Nonlinear Effects in Chromophore Doped Sol-Gel Photonic Materials

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Abstract. Linear and nonlinear optical effects have been studied in chromophore-doped gel hosts. Tetra-4-sulfonatophenylporphyrinato(II) (CuTPPS), and 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]-naphth[2,1-b][1,4]oxazine] (SP spirooxazine) species were entrapped within porous aluminosilicate hosts. Optical limiting effects and radiative up-conversion behavior in the CuTPPS-doped materials are described, and a six-level model is proposed based on experimental findings. Spirooxazine-containing specimens exhibiting photochromic effects were prepared, and cw and time-resolved spectroscopy methods are used to assess excited state band structures and the nature of guest-host interactions in the resultant gels.

Keywords: aluminosilicate gel, non-linear absorption, metalloporphyrin, spirooxazine, time-resolved spectroscopy

1. Introduction

The sol-gel preparative method provides a route by which a variety of novel solid state materials may be prepared. The tremendous inherent processing flexibility and potential for good optical transparency over extended regions of the visible and near IR spectrum make sol-gel materials of potential use in the development photonically-active media. Additionally, the solution synthetic aspect of sol-gel processing facilitates the incorporation of active species within the nanostructured sol-gel network. Finally, this method is easily adapted to the deposition of thin films on substrates such as optical fibers and planar waveguides by simple coating methods. The authors have focused on the characterization of fluence-dependent nonlinear effects in metalloporphyrin- and spirooxazine-doped gel specimens.
The host gel medium which serves as the basis of this work is prepared using di-sebutyloxylaminoxytriethoxysilane (DBATES), a silicon-aluminum double-alkoxide precursor which may be used to prepare porous 50:50 alumina-silica copolymers. The chemical structure of DBATES is given in Fig. 1. The preparation of chromophore-doped aluminosilicate gels, and the characterization of the gelation process using DBATES precursor, have been previously described by several groups [1–5]. The aluminosilicate host was chosen because of the open pore structure and the amphoteric nature of the double-alkoxide precursor. The open, interconnective pore structure of the resulting xerogels facilitates photo-induced molecular rearrangements in photochromic compounds, such as spirooxazine. The amphoteric nature of the precursor promotes gelation under neutral pH conditions; thus, pH-sensitive chromophores can be incorporated into the solid-state aluminosilicate host without undergoing decomposition.

1.1. NLO Effects in Metalloporphyrin-Doped Gels

We have previously reported the use of porphyrin-doped gels in conjunction with linear optical spectroscopy methods in the development of optode materials which may be used to identify Zn$^{2+}$(aq) and Cd$^{2+}$(aq) [3]. More recent studies have focused on distinction of group 12 ions from competing divalent aqueous cations, such as Cu$^{2+}$(aq), by remote optical interrogation methods. Cu(II)-porphyrin complexation is accompanied by an overall reduction in fluorescence yield from the first excited state, as is complexation with many other divalent transition metal ions; however, multiphoton-absorption and radiative relaxation from the second excited state become prominent in the copper(II) complexes. Hence, nonlinear spectroscopy is a very useful and sensitive method to distinguish between different types of metal centers in the metalloporphyrin complexes. Nonlinear effects in such systems are of potential utility in the development of novel NLO-active photonic media, such as optical limiting and luminescence up-conversion materials.

The protection of eyes and sensors from high-fluence optical sources has attracted much attention with the recent increase in the use of lasers in range finders, designators, LIDAR, and other remote sensing devices. Optical limiters utilize nonlinear materials whose optical transmittance decreases at elevated fluences. Several mechanisms lead to optical limiting behavior, such as excited-state absorption (or reverse saturable) absorption [6], two-photon absorption [7] thermal nonlinearity [8, 9], nonlinear refraction [10], and optically induced scattering [11]. Media currently being studied for optical limiting applications include bulk solids, thin films of organic and inorganic compositions, C$_{60}$ suspensions, and liquid crystals [12]. NLO-effects in chromophore doped sol-gel materials are the subject of much current investigation [13–15]; to authors’ knowledge, however, there is very little reported work on optical limiting characteristics of metalorganic complexes, such as metallophthalocyanines and metalloporphyrins, entrapped in gel hosts [5, 16].

