Covalent Grafting of Optically Active Molecules on Silica Gels

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Active organic molecules are grafted on the xerogel silica matrix by using functionalized alkoxides f-R'-Si(OEt)$_3$, where f is a chemical function and R' is an alkyl spacer to limit the degrees of freedom of the molecules. Organic-inorganic hybrid films are prepared in which optically nonlinear DR1 chromophores are covalently bound to the silica network. These films exhibit a large and stable second-order nonlinear coefficient from second harmonic generation experiments. Protoporphyrin molecules are attached double covalently to the xerogel matrix via flexible organic spacers. Persistent spectral holes are still burnt with moderate fluency at 120 K.

Introduction

The sol-gel process is now well known as a synthetic route for the preparation of molecule and cluster-doped xerogels in any desired shape, including thin films. Numerous materials and their applications have been proposed, such as catalysts, sensors, information recording materials, dye-laser materials (Avnir and Ottolenghi, 1992; Canva et al., 1995).

We have largely improved the properties of the xerogels in the last few years by modifying the synthetic procedures and by using organofunctional silicon alkoxides such as modified alkoxide precursors RSi(OEt)$_3$. R is a nonhydrolyzed permanent hydrophobic group (methyl and vinyltriethoxysilane are respectively noted as MTEOS and VTEOS) which decrease the mechanical tensions during the drying process. Owing to the improvement of the mechanical properties, the dense xerogels can be polished (one nanometer in surface roughness) and the optical quality is better (the optical transmission is of 92% at 633 nm for a cylindrical sample of 1 cm in thickness).

Functionalized alkoxides f-R'-Si(OEt)$_3$, where f is a chemical function such as amino or isocyanate group and R' is an alkyl spacer, can also be used to covalently graft active organic molecules on the xerogel matrix. This allows avoiding a phase separation and consequently increases the concentration of the guest molecules. We here focus our attention on the covalent grafting to limit the degrees of freedom of the active molecule. This leads to stabilizing second-order optical nonlinearities in hybrid films and reducing the hole width in persistent spectral hole-burning experiments.

Quadratic Optical Nonlinearity

A large variety of poled polymeric materials has been investigated for second-order nonlinear applications such as fast waveguide electrooptic modulation and frequency-doubling applications (Prasad and Williams, 1991; Burland et al., 1994). Concerning device applications, the major problem is the poor thermal and orientational stability of these poled materials. In the past few years, studies have also been focused on nonlinear sol-gel systems (Puccetti et al., 1991; Chen et al., 1993; Izawa et al., 1993; Yang et al., 1994; Kalluri et al., 1994; Lebeau et al., 1996). Sol-gel technology provides an attractive route to the preparation of a rigid amorphous inorganic matrix at ambient temperatures, which could slow down the molecular orientational motion which induces randomization.

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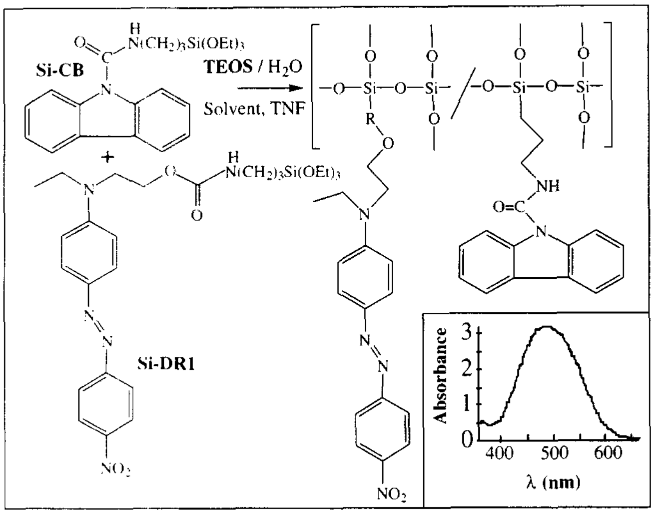

Figure 1. Copolymerization of modified silane monomers with TEOS.

