OPTICAL LIMITING AND UPCONVERTED LUMINESCENCE IN METALLOPORPHYRIN-DOPED SOL-GELS

Kai Dou, Xiaodong Sun, Xiaojun Wang, Robert Parkhill, Yin Guo and Edward T. Knobbe

Department of Chemistry and the University Center for Laser and Photonics Research, Oklahoma State University, Stillwater OK 74078, U.S.A.
Department of Physics, Georgia Southern University, Statesboro GA 30460, U.S.A.

(Received 23 February 1998; accepted in revised form 30 March 1998 by F.J. Di Salvo)

In this paper, optical limiting and upconverted luminescence have been demonstrated in metalloporphyrin of ZnTPPS-doped aluminosilicate sol-gel hosts. The photo-upconverted radiative emission was observed and believed to result from the radiative recombination of the second excited singlet state. Intensity of the upconverted luminescence was found to be saturated as a function of excitation intensity. Optical limiting associated with reverse saturable absorption was observed. These effects are attributed to the higher excited state absorption. A method for determining absorption cross-section of excited states was developed by using dynamic calculation to fit the intensity dependence of upconverted intensity. The absorption cross sections of the excited singlet and triplet state were estimated. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: A. polymers, D. optical properties, E. luminescence, E. nonlinear optics.

1. INTRODUCTION

Sol-gel synthesis methods [1] have been found to exhibit significant advantages in preparing solid state optical materials for making photonic devices and studying their photophysical properties [2–5]. The flexibility of the materials fabrication, good transparency in broad spectral range and incorporation of the embedded molecules can be realized in sol-gel systems. Photonic applications require solid state optical materials and these materials prepared by the sol-gel synthesis have been achieved in the fields of solid state laser media, thin film and coatings, optical limiting devices and chemical sensors [6–8]. For the optical limiting, dynamic mechanisms have been proposed [9] and in particular, one of these micromechanisms is associated with reverse saturated absorption (RSA) which emphasizes the absorption from higher excited states with elevated incident intensity. Investigations on RSA have been performed in solution and sol-gel media of phthalocyanines and metallophthalocyanines [8, 10, 11]. The work described here represents an extension of these earlier research results [12, 13] and exhibits experimental results for nonlinear absorption and emission of excited states in aluminosilicate gels doped with tetra-4-sulfonatophenylporphyrinatozinc (ZnTPPS).

The photophysical properties of porphyrin, metalloporphyrin and related compounds over both theoretical and experimental regimes have been extensively studied [14, 15] due to scientific interest and their potential applications in the field of photonics. Excited state processes are known to strongly affect photophysical properties of these compounds [16, 17]. Features of excitation, energy transfer, absorption and emission from excited states are related to the interaction between the excited states and the external light field and also related to the coupling between the excited states. Materials with reverse saturation absorption represent a class of attractive candidates for use in optical limiting and optical pulse compression. Several photophysical mechanisms for RSA have been proposed in the past years [18–25].
In the current paper, we demonstrate upconverted luminescence (UCL) and reverse saturation absorption in ZnTPPS-doped sol-gel media. It is believed that this is the first observation of upconverted luminescence and related reverse saturation absorption in ZnTPPS-doped sol-gel hosts. The upconverted emission is believed to associate with the radiative transition from the second excited singlet state to the ground state. The intensity saturation of upconverted fluorescence has been observed as a function of excitation intensity. These phenomena are considered to result from the higher excited state absorption which can be attributed to the stepwise two-photon absorption transition from both singlet and triplet states to their higher excited states via the first excited states. Herein, experimental measurement and corresponding dynamic analysis have been performed. The excited state absorption cross section is evaluated by fitting the experimental data. Experimental results are in a good agreement with dynamic calculation.