Nonlinear absorption and associated up-conversion fluorescence effects have been observed in the Cu(II)-porphyrin-doped ASE gels. These effects have been attributed to stepwise two-photon absorption events in both the singlet-like (singletsemiquinone) and triplet-like

![Figure 2. Chemical structure of tetra-4-sulfonatophenylporphyrinatocopper(II) (CuTPPS).](image)
(tripquartet) electronic manifolds of this system. The authors have proposed a six-level model for the Cu(II)porphyrin-dopant species. Fluence-dependent dynamics associated with excited state population densities and transition rates are presented. Rate equation analysis using a six-level model has been performed and good agreement has been achieved between experimental observation and parametrically-adjusted numerical calculations. The results indicate that intersystem crossing [17] and quartet-quartet absorption [18] events dominate the optically-nonlinear processes, especially in the case of elevated fluences, for CuTPPS-doped aluminosilicate gels.

1.2. Photochromism and Picosecond Time-Resolved Spectroscopy of Spirooxazine-Doped Gels

Photochromism in compounds such as spiropyrans and spirooxazines is a novel and technologically important phenomenon which may be summarized as a photo-induced molecular rearrangement process. In general, the rearranged form has different absorption and, in the case of fluorescent species, luminescence spectra with respect to those of the original molecular form [19]. Thus photochromism is correlated with fluence-dependent changes to the number density of electronic states (and the population of those states) in such media. Among the important optical characteristics of photochromic media are excitation-induced perturbations to the absorption and fluorescence spectra, which may be utilized to probe fundamental structural changes to the parent molecule. The effects of environmental factors on a photochromic dopant, such as matrix and solvent interactions, are also of substantial importance, and permit the assessment of guest-host interactions by observing subtle changes in the optical characteristics of such compounds entrapped in solid state media.

Spirooxazines comprise a collection of photochromic compounds which have been well characterized [20–22]. A dilute alcoholic solution containing 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphth[2,1-b][1,4]oxazine], a particularly efficient photochromic compound, is colorless in the absence of a suitable photoexcitation source but becomes intensely blue upon exposure to ultraviolet light. Alcoholic spirooxazine solutions are also observed to be highly fluorescent, a characteristic which may be explored for the purpose of detailing guest-host interactions.

Photochromism in spirooxazine compounds generally involves the reversible breakage of a C–O bond in the oxazine ring to form a merocyanine structure. The normal chemical structure and of the 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphth[2,1-b][1,4]-oxazine], and the mechanism of the formation of the UV-induced merocyanine form, are shown in Fig. 3.

Changes in the photochromic reaction may be used to probe the changes which occur in sol-gel media during processes such as polymerization, aging and/or drying [4, 23, 24]. Little, however, is known about solid state interactions between spirooxazine guest species.

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![Chemical structure](image-url)

*Figure 3. Chemical structure of the 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphth[2,1-b][1,4]oxazine] before and after UV irradiation.*
entraped in rigid oxide matrixes. Herein, the authors report preliminary results associated with absorption and fluorescence spectroscopy (cw and time-resolved) studies in spirooxazine-doped ASE gels. These studies are used to postulate radiative (i.e., $S_2 \rightarrow S_0$) and non-radiative (e.g., internal conversion, intersystem crossing) rates in the spirooxazine dopant, and to probe guest-host interactions in the ASE medium containing small amounts of residual solvent.

2. Experimental Methods

2.1. Materials

CuTPPS was obtained from Midcentury. 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3′(3H)naphth[2,1-b]-[1,4]oxazine], (referred to as SP hereinafter) was generously supplied by Prof. Meigong Fan. Detailed discussion regarding the synthesis of this compound is available elsewhere [25]. Di-(sec-butoxy)aluminoxytriethoxysilane (DBATES) was obtained from United Chemical Technology and used without further purification. Anhydrous reagent grade isopropanol was purchased from Fisher Scientific Company. Water was deionized and distilled.

