recorded in transmission and computer-converted to OD. The light of a white lamp transmitted through the sample was recorded, before and after burning, with a red-sensitive PM (R943−02 from Hamamatsu) placed behind a HRP 600 Jobin Yvon monochromator (inverse linear dispersion 1.2 nm/mm) and the signal followed with a picoammeter. The same monochromator, diode laser, and cryostat (for low-temperature measurements) were used for measurements of the fluorescence spectra.

Results

In Figure 1 the room-temperature absorption spectra of *cis*-TABC in matrices of PVB (curve 1) and TEOS (curve 2) are presented. As mentioned in the Introduction, the spectra of the two isomers are very close; therefore, for the sake of clarity, only the spectra of the *cis*-isomer are drawn, whereas the corresponding data for the *trans*-isomer are not shown in this figure. These spectra closely correspond to spectra in organic solvents.[9−15] However, in the solid samples a short-wavelength rise of the optical density is observed that is evidently due to light scattering. Scattering is weaker in PVB, but below 400 nm the host itself begins to absorb light. The maximum of the long wavelength absorption band $Q_x(0,0)$ of the *cis* isomer pigment in PVB (792.7 nm) is slightly red-shifted by 1 nm relative to its position in the TEOS host. A larger difference is observed for the bandwidth (fwhm, full width at half maximum), which is considerably greater in the TEOS host (450 cm^{-1}) than in PVB (390 cm^{-1}).

Analogous broadening of the $Q_x(0,0)$ band is observed in the spectra of *trans*-TABC in the TEOS host, but the red shift in passing from the TEOS matrix to PVB is larger, viz. 3.1 nm. A comparison of the spectra of the cis and trans isomers shows that the influence of the two matrices on the $Q_x(0,0)$ band position is opposite: by passing from the cis to the trans isomer, the band is red-shifted (from 792.7 to 793.5 nm) in the PVB host, while it is shifted to the blue (from 791.7 to 790.4 nm) in the TEOS host.

The fluorescence spectra were measured at 300, 80, and 5 K. In the room-temperature fluorescence spectrum of *cis*-TABC obtained at laser diode excitation ($\lambda_{exc} = 789.2$ nm), shown as an example in Figure 1, curve 3, two distinct bands are seen: the 0−0 band at 793.0 nm and the combined vibronic band at 840.3 nm ($\Delta\nu \approx 710$ cm^{-1}). Although neither the position of the 0−0 band nor its intensity were corrected for reabsorption, one may state that the fluorescence spectrum shows approximately mirror symmetry with respect to the long wavelength part of the absorption spectrum ($\Delta\nu \approx 702$ cm^{-1}).

At liquid-helium temperature, due to increased reabsorption, only the vibronic bands of the fluorescence spectra were reliably recorded. At 5 K under selective laser excitation, noticeable narrowing of the vibronic band takes place. For example, the fwhm of the 837.1 nm band (see Figure 1, curve 4) is about 170 cm^{-1} versus roughly 600 cm^{-1} at room temperature (the monochromator band-pass $\Delta\nu_{mon}$ was only ~ 3 cm^{-1}). The peak position of the vibronic band moves accordingly with the wavelength of the laser excitation, which is indicative of inhomogeneous broadening of the electronic spectra. Similar behavior is observed at 80 K, showing that inhomogeneous broadening is still predominant at this temperature. It should