We report quadratic nonlinearities of a sol gel material, which contains a second-order chromophore (Disperse Red 1: DR1) and a charge transporting molecule (carbazole groups) covalently attached to the silica based polymer backbone (Chaput et al., 1996). Carbazole attached alkoxysilane (CB-Si) was synthesized by reacting carbazole-9-carbonyl chloride with 3-aminopropyltriethoxysilane in benzene in the presense of pyridine at room temperature. The hydroxy group of the DR1 azobenzene dye reacted with isocyanate group of the silicon precursor (3-isocyanatopropyltriethoxysilane) in pyridine.

Coating solutions were obtained from copolymerization of the modified silane monomers with tetraethoxysilane (TEOS) (Figure 1). Thin films were prepared by spin-coating on different substrates and were dried at 120°C. Alignment of the nonlinear optical side groups in the sol-gel polymer films was achieved at 160°C by single-point corona poling technique.

As shown in Figure 2, for a gel film prepared with a spin-coating rotation speed of 4,000 rpm, visible spectra exhibited the usual absorption band due to the azobenzene chromophore with a maximum of absorption located at 485 nm. After poling, the absorbance decreased due to the alignment of the dipole moments of azo chromophores. The order parameter was stable after poling with only a slight decrease after 22 days from 0.23 immediately after poling to 0.21.

Thicknesses of the films and refractive indices at 632.8 nm were determined before and after poling for samples spin-coated on glass substrates, previously covered with a 40 nm-thick gold layer by using the well-known attenuated total reflexion method (Dumont et al., 1991). Additional measurements were made on glass-deposited samples by recording in transmission at variable incidence angles the interference fringes resulting from multiple reflections in the film. The film thickness varies from 0.8 to 4.5 μm depending on the angular speed.

For the gel film prepared with a spin-coating rotation speed of 1,500 rpm, the refractive index before poling was found to be $n = 1.732 \pm 0.001$. Immediately after the heating/poling process (thickness of 1.582 ± 0.003 μm), the indices were respectively $n^0 = 1.701 \pm 0.003$ (ordinary index) and $n^e = 1.780 \pm 0.004$ (extraordinary index). The appearance of a positive birefringence after poling results from the expected orientation of the chromophores perpendicular to the layer plane.

The refractive index dispersion was determined by Kramers-Kronig analysis of the visible absorption spectrum (Cardona, 1969). The dispersion curves obtained for each polarization were fitted to a one-resonance Sellmeier equation in the range 600–1,500 nm (Figure 3). The order parameter value deduced from birefringence measurement (Page et al., 1990) is 0.18, consistent with the relative decrease of the maximum absorbance of a glass-deposited sample observed after poling.

The second harmonic generation was performed on poled samples at 1.0642 μm with a Q-switched Nd:YAG laser. The second harmonic coefficient d_{33} was found 118 pm/V shortly after poling, 107 pm/V after two months, and 80 pm/V after one year. The value was obviously lower outside the resonance range ($d_{33} = 34$ pm/V at 1.34 pm/V). Although higher quadratic coefficients have been reported shortly after poling for the red 17 chromophore in a gel matrix (Lebeau et al., 1996), our new sol-gel system clearly shows a significant improvement in quadratic nonlinear stability compared to pre-

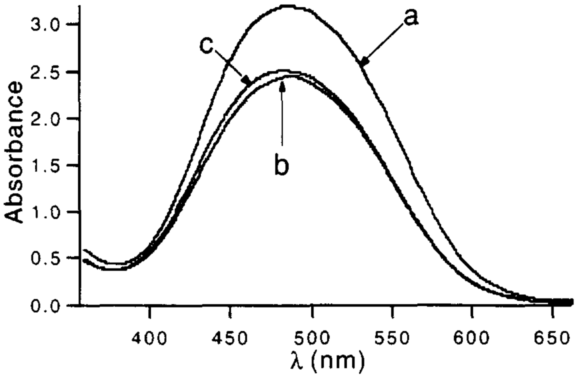

Figure 2. Absorbance spectra of a 4,000 rpm DR1/carbazole gel film.

