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Mo_6Cl_{12}-Incorporated Sol-Gel for Oxygen Sensing Applications

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Abstract. Excitation of hexanuclear molybdenum complexes such as Mo_6Cl_{12} and its derivatives in the ultraviolet results in a strongly red-shifted luminescence centered at 750 nm. Since oxygen efficiently quenches the luminescence, these thermally stable inorganic complexes are candidate lumophores for real-time, high temperature optical fiber based sensing of oxygen. Sol-gel films containing the acetonitrile complex of Mo_6Cl_{12} were deposited on quartz substrates by dip coating. After drying, the films were heated at 200°C for 1 h. The luminescence lineshapes of films before and after heating were unchanged, indicating that heating did not adversely affect the cluster photophysics. Compared to solutions of the acetonitrile complex, quenching by oxygen was smaller in the as-prepared films, but heating at 200°C for 1 h increased the quenching, apparently due to increased oxygen permeability resulting from the loss of water or other small molecules from the matrix. These results confirm the potential of hexanuclear molybdenum complexes such as $Mo_6Cl_{12}\cdot 2CH_3CN$ as the lumophores in fiber optic oxygen sensors that can operate up to 200°C.

Keywords: molybdenum cluster, sol-gel, optical fiber, oxygen sensor, high temperature, luminescence quenching

Introduction

The ability to make *in-situ* measurements of oxygen concentrations is essential for medical applications and the real-time control of combustion and other industrial processes. Fiber optic probes that rely on the quenching of luminescent organic, inorganic and organometallic compounds [1–4] offer several advantages over electrochemical sensors and other designs. Fiber based sensors are small, flexible, able to probe remote locations under harsh conditions, and immune to electrical interference.

A key challenge in designing an optical fiber based oxygen sensor is integrating the lumophore with the fiber geometry. Usually dispersed in a polymer matrix at the tip of the fiber, the polymer/lumophore composite must have high oxygen permeability and adhere strongly to the fiber. Previously we devised a fiber optic based sensor [5] by immobilizing Mo_6Cl_{12} clusters at the tip of a fiber in a matrix of poly(trimethylsilyl-1-propyne) (PTMSP), which has the highest known O_2 permeability of synthetic polymers. The sensor had excellent room temperature performance and could detect changes of 0.1% absolute oxygen concentration in the 0–1.0% range, 0.5% in the 1–4% range, and 1% in the 4–10% range. However, the inherent temperature range

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of the sensor was limited since organic polymers like PTMSP cannot survive extended exposure to >250°C.

Commercially available fiber-based oxygen sensors are only useful at temperatures below 130°C [6], primarily due to the use of low thermal stability components. A high temperature fiber optic oxygen sensor must incorporate a thermally stable lumophore in a thermally stable porous matrix. One advantage of using derivatives of Mo_6Cl_{12} as lumophores is that the clusters are stable in air to ~300°C [7]. The long cluster lifetime (180 μs) and large Stokes shift (>300 nm) also simplify sensor design since the luminescence is easily detectable by integrating over the broad emission band, and simple filtering techniques can be used to separate the excitation (300–400 nm) from emission (550–900 nm) signals.

An attractive alternative to embedding lumophores in polymers is to encapsulate them in an inorganic matrix. Sol-gel systems are ideal candidates because they are stable to high temperature and it is possible to control the porosity of the films through the use of templating molecules, or by adjusting the sol-gel reaction conditions [8]. In addition, sol-gel chemistry is compatible with the surface chemistry of silica optical fibers ensuring strong adhesion of the matrix to the fiber. The principal challenge is to devise a sol-gel process that is benign to the lumophore during the preparation of the matrix, and which results in full dispersal of the clusters in the matrix. In addition, the matrix must retain sufficient porosity to allow real-time detection of changes in oxygen levels while minimizing leaching of the lumophore from the matrix. A brief report provides precedent for immobilizing Mo_6Cl_{12} in a sol-gel matrix without significantly affecting the absorption and emission of molybdenum cluster [9]. These results are expected since the photophysics of interest are due to electronic transitions confined to the $[Mo_6Cl_8]^{4+}$ cluster core [9, 10].

