

SPECTROSCOPIC DETERMINATION OF
METAL IONS USING A PORHYRIN
DOPED SOL-GEL DERIVED
SOLID STATE HOST

By

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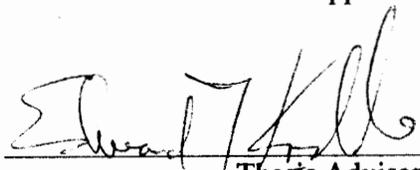
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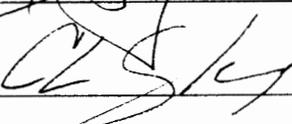
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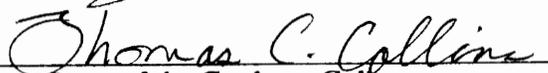
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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
I.A. Objectives and Thesis Overview.....	1
I.B. Background	2
I.C. Summary of Sol-Gel Science	6
I.D. Porphyrins	7
I.D.1. Optical Spectroscopy of Porphyrins	8
I.D.2. Optical Spectroscopy of Metalloporphyrins	9
I.E. Conclusions Based on Literature.....	12
I.F. Bibliography	12
II. SOL-GEL DERIVED SENSOR MATERIALS FOR USE IN AQUEOUS TRANSITION METAL ION DETECTION	14
II.A, Background.....	14
II.B. Experimental Methods and Procedures	14
II.C. Discussion of Results.....	17
II.C.1. Bulk Monolith Studies	17
II.C.2. Thin Film Studies.....	20
II.D. Summary and Conclusions	22
II.E. Bibliography.....	23
III. CONTINUOUS AND TIME RESOLVED LUMINESCENCE SPECTROSCOPY OF SULFONATOPORPHYRIN DOPANTS IN SOL-GEL HOSTS	24
III.A. Introduction	24

III.B. Experimental Methods and Procedures	25
III.C. Discussion of Results.....	26
III.D. Summary	30
III.E. Bibliography	31
IV. MULTIPHOTON SPECTROSCOPY IN METALLOPORPHYRIN- DOPED GELS	32
IV.A. Introduction	32
IV.B. Experimental	33
IV.C. Discussion of Results	34
IV.C.1. Nonlinear Absorption.....	34
IV.C.2. Up-Converted Luminescence	35
IV.D. Summary and Conclusions.....	38
IV.E. Bibliography	39
V. SUGGESTIONS FOR ADDITIONAL STUDY.....	40

LIST OF FIGURES AND TABLES

Figure/Table	Page
1.1. Hydrolysis and Condensation of Tetramethoxysilane	6
1.2. Structure of TPPS and MeTPPS.....	8
1.3. Energy Level Diagram for TPPS	9
1.4. Energy Level Diagram for TPPS and MeTPPS	10
1.5. Energy Level Diagram for CuTPPS.....	11
2.1. Emission Spectrum of TPPS Doped Aluminosilicate Bulk Sample	18
2.2. Excitation Spectrum of TPPS Doped Aluminosilicate Bulk Sample.....	19
2.3. Transduction Behavior of TPPS Doped Bulk Sample	20
2.4. Emission Spectrum of TPPS Doped Thin Film	21
2.5. Excitation Spectrum of TPPS Doped Thin Film.....	21
3.1. Schematic Setup for Time Resolved Measurements.....	26
3.2. Emission Spectra for TPPS, CdTPPS and ZnTPPS	27
3.3. Radiative Decay Curves for ZnTPPS and CdTPPS	29
3.4. Radiative Decay Curve for TPPS.....	29
T.4.1. Concentrations for CuTPPS Doped Samples.....	33
4.1. Nonlinear Absorption in CuTPPS Doped Aluminosilicate Gels	36
4.2. Up-Converted Luminescence of CuTPPS Doped Aluminosilicate Gels	38

CHAPTER I

INTRODUCTION

I.A. OBJECTIVES AND THESIS OVERVIEW

Among the main objectives of this research is the development of a material suitable for quantification of aqueous transition metal ions in ground water and surface water environments. Preliminary research findings toward this ultimate goal are presented herein. Studies of a water soluble metal chelating species doped into a sol-gel derived aluminosilicate host are presented in the following chapters. Chapter 2 focuses on the luminescent behavior of a water soluble porphyrin and the zinc analog of the porphyrin in an aluminosilicate host. The work presented in Chapter 2 includes the transduction behavior (in this case, transduction is associated with detection by studying perturbations induced by analyte species) of dye doped bulk monolith and thin film samples.

Chapter 3 describes continuous and time-resolved luminescence spectroscopy of the water soluble porphyrin metal chelate and the zinc and cadmium adducts of the porphyrin. The work done in Chapters 3 and 4 is associated with more specific methods for the determination of particular transition metal complexes. Nonlinear optical techniques including nonlinear absorption and up-converted luminescence were used to characterize an aluminosilicate doped with the copper porphyrin. Those results are reported in Chapter 4.

I.B. Background

Organic dyes (organic molecules which absorb visible light) are of interest for use in remote chemical sensor applications because they possess large absorption and emission cross sections, which permit enhanced signal to noise ratios to be obtained during spectroscopic measurements. In addition, organic chromophores are particularly sensitive to ambient conditions due to their conjugated π -electron systems, which are largely unshielded and therefore easily perturbed by their local surroundings. Thus, small fluctuations in parameters such as oxygen concentration, pH, temperature, or metal ion activities can result in measurable variations of the absorption and/or luminescence characteristics of select probe dye molecules.¹⁻⁴ A recent publication by K. Wang and coworkers, for example, has shown that the organic dye molecule, 4-(2-pyridylazo)resorcinol, can be used in opto-chemical transducer probes for the quantification of various analytes, including aqueous Zn^{2+} , through the observation of changes in optical absorption behavior.⁵

Various researchers have investigated the preparation of optical probe devices based on organic dye dopants in dielectric host media.¹⁻⁴ A dielectric material has a wide band gap which allows for transmission of light over the visible spectrum, thereby allowing visible light to interact with dopant probe molecules without host matrix-induced optical absorption losses. Presently, the matrix which is used to support the organic probe molecules remains a problematic issue. When considering the use of a host for chemical sensor applications, it is (a) desirable to maintain good mechanical and chemical stability while (b) realizing high transparency over the wavelength range(s) of interest and (c) simultaneously achieving rapid mass transport of analyte species. The general approach which has been utilized involves the entrapment of dye molecules within organic polymer host matrices such as silicone, polymethyl methacrylate, polyvinyl chloride or polyvinyl alcohol.³⁻⁶ Rigid organic polymers, however, tend to

have slow diffusive transport properties, due to their nonporous nature. In addition, chromophoric compounds tend to exhibit poor photostability characteristics in organic polymer matrices due to the very high chemical reactivities possessed by organic dye molecules when optically pumped to excited states.⁷ Energetically excited dye species often photodecompose when in intimate physical contact with the types of chemical functionalities that are typically found in organic polymer matrices. Thus, stable dielectric hosts having improved compatibility with organic dye molecules are of much interest for the development of sensor materials.

Sol-gel derived hosts, as a result of their inorganic nature, are substantially more chemically inert than transparent, rigid organic polymer hosts.⁸ These materials are prepared at low temperatures (typically room temperature), as opposed to conventional glasses which are prepared from high temperature melts, thus allowing incorporation of organic dye molecules without destroying the organic species. Various research groups have recently demonstrated that organic laser dyes exhibit photostability characteristics which are orders of magnitude larger in sol-gel host media than in organic polymer hosts.⁹⁻¹¹ Research performed by Gromov *et al.* pertaining to the photodegradation of modified polymethyl methacrylate doped with rhodamine 6G, for example, showed photobleaching (due to decomposition of the dye) after 180 pulses using excitation at 532 nm.¹² Knobbe *et al.* reported research performed on an organically modified silicate system (ORMOSIL) doped with rhodamine 6G. These sol-gel derived media showed greatly improved photostability characteristics with respect to comparable organic polymer hosts. Laser oscillation was reported to continue after more than 3000 excitation pulses upon excitation at 525 nm.⁹

Sol-gel derived aluminosilicate host materials have received considerable attention as solid state host materials for various applications.¹³⁻¹⁶ Pouxviel *et al.* presented research involving di-secbutoxyaluminumoxytriethoxysilane sol-gel precursor.¹³ Using 8-hydroxy-1,3,10-trisulfonato pyrene (pyranine) as a pH indicator, Pouxviel has

shown that hydrolysis and subsequent polycondensation of di-secbutoxyaluminoxy-triethoxysilane proceeds under near neutral pH conditions. The lack of leaching behavior of the dopant from aged areogels or dried xerogels was demonstrated, thus showing that the dye molecules are entrapped or chemically bound to the matrix. Pyranine is known to be triply ionized (three SO_3^- groups) under neutral pH conditions. Thus, there is the possibility that the molecules are electrostatically bound to the inorganic network, which typically contains a large number of polar species such as Al-OH groups. However, the absence of a pronounced shift in either the absorption or the emission spectra during the sol-to-gel transformation indicates that it is unlikely that there is any significant bonding between pyranine and the host network.

The sol-to-gel transformation of aluminosilicates has been widely investigated.¹⁴ Upon addition of water to the precursor, the alkoxy groups attached to the aluminum atoms are rapidly hydrolyzed.¹⁴ The resulting Al-OH groups keep the sol at the neutral pH value. Al²⁷ NMR showed that polymerization is primarily due to the formation of Al-O-Al linkages, first involving tetrahedrally coordinated aluminum species and later octahedrally coordinating to siloxane and other aluminum species, leading to a three dimensional particle growth.

One of the key issues involved in the development of sensor materials is one of probe response time. Optode (term commonly used to denote the optical equivalent of an electrode) response time is a function, at least in part, of analyte transport rates into the active region of the sensor. The controllable pore morphology of sol-gel derived materials offers a mechanism by which rapid mass transport of small molecules and ions through the solid state medium can be facilitated, while the larger probe species remain entrapped inside the cage-like network structure. Pore size and pore size distribution has been extensively studied for a variety of sol-gel preparative methods.¹³ Yamane and Okano¹⁷ have shown that by varying only the temperature of gellation of identically prepared samples the porosity of samples prepared from tetramethoxysilane were 30.5

and 51.7%. These porosities were measured for samples dried at 54 and 70 °C, respectively, for the samples.