(a) Before poling; (b) shortly after poling; (c) 22 days after poling.

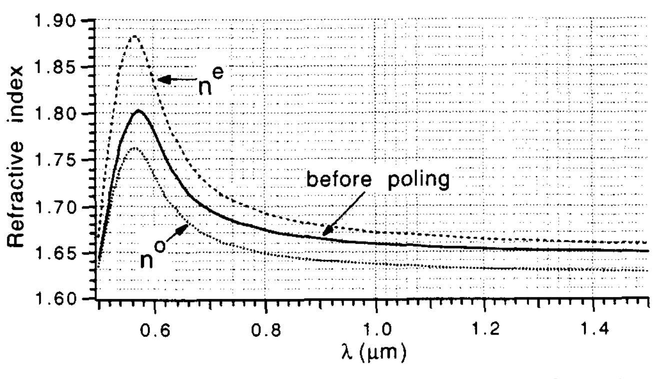

Figure 3. Refractive index dispersion resulting from the Kramers-Kronig analysis of the absorption spectra.

(a) Before poling; (b) immediately after poling.

viously proposed nonlinear gels (Chen et al., 1993; Izawa et al., 1993; Yang et al., 1994; Kalluri et al., 1994; Lebeau et al., 1996).

Persistent Spectral Hole Burning

Since the discovery in 1974 (Kharlamov et al., 1994; Gorokhovskii et al., 1974) of persistent spectra hole burning (PSHB) in the absorption spectra of organic molecules in solids at low temperature, considerable work has been done in ordered (crystals) or disordered (polymer, glasses) organic matrices. Until now, only a few data has been comparatively obtained for inorganic or hybrid organic-inorganic hosts.

The principle of PSHB is simple. A sample in which a chromophore has been diluted is cooled down to very low temperatures (4 K typical). At such temperatures, the absorption spectrum of each molecule is usually very narrow, with sharp vibronic lines, or so-called homogeneous lines. If the dopant molecule is in a disordered environment (at a less extent, this is also valid in crystals which are never perfect), as each molecule is placed in a different site, each molecule experiences a different site shift which gives rise to an inhomogeneous broadening. The disorder is then responsible for the fact that the absorption spectra remain very broad even at extremely low temperatures. PSHB is a method based on the use of high selective laser source and selective photochemistry to remove the inhomogeneous broadening.

A narrow laser source tuned on the inhomogeneous band selects a sub-ensemble of isoenergetic molecules which have coincident homogeneous absorption lines. This sub-ensemble is named a class of molecules or a site. Only the laser selected molecules are excited to their electronic state (usually the lowest one). The key point is now the following: if some of the selected sites are disturbed due to a chemical or a structural photoinduced change of the guest molecule itself or of the solvent cage, then the spectra of these molecules will be modified or only shifted, resulting in the fact that these molecules will not absorb anymore the excitation light. A dip will appear in the inhomogeneous absorption band at the excitation wavelength. This dip is usually called a spectral hole. In absence of saturation, the width of the hole equals two times the homogeneous width. At low temperature, the photoinduced chemical or structural change can be thermally irreversible and the burned hole is persistent over very long time, if the temperature is kept very low.

PSHB is a powerful tool to achieve high resolution spectroscopy of complex molecules in disordered media to study subtle photochemical events at a microscopic level in the solid state, to learn about guest-host interactions, and also to store information data (1 hole = 1 bit) in frequency space. Such a domain connected with applications is a very active research field: not only can very high capacity optical memories be imagined but, combining the use of selective frequency materials with holography, short pulse techniques or electric field control, this enables the investigation of new applications in the fields of image processing, real time holography, data pulse shaping, and optical computation processor (Moerner, 1988).