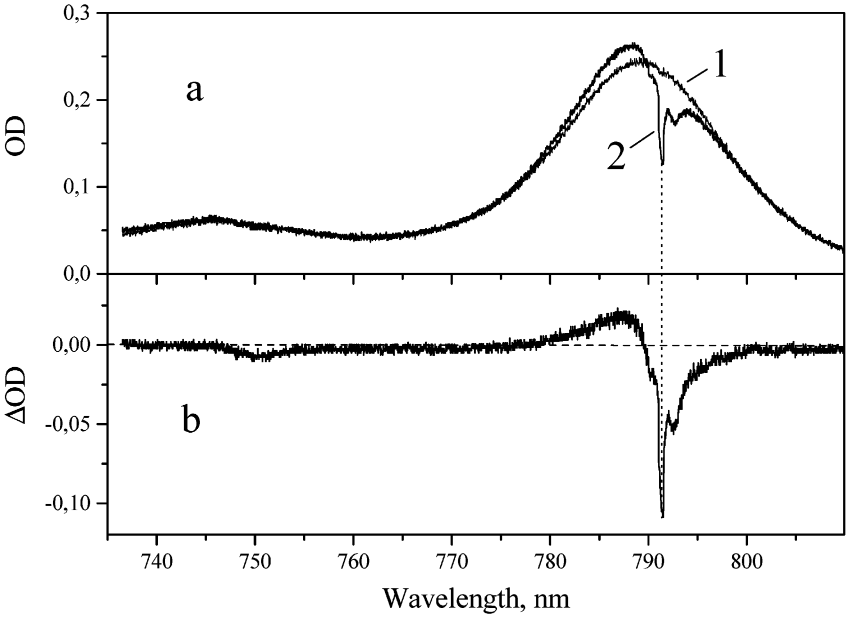

Figure 2. PSHB in the $Q_x(0,0)$ band of *cis*-TABC/TEOS at 5 K. (a) Absorption spectra before (1) and after hole-burning (2) by laser radiation (791.3 nm) during 420 s (P_b = 4 mW cm^{-2}) plus 120 s (P_b = 40 mW cm^{-2}). (b) Spectral hole profile as difference spectrum: (2) minus (1).

be emphasized that we did not observe the effect of fluorescence line narrowing, which gives discrete emission spectra with line widths of only a few wavenumbers[23−25] for the TABC isomers (see also the Discussion).

The $Q_x(0,0)$ band of the TABC isomers under study in both matrices is blue-shifted by several nanometers and considerably narrowed in going from 300 to 5 K. For instance, on cooling the *cis*-TABC/TEOS sample to 5 K, the band at 791.7 nm shifts to 789.1 nm and narrows from 450 to 330 cm^{-1} (the low-temperature spectrum in the $Q_x(0,0)$ band region is shown in Figure 2, curve 1).

Our main aim was to find out the ability of the chosen materials to manifest PSHB. As experiments have shown, the $Q_x(0,0)$ band is indeed, as mentioned above, broadened inhomogeneously at 5 K. Thus, the exposure of *cis*-TABC/TEOS to laser radiation at λ_b = 791.3 nm results in the burning of a persistent spectral hole in the band contour (Figure 2a, curve 2). The burning conditions are indicated in the figure caption. The spectral hole consists of the zero-phonon hole (ZPH) and a pseudo-phonon sideband, or “wing”. As shown in Figure 2a, it was possible to burn out a sufficiently large number of *cis*-TABC molecules under such conditions and to cause appreciable changes in the entire inhomogeneous contour of the absorption band.

The difference spectrum obtained by subtracting the spectrum after hole burning from the initial spectrum is displayed in Figure 2b. It is seen from Figures 2a and 2b that, on the short-wavelength side from the ZPH, an additional absorption arises, which is evidence of the spectral manifestation of a photoproduct. Figure 2b shows explicitly that the spectral hole, burned in the $Q_x(0,0)$ absorption band, is accompanied by a broad and shallow hole at 750 nm in the vibronic $S_1 \leftarrow S_0$ absorption band. In the case of the trans isomer of TABC in the TEOS gel matrix, a persistent spectral hole is formed in an analogous way. The difference absorption spectra in the spectral hole region for all four systems studied are compared in Figure 3.

In organic polymeric PVB matrices PSHB is also observed for both TABC isomers, but the characteristics of the spectral holes are somewhat different. Figure 3 shows that the ZPHs of the spectral holes are significantly narrower for the organic PVB host ($\Delta\nu_{ZPH} \approx 2$ cm^{-1}) than for the inorganic TEOS host ($\Delta\nu_{ZPH} \approx 11$ cm^{-1}), under practically identical burning and recording conditions ($\Delta\nu_{mon} \approx 2$ cm^{-1}). We notice that the measured values of $\Delta\nu_{ZPH}$ in PVB are limited by the spectrometer resolution $\Delta\nu_{mon}$, meaning that the true values of $\Delta\nu_{ZPH}$ may be noticeably smaller. Furthermore, for the PVB samples additional absorption on the short-wavelength side from the ZPH seems to be of less intensity than for the TEOS samples.