2. EXPERIMENTAL METHODS

Metal tetra-4-sulforatophenylporphyrins of ZnTPPS were received from Midcentury and used without further purification. Molecular structure for ZnTPPS are plotted in Fig. 1 along with TPPS’s structure as a comparison. Specimens were dissolved in ethanol and mixed with aluminosilicate sol-gel forming a gel in a range of concentration from $5 \times 10^{-6}$ to $1.5 \times 10^{-4}$ molar. Aluminosilicate gel bulk, doped with metalloporphyrins, were prepared similarly to the method previously reported by J.C. Pouxviel and his colleagues [2, 3]. The aluminosilicate gels were put directly into polystyrene cuvettes coated with parafilm. The bulk samples were subsequently allowed to slowly dry for approximately 10 weeks prior to experimental measurements.

The excitation source for nonlinear absorption and inverse saturation absorption measurement was an excimer laser (Lambda Physik, model 120iL at output wavelength of 308 nm) pumped dye laser (Lambda Physik, model LPD3000CES). The wavelength range of the output dye laser, employing a Rhodamine 6G in methanol gain medium, was tunable over the 565–610 nm. The pulse width of the dye laser was measured to be 15 ns. An excitation wavelength of 584 nm was used for nonlinear absorption measurement. Output maximum of incident pulse energy from dye laser was 4.2 mJ per pulse. A set of neutral density filters was used to attenuate the laser incident energy during the intensity dependent measurement. The laser beam was focused to a 80 μm spot inside the sample by using 20 cm focal length lens. A dual-channel Rm6600 Universal Radiometer was used to detect incident and transmitted energies.

Fig. 1. Molecular structures for (a) metal-free porphyrin and (b) zinc porphyrin.

Photo-upconverted luminescence spectra were determined by using the same excitation system as the nonlinear absorption experiment. An excitation wavelength of 584 nm was selected. Detection of upconverted luminescence was achieved using a Spex model F112A fluorometer (0.22 m double grating spectrometer, thermo-electrically cooled R928 PMT detector). Absorption spectra were measured with a Cary 5 spectrophotometer. All spectra were corrected for instrumental response and all measurements were performed at room temperature.

3. EXPERIMENTAL RESULTS

Photophysical features for zinc porphyrins are characterized by the excited state processes of $d$-electrons from the transition ions and delocalized $\pi$-electron
Fig. 3. Dynamic model with multi-energy levels for metalloporphyrin systems. \(S\) and \(T\): singlet and triplet states \(\{\sigma\}\): absorption cross sections, \(\{\tau\}\): decay time constants, \(\tau_{ST}\) and \(\tau_{T}\): intersystem crossing constants.

Fig. 4. Transmittance vs excitation energy shows the reverse saturation absorption in ZnTPPS gel at pumping wavelength of 584 nm.

Fig. 5. Upconverted luminescence centered around 480–500 nm (1) at excitation wavelength of 584 nm with excitation density of 4 MW cm\(^{-2}\) and (2) compared to excitation of 385 nm.

Fig. 2. Absorption spectra for ZnTPPS-doped gels at a concentration of \(\times 10^{-3}\) mol.

from the porphyrin ring. Differences of the central metal ions in metalloporphyrins may lead to changing optical properties in excitation, absorption and emission. Hence, much attention will be paid to absorption, nonlinear transmission and intensity-dependent emission related to the excited states in metalloporphyrins.

Absorption spectrum is shown in Fig. 2 for ZnTPPS gels. Two main absorption bands are found in the region of 400–420 nm and 500–650 nm which are known as the porphyrin \(B\) and \(Q\) band, corresponding to absorption transitions of \(S_2 \rightarrow S_0\) and \(S_1 \rightarrow S_0\), respectively. Schematic energy level diagram for ZnTPPS is shown in Fig. 3. Both \(B\) and \(Q\) bands are composed of absorption subbands. Metalloporphyrin ZnTPPS shows the similar structure of \(B\) and \(Q\) absorption bands to CuTPPS [12]. But \(Q\) absorption band for TPPS with at least four absorption peaks is obviously different from that for ZnTPPS. No obvious change of absorption structure can be observed in absorption spectra between solution and sol-gel of metalloporphyrins.