However, to make these potential applications exist in the future, two main problems will have to be solved. One is to find highly efficient and thermally stable systems to achieve very high rates for writing data or processing, and the second one is to find systems in which persistent and narrow stable holes can be burnt at temperatures as high as possible. As mentioned above, few articles have been concerned with spectral hole-burning data of organic molecules in sol-gel solids. We summarize our main results obtained on porphyrin and quinizarin doped inorganic or hybrid organic-inorganic xerogels, and we report on the promising behavior of such systems at high temperatures (> 100 K).

Background: prerequisites for high temperature PSHB

Two main points have to be fulfilled. First, the microscopic photoinduced process responsible for the hole appearance has to give rise to a stable photoproduct. This is mainly determined by the height of the product-photoproduct barrier which should be high enough to eliminate any possibility of reconversion. Second, the change of the hole width and the hole shape with increasing the temperature has to be minimized. A burnt hole reflects two contributions: one is the zero-phonon hole; the second is the phonon side band whose importance is determined by the linear electron-phonon coupling. The Debye-Waller factor α_D measures the relative importance of these two contributions (Rebane and Rebane, 1993).

$$\alpha_D = \frac{A_{\mathrm{ZPH}}}{A_{\mathrm{ZPH}} + A_{\mathrm{PSB}}}$$

where A_{ZPH} and A_{PSD} are the areas of the zero phonon hole and of the phonon side band, respectively. For strong electron-phonon coupling $\alpha_D \approx 0$; for weak coupling $\alpha_D \approx 1$. In a simple model for linear electron-phonon coupling, the following temperature dependence for α_D is predicted (Rebane et al., 1993)

$$\alpha_D(T) = \exp\left[- S \coth\left(\frac{\Delta E}{2kT} \right) \right]$$

where ΔE is the energy difference between the maximum of the phonon side band and the zero phonon line, and S, the Huang-Rhys factor, is the Stokes shift in emission or absorption, that is, the average energy imparted to vibrations in the vibronic transition. The decrease of α_D when increasing temperature will be minimum is S is small and ΔE large. The value of ΔE is related with the most probable energy of the phonon distribution. Stiff lattices with nearly no soft modes at energies lower than 10 cm^{-1} will be favorable. Hosts with three-dimensional cross-linked networks like in inorganic or hybrid xerogels look very suitable. For a porphyrin derivative dispersed in various xerogel hosts, we reported yet the following observations: the value for ΔE is about 15 cm^{-1}, not strongly different from polymers. However, the values of α_D is increased in hybrid matrices with bulky organic groups: a monotonic decrease of the phonon side band is observed from MTEOS, VTEOS to ATEOS host (Kulikov et al., 1997). However, in such systems, the highest temperature until PSHB was still observed was not greater than 40–50 K.

Grafting of porphyrins on gel backbone

To increase the rigidity of the host as well as to limit the degrees of freedom of the active molecule, so as to reduce the contributions of librational movements to the hole width, the dopant was grafted to the host. Porphyrin-type molecules were first double covalently attached on a sol-gel precursor by using amidation of protoporphyrin IX with aminopropyltriethoxysilane. Doped xerogels were then elaborated by hydrolysis of alkoxides, permitting the copolymerization of the alkoxysilane modified porphyrins with usual sol-gel precursors (TEOS, VTEOS or MTEOS). This was the first preparation of doped xerogels in which porphyrin molecules were grafted to the gel network via flexible organic spacers.

Amidation of Protoporphyrin IX by Functionalized Alkoxide. Alkoxysilane modified porphyrin was prepared from protoporphyrin IX (PP-IX) and 3-aminopropyltriethoxysilane (APTES), supplied by Aldrich and Fluka, respectively, and used without further purification. Coupling was accomplished through the amidation of the carboxylic acid groups with 1,1'-carbonyldiimidazole (CDI) (Figure 4) (Woodburn et al., 1992).