2.2. Sample Preparation

Bulk aluminosilicate gel monoliths, doped with chromophoric guest species, were prepared by a method similar to one previously described by Pouvviel and others [1–5]. This preparation involves the dropwise addition of aqueous isopropanol, containing the soluble (e.g., CuTPPS or SP) dopant species, into a 50:50 mixture (by volume) of DBATES and isopropanol. The volumetric ratio of water: isopropanol: DBATES in the precursor solution was 1:6:3. The hydrolyzed aluminosilicate sol was cast directly into $1 \times 1 \times 4.5$ cm$^3$ polystyrene cuvettes and subsequently covered with parafilm for gelation and aging.

CuTPPS-doped ASE specimens prepared in this manner were observed to gel at room temperature over a period of three days. The bulk samples were subsequently allowed to slowly dry, under ambient conditions, for approximately 8 weeks prior to making experimental measurements. Initial dopant concentrations in the sols ranged from $1 \times 10^{-6}$ to $1 \times 10^{-4}$ M. The dopant number densities ($N_D$) of entrapped CuTPPS in the xerogel specimens were calculated, based upon the final dimensions of the dried bulk monoliths, to range from $1.5 \times 10^{15}$ cm$^{-3}$ to $1.5 \times 10^{17}$ cm$^{-3}$.

Spirooxazine-doped specimens were prepared using an initial chromophore concentration of $1 \times 10^{-4}$ M in the precursor solution. The aged SP-containing gels were allowed to dry under ambient conditions for 2 and 3 weeks. The gels obtained at this time were not completely dried; fully dried SP-doped xerogels did not retain their photochromic activity. The final SP dopant number densities ($N_D$) in the partially dried gels was calculated to be $8.2 \times 10^{16}$ cm$^{-3}$, based on final specimen dimensions.

2.3. Nonlinear Absorption and Luminescence Up-Conversion

A schematic diagram of the experimental setup for nonlinear absorption is shown in Fig. 4 and described elsewhere [5]. An excimer laser (oscillating at 308 nm) pumped dye laser was used as the excitation source. A rhodamine 6G: methanol solution served as the gain medium in the dye laser. The dye laser output was determined to have a 16 ns pulse width (FWHM); laser output was tuned to 584 nm. Nonlinear absorption measurements were conducted using incident pulsed energies which ranged up to a few microjoules per pulse. The incident energy was monitored for each pulse by placing a beam splitter behind a neutral density filter which reflected 10% of the incident energy to an energy probe (at location A) orthogonally positioned.

![Figure 4](image)

Figure 4. Schematic diagram of experimental setup for optical nonlinear absorption measurements.
with respect to the beam. The balance of the laser energy was focused, using a 200 mm focal length lens, to a spot (≈20 μm) inside the sample. The best focus within the sample was obtained using the Z-scan method [26].

Up-converted luminescence studies were performed using the same excitation system. Emission measurements were made using a Spex model FI12A fluorometer. Absorption spectra were determined using a Cary 5 spectrophotometer. All spectra were corrected for instrumental response, and all measurements were performed at room temperature.

2.4. Picosecond Time-Resolved Spectroscopy

Time-resolved luminescence measurements of the SP-entrapped gels utilized a frequency-doubled dye laser (5 ps pulse width; 82 MHz repetition rate). 300 nm output from the dye laser was obtained upon frequency doubling of the 600 nm oscillation produced upon pumping via modelocked Nd:YAG laser (Spectral Physics 3800; frequency doubled 532 nm output). Temporal luminescence characteristics were obtained using a 0.5M dispersing monochromator in conjunction with a synchronscan streak camera (Hamamatsu C5690, temporal resolution <2 ps). The overall time resolution of detection system, including jitter, was less than 20 ps (apparatus schematically shown in Fig. 5). The pump source was 160-W UV Lamp with the intensity of 11,600 μW/cm².

3. Results and Discussion

3.1. Nonlinear Absorption and Up-Converted Luminescence of CuTPPS Dopant

A simplified six-level system for CuTPPS, which is subsequently used in the rate equation model, is given in Fig. 6; the singlet-like singlet-doublet manifold is designated D, while the triplet-like triplet-quartet manifold is designated T. No significant changes in the absorption features of the dopant were observed as the material evolved from the liquid phase sol to the fully dried.