There are a number of examples of immobilized lumophores for oxygen sensing applications [4]. The most commonly used lumophore has been $Ru(dpp)_3{}^{2+}$, which has been embedded in a sol-gel matrix as the coating of an optical fiber sensor in an evanescent wave configuration [11], as well as on planar substrates. A copper containing zeolite immobilized on the end of an optical fiber was used to measure oxygen concentrations at temperatures >425°C, demonstrating that a fiber based oxygen sensor could be fabricated to withstand high temperatures [12]. In this paper, we describe the immobilization of the acetonitrile complex of Mo_6Cl_{12} in a sol-gel matrix and show that the immobilized lumophore retains its luminescence after thermal ageing of the composite at 200°C for 1 h.

Experimental

Materials

All glassware was oven-dried prior to use. Acetonitrile (Spectrum Chemical Company, HPLC grade) was dried over CaH_2 and distilled prior to use. Tetraethyl orthosilicate (TEOS) (Aldrich, 98%) and hydrochloric acid (CCI, electronics grade) were used as received. Molybdenum dichloride (Cerac, Inc.) was purified as described elsewhere [7]. The acetonitrile complex of Mo_6Cl_{12} was prepared by placing dry, purified Mo_6Cl_{12}(100 mg) into a cellulose Soxhlet extraction thimble. After assembling the Soxhlet apparatus and flushing the system with nitrogen, the Mo_6Cl_{12} was extracted with 250 mL of dry acetonitrile for one week. Concentration of the resulting clear yellow solution to 10 mL gave an orange-yellow solution of the acetonitrile complex (cluster concentration $\sim 2 \times 10^{-3}$ M). Corning type 7980 fused quartz microscope slides ($3'' \times 1'' \times 1$ mm) were obtained from Technical Glass Products and were cut into 1.25×2.45 cm pieces. Slides were handled with gloves and tweezers in order to minimize surface contamination and then washed with Alconox, rinsed with distilled water, soaked in a base bath (~5 M NaOH in 95% ethanol), rinsed with distilled water, and stored in distilled water until use.

Film Deposition

Sol-gel films were dip-coated onto quartz slides. A typical stock solution for the coating process was prepared as described below. The acetonitrile complex (1.4 mL, 3 μmol) was added with stirring to TEOS (2.0 mL, 9.0 mmol) in a 10 mL Erlenmeyer flask. Water (0.65 mL, adjusted to pH = 1 with HCl) was added and the solution was stirred for 1 hour at room temperature. The stir bar was removed from the flask and the solution was heated in an oil bath at 70°C for 2.5 h. The solution was then transferred to a 20 mL glass scintillation vial, capped, and aged at room temperature until use.

Just prior to deposition, the slides were removed from the distilled water and dried under a stream of nitrogen. Slides were dipped by hand at a rate of ~1 mm/sec with no hold time and placed directly into a scintillation vial. The vial was capped, and stored on its side to minimize flow of the solution. The vial containing the sol-gel solution was capped after each dip coat in order to minimize evaporation. The best results were obtained using a three-dip coat process with the first coat applied after the solution had aged for 64.5 h. The second and third coats were applied 10 and 37 min after the first coat. After drying at room temperature in a capped vial for 2 weeks, the films were thermally cured in air at 70°C for 24 h.

Optical Characterization

The absorption spectrum was measured using a Perkin-Elmer Lambda 40 series double beam UV/vis spectrometer. Data analysis was performed using the UV Win lab (version 2.80.03) software package supplied with the instrument. Fluorescence measurements were performed using a Fluorolog-3 instrument from Instruments S.A., Inc. The excitation optics consisted of a 450W Xe lamp, followed by a 330 nm ruled grating and a 270–380 nm bandpass filter (Oriel 1124) to remove undesired Xe lines. The detection optics consisted of a 600 nm long wave pass filter (CVI) followed by a 630 nm holographic grating and multi-alkali photo multiplier tube at 950V (Hamamatsu R928). Data processing was performed using the Datamax (version 2.2) software package supplied with the instrument. The excitation beam was centered at 313 nm with a 5 nm bandpass and the emission monochromator was scanned from 550 to 850 nm in 1 nm steps. The emission spectra have been corrected for both the spectral response of the 630 nm emission grating and the photo multiplier tube.