Probe response time may also be affected by interaction between the analyte under study and the host matrix. A recent publication by Liu *et al.* presents adsorption behavior of cadmium and zinc metal ions on silica and alumina particles as a function of ionic concentration at 25 °C and pH 6-6.5.¹⁸ 1.89×10^{-10} mol/cm² Cd²⁺ was adsorbed from a 4.66×10^{-3} M Cd²⁺ aqueous solution onto Al₂O₃ particles, and 2.86×10^{-10} mol/cm² Zn²⁺ was similarly adsorbed from a 4.49×10^{-3} M solution. In the case of SiO₂, 9.28×10^{-11} mol/cm² Cd²⁺ was adsorbed from a 6.5×10^{-4} aqueous solution of cadmium and 1.36×10^{-10} mol/cm² Zn²⁺ was adsorbed from a 7.81×10^{-4} M solution of zinc. These results indicate that limited interaction occurs between zinc and cadmium ions on either alumina or silica surfaces. Studies to determine the number of active hydroxyl groups on the surfaces of the alumina and silica particles were not presented.

The sol-gel preparative method has proven to be an effective means by which to incorporate a variety of water and/or alcohol soluble species into an inert, porous, solid state host.⁹⁻¹⁸ These inherent characteristics may ultimately prove to be advantageous in the development of a remote fiber-optic based sensor. Previous investigations have shown that chromophore-doped silica gels may be used to detect changes in pH by observing luminescence perturbation of pyranine.¹⁵ More recently, Avnir and coworkers included a variety of organic guest species (none of which were porphyrin molecules) doped into sol-gel glasses; they were able to detect changes in absorption spectra for a variety of analytes, including Fe²⁺, Al³⁺, Cu²⁺ and Ni²⁺.²⁰ Sol-gel derived media have been investigated for the purpose of developing optically interrogated sensors. The research described in this thesis involves the incorporation of a new probe molecule (from the porphyrin class) incorporated into porous oxide hosts. Classical (continuous wave and luminescence) and highly novel (time-resolved luminescence, multiphoton

absorption and up-converted photoluminescence) optical characterization methods have been utilized.

I.C. Summary of Sol-Gel Science

The Introduction section of this chapter presented properties of sol-gel derived materials (controllable pore morphology, entrapment of dye molecules, and inertness with respect to the entrapped dye molecules) which show the applicability of sol-gel derived materials for use as an opto-chemical probe host.⁹⁻¹⁸ These properties are a function of the reaction conditions and subsequent treatment of the gels. Solid state media are achieved through a two step reaction which involves the hydrolysis of an alkoxide precursor, such as tetramethoxysilane, followed by polycondensation. In the case of tetraalkoxysilanes, siloxane chains are formed by the elimination of alcohol and water (Figure 1.1). Pore morphology may be controlled by various methods during either the hydrolysis or condensation. Such methods include addition of either water or an appropriate alcohol before hydrolysis, control of temperature during condensation (gellation) and/or addition of catalysts.^{13,17}

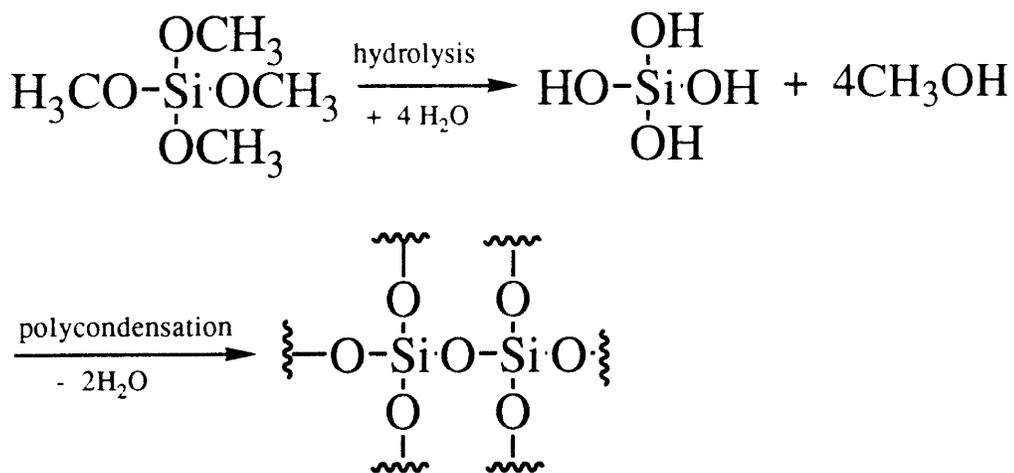


Figure 1.1. Hydrolysis and condensation of tetramethoxysilane.

I.D. Porphyrins

The family of porphyrin molecules lend themselves for use as "luminoionophoric" probe molecules (molecules whose luminescence behavior depends upon the activity of various ionic species), as the high degree of molecular conjugation in this family gives rise to intense absorption and, frequently, luminescent emission peaks. Porphyrin molecules, such as tetra(4-sulfonatophenyl)porphyrin (TPPS), are promising candidates for use in a transition metal ion optode. These conjugated compounds (see Figure 1.2) are well known for their luminescence behavior under blue-green excitation.¹⁹⁻²⁰ This conjugated π -electron structure incorporates four nitrogen atoms through the constituent heterocyclic rings. For the purpose of this work, the salient feature of the porphyrins involves the four-fold ensemble of heterocyclic nitrogen atoms which are capable of forming tetradentate complexes with aqueous transition metal ions. This is especially true of divalent species such as zinc, cadmium and copper. Complex formation with appropriate metal ion species is accompanied by perturbations to the conjugated porphyrin π -electron system and to the overall molecular symmetry. These changes are, in general, readily detected by spectroscopic methods. This assessment has been verified by a substantial amount of research performed in the area of luminescence spectroscopy of porphyrin and analogous metal-porphyrin complexes.¹⁹⁻²⁰ The bound metal ion may exist either in the ligand plane, resulting in a D_{4h} site symmetry (as opposed to the D_{2h} symmetry of a free porphyrin), or out of the heterocyclic molecular plane, thereby yielding a complex possessing C_{4v} symmetry. Perturbations to the luminescence spectra, as a function of complex formation, are attributed to various effects including (1) a change in the molecular symmetry of TPPS from D_{2h} to D_{4h} or C_{4v} , (2) changes to the radiative relaxation manifold due to vibrational effects associated with the heavy metal ion, and (3) the formation of metal-ligand charge transfer bands, especially when metal ion d orbitals are available for bonding with the ligand.

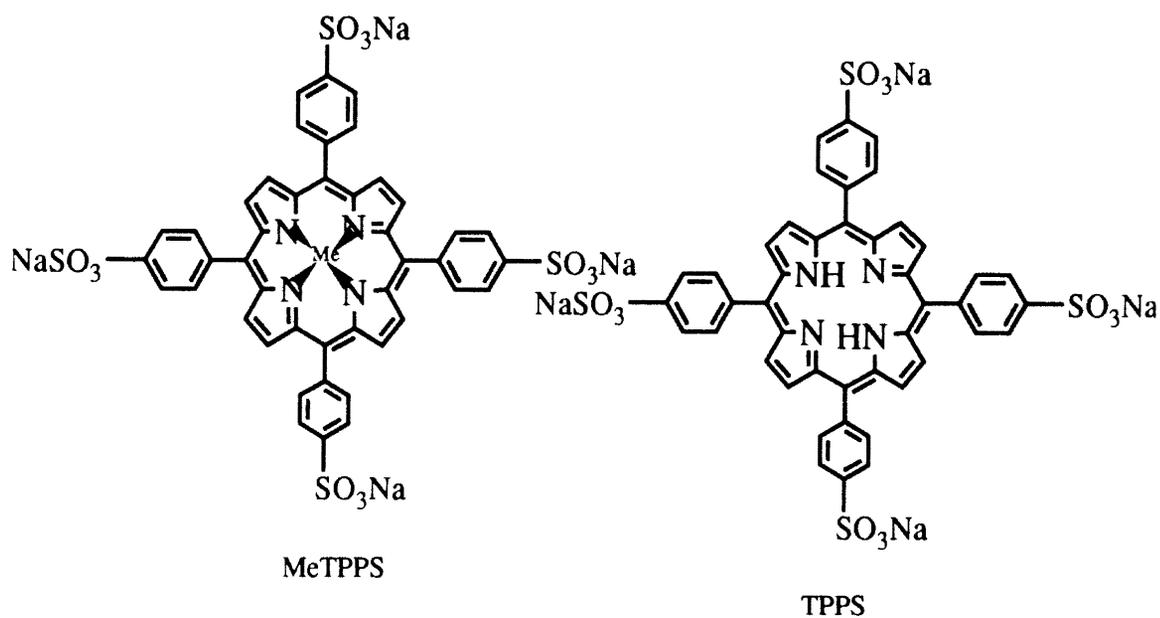


Figure 1.2. Structure of a representative metal complex of TPPS and TPPS.

I.D.1. Optical Spectroscopy of Porphyrins

Luminescence effects in the porphyrin family arise from two distinct excitation bands typically referred to as the Q- and B- (or Soret) bands. The Q-band is the first excited singlet state while the B band corresponds to the second excited singlet level (see Figure 1.3). This nomenclature was first introduced by Platt.²² In this nomenclature, B implies a strongly allowed transition and Q a quasi-allowed transition. Free porphyrin molecules, such as TPPS (Figure 1.2), typically possess a pair of Q and a pair of B sub-bands¹⁹, which arise due to splitting of these singlet states as a function of the D_{2h} molecular symmetry. The Q-band splitting results in the so-called Q_x and Q_y sub-bands, as indicated in Figure 1.3. Thus, porphyrin species usually exhibit a characteristic four-band series of visible wavelength absorption peaks due to the splitting of these states. Direct excitation of the Q_y level leads to very fast radiationless decay to the lower Q_x level. Radiative relaxation may occur from the Q_x level to one of the vibrational levels of

the ground state (S_0). Free porphyrin molecules typically have two emission bands. The first results from relaxation from the Q_x level to the lowest vibrational ground state level, denoted $Q_x(0,0)$. The second peak results from relaxation out of the bottom of the Q_x state to a higher lying vibrational state in S_0 which is associated with a single phonon vibrational relaxation mode. This event is typically denoted as the $Q_x(0,1)$ emission peak.