Figure 5. Schematic diagram of experimental setup for time-resolved measurements of photochromic compound-doped gels.

Figure 6. Six-level energy level diagram for CuTPPS.
xerogel state. A four-fold increase in the peak optical density was found to correlate well with the expected shrinkage-induced increase in the absorption cross sectional area; thus it is postulated that the entrapped CuTPPS molecules exist primarily in large pores and do not have substantive electronic interaction with the entrapping aluminosilicate network.

The 584 nm excitation wavelength was selected such that the low energy tail of the $D_1$ band could be selectively probed, and strong linear absorption effects were avoided. Intensity-dependent nonlinear transmission plots are shown in Fig. 7 for the three dopant densities studied. For all specimens examined, absorption was found to be a linear function of the incident energy under very weak illumination conditions. All of the CuTPPS-doped aluminosilicate samples exhibited a nonlinear absorption behavior (intensity-related decrease in transmissivity) at intermediate incident energies, as shown in Fig. 7. Saturation of this effect was observed above a critical energy, $E_c$, over which the transmissivity once again behaved in a more or less linear manner. $E_c$ was found to be a function of dopant concentration, i.e., increased dopant densities were found to correlate with elevated $E_c$ values. No visible sample bleaching or burning was observed over the reported incident energy range.

The authors conclude from the saturation behavior shown in Fig. 7 that strong excited state absorption occurs in these materials [16, 27]. The observed optical limiting behavior indicates that the excited state absorption cross-section is larger at 584 nm than the ground-state absorption cross-section.

Nonlinear transmissivity effects may be explained by depopulation of the ground state and subsequent absorption from optically excited states, presumed to be the first excited doublet and quartet states, to higher lying levels in the doublet and quartet manifolds. Luminous up-conversion can result, in conjunction with such multiphoton absorption processes, from radiative relaxation out of higher lying excited states (see Fig. 6) [28–30]. In the case of CuTPPS, the second excited singlet band, $D_2$, can be populated by two-photon absorption of 584 nm photons from the electronic ground state, $D_0$, through the $D_1$ band to the higher lying $D_n$ band(s). Internal conversion (ic) from the $D_n$ state(s) leads to nearly instantaneous population of the $D_2$ band. Subsequent radiative relaxation from $D_2$ to the ground state yields blue photon emission, peaked at 434 nm. A typical spectrum of the observed up-converted blue emission, resulting from 584 nm excitation, is shown in Fig. 8.

To quantitatively investigate this behavior, up-converted photon emission intensity was measured as a function of excitation pulse intensity. Figure 9 shows the experimentally-determined blue emission intensity ($\lambda_{em} = 434$ nm) as a function of the excitation intensity at 584 nm (circles with error bars). The data shown represent the characteristics for a specimen having a dopant $N_0$ of $1.5 \times 10^{17}$ cm$^{-3}$; other samples had similar behavior. Up-converted fluorescence intensity was found to rapidly increase relative to the pump intensity over the low to intermediate intensity range. Blue emission was found to saturate at essentially the same energy, $E_c \sim 600 \mu$J, as that seen for the onset of linear transmission in the earlier studies (Fig. 7(c)). This may be explained by heavy saturation of the $D_1$ band under elevated excitation fluences. In a simple four-level system, the intensity of the up-converted blue emission would be expected to proportionally increase as a function of the excitation intensity. Such behavior is, however, inconsistent with the experimental observation, as strong saturation effects occur at elevated fluences.
Optical limiting effects have been attributed to intersystem crossing, i.e., nonradiative relaxation from the $D_1$ band to the lowest lying quartet level, $^4T_1$. The excited quartet $^4T_1$ level has a long lifetime (on the order of a few milliseconds), due to the forbidden nature of relaxation to the singlet-doublet ground state, $D_0$ [31]. During intense excitation, the initial portion of the incident laser pulse can be reasonably expected to excite a large portion of the irradiated metalloporphyrin molecules to the $D_1$ band. It appears that a substantial number of this excited population relaxes to the $^4T_1$ level and remains in the quartet manifold ($^4T_1 \leftrightarrow ^4T_n$) during the balance of the exciting ns pulse. This hypothesis correlates well with prior studies showing that inverse intersystem crossing ($^4T_n \rightarrow D_2$) in metalloporphyrins is a highly improbable event [28]. Temporally-resolved emission studies of the CuTPPS-doped specimens demonstrated that upconverted emission behavior is too fast to be based upon a triplet-like intermediate state, indicating the absence of a contribution from quartet level ($^4T_1$) annihilation [28, 32], which could also lead to population of the $D_2$ band. Thus, our measurements indicate that guest CuTPPS molecules which undergo electronic intersystem crossing (isc) into the quartet manifold make no subsequent contribution to up-converted luminescence. This is one of several possible mechanisms by which the type of saturated emission behavior seen in Fig. 9 may be explained. The proposed model is supported by the observation that only extremely weak fluorescence is detected for the transition from the $D_1$ band to the ground state, indicating that isc may dominate these transition processes as a result of heavy atom effects [33].
3.2. Rate Equation Analysis: CuTPPS Dopant in ASE Gels