Intensity-dependent nonlinear transmission is shown in Fig. 4 for ZnTPPS gels with \(\times 10^{-3}\) molar at 584 nm excitation. All of these samples with different concentrations show the reverse saturation absorption in a range of excitation wavelength of 570–600 nm. Absorption is found to be a linear function of incident energy during very weak excitation. The transmittance decreases in a range of intermediate incident intensity, which implies absorption increasing with elevated excitation. Saturation appears above the saturated intensity, which is concentration-dependent. We think that absorption from the higher excited states takes place in these samples based on the optical transmittance vs excitation intensity.

Figure 5 exhibits typical spectra of the photo-upconverted luminescence. Both emissions from \(B\) and \(Q\) band can be observed with normal excitation
of 385 nm. Upconverted luminescence peaking around 480–500 nm for ZnTPPS gels is recorded by using selective excitation of 584 nm which corresponds to the absorption of $S_1 \rightarrow S_0$ transition. The upconverted luminescence is recorded as a function of excitation intensity in Fig. 6. The upconverted emission intensity is found to be nearly square of excitation intensity and increase rapidly within a regime of weak excitation. The saturation of the upconverted emission is found in Fig. 6 during intermediate and strong excitation.

4. DISCUSSION

Nonlinear absorption and related upconverted luminescence can be well understood with multi-level model shown in Fig. 3. For the selective excitation of 584 nm, molecules in the ground state $S_0$ are excited into the first excited singlet state $S_1$. The portion of electrons in $S_1$ may deexcite to the ground state in radiative and nonradiative transition and partly decay to the first excited triplet state $T_1$ through the nonradiative intersystem crossing. On the other side, electrons in $S_1$ can be subsequently excited to the higher excited singlet state $S_n$ during high excitation fluxes and analogously electrons in $T_1$ absorbing the incident photons transit to the higher excited triplet state $T_n$. Both reabsorption from $S_n \rightarrow S_1$ and $T_n \rightarrow T_1$ may lead to the increasing absorption (inverse saturated absorption). Due to the short lifetime for the higher excited states electrons in $S_n$ and $T_n$ nonradiatively decay rapidly to the lower lying levels even to the $S_1$ and $T_1$, respectively. Electrons in $T_1$ will give rise to fluorescence or relax nonradiatively to the ground state. Electrons in $S_2$ can be populated through the electron decay from $S_n$. Consequently, at intense excitation electrons resided in $S_2$ may transit directly to the ground state by radiative recombination of $S_2 \rightarrow S_0$, resulting in the upconverted luminescence in 480–500 nm for ZnTPPS gels as observed in Fig. 6. The higher excited state absorption, i.e., transition from the first singlet and triplet excited states to their corresponding higher excited state levels is supposed to be responsible for transmittance decrease with elevated excitation intensity and photo-upconverted radiation. These effects are thought to result from the multiphoton absorption processes.

The reverse saturation absorption is analyzed by studying the correlation of absorption coefficient and excitation intensity. The systematic absorption coefficient in the multi-level system in Fig. 3 is described as a function of excitation intensity by

$$\alpha = \frac{\sigma_e}{(1 + I/I_{SA})} + \frac{\sigma_s}{(1 + I/I_{SA})}. \tag{1}$$

$\alpha$ contains the absorption contribution from the ground state and the excited states. The saturation intensity $I_{SA}$ is given by $I_{SA} = h\omega/\sigma_g \tau_e$, where $\tau$ denotes the effective lifetime of excited states in the multi-energy-level system. $\sigma_e = (\sigma_{TE} + \sigma_{SE} \tau_S)/(\tau_T + \tau_S)$ stands for the effective absorption cross-section for the excited states including the contribution of excited singlet and triplet states. In ZnTPPS doped gels, $\tau_T/\tau_S$ is about $10^3$ and it turns out $\sigma_e = \sigma_{TE}$. One abstracts the absorption cross section by using (1) to fit the intensity dependence of absorption.