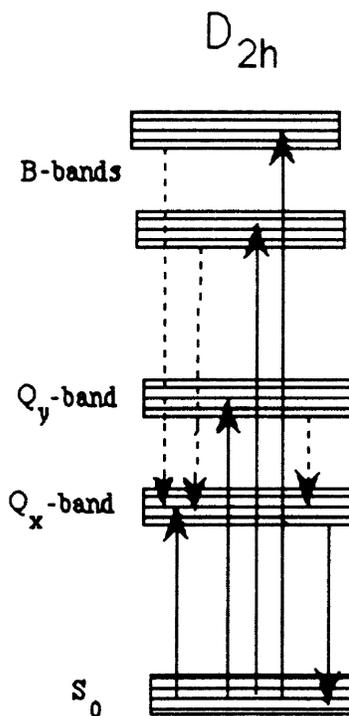


Figure 1.3. Energy level diagram for a TPPS.

I.D.2. Optical Spectroscopy of Metalloporphyrins

Upon complex formation with small ions, molecular symmetry is generally raised to D_{4h} , which is a configurational symmetry that is not associated with singlet state splitting (Figure 1.4); thus, the absorption and luminescence spectra of D_{4h} complexes tend to be distinctly different from the D_{2h} parent. Metalloporphyrins tend to exhibit a two-band absorption spectrum (rather than four-band spectra associated with the separate

sub-bands). Like the free parent porphyrin, Q-level (first excited singlet) excitation of a metalloporphyrin complex is generally associated with twin emission peaks; Q(0,0), emission related to emission from the first excited singlet to the ground state, and Q(0,1), related to emission from the vibronically excited first excited singlet to the ground state. In the case of radiative relaxation out of the first excited singlet state, metalloporphyrin complex emission bands are generally higher in energy, due to the lack of Q-band splitting.

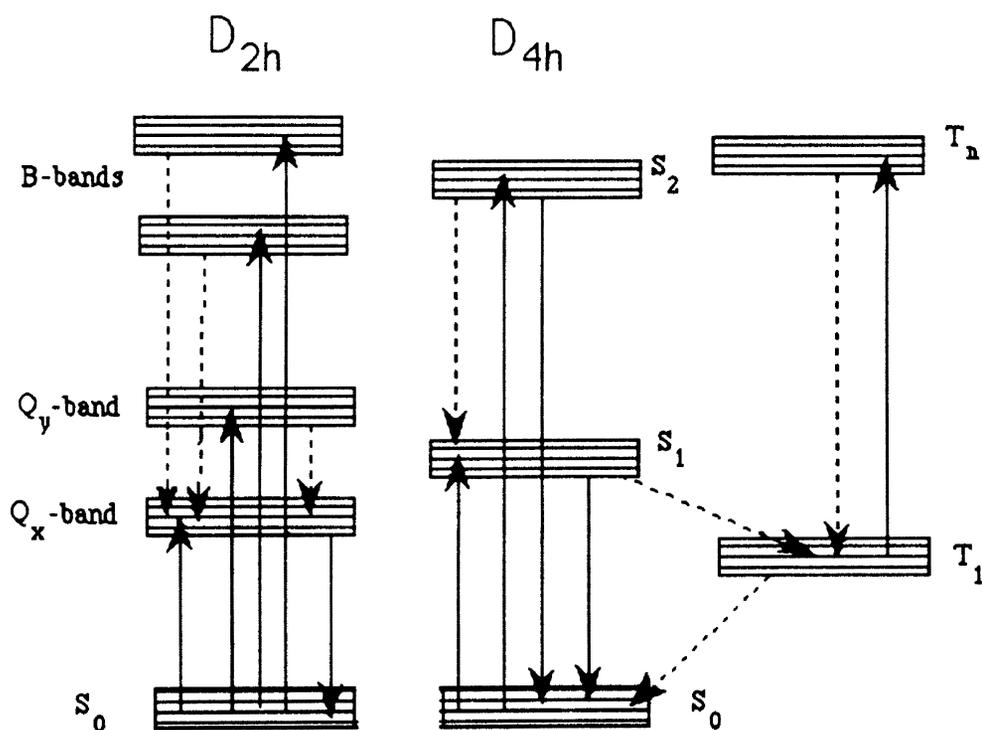


Figure 1.4. Energy level diagram for TPPS and metal complex of TPPS.

When complexed to a metal containing an unpaired d electron, such as Cu(II), the singlet excited states of the system become doublets (called singdoublets) while the triplet excited states become doublets, quartets and sextets (called tripdoublets, tripquartets and tripsextets, respectively) (see Figure 1.5, the tripquartet and tripsextet states have been combined into a single 4T_1 manifold for simplicity). The tripdoublets and singdoublets have been combined in the indicated doublet (D_i) manifold as

conventionally done, for simplicity.²¹ Excitation from the ground state (D_0) to the tripdouplet states is highly forbidden due to spin-related selection rules: thus, only the singdouplet states effectively participate in absorption and luminescence phenomena of metalloporphyrin compounds. Similarly, transitions into the tripsextet states are highly forbidden and can be disregarded in most cases. Only the singdouplet and tripquartet (4T_i) manifolds need to be considered in most instances, unless very high resolution optical spectroscopy (such as the observation of Stark-splitting) is being performed. However, emission from 4T_i levels is spin forbidden, and is typically not observed at temperatures $> 77\text{K}$.

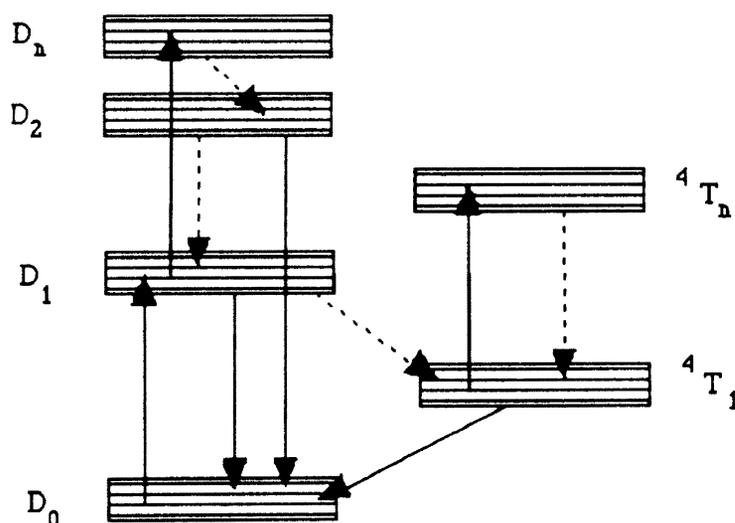


Figure 1.5. Energy diagram for TPPS complexed with a metal containing one odd electron.

In both the free porphyrin and metalloporphyrin complexes, intersystem crossing out of the singlet manifold leads to population of the triplet manifold. The probability of intersystem crossing and vibronically-coupled relaxation events are known to be greatly enhanced by the presence of heavy metal ions.²²⁻²³ Thus, the formation of metal ion complexes by porphyrin probe molecules is usually accompanied by dramatic perturbations to absorption and luminescence characteristics. The focus of the present

work involves the study of metal ion complex-induced perturbation effects in porphyrin-doped sol-gel materials.

I.E. Conclusions Based on Literature

As previously stated, optical transitions of porphyrin molecules in solution have been extensively studied; little, however, is known about their properties in solid state oxide hosts. The sol-gel preparative method provides a route by which these organic chromophores may be incorporated into such a host system. We have selected a solubilized porphyrin analog, the sodium salt of tetra-4-sulfonatophenylporphyrin (TPPS), for study in an aluminosilicate sol-gel host. The inherent properties of porphyrin molecules makes them an ideal candidate for use as an optical probe molecule for optode materials.

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CHAPTER II

SOL-GEL DERIVED SENSOR MATERIALS FOR USE IN AQUEOUS TRANSITION METAL ION DETECTION

II.A. Background

The approach under investigation involves the preparation of porous films which are sensitized to one or more analyte species by the entrapment of organic probe molecules. The work described herein is associated with the preliminary investigation of an opto-chemical probe material whose luminescence and absorption behavior vary as a function of aqueous Zn^{2+} activity. Early sections of this chapter involve TPPS and zinc(II)-TPPS metalorganic complex (ZnTPPS) species that have been doped into solid state aluminosilicate hosts to compare the metal complex to the parent porphyrin in the solid state host. Differences between emission and excitation spectra of the two entrapped species are described. Later sections include optode characterization studies, including the observation of Zn-complex formation in TPPS-doped gels upon exposure to an aqueous Zn(II) solution (as determined by luminescence spectroscopy). Preliminary results indicate that optode materials of this type may be developed for the purpose of continuous, real time monitoring of specific analyte species in aqueous environments.

II.B. Experimental Methods and Procedures

Metalloporphyrin complexes are known to decompose into a mixture of complexed neutral and dissociated ionic species under mildly acidic conditions, especially in the case of large or weakly-bound metal ions.¹⁻² Thus, an aluminosilicate

host was chosen for study because polymerization from the metal alkoxide precursor proceeds at room temperature under neutral pH conditions.

Aluminosilicate sols were prepared by the method described by Pouxviel and coworkers³. A 9 ml volume of di-sec-butoxyaluminumoxytriethoxysilane (used as received from Hüls) was diluted with 9 ml of isopropyl alcohol in a polyethylene beaker. Isopropanol is a mutual solvent for the organometallic precursor and water and also serves as a diluent such that the rates of hydrolysis and condensation of the reactive aluminoxy group are slowed. A solution containing 2 ml of deionized water and 9 ml of isopropyl alcohol (reagent grade purchased from Fisher Scientific and used without further purification) was slowly added at room temperature, in a dropwise fashion, to the aluminosilicate solution in a polyethylene beaker with vigorous stirring. The total volumetric water : isopropanol : aluminosilicate ratios were 2:18:9. Thus, the molar ratio of the aluminosilicate alkoxide to water was 4.4:1. Hydrolysis was allowed to proceed at room temperature for approximately one hour. After the initial hydrolysis period, TPPS and ZnTPPS (purchased from Midcentury Chemicals and used without further purification) dopants were separately dissolved directly into the aluminosilicate sol such that the porphyrin dopant concentration in the aluminosilicate sol was 0.1 mM.