Measurements of cluster fluorescence in solution were performed by placing the solution in a quartz cuvette sealed with an airtight septum. Spectra were measured in laboratory air and high purity nitrogen (AGA, Inc, 99.999%). All gases were bubbled through the solution for 10 to 15 min at a rate of ~10 mL/min prior to obtaining spectra. Measurements of the sol-gel immobilized clusters were made in the same manner. The film-coated side of the quartz slide was irradiated at an angle of ~40° with a 90° angle maintained between the excitation beam and detector. The slides were purged *in-situ* and care was taken not move the excitation spot between measurements in the different gas environments.

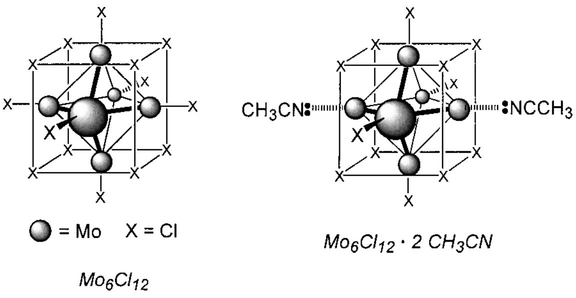

Figure 1. Luminescent molybdenum clusters.

Results and Discussion

Developing a high temperature oxygen fiber sensor based on Mo_6Cl_{12} requires a scheme for embedding the clusters in a matrix while retaining their unique optical properties. In addition, the matrix must have high oxygen permeability and adhere strongly to the optical fiber. These requirements can be satisfied by using a sol-gel matrix to immobilize the clusters at the tip of high temperature silica fibers, such as a commercially available gold clad silica fiber rated for long term operation up to 750°C [13]. The silanol terminated surface of the fiber ensures excellent adhesion to the matrix, and prior work has shown that the oxygen permeability of sol-gel matrices can be tailored by appropriate choice of reaction conditions [8].

The process for embedding the luminescent clusters must be compatible with the solubility and chemical reactivity of Mo_6Cl_{12}. There are two open coordination sites in the hexanuclear Mo_6Cl_{12} structure (Fig. 1). In the solid state, both sites are occupied by bridging chlorides from adjacent clusters resulting in a polymeric structure. In polar solvents such as ethanol or 6 M HCl, solvent displaces the bridging chlorides and the clusters dissolve to give the monomeric complexes. Ethanol/HCl mixtures are common solvents for sol-gel syntheses [8, 14], but Mo_6Cl_{12} clusters tend to form precipitates with oxo bridging ligands and precipitate from solution. We elected to use the acetonitrile complex of Mo_6Cl_{12} ($Mo_6Cl_{12}\cdot 2CH_3CN$) in sol-gel syntheses since acetonitrile has been used successfully as a co-solvent [14]. Stirring Mo_6Cl_{12} in acetonitrile for several days will eventually yield concentrated orange-yellow solutions of the acetonitrile complex. We found that the complex is more conveniently prepared by loading Mo_6Cl_{12} into the thimble of a Soxhlet extractor and exhaustively extracting with dry acetonitrile. The use of dry solvent is important as it minimizes formation of less soluble oxygen-bridged complexes.

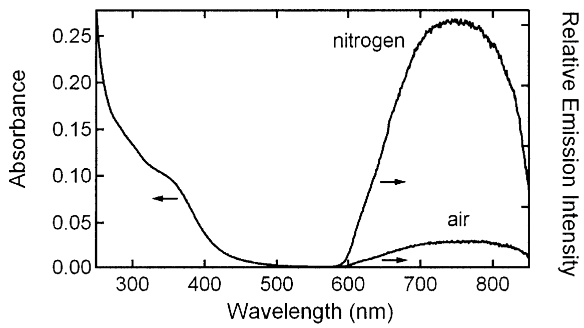

Figure 2. Absorption and emission spectra of the acetonitrile complex of Mo_6Cl_{12} in acetonitrile. The cluster concentration is 4×10^{-5} M. The emission spectra demonstrate oxygen quenching by a factor of 9.6 between (a) nitrogen (99.999%) and (b) laboratory air (~20% oxygen).