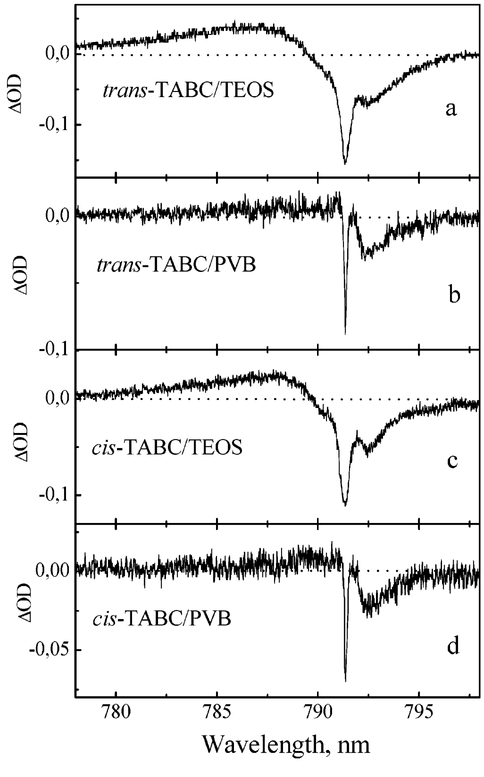

Figure 3. Profiles of persistent spectral holes in the $Q_x(0,0)$ band of *trans*-TABC (a,b) and *cis*-TABC (c,d) in the PVB matrix (b,d) and TEOS xerogel (a,c) burned by laser radiations at 5 K (λ_b = 791.3 nm, P_b = 40 mW cm^{-2}, t_b = 120 s (a,c) and 180 s (b,d)).

The prospect of using the materials under study for practical applications is determined by several factors, including the

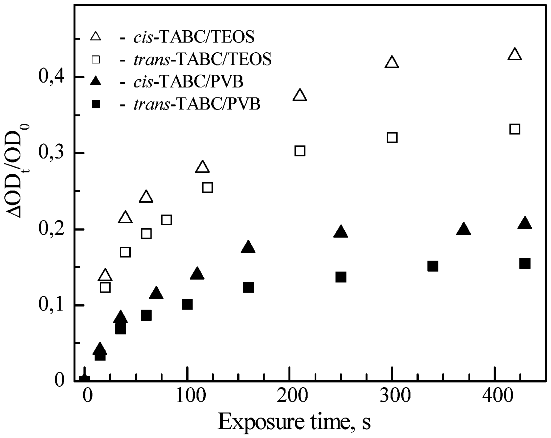

Figure 4. Dependences of relative optical density changes at the burning light wavelength ($\lambda_b = 791.3$ nm, $P_b = 4$ mW cm^{-2}) on the exposure time for the TABC isomers in the PVB and TEOS hosts.

spectral hole-burning efficiency. Figure 4 demonstrates the results of the investigation of the relative optical density changes $\Delta OD_t/OD_0$, where ΔOD_t is the measured decrease in optical density at the burning wavelength as a function of the exposure time t, and OD_0 is the initial optical density at the same wavelength at $t = 0$. The obtained dependences 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.

Discussion

The main result of this study is to have established the capability of substituted tetraazabacteriochlorin isomers to exhibit PSHB. The mechanism of this process and its specific features are discussed below.

