

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

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Abstract. Organic chromophores are of interest for use in remote luminescent chemical sensor applications, as they can be highly sensitive to conditions such as oxygen concentration, pH, temperature, metal ion activity, etc. Small fluctuations in local environmental parameters can lead to substantial perturbations in the optical properties of select organic probe molecules. Lifetime studies were performed on the S_1 emission of tetra-4-sulfonatophenylporphyrin and the zinc (II) and cadmium (II) adducts in sol-gel derived aluminosilicate hosts. Vibronically-coupled quenching was observed to occur as a function of the complexed transition metal ion.

Keywords: sol-gel, tetra-4-sulfonatophenylporphyrin, time-resolved luminescence

1. Introduction and Background

Sol-gel synthesis provides a method by which a variety of solid state materials are readily prepared. A great deal of inherent flexibility exists in relation to sol-gel materials preparation. Fabrication of samples having a variety of compositions (including silica and modified silicates) and configurations (such as thin films, fibers, and bulk monoliths) is readily achieved via this method.

Sol-gel derived thin films have a number of characteristics which make them of potential use in the development of remote, optically-coupled chemical sensor media. Sol-gel films can exhibit good transparency over extended regions of the visible and near IR spectrum and they often are made to be chemically inert. Undensified films are typically quite porous; thus the transport of various analyte species, in either gas or liquid phase, is facilitated. In addition, water and/or alcohol-soluble probe species are readily entrapped within the nanostructured sol-gel network. Finally, the solution synthetic approach is easily adapted to the deposition of thin films on optical fiber substrates by a variety of coating methods. These combined attributes facilitate the development of sol-gel based opto-chemical sensor media. Sensor interrogation in such systems may be accomplished by a vari-

ety of methods including the continuous monitoring of analyte-induced changes to absorption and/or emission spectra of the probe dopant species.

The family of porphyrin molecules lend themselves for use as a "luminoionophoric" probe molecules, as the high degree of molecular conjugation in this family gives rise to intense absorption and, frequently, luminescent emission peaks. This conjugated π -electron structure incorporates four nitrogen atoms through the constituent heterocyclic rings (see the chemical structure of the sulfonatoporphyrin molecule represented in Figure 1). For the purpose of this work, the salient feature of the porphyrins is that the heterocyclic nitrogen atoms are capable of forming tetradentate complexes with divalent transition metal ions in solution. Complex formation with appropriate metal ion species is accompanied by perturbations to the conjugated π -electron system and to the overall molecular symmetry which may be detected spectroscopically.

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 2). Free porphyrin molecules, such as the one indicated in Figure 1, typically possess a pair of Q and a pair of B sub-bands [1], which arise due to splitting of these singlet states as a function of the D_{2h} molecular

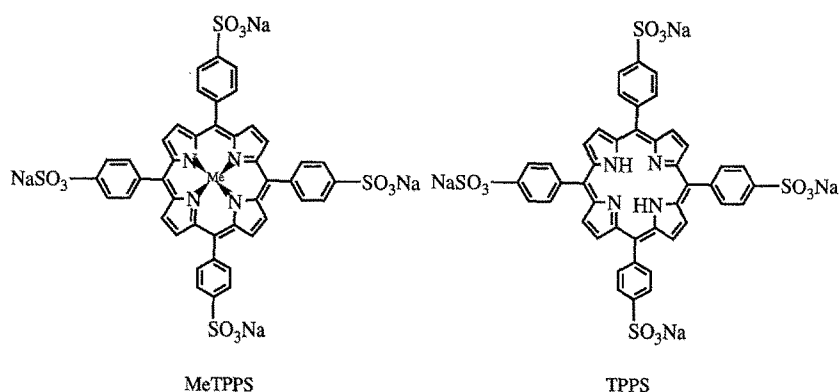


Fig. 1. Structure of tetra-4-sulfonatophenylporphyrin (TPPS) and a representative metal complex of TPPS.