Bulk gel samples were prepared by casting 1.75 ml of the sol into semimicro polystyrene cuvettes (4.5 cm x .3 cm x 1.0 cm), which were subsequently covered with parafilm. Gellation was observed to occur, at room temperature, over a period of approximately three days. Two perforations (using pencil lead) were made in the parafilm upon gellation. These perforations were very gradually enlarged over a period of two weeks until the smell of isopropanol was no longer detected. Subsequently, the parafilm covering was removed. The dried xerogel monoliths had final dimensions of approximately 17 × 2 × 4 mm and a calculated dopant number density of $4.7 \times 10^{18} \text{ cm}^{-3}$. This calculation was performed by multiplying the initial concentration ($1 \times 10^{-4} \text{ M}$) by Avogadro's number ($6.02 \times 10^{23} \text{ molecules/mol}$) to give the number of molecules per

volume in each sample. This result was multiplied by the shrinkage factor (the final volume of the xerogel divided by the initial volume of the sol in each cuvet).

Thin film preparation involved the use of a dip-coating apparatus (designed and built with assistance from the Physics and Chemistry Instrument Shop). The previously described porphyrin-doped aluminosilicate sol, diluted by a 3:1 volume ratio of isopropanol to the hydrolyzed sol, was used to dipcoat borosilicate glass microscope slides which had been previously cleaned with Palmolive dishwashing detergent and dried with acetone. The slides were withdrawn from the diluted sol at a rate of 16 cm/min. This rate was found to provide the most stable film structure. Samples were placed into a 250 ml polyethylene beaker and covered with a petri dish. The thin films were allowed to dry overnight under ambient conditions. Atomic force microscopy (AFM) studies performed by Park Scientific Laboratories showed that the thin film samples prepared in this manner had a thickness of 0.8 nm.

Emission and excitation spectra of the bulk samples were measured using a Spex model F112A spectrofluorimeter; all spectra were corrected using Spex's Mcorrect and Xcorrect software files.

Opto-chemical transduction behavior of TPPS-doped aluminosilicate gels was studied by placing deionized water-saturated gel samples into a 2 mM solution of ZnCl₂ which had been dissolved into deionized water and maintained in a polystyrene cuvet. The time evolution of changes in the luminescence behavior of the entrapped probe molecules was spectroscopically determined. Thin film luminescence measurements were performed by placing the glass slide in a quartz cuvet with a diffuse scattering surface mounted immediately behind the slide at 180 degrees to the beam in order to reflect transmitted light excitation back into the sample. Bulk samples were measured in the front face configuration, while thin film measurements were obtained in the right angle configuration of the spectrofluorimeter.

II.C. Discussion of Results

II.C.1. Bulk Monolith Studies

The room temperature emission spectra of TPPS and ZnTPPS dopants, incorporated into sol-gel derived aluminosilicate hosts, are shown in Figure 2.1; the excitation wavelength, λ_{ex} , was 430 nm. It can be seen that the ZnTPPS complex has two easily resolvable emission bands centered at 605 and 650 nm. The two emission peaks have been associated, respectively, with relaxation from the porphyrin Q-band to a ground state, denoted Q(0,0), and one mode of vibrational emission from the Q-band, Q(0,1). In the case of the TPPS parent species, the D_{4h} symmetry of the metal complexed porphyrin ring has been lowered to D_{2h} , resulting in the splitting of Q-band into Q_x - and Q_y -bands (see Chapter 1).⁴ The excitation of Q_y (higher energy level of the Q-band sub-splittings) leads to very fast radiationless decay to the lower level, Q_x . The emission peaks of TPPS at 650 and 718 nm are then attributed to the transitions of $Q_x(0,0)$ and its vibronic overtone $Q_x(0,1)$, respectively. The weak features around 600 and 660 nm (shoulder), which have similar emission to ZnTPPS, are postulated to be due to the presence of metal porphyrin impurities.

By fitting the two major peaks of the normalized spectra at Figure 2.1 for both TPPS and ZnTPPS, it is calculated that the ratio of intensity of Q(0,1) to Q(0,0) for ZnTPPS is increased by approximately 60% in comparison to the relative ratio of $Q_x(0,1)$ to $Q_x(0,0)$ for TPPS. This increase in the ratio of the vibrational mode to the nonvibrationally coupled mode indicates that the perturbation by the central metal (Zn) greatly enhances the vibronic coupling. As the vibrational mode becomes more accessible, increased emission from this state is observed, along with a concomitant decrease in the relative emission intensity associated with the 0→0 transition.

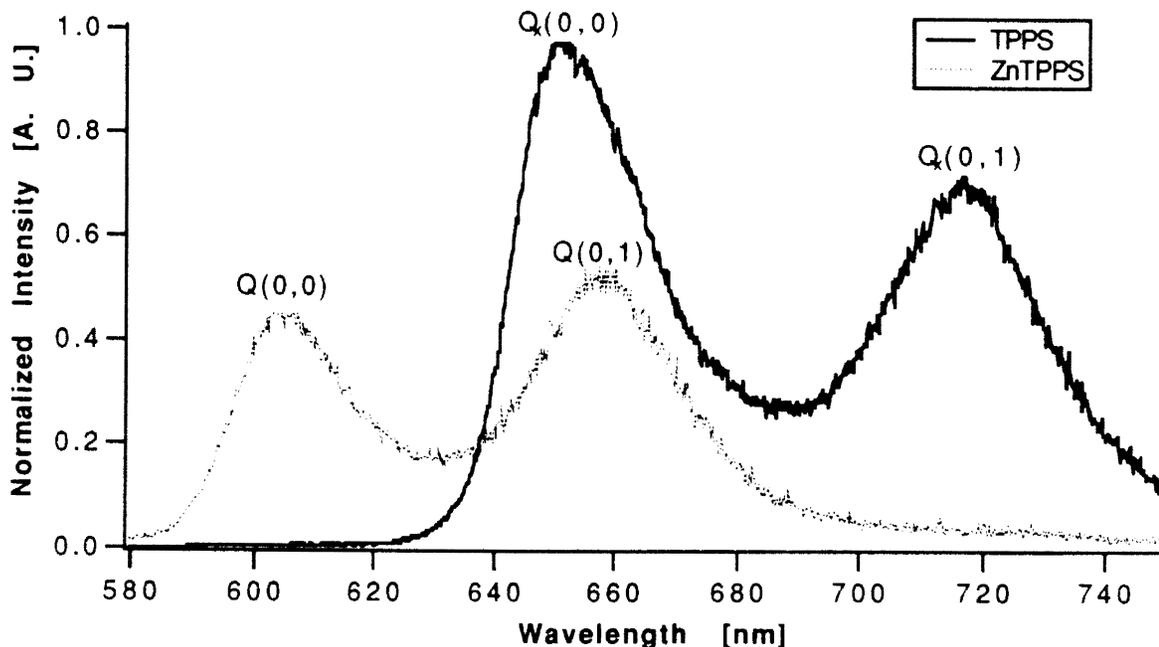


Figure 2.1. Emission Spectra of porphyrin doped aluminosilicate gels. $\lambda_{ex} = 430$ nm.

Room temperature excitation spectra of entrapped TPPS and ZnTPPS probes are shown in Figure 2.2; the emission wavelength, λ_{em} , was 648 nm. Although both samples possessed substantial emission intensity at 648 nm, it can be seen that the excitation mechanisms are distinctive, especially at lower photon energies. The TPPS- and ZnTPPS-doped samples exhibited similar band structure over the 350 to 450 nm wavelength range. This is the Soret absorption region, also known as the B-band (second excited singlet).⁴⁻⁵ Only the TPPS-doped aluminosilicate gel, however, was observed to exhibit an intense excitation via the Q-bands, with the primary excitation peaks located at 515 and 590 nm and distinguishable shoulders at 470, 505 and 545 nm.

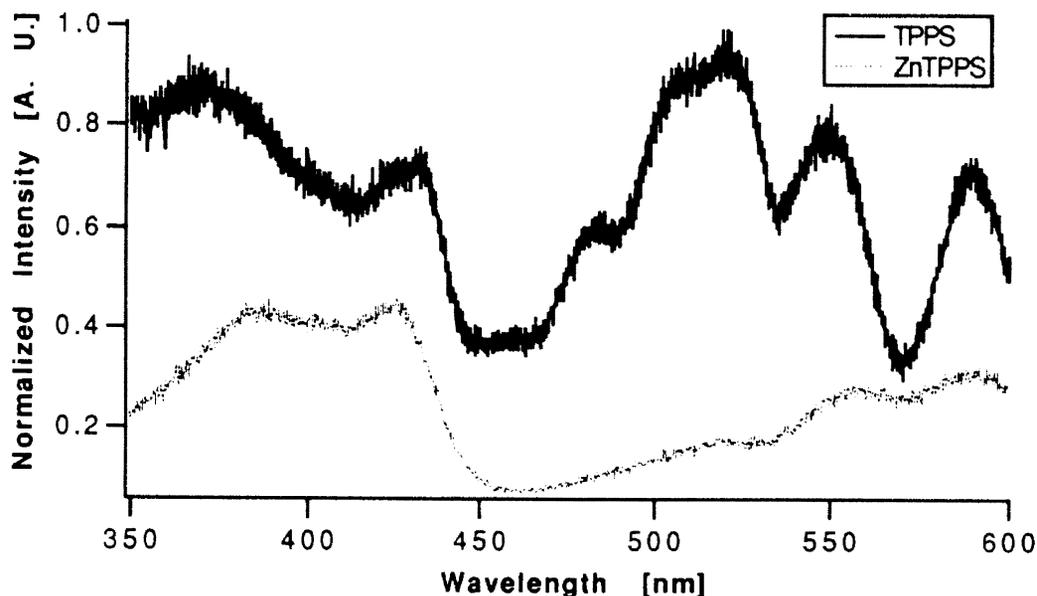


Figure 2.2. Excitation spectra of porphyrin-doped aluminosilicate gels. $\lambda_{em} = 648$ nm.