It is well-known that in tetrapyrrole macrocyclic free-base porphyrin derivatives NH tautomerism takes place.[26-31] This effect enables effective PSHB, which belongs to the "photochemical" type.[32,33] However, in our case this mechanism should be rejected for two reasons. First, the shift of the photoproduct absorption band (anti-hole) relative to the ZPH is small (about 60 cm^{-1}). Based on the data on quasi-line spectra of chlorins,[28-31] for which the origins of the photoproducts are blue-shifted by 500−1600 cm^{-1}, one may expect larger shifts for bacteriochlorins, since the nonequivalence of the two directions passing through the pairs of opposite nitrogen atoms is stronger for the latter. Second, direct attempts to burn holes in the quasi-line spectra of unsubstituted bacteriochlorin and searching for its photoproducts were unsuccessful.[17]

On the other hand, the pure nonphotochemical mechanism of PSHB based on tunneling between the levels of double-well potentials (two-level systems, TLS)[34] is also inapplicable. If this mechanism were operating, the anti-holes would be very close to the ZPH (shifted by <2 cm^{-1}) and located symmetrically on both sides from it. For example, symmetrical holes without signs of anti-holes were burned in the Q(0,0) band of Al-phthalocyanine tetrasulfonate in different hosts, including TEOS xerogel.[35] It is interesting to notice that even in relatively simple systems, the question of photochemical versus nonphotochemical hole burning mechanism remains controversial.[36] Recently, Reinot et al.[37] have proposed a consistent model for the simulation of hole burned spectra, taking into account the electron−phonon coupling and dispersive kinetics. The model should be applicable to photochemical as well as to nonphotochemical hole burning.

Holes burned in the spectra of *cis*-TABC/TEOS and *trans*-TABC/TEOS are accompanied by anti-holes blue-shifted from ZPH. It should be mentioned here that the maximum of the additional photoinduced band does not correspond to the exact position of the anti-hole since the latter overlaps with the phonon wing of the hole, resulting in almost complete disappearance of the phonon wing and distortion of the anti-hole, due to the difference in signs of the two spectral features. Therefore, the true position of the anti-hole is closer to the ZPH. The character of the observed anti-holes shows that after photoexcitation the pigment molecules undergo certain transformations, which do not essentially change the conjugated bond system. We believe that this is associated with changes in the system of intermolecular H-bonds formed by the OH groups of the gel pores and the bridge nitrogen atoms of the macrocycle, analogously to photoinduced changes in the system of intramolecular H-bonds in quinizarin[38,39] and hypericin.[40] Another possibility is an increased nonplanarity of the macrocycle due to the enhancement of the interaction of TABC molecules with the surface of the pores in the excited state.

It is to be mentioned that for cresyl violet adsorbed on γ-alumina and silica gel a photoinduced H-transfer from the excited dye to the surface was proposed as the mechanism of PSHB.[41]

It is expedient to note an interesting peculiarity of the contours of the spectral holes displayed in Figure 3. The pseudo-phonon wings in all four spectra are shifted (to the red from ZPH) by the same amount, viz., by 18 cm^{-1}. Although the true phonon wings of the holes are almost canceled as a result of overlap with the photoproduct absorption (see above), they are still discernible in Figures 3a and 3c; their shift (to the blue from ZPH) is also 18 cm^{-1}. We interpret the independence of this frequency shift on the nature of the matrix to be a result of predominant manifestation in the electronic spectra of librations and/or other type of local vibrations of the pigment molecule as a whole that interact with phonons and pseudo-local vibrations of the matrices.

The spectral pattern of holes in Figures 3a and 3c is similar to that obtained by Al'shits et al. for perylene in frozen ethanol.[42] It was shown in ref 42 that additional absorption shifted to the blue from the ZPH belongs to a chemically different species, which undergoes further transformation on irradiating the sample by white light. Despite the great energy difference between our samples and perylene, the mechanism of PSHB may be similar due to the presence of active OH groups in the frozen ethanol matrix. Indeed, in the case of the *cis*-TABC/TEOS and *trans*-TABC/TEOS samples, the PSHB mechanism should be considered as belonging to the "photochemical" type and possibly assigned to the interaction with the OH groups present in the inorganic host. Possibly also, this interaction might explain why the holes are broader and the electron−phonon coupling stronger as seen from the appearance of the true phonon sideband on the blue side of the ZPH (Figures 3a and 3c).