The synthetic procedure described below was carried out under a dried nitrogen atmosphere and in subdued light. The carboxylic acid groups of PP-IX (0.2 mole) were first activated by using CDI (0.4 mole) in 5 mL dried dimethylformamide (DMF was previously stored over molecular sieves). The solution was stirred for 40 min at room temperature. Modification reaction has been monitored by thin-layer chromatography using $CHCl_3/CH_3OH$ (70/30) as eluent. A solution of APTES (0.4 mole) in dried DMF (1 mL) was added slowly to the above mixture. The stirring was continued for $3\frac{1}{2}$ h at room temperature. The solvent was then evaporated. The residue was dissolved in dichloromethane and the mixture was filtered on celite. The filtrate was quickly washed with water, isolated, and dried over anhydrous magnesium sulfate and filtered. The solvent from the filtered solution was removed by a rotary evaporator under vacuum. The residue gave 160 mg (yield 78%) of alkoxysilane terminated protoporphyrin IX. IR spectra of the amides (as KBr disks) were well resolved and the conversion of the PP-IX dicarboxylic acids into dicarboxamides was unequivocally shown by the loss of the carboxylic acid frequency at 1,730 cm^{-1} and the appearance of the amide frequency at 1,650 cm^{-1}. Structure of the as-prepared product was also confirmed by NMR and mass spectrometry.

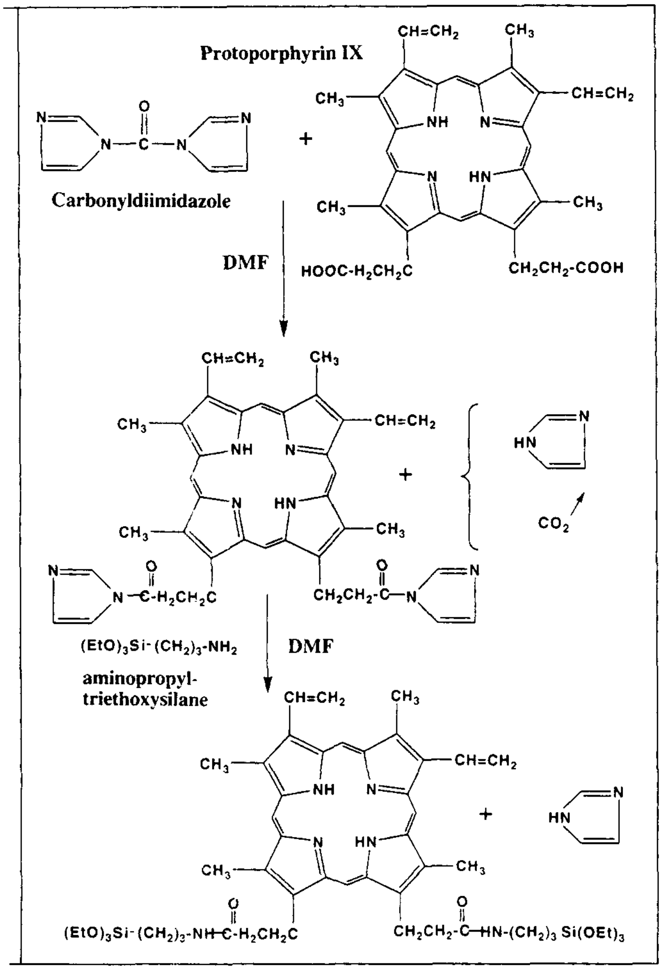

Figure 4. Different steps for the amidation of Protoporphyrin IX by functionalized alkoxide.