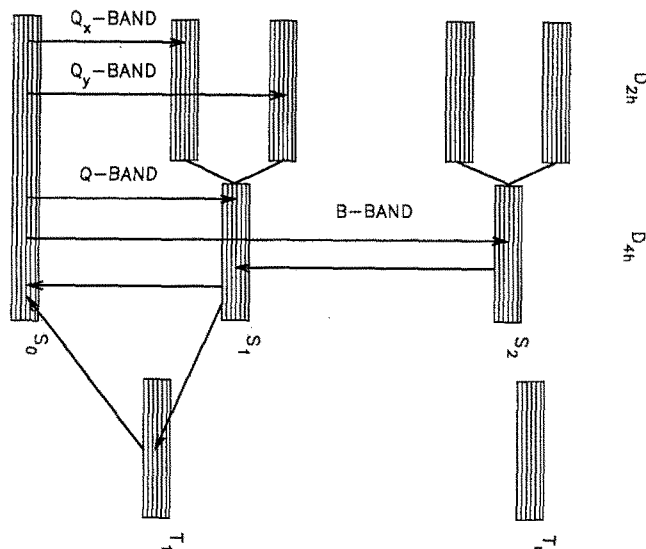


Fig. 2. Energy level diagram for TPPS and metal complexed TPPS.

symmetry. The Q-band splitting results in the so-called Q_x and Q_y sub-bands, as indicated in Figure 2. Thus, porphyrin species usually exhibit a characteristic four-band series of absorption peaks due to the splitting of these states. Direct excitation of the Q_y level leads to very fast radiationless decay to that of the lower Q_x vibronic sublevel. Hence, free porphyrin molecules typically have 2 emission bands, resulting from relaxation from the Q_x level to the ground state, denoted $Q_x(0, 0)$, and an emission event associated the single phonon vibrational relaxation mode, denoted $Q_x(0, 1)$. Upon complex formation, molecular symmetry is generally raised to D_{4h} , which is a structure that is not accompanied by singlet state splitting (Figure 2); thus, the absorption and luminescence spectra of the complexes tend to be distinctly different from the parent. Met-

alloporphyrins tend to exhibit a two-band absorption spectrum. Like the free parent porphyrin, Q-level excitation of a metalloporphyrin complex is generally associated with twin emission peaks; $Q(0, 0)$ and $Q(0, 1)$ associated with higher and lower emission energies respectively. 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.

In both the free porphyrin and metalloporphyrin complexes, intersystem crossing leads to population of the triplet manifold (designated T_1 in Figure 2). Both intersystem crossing 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 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, especially as they pertain to changes in the radiative lifetime.

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 system. We have selected a solubilized porphyrin analogue, the sodium salt of tetra-4-sulfonatophenylporphyrin (TPPS), for study in an aluminosilicate sol-gel host. The aluminosilicate host was chosen because polymerization from the metal alkoxide precursor proceeds at room temperature under neutral conditions. Metalloporphyrin complexes are known to decompose into a mixture of complexed neu-

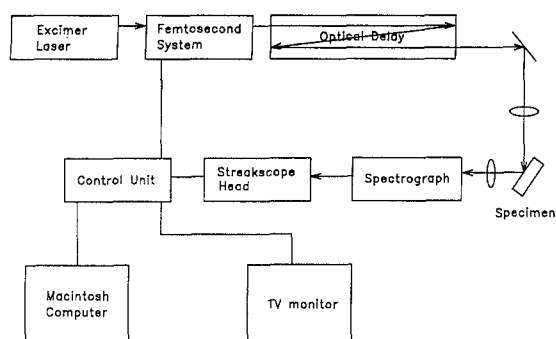


Fig. 3. Schematic setup for time resolved measurements.

tral and dissociated ionic species under mildly acidic conditions, especially in the case of large or weakly-bound metal ions [2, 3].

Prior studies have shown that complex formation between TPPS and zinc or cadmium proceeds within the sol-gel host under aqueous conditions. Perturbations to the excitation and emission spectra were reported. The present contribution seeks to investigate changes in the radiative lifetime of TPPS as compared to its zinc (ZnTPPS) and cadmium (CdTPPS) complexes within the solid state host. Correlations between radiative lifetime shortening and the mass of the complexed ion are presented.

2. Experimental

Bulk porphyrin-doped aluminosilicate sol-gel samples were prepared by a method similar to one described by Pouxviel and coworkers [4]. This synthesis involves the dropwise addition of aqueous isopropanol into a 50:50 mixture, by volume, of di-secbutoxyaluminumoxytriethoxysilane and isopropanol. The final ratio of water to isopropanol to di-secbutoxyaluminumoxytriethoxysilane in the precursor solution was 1:6:3. After mixing, the sol was cast into $1 \times 1 \times 4.5$ cm polystyrene cuvettes and covered with parafilm. In our preparation the porphyrin dopants were dissolved directly into the water of hydrolysis before addition into the sol. Initial concentrations in the sol were 1 mM. Samples prepared in this manner were observed to gel at room temperature over a period of two days. The specimens were slowly dried, under ambient conditions, for approximately two weeks prior to making the radiative lifetime measurements. The dried specimens retained approximately 90% 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 spectrofluorometer; 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 and optical delay generator. 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 540 A, 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.