Two absolutely different categories of absorptions are distinguishable depending on the ratio of $\sigma_e/\sigma_g$. $\sigma_e/\sigma_g < 1$ indicates the saturated absorption and $\sigma_e/\sigma_g > 1$ defines the reverse saturated absorption. $\sigma_e/\sigma_g = 5.5$ is obtained by fitting the experimental data in Fig. 5 and the reverse saturated absorption has been observed. The observed reverse saturated absorption is consistent with dynamic analysis, where the excited state cross-section is larger at excitation wavelength of 584 nm than that of the ground state.

Most interesting parameters of $\sigma_{SE}$ and $\sigma_{TE}$, representing the absorption transition of the upper singlet and triplet excited states, can be quantitatively investigated in the upconverted processes. The upconverted luminescence intensity of $I_{up}$ in the steady-state condition can be expressed to be

$$I_{up} = \left(\frac{I/I_{SA}}{1 + I/I_{SA}}\right)[1 + (\sigma_{TE}/\sigma_g)(I/I_{SA})]/(\tau_T/\tau_S)]. \tag{2}$$

$\sigma_{TE}$ is the absorption cross-section of the excited triplet state. The important parameters of $\sigma_{TE}$ may be abstracted from expression (2), which explicitly defines the relationship between the upconverted emission and the incident excitation intensity. Furthermore, the absorption cross-section $\sigma_{SE}$ for the excited singlet state can be
estimated similarly to $\sigma_{TE}$. Expression (2) is used to fit experimental data for obtaining value of $\sigma_{SE}$ and $\sigma_{SE}$. $\sigma_{S}$ is derived from the linear absorption spectrum, for example, $\sigma_{S} = 9.5 \times 10^{-18}$ cm$^2$ for ZnTPPS gels. $\sigma_{SE} = 5 \times 10^{-17}$ cm$^2$ mol$^{-1}$ and $\sigma_{TE} = 7.4 \times 10^{-17}$ cm$^2$ mol$^{-1}$ are obtained for ZnTPPS-doped gels in the data fitting in Fig. 6.

The transmittance decrease vs elevated excitation indicates the absorption enhancement as shown in Fig. 5. The absorption increase can be attributed to the absorption coming from the higher excited states, which induces the energy band population in the higher excited state and accordingly results in the radiative emission (referred to the upconverted luminescence) through the transition from the higher excited bands to the ground state. As a consequence, the intensity of the upconverted emission would be expected to proportionally increase as a function of excitation intensity. This is not consistent with the experimental observation.

The rapid increase and saturation of the upconverted emission intensity is found in the range of low and intermediate pump intensity as shown in Fig. 6. The heavy saturation of the $S_1$ band at higher excitation fluences may lead to the upconverted luminescence saturation of the higher excited states. In addition, the effect of the intersystem crossing between the singlet state $S_1$ and the triplet state $T_1$ on the upconverted emission should be taken into account throughout the excitation processes. In particular, the overlapping and coupling of the wavefunction of $d$-electron from transition metals and $\pi$-electron state from porphyrin skeleton would strengthen the intersystem crossing interaction and consequently lead to the enhancement of the electron transfer rate in the intersystem crossing. These may result in the saturation of the upconverted emission.

5. SUMMARY

Based on the investigation of linear and nonlinear optical properties in aluminosilicate sol-gel materials containing the sodium salt metalloporphyrins of ZnTPPS, we conclude that metalloporphyrins embedded in solid gels are a kind of competitive materials for optical limiting. Chromophore of ZnTPPS exhibiting the reverse saturation absorption plays an important role in the nonlinear optical absorption or the optical limiting. The stronger absorption of the higher excited states leads to both the reverse saturation absorption and the radiative upconversion. The upconverted luminescence results from the second excited singlet state of $S_2 \rightarrow S_0$, which also provides an evidence for the excited state absorption.

Acknowledgements—The authors would like to thank Dr. L. Mathews, D. Arbuthnot and R. Shelton for their helpful discussions and technical assistance. This work was supported by the National Science Foundation and the Office of Naval Research.

REFERENCES