This behavior is again attributed to changes in absorption spectrum from a four-banded (D_{2h} -type) to a two-banded (D_{4h} -type) structure associated with the presence of the metal ion. Thus, it is possible to distinguish between the existence of TPPS and ZnTPPS species in ASE gels through the use of either excitation or emission spectroscopy.

Preliminary studies regarding the transduction behavior of TPPS-doped ASE gels were conducted. Upon placement of monolithic deionized water-saturated sensor samples into a 2 mM $Zn(II)_{aq}$ solution at a pH of 7 (containing no buffer), the emission and excitation spectra of the doped gel samples were observed to slowly evolve from those associated with the ion-free parent species to spectral features associated with ZnTPPS complex. The spectral data were acquired at room temperature. Figure 2.3 shows the excitation spectrum ($\lambda_{em} = 605$ nm) of a transducer sample upon introduction of the analyte solution (time = 0 hr) and at a time approximately 5 hours later (time = 5 hr); the spectrum had evolved to approximately 90% of the final curve shown after approximately 3 hours. The luminescence feature being studied is one associated with

the radiative relaxation from the ZnTPPS complex. Thus, there are essentially no excitation phenomena seen for this emission band at time = 0. The excitation bands present at time = 0 are postulated to be a result of minute quantities of metal-ligand complex due to the presence of inherent impurity ions. Later, however, substantial amounts of ZnTPPS complex are expected to have formed under the conditions used. Dramatic evidence of complexation is seen at time = 5 hours, as excitation phenomena associated with vibrationally-coupled radiative decay paths are readily observed.

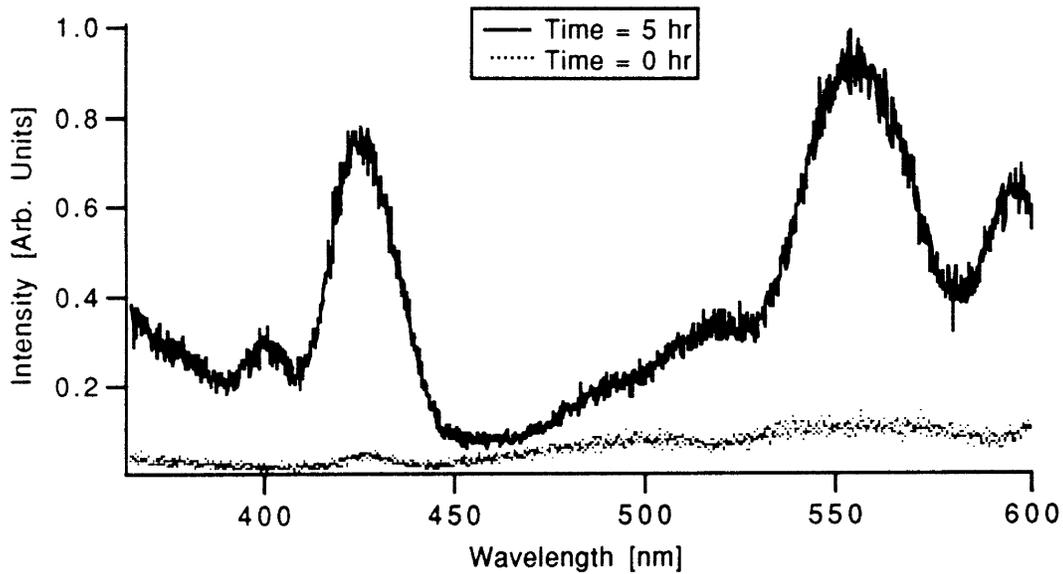


Figure 2.3. Transduction behavior of TPPS-doped aluminosilicate gel in the presence of $Zn(II)_{aq}$. Excitation spectra with $\lambda_{em} = 605$ nm.

II.C.2. Thin Film Studies

The room temperature emission spectra of the TPPS dopant in a sol-gel derived aluminosilicate thin film host is shown in Figure 2.4; the excitation wavelength, λ_{ex} , was 430 nm. The spectrum compares favorably with that observed in the bulk monolith sample. The room temperature excitation spectrum associated with an emission wavelength, λ_{em} , of 648 nm can be seen in Figure 2.5. Again, we see spectral features comparable to the doped bulk monolith. Collected intensities for the bulk and thin film

samples have not been compared due to the difference in experimental acquisition of the spectra (active volumes and collection geometry).

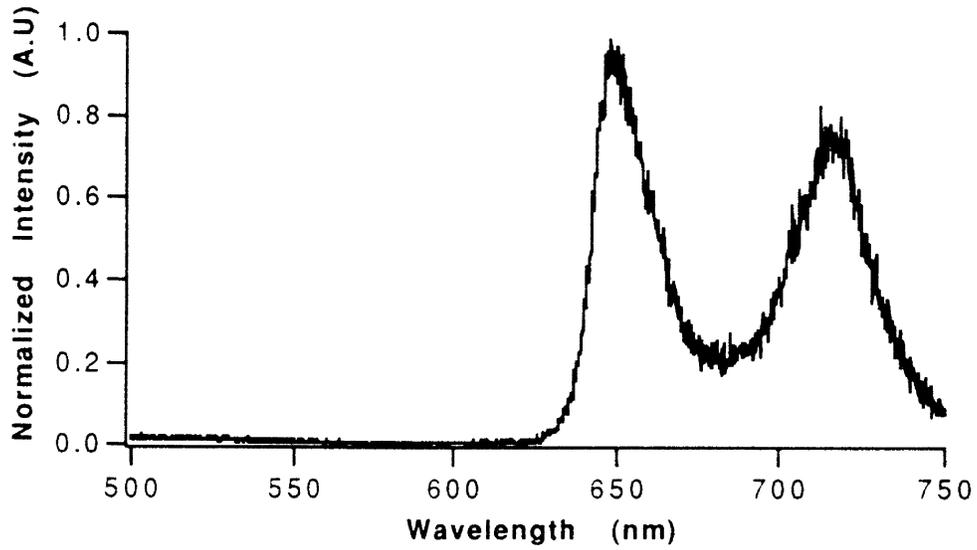


Figure 2.4. Emission spectrum of porphyrin doped aluminosilicate thin film.
 $\lambda_{ex} = 430$ nm.

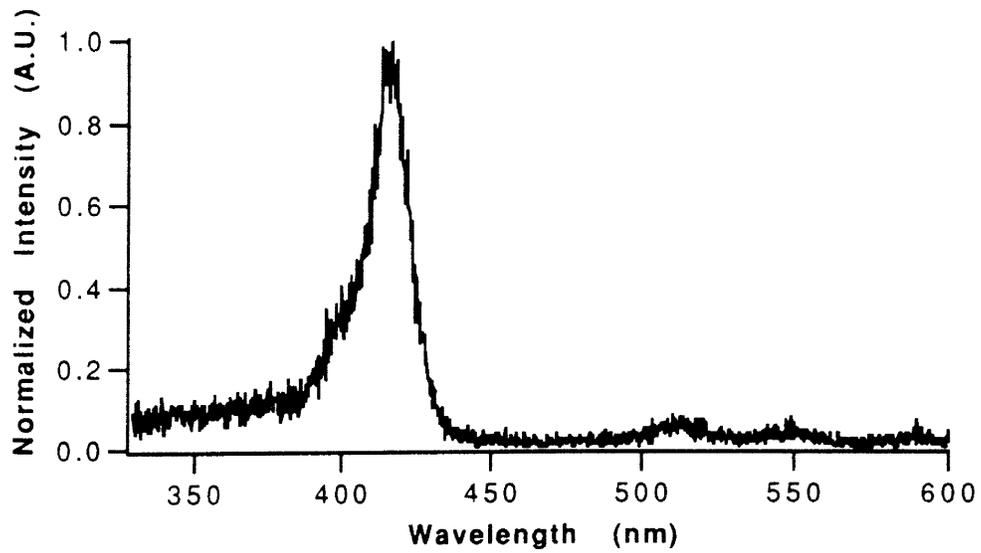


Figure 2.5. Excitation spectrum of porphyrin doped aluminosilicate thin film.
 $\lambda_{em} = 648$ nm.

The thin film was treated in the same manner as the bulk sample for the purpose of studying transducer characteristics. The film was placed into a 2 mM $\text{Zn(II)}_{\text{aq}}$ solution; emission and excitation spectra were monitored over a period of 24 hours. In the case of the thin films, no transduction behavior was observed.

The behavior of the thin films may be explained by the coherent forces in the deposited films. It is expected that bonding between the film and substrate for films 1 μm thick is large compared to the coherent forces in the film.⁶ In this case the film shrinks in a direction perpendicular to the substrate, resulting in the formation of dense films that bond firmly to the substrate. This yields comparatively nonporous films, a microstructure which severely limits the diffusion of ions through the film matrix.

II.D. Summary and Conclusions

It has been shown that TPPS, a luminescent member of the porphyrin family, may be doped into porous inorganic network matrices via sol-gel synthesis. TPPS-doped ASE xerogel materials were observed to maintain a substantial degree of the luminescence behavior commonly associated with TPPS in solution. It has also been shown that zinc-TPPS complexes display emission and excitation behavior in the ASE host matrix that are readily distinguished from the non-complexed parent species. The present work suggests that these species may be specifically identified in the solid state host by luminescence spectroscopy methods. Additional studies have shown TPPS-doped ASE gels behave as fluorescent opto-chemical transducer materials for the presence of $\text{Zn(II)}_{\text{aq}}$, although the monolithic test samples exhibited first order response times which are too long to be considered real time. Future research should be directed toward the investigation of mass transport properties of aqueous transition metal ion analytes through the porous inorganic thin film systems. In addition, kinetics of the metal-ligand and metal host complex formation should be studied under a variety of ambient conditions.

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CHAPTER III

Continuous and Time-Resolved Luminescence Spectroscopy of Sulfonatoporphyrin Dopants in Sol-Gel Hosts

III.A. Introduction

Previous studies have shown that complex formation between TPPS and zinc proceeds within the sol-gel host under aqueous conditions (Chapter 2). Perturbations to the excitation and emission spectra upon metal complexation were described in Chapter 2. The work presented in this chapter is associated with the investigation of changes in the radiative lifetime of TPPS as compared to its zinc (ZnTPPS) and cadmium (CdTPPS) complexes within sol-gel derived solid state hosts. Correlations between radiative lifetime shortening and the mass of the complexed ion, due to heavy ion effects, are presented.