According to the postulated mechanisms, quartet states must be taken into account when assessing the absorption and radiative relaxation processes which occur in CuTPPS at elevated incident energy intensities. Six-level rate equations are given in Eq. (1), where superscripts $D$ and $T$ refer to the singlet-like singlet-doublet and triplet-like triquartet manifolds, respectively; in Eq. (1), $Pump$ indicates the use of a Gaussian source term that represents the laser excitation at 584 nm. $n_D$ and $n_T$ denote the electron populations of the singlet-doublet and triquartet states. $\sigma_s$’s and $k$’s correspond to absorption cross-sections and decay rates. $k_{21}$ ($k_{12}$) represents the internal conversion rate, while $k_{isc}$ and $k'_{isc}$ are associated with intersystem crossing rates. $\sigma_{01}^D$ was calculated from the absorption spectrum to be $1.3 \times 10^{-17}$ cm$^2$ molecule$^{-1}$ at $\lambda_{ex} = 584$ nm. The sum of excited state absorption cross-sections, $\sigma_{a1}^p$ and $\sigma_{a2}^T$, were estimated to have values of $2.1 \times 10^{-17}$ cm$^2$ molecule$^{-1}$, by assuming absorption in the saturation region only results from excited state absorption. Decay rates were approximated using previously reported experimental results for similar metalloporphyrins; all parameters used in the computation are listed in Table 1. Internal conversion ($k_{21}^D$) and intersystem crossing rates ($k_{isc}$) were incorporated into the rate equations as adjustable parameters. Thus, the relative magnitudes of inter- and intra-manifold transitions can be assessed, based on the experimental, fluence-dependent optical measurements described above.

\[
\frac{dn_{D_0}}{dt} = -pump \sigma_{01}^D n_{D_0} + k_{10}^D n_{D_1} + k_{20}^D n_{D_2} + k'_{isc} n_{T_1} \\
\frac{dn_{D_1}}{dt} = pump \sigma_{01}^D n_{D_0} + k_{21}^D n_{D_2} - (k'_{isc} + k_{isc} + pump \sigma_{a1}^p) n_{D_1} \\
\frac{dn_{D_2}}{dt} = pump \sigma_{a1}^D n_{D_0} - (k_{10}^D + k_{21}^D) n_{D_2} \\
\frac{dn_{T_1}}{dt} = k_{isc} n_{D_1} - (k'_{isc} + pump \sigma_{a2}^T) n_{T_1} + k_{21}^T n_{T_2} \\
\frac{dn_{T_2}}{dt} = pump \sigma_{a1}^T n_{T_1} - k_{21}^T n_{T_2}
\]

(1)

The intersystem crossing rate, $k_{isc}$, was found to be approximately 10 times greater than the internal conversion rate $k_{10}^D$, suggesting that the intersystem crossing events dominate the relaxation processes out of the first excited ($D_1$) singlet-doublet band. This result is consistent with the study of triplet state formation via isc (from the singlet manifold) in copper phthalocyanines, where a quantum efficiency for such events is reportedly $\geq 70\%$ [30].