Spectrometry Data. ^1H, ^{13}C NMR spectra were recorded on a AC200 Bruker spectrometer. UV-visible absorption spectra were obtained in dichloromethane on a Shimadzu UV-160A spectrometer. FTIR spectra were recorded on a Michelson Bomem spectrometer. Plasma desorption mass spectra were performed on the time-of-flight (TOF) Depilx spectrometer (^{252}Cf source).

N,N' Bis(propyltriethoxysilane)-7,12 diethenyl-3,8,13,17-tetramethyl-21H,23H-porphyrin-2,18-dipropanamide

^1H NMR ($CDCl_3$): δ9.83 (s, 1H), 9.80 (s, 1H), 9.68 (s, 1H), 9.62 (s, 1H), 4x methane protons; 8.21 – 7.90 (m, 2H) 2x $\mathbf{CH}=CH_2$; 6.33 – 6.05 (m, 4H), 2x $CH=\mathbf{CH_2}$; 4.4 – 2.9 (36H), 4x ring methyl, 2x $(-O-\mathbf{CH_2}-CH_3)_3$, 2x $(-\mathbf{CH_2}-CH_2-CO-$, $-CH_2-\mathbf{CH_2}-CO-$, $-CO-NH-\mathbf{CH_2}-)$; 1.37 – 1.17 (m, 4H), $-\mathbf{CH_2}-CH_2-Si-$; 1.02 (t) 2x $(-O-CH_2-\mathbf{CH_3})_3$; 0.24 (t) 2x $-\mathbf{CH_2}-Si-$.

^{13}C NMR ($CDCl_3$): δ7.28, $-\mathbf{CH_2}-Si—$; 11.4, 12.4, ring CH_3; 18.2, $-O-CH_2-\mathbf{CH_3}$; 22.38, $-\mathbf{CH_2}-CH_2-CO-NH-$; 29.68, $-CH_2-CH_2-Si—$; 39.9, $-CH_2-\mathbf{CH_2}-CO-NH$; 41.9, $-NH-\mathbf{CH_2}-$; 58.1, $-O-\mathbf{CH_2}-CH_3$; 96.67, meso carbons; 121.1, $CH=\mathbf{CH_2}$; 129.9, $\mathbf{CH}=CH_2$; 134 – 136, pyrrole carbons; 173, $-\mathbf{CO}-NH-$.

Gel Process. The experimental procedure can be described as follows: raw materials zirconium butoxide $Zr(OBu)_4$ and silicon precursor (TEOS, VTEOS or MTEOS) in the molar ratio 1:4 were mixed in a dry atmosphere using chloroform as a solvent and stirred for several minutes. The volume ratio chloroform:alkoxides was kept at 1:1. The mixture was doped with the alkoxysilane modified porphyrin in chloroform solution in order to obtain a doping concentration of 10^{-3} mol·l^{-1}. The hydrolysis was carried out in a Petri dish by using the moisture in ambient atmosphere. The gelation was observed within one week at room temperature and the aging was performed for one month. Due to the condensation substep, proceeding with solvent evaporation, the contraction of the volumic sample was 90%. Xerogels exhibited a glassy aspect and did not require prior polishing for optical measurements.

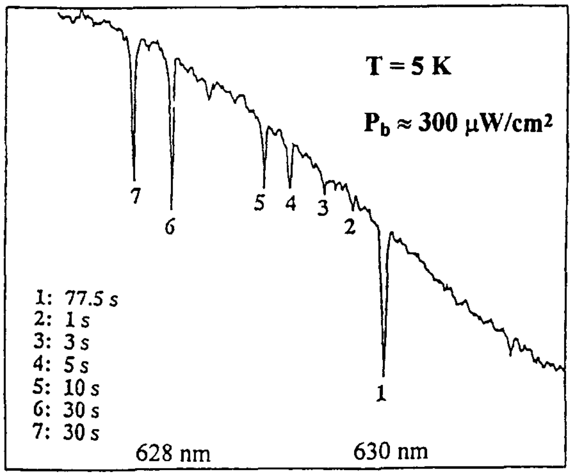

Figure 5. Holes burnt at 5 K.