Intersystem crossing leads to population of the triplet manifold (designated T_1 in Figure 1.4) in both the free porphyrin and metalloporphyrin complexes. Both intersystem crossing probabilities and vibronically-coupled relaxation events are known to be highly influenced by the presence of heavy metal ions. Thus, the formation of metal ion complexes by porphyrin probe molecules is usually accompanied by ion-specific perturbations to absorption and luminescence characteristics. The focus of the work described in this chapter involves the study of metal ion complex-induced perturbation effects in porphyrin-doped sol-gel materials.

III.B. Experimental

Bulk porphyrin-doped aluminosilicate sol-gel samples were prepared by the method discussed in Chapter 2. The dried specimens retained approximately 70% of their initial volume. Dopant number densities were calculated to be 6.7×10^{17} molecules/cm³.

Continuous wave emission spectra were determined using a Spex Industries model F112 spectrofluorimeter; spectra were corrected for instrument response. The excitation wavelength, λ_{ex} , was 540 nm.

Lifetime measurements were performed using a Hamamatsu picosecond photoluminescence lifetime spectroscopy system (streakscope head model C4334, 10 psec resolution, multi-pulse analysis mode). The luminescent signal was collected with a 200 mm focal length Chromex model CP-200 spectrometer. The Hamamatsu system was optically triggered using a fast photodiode (Thorlabs) and optical delay generator (Hamamatsu model number C1097). The excitation source used was a Lambda Physik LEXtra 200 excimer laser (with extended cavity, 10 ns pulse width oscillating at 308 nm) pumped Lambda Physik LPD 500 fs femtosecond dye laser system. This system yields tunable pulses having a nominal temporal pulsewidth of 500 fs. Coumarin 540A, dissolved into dimethylformamide, served as the gain medium in the distributed feedback dye laser (DFDL) stage. The laser was tuned to oscillate at 540 nm with a nominal output of 100 μ J per pulse. A schematic diagram of this apparatus is shown in Figure 3.

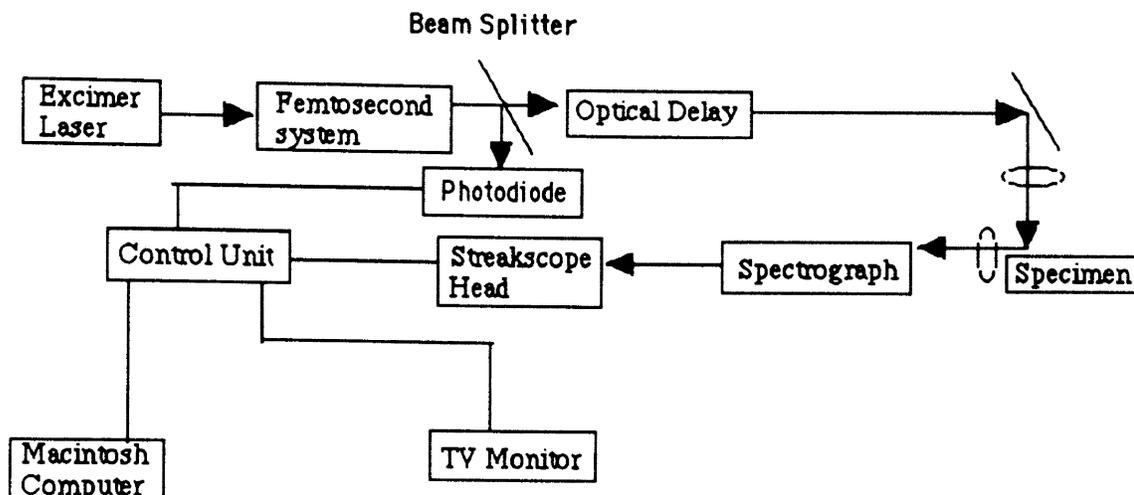


Figure 3.1. Schematic setup for time resolved measurements.

III.C. Discussion of Results

Continuous wave emission spectra of TPPS-, CdTPPS- and ZnTPPS-doped gels are indicated in Figure 3.2. The three spectra have been normalized with respect to the more intense 720 nm parent porphyrin emission band. It was found that substantial demetallation of the porphyrin occurred in the CdTPPS-doped specimen while drying, despite the use of the benign aluminosilicate processing conditions. Thus, a mixture of free TPPS and complexed CdTPPS were found to exist in this sample. A TPPS background "equivalent" was calculated, based on relative TPPS peak height intensities and was subtracted from the CdTPPS-doped gel emission spectrum in order to make the salient complex-related features more apparent.

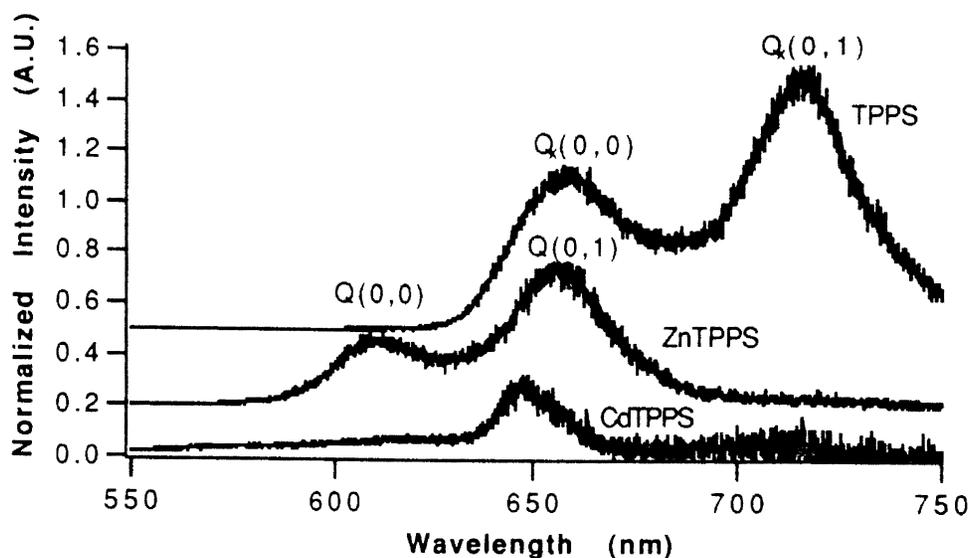


Figure 3.2. Emission spectra for TPPS, ZnTPPS and CdTPPS. $\lambda_{ex} = 540$ nm.

Radiative relaxation from the first excited singlet state of the porphyrin dopants is readily observed in these specimens. The two TPPS emission peaks correspond to the $Q_x(0,0)$ and $Q_x(0,1)$ radiative transitions centered at 655 and at 720 nm, respectively. The 605 and 650 nm emission bands observed for CdTPPS- and ZnTPPS-doped gels have been attributed to the $Q(0,0)$ and $Q(0,1)$ transitions, respectively. Significant quenching of the overall luminescence for the complexed species with respect to the parent molecule can be attributed, at least in part, to intersystem crossing from the singlet to the triplet manifold. This is a phenomenon which is promoted by the heavy metal effect which is a key feature of the work presented in this chapter. Luminescence from the triplet manifold is not observed at room temperature for any of the porphyrin species studied.

Inspection of Figure 3.2 reveals that the CdTPPS-doped gel exhibits very weak non-vibronically coupled luminescence peak at 605 nm. This indicates that the perturbation by the heavier metal ion, cadmium(II), greatly enhances vibronic coupling ($Q(0,1)$ over $Q(0,0)$) with respect to zinc(II). An indication of the magnitude of this effect can be developed by taking a simple ratio between the peak intensity values of

Q(0,1) and Q(0,0) transitions for the metal complexes and the $Q_x(0,1)$ and $Q_x(0,0)$ bands in the parent. This value is computed to be 2.1 for the ZnTPPS-doped sample, 4.2 for the CdTPPS-doped sample, and 1.6 for the TPPS-doped sample. It is expected that this relationship is strongly correlated to other relaxation phenomena, including the radiative fluorescence lifetime.

The fluorescence decay curves of the CdTPPS and ZnTPPS-doped specimens, using subpicosecond excitation pulses at 540 nm and relaxation from the Q(0,0) band (605 nm peak), are shown in Figure 3.3. Lifetimes were found to be 580 psec for CdTPPS and 2.13 nsec for ZnTPPS, using a single exponential decay model. Using this approach, a good fit to the data over approximately 5 lifetime periods was obtained. TPPS was not observed to have measurable luminescence at 605 nm using the experimental apparatus described. The radiative relaxation rate of TPPS-doped gel, seen in Figure 3.4, was subsequently measured for the $Q_x(0,0)$ band (655 nm). A decay lifetime of 14 ns was measured, again using a single exponential decay fit. As expected, the lifetime was found to be relatively long for the free porphyrin (no ion-induced vibronic metal-ligand interactions) as compared to the lifetime of the ZnTPPS complex.^{1,2} The shortest lifetime was found in association with the heavier cadmium(II) complex. This behavior can be attributed to vibronic coupling, which is greatest for CdTPPS and has essentially no contribution in the case of TPPS. Vibrationally-activated nonradiative decay events (probably in association with intersystem crossing into the triplet manifold³) leads to lower overall luminescence intensities and to concomitantly faster radiative decay rates.