The spectroscopic features of the acetonitrile complex are shown in Fig. 2. Excitation of Mo_6Cl_{12} clusters in the UV ($\lambda < 400$ nm) leads to a long lived triplet state, which decays to the ground state with emission of red luminescence centered at ~750 nm. The large Stokes shift of the emission (>300 nm) greatly simplifies the design of a reflection mode fiber sensor since photons over the entire emission band can be collected and the UV pump signal can be removed using simple band pass filters. In addition, the high quantum yield (0.19 in CH_3CN [15]) allows simple sources such as pen lamps to be used as the UV source. Excitation spectra were obtained by pumping at 313 nm while scanning the emission from 550 to 850 nm. The absorbance of the solutions used for these experiments were adjusted to ~0.1 at 313 nm in order to minimize self-quenching effects. Using reported extinction coefficients for Mo_6Cl_{12} clusters ($\varepsilon = 3000$ L mol^{-1}cm^{-1}) [16, 17], we estimate the concentrations to be 4×10^{-5} M. A concern is whether the clusters in the matrix exist as isolated species or as aggregates. Having the former is important to avoid decreases in luminescence due to self-quenching. We believe that in solution, $Mo_6Cl_{12}{\cdot}2CH_3CN$ is monomeric since the luminescence intensity and quenching behavior of its solutions are comparable to those of molybdenum clusters (e.g. $Mo_6Cl_{14}^{2-}$), which are known to be monomeric. In addition, the luminescence intensities scale linearly with changes in concentration.

The excited states of Mo_6Cl_{12} clusters are efficiently quenched by oxygen. Spectra for $Mo_6Cl_{12}{\cdot}2CH_3CN$ solutions measured in room air and under nitrogen are shown in Fig. 2. The data show a quenching factor of 9.6, with the luminescence intensity and lineshape returning to their original values upon equilibration. Luminescence quenching data for Mo_6Cl_{12} clusters typically follows the Stern-Volmer equation, $I/I_0 = 1/(1 + K_{sv}[O_2])$, where I and I_0 are the luminescence intensity in the presence and absence of oxygen of concentration $[O_2]$ and K_{sv} the Stern-Volmer constant [5].

A standard TEOS based process was used to embed the acetonitrile complex in a sol-gel matrix [14]. A requirement is that the sol-gel film be sufficiently porous to allow rapid diffusion of oxygen through the matrix. A series of experiments that lead to sol-gel matrices with different oxygen permeabilities have been reported [8]. Using those conditions as a starting point, we prepared a solution of TEOS, $Mo_6Cl_{12}{\cdot}2CH_3CN$ dissolved in acetonitrile, and aqueous HCl, and then aged the solution at 70°C for 2.5 h. Since acetonitrile is known to increase the rates of sol-gel reactions [14], we monitored the change in the viscosity of the solution and dip-coated clean quartz substrates at regular intervals. Drying at room temperature for ~2 week followed by heating at 70°C for 24 h gave clear films that adhered strongly to the substrate. These films glow brightly when illuminated with a hand held UV lamp.

The data in Fig. 3 show that the emission lineshape for the clusters is unchanged when incorporated into the sol-gel matrix. This is consistent with numerous observations that the cluster/solvent interactions do not significantly affect the electronic structure of the hexanuclear core, and it is these electronic transitions that are responsible for the red luminescence. Using oxygen permeabilities reported for similar sol-gel films [8], we estimate that the time constant for a fiber sensor with the acetonitrile complex embedded in a 1 μm thick sol-gel film will be ~1 sec.

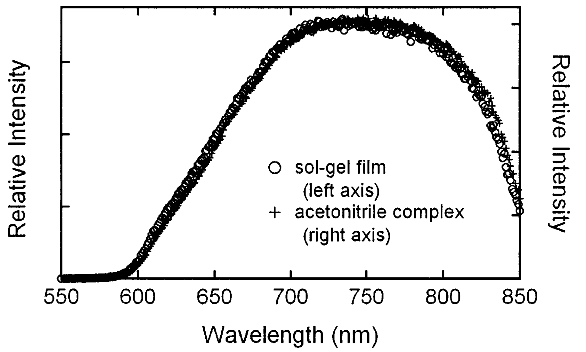

Figure 3. Emission spectra of $Mo_6Cl_{12}{\cdot}2CH_3CN$ demonstrating no change in the cluster lineshape between the CH_3CN solution and the sol-gel matrix.