3. Discussion of Results

Continuous wave emission spectra of TPPS-, CdTPPS and ZnTPPS-doped gels are indicated in Figure 4. 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.

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

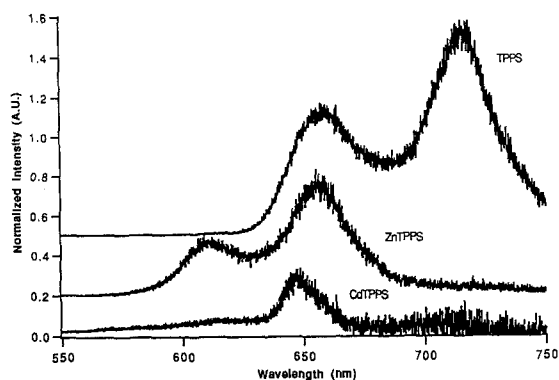
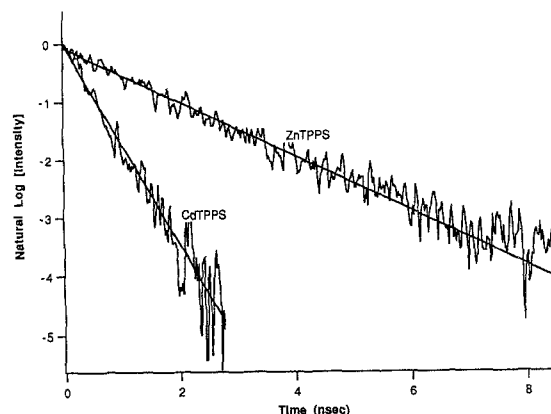


Fig. 4. Emission spectra for TPPS, ZnTPPS and CdTPPS, $\lambda_{\text{ex}} = 540$ nm.

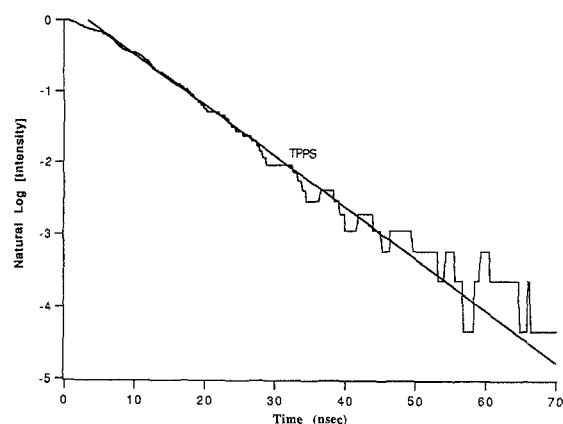
complexed species with respect to the parent molecule can be assessed at least in part to intersystem crossing from the singlet to the triplet manifold via the heavy metal effect.

Inspection of Figure 4 reveals that the CdTPPS-doped gel exhibits very weak nonvibronically coupled luminescence peak at 605 nm. This indicates that the perturbation by the heavier metal ion, cadmium(II), greatly enhances vibronic coupling with respect to zinc(II). A simple 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 should be correlated with other sorts of relaxation phenomena such as the radiative lifetime.

The radiative decay curves of the CdTPPS and ZnTPPS-doped specimens, with subpicosecond excitation pulses at 540 nm and relaxation from the $Q(0, 0)$ band (605 nm peak), are shown in Figure 5a. Lifetimes were found to be 580 psec for CdTPPS and 2.13 nsec for ZnTPPS, using a single exponential decay curve. Using this model, 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 5b, 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



(a)



(b)

Fig. 5. a) Radiative decay curves for ZnTPPS and CdTPPS with the straight lines representing single exponential fits. b) Radiative decay curve for TPPS with the straight line representing a single exponential fit.

porphyrin (no vibronic metal ligand interactions) as compared to the lifetime of the ZnTPPS complex [1, 5]. 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 manifold [6], leads to faster radiative decay rates and lower overall luminescence intensities.

These results are significant, as they provide a very sensitive method by which one might 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 3 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.

4. Summary

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.

Acknowledgments

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