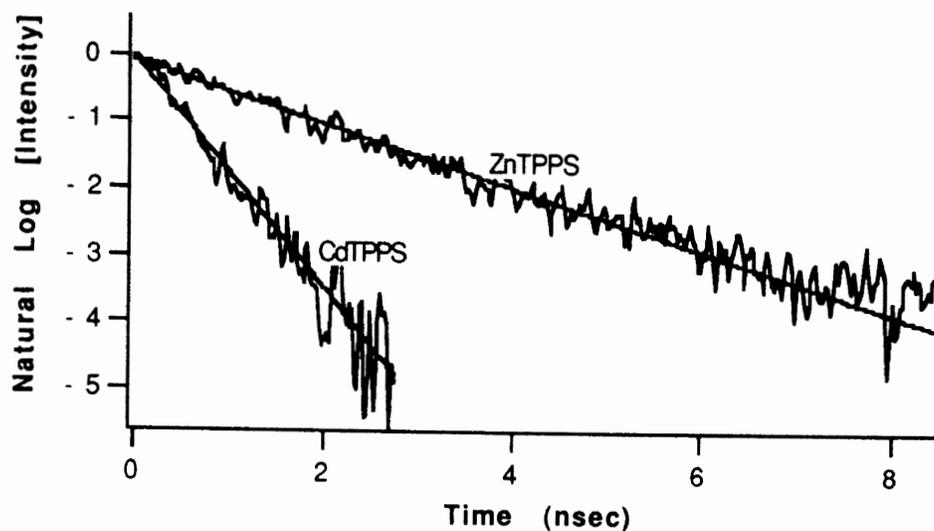


Figure 3.3. Radiative decay curves for ZnTPPS and CdTPPS with the straight lines representing single exponential fits.

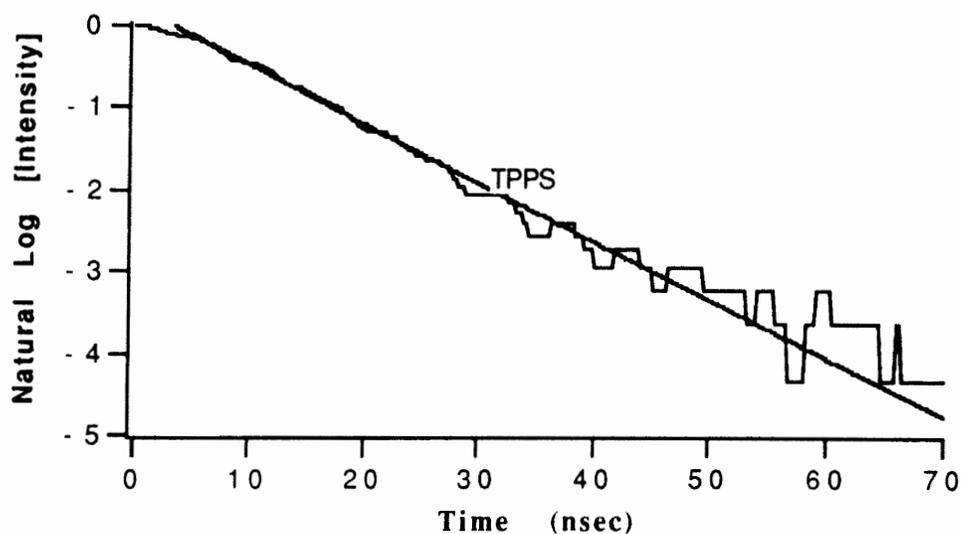


Figure 3.4. Radiative decay curve for TPPS with the straight line representing a single exponential fit.

These results indicate that time-resolved spectroscopy is a very sensitive method to assess the relative activity of a mixture of transition metal ion analytes present in solution, as they might typically be found in a real sample. The continuous wave spectral features of these three species in the sol-gel host are similar enough that the relative

activities of each of them in such a mixture would be exceedingly difficult to resolve. The development of an optically-coupled sensor depends, of course, upon the ability to distinguish between closely related species and to quantify them if two or more are simultaneously present. Only through the development of secondary and possible tertiary analytical techniques can such assessments be made. The present work indicates that radiative lifetime determination can be a very sensitive spectroscopic method with regard to transition metal ion differentiation in metalorganic complexes.

III.D. Summary of Time-Resolved Luminescence Studies

Transition metal ion-induced perturbations to the luminescence properties of tetra-4-sulfonatophenylporphyrin doped into an aluminosilicate host were characterized. The complexes selected for study were ZnTPPS and CdTPPS. Significant quenching and a concomitant reduction in radiative lifetimes were observed in the samples as a function of the complexed transition metal ion. CdTPPS was shown to have the greatest vibronic coupling which resulted in the lowest luminescence intensity and the shortest radiative decay lifetime. These studies have demonstrated that closely related metalloporphyrin species are readily distinguished from one another in the gel host by characterization of the radiative decay rate.

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CHAPTER IV

MULTIPHOTON SPECTROSCOPY IN METALLOPORPHYRIN-DOPED GELS

IV.A. Introduction

Porphyrin molecules which are complexed to a metal ion containing an unpaired d electron comprise a family of compounds which possess an extensive series of doublet and quartet vibronic levels (Section I.D.2.). In the case of CuTPPS, the singlet and triplet energy level system of the porphyrin ring become doublets (including singdoublets and tripdoublets) and quartets¹, due to the exchange interaction between the one unpaired electron from copper and the porphyrin (π, π^*) states. Linear and nonlinear (NLO) effects associated with electronic transitions in these compounds have been characterized theoretically and experimentally². The work presented in this chapter involves the investigation of excited state absorption and up-converted luminescence behavior of a metalloporphyrin dopant, tetra-4-sulfonatophenylporphyrinatocopper (II) sodium (CuTPPS) entrapped within a solid state aluminosilicate host.

Excited state absorption involves the absorption of a photon by a molecule which is already in an electronically excited state. This may occur through a virtual or real energy level. In the case of CuTPPS this process takes place through the first excited doublet (Q-band) level (see Figure 1.5). In the up-conversion luminescence process, low energy photons are converted into higher energy photons. In the case of CuTPPS, this results from nonlinear absorption and population of the second excited doublet level. Up-converted photons result from relaxation to the ground state from higher lying energy levels attained via multiple photon absorption.

The work presented in this chapter involving such processes is believed to be the first description of nonlinear absorption and radiative up-conversion associated with solid

state media containing metalloporphyrin-dopants. These effects have been attributed to multiphoton absorption of species through both doublet and quartet manifolds. A mechanism such as this has previously been cited by P.D. Fuqua and coworkers ² as having a probable contribution to excited state absorption in a related system, phthalocyanine-doped SiO₂ gel.

IV.B. Experimental Methods and Procedures

Bulk aluminosilicate gel monoliths doped with the CuTPPS complex, were prepared by the method discussed in Chapter 2. Gellation of the samples occurred over a period of three days at room temperature. The bulk samples were subsequently allowed to dry slowly, under ambient conditions, for 8 weeks. Initial dopant concentrations in the sols and calculated number densities for the resultant xerogels are shown in Table 4.1. The final number densities (N_D) of CuTPPS dopant in the solid state materials were calculated based upon the final dimensions of the dried bulk monolithic specimens.

Table 4.1 Concentrations in the sol (M) and gel (cm⁻³) states for CuTPPS doped aluminosilicate hosts.

Initial Concentration (M)	Number Density (cm ⁻³)
1×10^{-6}	1.5×10^{15}
1×10^{-5}	1.5×10^{16}
1×10^{-4}	1.5×10^{17}

Nonlinear absorption and up-converted luminescence were measured following an experimental procedure similar to one described by J.W. Perry and coworkers ⁴. The excitation source used was an excimer laser (Lambda Physik, model 120i oscillating at 308 nm) pumped dye laser (Lambda Physik, model LPD 3000 CES) system. Rhodamine

6G dissolved into methanol was used as the gain medium in the dye laser; the pulse width (FWHM) of the dye laser output was measured to be 16 ns. During both nonlinear absorption and up-converted luminescence measurements the excitation wavelength, λ_{ex} , was 584 nm (17123 cm^{-1}). Nonlinear absorption measurements were conducted using incident pulse energies of up to a few mJ per pulse; a set of neutral density filters was used to attenuate the dye laser input energy. An R = 10% beam splitter was used to direct a small portion of the total incident energy to an energy probe positioned at 45 degrees with respect to the beam. The balance of the laser energy was focused, using a 200 mm focal length lens, to a spot ($d = 20 \text{ }\mu\text{m}$) inside the sample where the best focus was obtained by Z-scan measurements ⁴. Both incident and transmitted energies were measured externally during each excitation pulse using a Laser Precision Corp. energy probe model number RJP-637 and a Tektronix 2440 oscilloscope. Up-converted luminescence studies were performed using the same excitation system. Emission measurements were made using a Spex Fluorolog fluorometer (using a thermoelectrically cooled R928 PMT detector). All luminescence spectra were corrected for instrument response using Spex's Mcorrect software files.

IV.C. Discussion and Results

IV.C.1. Nonlinear Absorption

Nonlinear transmission plots are shown in Figure 4.1 as a function of the incident energy for the three values of dopant number densities studied. In all cases, absorption was found to be a linear function of the incident energy under very weak illumination conditions. All specimens studied exhibited a nonlinear absorption behavior (intensity-related decrease in transmissivity) at intermediate energies. This is associated with intersystem crossing, in which a molecule crosses from the first excited singdoublet (D_1)

level into the triplet manifold. Subsequent absorption arises between the triplet (4T₁) and higher lying states in the triplet manifold (4T₁) (Figure 1.5), resulting in the observed phenomenon. Saturation of this effect was observed at a critical energy, E_c, which was found to be a function of dopant concentration. Nonlinear transmissivity effects may be explained by excitation from the doublet ground state to the excited D₁ state and by subsequent absorption from optically excited states D_{1-n}, presumably from the first excited doublet and/or quartet states to higher lying levels in the doublet and/or quartet manifolds (Figure 1.5). No visible sample bleaching or burning was observed over the reported incident energy range.

Following the energy-level diagram indicated for d¹ metal-TPPS complexes (Figure 1.5), ΔE₁(D₀→D₁) and ΔE₂(D₀→D₂) were determined from absorption spectra to be 18,622 and 24,196 cm⁻¹, respectively in the case of Cu(II)TPPS.

IV.C.2. Up-Converted Luminescence

Luminescent up-conversion generally results from radiative relaxation out of higher lying excited states following multi-photon absorption processes similar to those indicated by the nonlinear absorption studies described in the previous section. The second excited doublet band or Soret band, D₂, can be populated by sequential photon absorption from the ground state, D₀, through the D₁ band to higher lying D_n bands. Molecular populations at these levels can rapidly relax, in a nonradiative fashion, to the D₂ band. Subsequent radiative relaxation from D₂ to D₀ results in the emission of blue photons peaked at 434 nm (23,041 cm⁻¹).