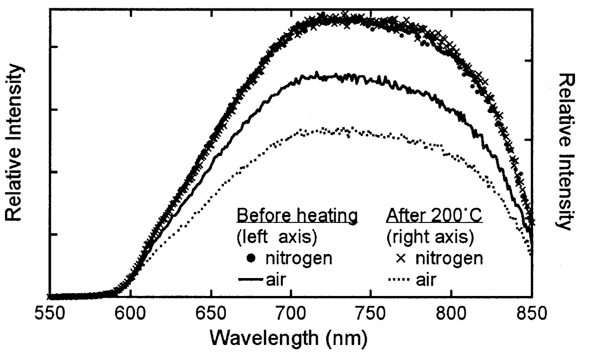

Figure 4. Emission spectra of the cluster incorporated matrix (i) before heating (left axis) and (ii) after heating to 200°C for 1 h (right axis), showing no change in the lineshape. Oxygen quenching by a factor of 1.3 before and 1.7 after heat cycling is observed.

Several films were aged at 200°C for 1 h to simulate operation of the sensor at high temperatures. The emission spectra measured before and after heating in air at 200°C for 1 h are shown in Fig. 4, left and right axis respectively. The emission lineshapes before and after heating are identical; again demonstrating that heating of the sol-gel immobilized clusters does not affect the electronic structure of the hexanuclear core. However, the decrease in luminescence due to quenching by oxygen is $\sim 2\times$ for the heat-treated sample compared to $9.6\times$ for the clusters in acetonitrile (Fig. 2). There are two likely scenarios that could explain the difference in quenching between solution and sol-gel film. First, quenching may be limited by poor accessibility of oxygen to the clusters. This can be overcome by the use of templating molecules or changes in the drying conditions used for the preparation of the films. We note that the quenching for the film aged at 200°C is slightly larger than that for the control film, and thus the difference in quenching behavior is at least partially related to an increase in the porosity of the films during heating. Such effects have previously been ascribed to the loss of water from the matrix [18]. A second possibility is that the clusters may form aggregates in the sol-gel matrix leading to self-quenching, which we plan to address by comparing the luminescence lifetimes for clusters in solution and embedded in sol-gel matrices.

There are other examples where lumophores in sol-gel matrices have been thermally aged at elevated temperatures. For these, heating was motivated by the need to refine the sol-gel process rather than high temperature sensing of oxygen. High temperature aging is commonly used to remove water and solvent molecules from the sol-gel matrices, and as a consequence increases porosity. For example, $Ru(bpp)_3^{2+}$ was embedded in sol-gel films and the films were aged at temperatures as high as 300°C [19]. A related study of the oxygen induced quenching of luminescence from $Ru(bpp)_3^{2+}$ as a function of the aging temperature and time [18] showed increased quenching rates that were ascribed to an increased porosity of the sol-gel film.

A critical parameter in a high temperature sensor based on luminescence quenching is the long-term stability of the lumophore. We note that the data of Fig. 4 were acquired from a ~1 year old film that had been thermally cycled to 200°C five times. Despite the repeated cycling, the luminescence intensity of the film did not diminish, but rather increased. While the reason for the change in luminescence is not certain, it is likely related to the continued evolution of the sol-gel matrix. Preliminary *in-situ* measurements show that the cluster emission intensity decreases from room temperature to 140°C and then is constant to 200°C. Based on our previous room temperature sensor results [5], the luminescence intensity is sufficient for high temperature fiber sensor operation.

Conclusions

We have developed a scheme for embedding luminescent hexanuclear molybdenum chloride clusters in sol-gel matrices via the acetonitrile complex ($Mo_6Cl_{12}\cdot 2CH_3CN$). Spectroscopic measurements show that the photophysics of the clusters are unchanged by the immobilization process. After heating the cluster/sol-gel composite to 200°C, oxygen quenching of the cluster luminescence was preserved. These results provide a route for development of a silica fiber based high temperature oxygen sensor.

Acknowledgments

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