The situation is quite different in the case of the PVB host, in which a mechanism similar to that in TEOS can be ruled out. Most probably, the PSHB mechanism for *cis*-TABC/PVB and *trans*-TABC/PVB samples is the true nonphotochemical one based on TLS flipping. The spectral holes burned in the PVB samples are considerably narrower than in the TEOS host. The homogeneous line width is evidently broader for the latter. In the review of ref 43, analogous facts in narrow-band PSHB-experiments at very low temperatures were interpreted as a result of a “higher degree of freedom of the guest molecules on the *surface*, as compared to molecules incorporated in the *bulk* of the host”. In our case the increase in the fwhm of the ZPH for the TEOS host is apparently associated with fluorescence quenching, i.e., shortening of the S_1 (Q_x) state lifetime.

The fluorescence quantum yield (φ_F) of *trans*-TABC and *cis*-TABC is low. For toluene solutions at room temperature the values of φ_F are 0.007 and 0.004, respectively; the corresponding values of the fluorescence lifetime, τ_F, are 160 and 75 ps.[14] In the TEOS gel host the φ_F values are many times lower since the fluorescence signal could not be detected at all for the cis isomer and was extremely weak for the trans isomer. Correspondingly, the τ_F values must be much shorter than in solution. If we assume that the fwhm of ZPHs of the holes in Figures 3a and 3c is completely due to τ_F shortening via the uncertainty relationship, the τ_F value for both TABC isomers may be estimated to be 1 ps, that is shorter by 2 orders of magnitude than in solution at 300 K. The corresponding value of φ_F, obtained assuming that φ_F changes in proportion with τ_F, is on the order of 10^{-5}, which is in qualitative agreement with our experimental data on fluorescence intensity. The reason for this strong quenching may be photoinduced electron transfer to the matrix.

The inhomogeneous broadening of the $Q_x(0,0)$ band is also larger for the TEOS hosts than for the PVB hosts, by 60−80 cm^{-1} at 300 K and 40−60 cm^{-1} at 5 K. We obtained an analogous result earlier for metal 1,2-naphthalocyanine[44] and attributed it to the protonation of bridge nitrogen atoms of the pigment. Since the broadening effect is not very strong (the relative shifts of the 0−0 transition for different centers, leading to this broadening, are in the order of 100 cm^{-1}), it is better to call this type of protonation partial or hydrogen bonding protonation. It is important to note here that the formation of dicationic forms of bacteriochlorins (protonation of the central tertiary nitrogen atoms) results in large bathochromic shifts of the $Q_x(0,0)$ and $Q_y(0,0)$ bands (for example, respectively, 910 and 2420 cm^{-1} for octaethylbacteriochlorin, 950 and 2950 cm^{-1} for tetraphenylbacteriochlorin).[45] The formation of cations of azaporphyrin metal complexes due to protonation of bridge nitrogens also gives considerable shifts to the red (ca. 900 cm^{-1} for the Q(0,0) band).[16] The second cause of the inhomogeneous broadening under consideration may be associated with the peculiarities of the incorporation of the dopant molecules into the nanosized pores of the silicate matrix. The distribution in the matrix pore sizes (from several to tens of nanometers) will result in differences in the guest−host interaction for different sites. Specifically, part of the dopant molecules localized on the surface of relatively large pores may be in a semi-isolated state which will increase the scatter of the site parameters.

The experiments have demonstrated that the efficiency of the phototransformation of the TABC isomers (the main parameter determining the hole-burning rate) depends essentially on the nature of the matrix environment. The qualitative analysis of the time dependences of the relative depth of the spectral holes has shown that, at equal exposure time, holes are burned more efficiently in the TEOS host than in the PVB host (Figure 4). The maximum relative depth of ZPH in the inorganic TEOS matrix is approximately twice as large as in the organic polymer, reaching, e.g., for *cis*-TABC/TEOS ∼ 42% of the initial OD at the burning wavelength after photoirradiation for ca. 400 s. In our opinion, essential influence of the silicate xerogel on the efficiency of phototransformations of the TABC isomers is associated with the alteration of intermolecular H-bonds involving the matrix OH groups on the photoexcitation of the guest molecule (see above). Higher efficiency of PSHB and larger hole depth for *cis*-TABC/TEOS than for *trans*-TABC/TEOS (see Figure 4) are, most likely, due to steric hindrances for the surface OH groups to form such bonds with the nitrogen atoms of the macrocycle.