Up-converted photon emission intensity was measured as a function of the excitation energy (λ_{ex}=584 nm; Figure 4.2.). The data shown represent the characteristic behavior of the sample having a dopant N_D of 1.5x10¹⁷ cm⁻³; other samples behaved similarly. Up-converted fluorescence intensity was found to increase rapidly as a

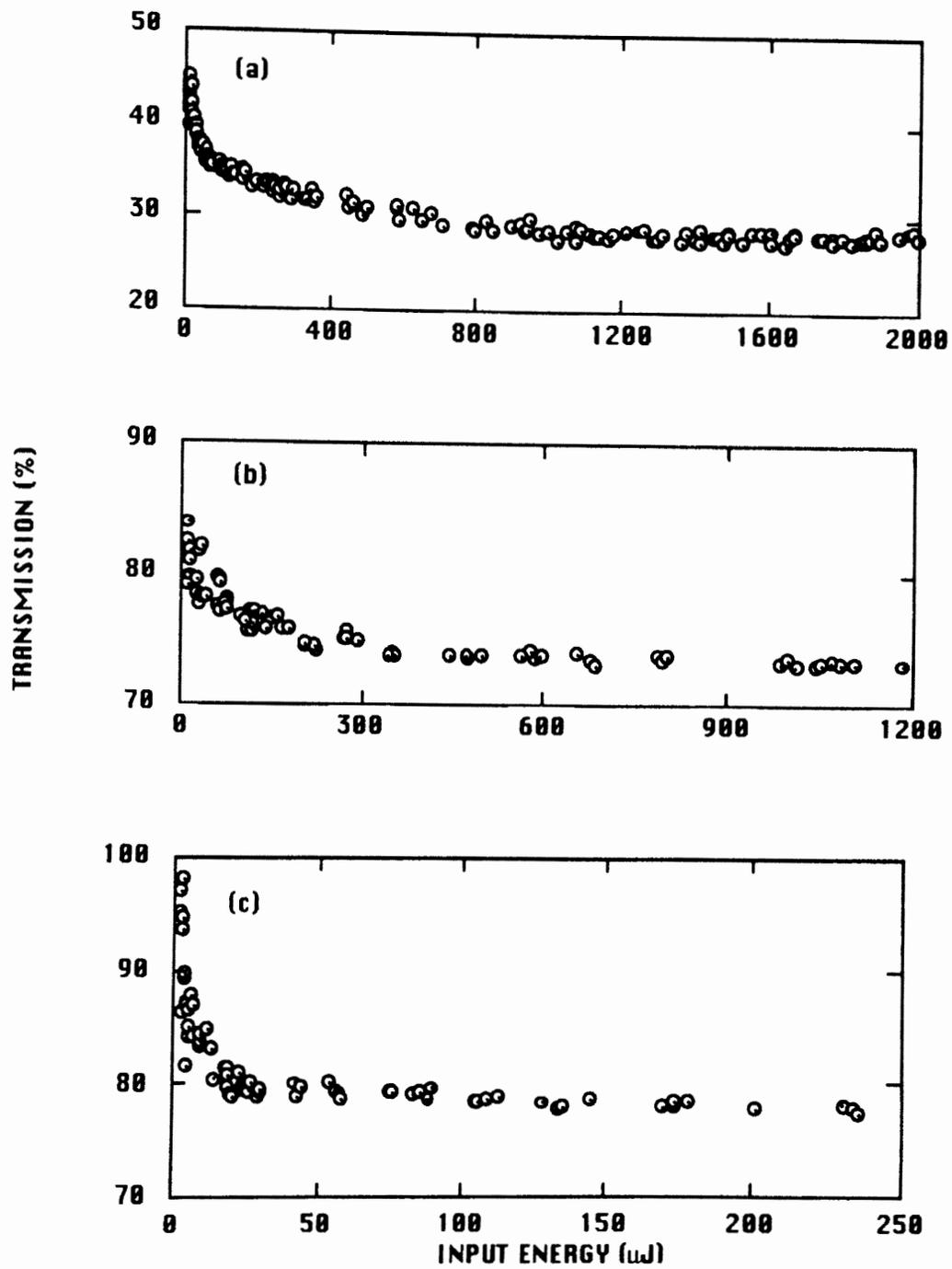


Figure 4.1. Nonlinear absorption in CuTPPS-doped aluminosilicate gels (a) $N_D=1.5 \times 10^{17} \text{ cm}^{-3}$; (b) $N_D=1.5 \times 10^{16} \text{ cm}^{-3}$; (c) $N_D=1.5 \times 10^{15} \text{ cm}^{-3}$.

function of the pump fluence over the low to intermediate intensity range. This behavior was found to saturate at essentially the same energy, E_c , as that seen for the onset of nonlinear transmission (Figure 4.1a). This may be explained by heavy saturation of the D_1 band under elevated excitation fluences. As a consequence, the intensity of the up-converted blue emission is expected to be quadratically proportional to the excitation intensity, as two photon absorption is required in order to populate the D_2 band; subsequent radiative relaxation from D_2 is associated with the emission of a blue photon. A quadratic fluence/emission intensity relationship is not consistent with the experimental observations, however, as strong saturation effects were observed. We believe these effects can be attributed to intersystem crossing, i.e., nonradiative relaxation from the lowest level of D_1 band to the lowest lying quartet level, 4T_1 . The quartet 4T_1 level has a long lifetime (on the order of a few milliseconds), due to the forbidden nature of relaxation to the doublet ground state, D_0 . During intense excitation, the initial portion of the incident laser pulse is expected to excite essentially all of the porphyrin molecules to the D_1 band. It appears that a substantial portion of this population relaxes to the 4T_1 level and remains in the triplet manifold (4T_1 - 4T_n) during the balance of the exciting laser pulse. Molecules which intersystem cross into the triplet manifold make no subsequent contribution to the up-converted luminescence as relaxation from the D_2 state is essentially precluded. This mechanism would result in the saturation of up-converted emission behavior indicated in Figure 4.2. This proposed model is supported by the observation that extremely weak fluorescence is detected for the transition from the D_1 band to the doublet ground state, indicating that intersystem crossing from D_1 into the triplet manifold may be prevalent due to heavy atom effects.

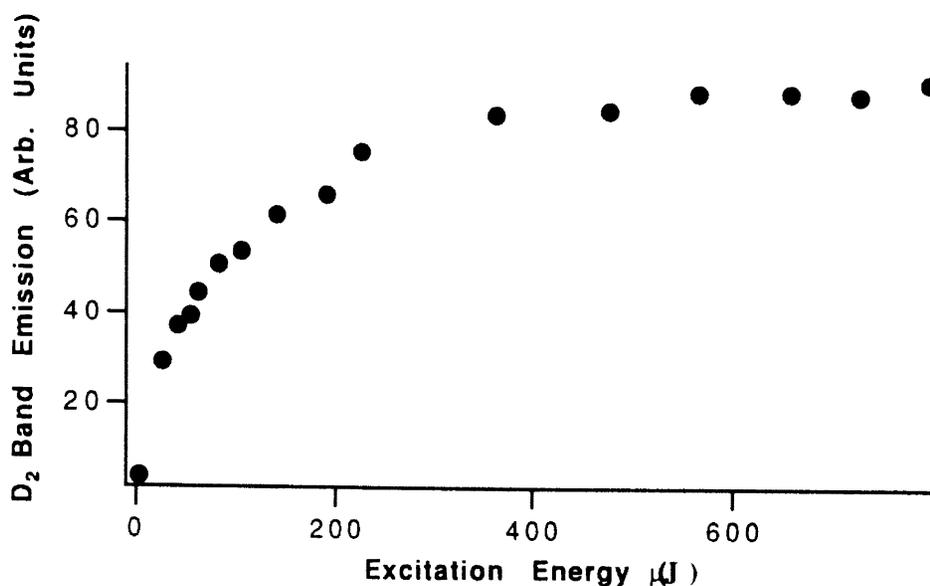


Figure 4.2. Up-converted luminescence as a function of excitation energy. CuTPPS $N_D = 1.5 \times 10^{17} \text{ cm}^{-3}$. $\lambda_{ex} = 434 \text{ nm}$.

IV.D. Summary and Conclusions

Nonlinear absorption and radiative up-conversion have been observed in sol-gel derived aluminosilicate materials containing CuTPPS. These phenomena have been attributed to excited state transitions originating from the D₁ band. Up-converted luminescence is associated with stepwise two photon absorption via the first excited doublet band of CuTPPS and subsequent relaxation from the D₂ doublet ground states. Saturation effects were observed at laser pulse energies greater than the critical energy E_c . This behavior is attributed, at least in part, to intersystem crossing into the long lived quartet manifold. Such spectroscopic methods may be used to distinguish between closely related species, such as Zn(II) and Cd(II), when employed in optode materials studies.

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CHAPTER V

SUGGESTIONS FOR ADDITIONAL STUDY

It was shown in the preceding chapters that porphyrin molecules have different electronic properties when chelated to various transition metals. This promising result coupled with the failure of the thin films to produce positive results in the area of metal ion migration through the material lead toward the possibility of evanescent sensing. This method involves the fact that if a light beam is directed into a glass fiber, which is surrounded by a medium of lower refractive index, a part of the beam will be transmitted by total internal reflection at the core/cladding interface. The resulting standing wave will penetrate over a small distance into the lower refractive index material where it can interact with molecules. Thus, the medium of lower refractive index will absorb energy from the evanescent field at frequencies specific to the substance.

The interacting molecules may be covalently bound to derivitized glass beads, such as aminopropyl glass beads, through a reaction similar to amino acid bonding. These beads may then be attached to the optical-fiber. The preferable method would involve direct bonding of the probe species to the cladding. One such cladding material is the polyalkylsiloxane type ($RR'-Si-O-$). The R groups may be converted into an amino group which would allow the same type of reaction previously discussed.

The response times of a material derived from a porphyrin molecule remain a problematic area in that porphyrins are inherently slow in complexing metals. This problem may be resolved by displacement of one metal with another. It is known that zinc displaces cadmium in porphyrin-cadmium complexes. The time for this displacement to occur is dramatically less than complexation of the zinc to the uncomplexed parent. This helps alleviate the kinetics problem; however, the sensor would have to be regenerated after every few minutes of use.

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