Burning times are shown in the insert. The burning power was in the order of 0.3 mW·cm^{-2}. Hole widths are laser limited.

Results

PSHB performances

As shown in Figure 5, we burnt several holes at 5 K using different burning times. Previously burnt holes are not erased when a new hole is burnt on their "blue" or "red" side. Also, no phonon side bands in the hole burnt spectra could be recorded which means that the Debye-Waller factor α_D should be quite large in these systems approaching the value one. The hole-burning quantum efficiency is calculated according to the following equation (Horie et al., 1992)

$$\Phi_{hb} = \frac{[d(-\Delta A)/dt]_{t=0} \cdot \Delta\omega_h / \Delta\omega_i}{10^3 \cdot I_0 (1 - 10^{-A_0}) \cdot \epsilon_p}$$

where A is the absorption, ϵ_p is the molar extinction coefficient, I_0 is the incident laser intensity on the sample, $\Delta\omega_h$ and $\Delta\omega_i$ are the homogeneous and the inhomogeneous bandwidth, respectively. From our experimental data, we evaluated $\Phi_{hb} \approx 1.2 \times 10^{-2}$ in the case of VTEOS samples.

Holes are easily burnt (in 1 s with $Pb \approx 0.2$ mW·cm^{-2}), and they remain quite narrow (less than 2 cm^{-1}) even at temperatures as high as 20 K. Increasing the temperature makes the holes broaden rapidly (Figure 6). Detectable holes are burned with moderate fluences (2 to 5 mW·cm^{-2}) during 5 min) at 120 K. However, at this temperature, the hole is quite broad (FWHM = 120 to 130 cm^{-1}), and it disappears when $T > 150$ K. The photochemical event responsible for PSHB is the rotation of the inner protons of the porphyrin cycle. As expected, holes disappear at 150 K because the inner protons begin to rotate freely. This limitation should be easily overcome by using other photochemical mechanisms like, for instance, a photoinduced electron transfer reaction between a donor molecule and an electron trap, which should be deep enough to prevent detrapping at room temperature. Comparative data on PSHB performances for organic molecules in inorganic hosts are given in the Table 1.

Thermal cycling experiments and spectral diffusion

A persistent burnt hole can be used to probe the changes with time occurring in the local environment around burnt molecules. A glass like structure is basically metastable and will spontaneously change with time. These changes will result in a broadening of the burnt hole. This phenomenon which results in a spreading of the frequencies of the burnt molecules over the inhomogeneous spectrum is called spectral diffusion. It is strongly material structure dependent: for instance, spectral diffusion is not expected to play a role in well-ordered systems like crystals. Evidences for the occurrence of spectral diffusion in a material can also be obtained with a thermal cycling PSHB experiment. The experimental procedure is as follows: a hole is burned at a low temperature T_1 and its width is measured Γ_{h1}; then the temperature is raised to $T_2 > T_1$ and kept at this temperature for a time t. Finally, the temperature is decreased to T_1 and the holewidth is measured again Γ_{h2}. If there is no spectral diffusion, the thermal cycle should be reversible and $\Gamma_{h1} = \Gamma_{h2}$ is expected.

Table 1. PSHB Performances for Organic Molecules in Inorganic Hosts

T (K)	Host	Guest	Γ_{inh} (cm^{-1})	Γ_{hole} (cm^{-1})	P_b (mW/cm^2)	t_b (s)	λ_b (nm)	Ref.
77	γAl_2O_3	quinizarin DAQ	1,000	15	12	500	570	Basché and Braüchle (1991)
80	Sol-gel AlOSi	quinizarin DAQ	200	38	20	600	575	Veret-Lemarinier (1995)
80	Zeolite $AlPO_4$-5	ZnPhthalocyanine	450	19	13	100	655	Ehrl et al. (1994)
90	γAl_sO_3	OctaEthyl-Porphin	280	54	3.7	900	612.8	Sauter and Braüchle (1992)
120	Sol-gel Zr VTEOS	PP-IX grafted	440	124	4.5	300	629	Veret-Lemarinier et al. (1995)
140	Semiconductor TiO_2	ZnTTBP	390	≈ 200	3.8	1,200	627.8	Machida et al. (1993)