Some spectroscopic data acquired in this work deserve special comments. To begin with, the maximum of the vibronic band at 837.1 nm in the fluorescence spectrum of *cis*-TABC/PVB at 5 K (Figure 1, curve 4) is shifted relative to the position of the exciting laser radiation line (i.e., of the purely electronic $S_1 \rightarrow S_0$ transition frequency) by ca. 725 cm^{-1}. According to the data of the quasi-line fluorescence spectra of unsubstituted bacteriochlorin obtained in *n*-octane at 77 K[16] and 4.2 K[18] and in *n*-hexane at 4.2 K,[17] vibronic transitions with excitation of two normal modes in the S_0 state, of ∼720 and ∼728 cm^{-1} frequencies, correspond to the analogous band of the parent compound. Relying on the correlation between the properties (frequencies and symmetry) of normal vibrations of chlorin and bacteriochlorin,[18] one may state that in the case of tetraazachlorin the hydrogenation of the second (opposite) pyrrole ring, i.e., the formation of tetraazabacteriochlorin, will not essentially influence the nature of the normal modes which are active in vibronic spectra. The data on quasi-line fluorescence spectra of tetraazachlorin show that in the corresponding spectral interval two active vibrations also appear, having frequencies of 693 and 716 cm^{-1} (*n*-octane at 77 K).[46] The normal-coordinate analysis, carried out in parallel,[46] showed that skeletal deformations (changes in the angles in the pyrrole rings, deformation of aza bridges, etc.) bring the main contribution into these modes. Therefore, the vibronic band in the fluorescence spectrum of *cis*-TABC/PVB at 837.1 nm must be of the same nature. It is to be noted that in refs 13 and 14 the interval between the relevant band and the 0−0 band in the low-temperature fluorescence spectra of *cis*- and *trans*-TABC is given as ∼600 cm^{-1}. It follows from the above data that this value is underestimated, undoubtedly due to the fact that the effect of reabsorption on the measured position of the fluorescence 0−0 band was not taken into account.

The broad and shallow spectral hole appearing in the 750 nm range of the difference spectrum of *cis*-TABC/TEOS (Figure 2b) corresponds to vibronic transitions involving vibrational sublevels of the S_1 state of the molecules which were burned out in their $S_1 \leftarrow S_0$ 0−0 band (in this range difference spectra of all samples are similar). The distance from this hole to the ZPH is ca. 700 cm^{-1}. The vibrations in the S_1 state, which are responsible for this spectral feature, must be of the same nature as those considered in the preceding paragraph. More than likely, the shortening of the appropriate vibronic levels lifetimes leading to homogeneous broadening of spectral bands causes the broadening of this hole.

The absence of fine-structured fluorescence spectra of the investigated systems at liquid-helium temperature and under spectrally selective laser excitation (Figure 1, curve 4) may be caused by one of two reasons, or both. First, as shown in Figure 4, the hole burning is rather fast and during adjustment for measuring the fluorescence spectrum, the saturation of the hole may occur. In this case the laser excitation will occur via the phonon wings, i.e., without the benefit of the high selectivity as achieved when exciting in the zero phonon line (ZPL). Second, even in a solid matrix at 5 K, a nonplanar large molecule like the TABC pigment may undergo some kind of conformational rearrangement in the excited S_1 state. The fixed frequency of the exciting light will thus give a large distribution of frequencies of the emitting centers, experiencing different conformational rearrangement. For liquid solutions the existence of such rearrangement was established earlier.[13,14]

Conclusions

We have found that for the TEOS xerogel and PVB matrices doped with *cis*-TABC and *trans*-TABC, especially selected tetrapyrrole pigments which have an intense $Q_x(0,0)$ 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 our 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 $Q_x(0,0)$ 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 are 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.