The intensity of up-converted fluorescence for any fixed value of incident energy, $I_{D_1}$, can be obtained by the following:

\[
I_{D_1} \propto \int_0^\infty n_{D_1}(t) \, dt
\]

(2)

The calculated results are shown as the solid curves given in Fig. 9. The solid line indicates the expected $D_2$ emission intensity if one includes the effect of intersystem crossing, using the indicated parameters and assuming a high $D_1 \rightarrow 4T_1 (\geq 70\%)$ intersystem crossing efficiency. The dashed line indicates the computed blue fluorescence intensity as a function of the incident excitation energy which could be expected if one considers only the singlet manifold transitions. A quadratic dependence was experimentally observed at relative low excitation power densities, but a nearly linear behavior is noted for energies above $E_c$. Our results clearly indicate that a six-level model, which includes the effects of efficient isc pathways, describes the behavior of this system much more accurately than does a simple model which includes only singlet manifold transitions.

Figure 10 shows the computed electronic populations, $n_{D_0}$ and $n_{T_1}$, in the $D_0$ and $4T_1$ levels as a function of time during and immediately following the laser pulse excitation. For relative low incident energy densities (dotted curves), $n_{D_0}$ is calculated to be greater than $n_{T_1}$ over the entire pulse duration period. As the laser power increases to intermediate levels (dashed curves), however, $n_{T_1}$ is expected to exceed $n_{D_0}$, at some critical energy density.

The time when $n_{T_1}$ is predicted by the model to exceed $n_{D_0}$ occurs at earlier times under conditions of higher incident fluences. It is under such conditions that the optical absorption may be dominated by quartet-quartet transitions, behavior which is consistent with our experimental observations ($\sigma_{a2}^T$ has been assumed to have the same value to $\sigma_{01}^D$ in the calculation).

3.3. Photochromism and Fluorescence Effects in SP-Doped Gels

Freshly prepared gels containing spirooxazine were yellow in color and exhibited rapid, reversible
Table 1. Parameters used for rate equation calculations.

<table>
<thead>
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<th></th>
<th>(01) (cm(^2) mol(^{-1}))</th>
<th>(1n) (cm(^2) mol(^{-1}))</th>
<th>(k_{10}) (sec(^{-1}))</th>
<th>(k_{20}) (sec(^{-1}))</th>
<th>(k_{21}(k_{so})) (sec(^{-1}))</th>
<th>(k_{nc}) (sec(^{-1}))</th>
<th>(k_{nc})' (sec(^{-1}))</th>
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</thead>
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<td>(1.3 \times 10^{-17})</td>
<td>(0.8 \times 10^{-17})</td>
<td>(5 \times 10^{10})(^a)</td>
<td>(5 \times 10^{12})(^b)</td>
<td>(1 \times 10^{12})</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Quartet system</td>
<td>(1.3 \times 10^{-17})</td>
<td>(1.3 \times 10^{-17})</td>
<td>--</td>
<td>(1 \times 10^{11})(^c)</td>
<td>--</td>
<td>(5 \times 10^{11})</td>
<td>(4 \times 10^{10})(^d)</td>
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<tr>
<td>Intersystem crossing</td>
<td>--</td>
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\(^a\)From Ref. [30].
\(^b\)From Refs. [28] and [30].
\(^c\)From Ref. [15].
\(^d\)From Ref. [31].

Figure 10. Calculated population of the electronic ground state, \(D_0\), and the lowest quartet state, \(^4T_1\), as a function of time. Dotted, dashed and solid lines represent light, intermediate and heavy excitation fluences, respectively.

photochromic behavior. Drying of the SP-doped gels significantly changed their photochromic characteristics. Fully dried ASE xerogels ceased to exhibit photochromic effects; thus, partially dried gels (two-week and three-week drying times) were selected for study.