Γ_{inh} is the width of the inhomogeneous absorption band; Γ_{hole} is the width of the hole; P_b, t_b, λ_b are the burning conditions (respectively the power, the time and the wavelength).

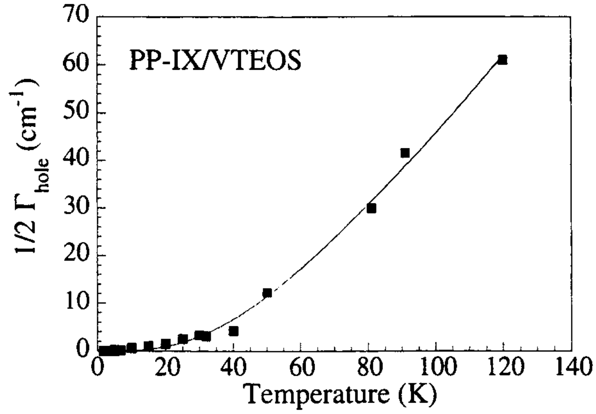

Figure 6. Temperature dependence of the homogeneous width of PP-IX grafted to the siloxane network of a VTEOS xerogel.

In the case of spectra diffusion, irreversible changes have occurred during the thermal cycle and $\Gamma_{h2} > \Gamma_{h1}$.

In VTEOS:PP-IX grafted sample, we burnt holes at a high temperature and we measured their hole width (Veret-Lemarinier et al., 1995). Then, the temperature was lowered and the holewidth measured again. The experimental results (Figure 7) show that no narrowing of the burnt hole is observed when the temperature is lowered. This strong evidence that the main contribution to the holewidth is due to spectral diffusion, which appears as a negative consequence of the grafting.

Conclusion

By covalent grafting, one can both limit the degree of freedom of the optically active molecules and prepare polyfunctional systems. Anchoring of the guest system tends to reduce the width of the homogeneous absorption band of porphyrins, allowing the persistent spectral hole burning above 100 K. Besides, the covalent grafting stabilizes the orientation anisotropy induced by static electric field. This allows to prepare materials with large and stable quadratic nonlinearities for frequency-doubling applications.

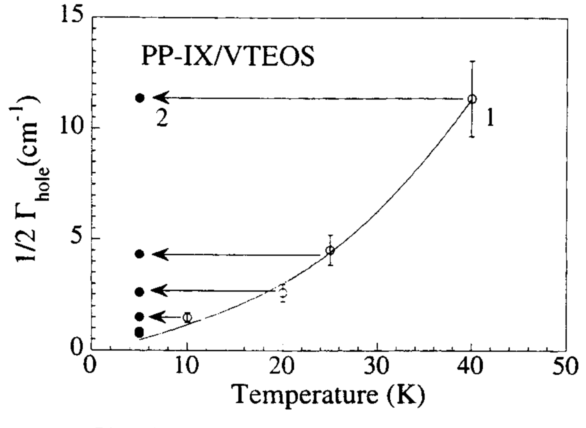

Figure 7. Simple temperature cycle experiment for PP-IX grafted to the siloxane network of a VTEOS xerogel.

Hole is burnt at high temperature (white circles) and then read again at low temperature (black circles). No hole narrowing is observed.

Finally, we have recently shown that gels with covalently attached push-pull azobenzene and carbozole moieties present both quadratic nonlinearities and photoconductive properties. This led to the synthesis of the first photorefractive sol-gel materials for holographic image storage (Chaput et al., 1996).

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