Acknowledgment. This work was performed with partial financial support from the Belarusian Republican Foundation for Fundamental Research (Grant F03-072) and Program de Bourses de Recherche Scientifique et Technique de l'OTAN (NATO/France-East European Countries).

References and Notes

(1) *Persistent Spectral Hole Burning: Science and Applications, Topics in Modern Physics*, Vol. 44; Moerner, W. E., Ed.; Springer: Berlin, 1988.

(2) Rebane, A. Femtosecond time-and-space domain holography. In *Trends in Optics, Research, Developments and Applications*; Consortini, A., Ed.; Academic Press: San Diego, 1996.

(3) Chanelière, T.; Fraigne, S.; Galaup, J.-P.; Joffre, M.; Le Gouët, J.-L.; Likforman, J.-P.; Ricard, D. *Eur. Phys. J. − Appl. Phys.* **2002**, *20*, 205.

(4) Fraigne, S.; Galaup, J.-P.; Le Gouët, J.-L.; Bousquet, B.; Canioni, L.; Joffre, M.; Likforman, J.-P. *J. Opt. Soc. Am.* **2003**, *B20*, 1555.

(5) Galaup, J.-P.; Fraigne, S.; Le Gouët, J.-L.; Likforman, J.-P; Joffre, M. *J. Lumin.* **2004**, *107*, 187.

(6) Turukhin, A. V.; Gorokhovsky, A. A.; Moser, C.; Solomin, I. V.; Psaltis, D. *J. Lumin.* **2000**, *86*, 399.

(7) Fraigne, S.; Rice, J. H.; Galaup, J.-P. *J. Lumin.* **2001**, *94−95*, 649.

(8) Fraigne, S.; Galaup, J.-P. *J. Lumin.* **2002**, *98*, 231.

(9) Makarova, E. A.; Korolyova, G. V.; Lukyanets, E. A. *Zh. Obshch. Khim.* **1999**, *69*, 1356.

(10) Makarova, E. A.; Korolyova, G. V.; Tok, O. L.; Lukyanets, E. A. *J. Porphyrins Phthalocyanines* **2000**, *4*, 525.

(11) Shushkevich, I. K.; Pershukevich, P. P.; Makarova, E. A.; Solovyov, K. N. *Zh. Prikl. Spektrosk.* **2001**, *68*, 669.

(12) Miwa, H.; Makarova, E. A.; Ishii, K.; Lukyanets, E. A.; Kobayashi, N. *Chem. Eur. J.* **2002**, *8*, 1082.

(13) Shushkevich, I. K.; Pershukevich, P. P.; Makarova, E. A.; Solovyov, K. N.; Tusov, V. B. *Zh. Prikl. Spektrosk.* **2003**, *70*, 137.

(14) Kuzmitsky, V. A.; Makarova, E. A.; Pershukevich, P. P.; Shushkevich, I. K.; Solovyov, K. N.; Tusov, V. B. *Chem. Phys.*, **2004**, in press.

(15) Hashimoto, T.; Choe, Y.-K.; Nakano, H.; Hirao, K. *J. Phys. Chem. A* **1999**, *103*, 1894.

(16) Gurinovich, G. P.; Sevchenko, A. N.; Solovyov, K. N. *Spectroscopy of Chlorophyll and Related Compounds* (in Russian), Nauka i Tekhnika: Minsk, 1968 (section on quasi-line spectra written by K. N. Solovyov and S. F. Shkirman).

(17) Thijssen, H. P. H.; Völker, S. *Chem. Phys. Lett.* **1981**, *82*, 478.

(18) Arabei, S. M.; Egorova, G. D.; Solovyov, K. N.; Shkirman, S. F. *Zh. Prikl. Spektrosk.* **1982**, *36*, 616.

(19) Arabei, S. M.; Egorova, G. D.; Solovyov, K. N.; Shkirman, S. F. *Opt. Spektrosk.* **1985**, *59*, 489.

(20) Arabei, S. M.; Egorova, G. D.; Shkirman, S. F. *Zh. Prikl. Spektrosk.* **1986**, *45*, 239.