The optical absorption spectra of SP-doped aluminosilicate gels (two-week drying period) are shown in Fig. 11. Prior to UV-irradiation, three principal absorption bands, centered at 295 nm, 430 nm, and 550 nm, are distinguishable. The intense band is tentatively ascribed to the \(S_0 \rightarrow S_2\) transition, while the 430 nm peak has been assigned to the \(S_0 \rightarrow S_1\) transition. The 550 nm peak is attributed to the merocyanine form of the dye. After irradiation with a 365 nm source (10,000 \(\mu W/cm^2\)) for 2 minutes at room temperature (Fig. 11), the samples became purple in color. This color change corresponds to a large increase in the intensity of the 550 nm absorption peak, indicating substantial conversion of SP to the merocyanine form. The merocyanine form is postulated to be stabilized by the gel structure itself, which contains a high number density of polar species such as Si-OH and Al-OH group [34]. It should be noted that the merocyanine form is represented by a mixture of four isomers [35]. While our experiments do not distinguish between different isomers, the distribution of isomers may be solvent dependent and that those with intramolecular hydrogen bonds may be favored in non-polar media.
In the partially dried gel hosts the colored mero-
cyanine was observed to decay, over a period of ap-
proximately 5 minutes at room temperature, to the
colorless form. The decay kinetics of the colored form
of merocyanine was found to deviate considerably from
first order reaction kinetics, a result which is consis-
tent with the decay of spiropyran in organic polymer
matrices [36]. Constraining interactions between the
photochromic guest compound and the aluminosilicate
host material can cause the thermalization process in
the solid state sol-gel media to be much slower than
that in alcoholic solution.

Continuous wave fluorescence spectra of the ASE-
entrapped SP species are shown in Fig. 12. The
spectrum of SP prior to UV-irradiation shows only
one principal luminescence peak centered at 435 nm
(Curve 1; \( \lambda_{ex} = 375 \) nm). After 2 minutes irradiation
with 365 nm light, a second emission peak arose at
519 nm (Curve 2, \( \lambda_{ex} = 375 \) nm). Five minutes after
observation of Spectrum 2, the broad 519 nm emission
band had nearly disappeared (Curve 3). UV-induced
appearance of the 519 nm emission band was found
to be completely reversible with dark storage. The
519 nm luminescence peak has been attributed by
relaxation rate from second singlet state to the ground state.

The influence of solvent evaporation may be distinguished by comparing Curves A and B in Fig. 13. The three-week dried gel (corresponding to Curve B) exhibited $t_1$ and $t_2$ components that were substantially longer (1100 ps and 110 ps; fractional intensity components $f_{t_1} = 0.17$ and $f_{t_2} = 0.83$, respectively) than in the case of the gel which was dried for a two-week period. The lifetime increases correspond to retardation of the $S_2$ depopulation rate by approximately 20%. This result indicates that the molecule is strongly influenced by the local surroundings, and provides some insight regarding the mechanism for loss of photochromic characteristics in such media. Longer drying times correspond to lower solvating alcoholic activities in the gel host, thereby increasing SP interaction with the ASE matrix. As interaction with the rigid gel matrix increases, molecular reorientations become more difficult and photochromic behavior is impeded. It is through the use of modified gel hosts, such as those achieved using ethyl-modified silicon alkoxide precursors by Avnir and co-workers [23, 38], that fully dried photochromic materials based on dopants such as spirooxazine may be prepared.

4. Summary and Conclusions

Chromophore-doped aluminosilicate gels have been prepared, and nonlinear characteristics have been assessed as a function of dopant number densities, excitation fluence, and residual solvent content. CuTPPS-doped gels exhibit optical limiting and radiative upconversion effects which have been attributed to excited state absorption in the triquartet manifold and radiative decay from higher-lying singlet doublet states. The observation of photochromic effects in spirooxazine-doped gels were correlated with postulated energy level structures which were assigned through the use of linear and nonlinear spectroscopy methods. Such methods have proven to be a powerful approach to the assessment of excited state electronic structures and the investigation of nonlinear characteristics in photonically-active media.

Acknowledgments

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