(21) Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33.

(22) Brinker, C. J.; Scherer, G. W. In *Sol−Gel Science: The Physics and Chemistry of Sol−Gel Processing*; Academic Press: New York, 1990.

(23) Personov, R. I.; Al'shits, E. I.; Bykovskaya, L. A. *Pis'ma Zh. Exp. Teor. Fiz.* **1972**, *15*, 609.

(24) Personov, R. I.; Al'shits, E. I.; Bykovskaya, L. A. *Opt. Commun.* **1972**, *6*, 169.

(25) Personov, R. I. In *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*; Agranovich, V. M., Hochstrasser, R. M., Eds.; North-Holland: Amsterdam, 1983; p 555.

(26) Zalesskii, I. E.; Kotlo, V. N.; Sevchenko, A. N.; Solovyov, K. N.; Shkirman, S. F. *Dokl. Akad. Nauk SSSR* **1972**, *207*, 1314.

(27) Solovyov, K. N.; Zalesskii, I. E.; Kotlo, V. N.; Shkirman, S. F *Pis'ma Zh. Exp. Teor. Fiz.* **1973**, *17*, 463.

(28) Völker, S.; Macfarlane, R. M. *Mol. Cryst. Liq. Cryst*. 1979, *50*, 213.

(29) Shkirman, S. F.; Arabei, S. M.; Egorova, G. D. *Zh. Prikl. Spektrosk.* **1979**, *31*, 817.

(30) Völker, S.; Macfarlane, R. M. *J. Chem. Phys*. **1980**, *73*, 4476.

(31) Arabei, S. M.; Egorova, G. D.; Solovyov, K. N.; Shkirman, S. F. *Zh. Prikl. Spektrosk*. **1984**, *40*, 92.

(32) Gorokhovskii, A. A.; Kaarli, R. K.; Rebane L. A. *Pis'ma Zh. Exp. Teor. Fiz.* **1974**, *20*, 474.

(33) Völker, S.; van der Waals, J. H. *Mol. Phys.* **1976**, *32*, 1703.

(34) Hayes, J. M.; Small, G. J. *Chem. Phys*. **1978**, *27*, 151.

(35) Galaup, J.-P.; Fraigne, S.; Landraud, N.; Chaput, F.; Boilot, J.-P. *J. Lumin.* **2001**, *94−95*, 719.

(36) Reinot, T.; Dang, N. C.; Small, G. J. *J. Lumin.* **2002**, *98*, 183.

(37) Reinot, T.; Dang, N. C.; Small, G. J. *J. Chem. Phys.* **2003**, *119*, 10404.

(38) Drissler, F.; Graf, F.; Haarer, D. *J. Chem. Phys.* **1980**, *72*, 4996.

(39) Breinl, W.; Friedrich, J.; Haarer, D. *J. Chem. Phys.* **1984**, *81*, 3915.

(40) Arabei, S. M.; Galaup, J.-P.; Jardon, P. *Chem. Phys. Lett.* **1995**, *232*, 127.

(41) Basché, T.; Bräuchle, C. *J. Phys. Chem*. **1988**, *92*, 5069.

(42) Al'shits, E. I.; Kharlamov, B. M.; Personov, R. I. *Zh. Prikl. Spektrosk.* **1986**, *45*, 559.

(43) Völker, S. *Annu. Rev. Phys. Chem*. **1989**, *40*, 499.

(44) Arabei, S. M.; Galaup, J. P.; Pavich, T. A.; Solovyov K. N. *J. Lumin.* **2001**, *94−95*, 767.

(45) Keegan, J. D.; Stolzenberg, A. M.; Lu, Y.-C.; Linder, R. E.; Barth, G.; Moscowitz, A.; Bunnenberg, E.; Djerassi, C. *J. Am. Chem. Soc.* **1982**, *104*, 4305.

(46) Gladkov, L. L.; Shkirman, S. F.; Konstantinova, V. K.; Makarova, E. A.; Solovyov, K. N. *Zn. Prikl. Spektrosk.* **2002**, *69*, 707.