

# An optical temperature sensing system based on encapsulation of a dye molecule in organosilica sol–gels

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## Abstract

The design of an optical sensor system for detecting ambient temperature is reported. The sensor element comprises of a dye molecule encapsulated in a stable organosilica sol–gel matrix that exhibits changes in its color when subjected to temperature changes. These temperature-dependent changes in optical properties of the encapsulated dye are utilized to translate a thermal signal to an optical output for use as a simple optical temperature sensor. The response of the system is reversible with respect to variations in temperature. The results show that system may be used as a simple, easy-to-use, cost-effective temperature sensing device which may find potential utility in several specialized areas such as designs of embedded fiber optics sensors in civil infrastructures, sensors for underwater and marine environments as well as common uses related to display and alert systems for visual estimation of temperature.

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## 1. Introduction

Temperature is a critical physical parameter and is necessary to define the state of any system. As such, its precise and accurate determination is of fundamental significance in science and technology [1]. Temperature sensors span a wide range of designs and signal transduction approaches [2,3]. Because of intrinsic interferences from environmental factors, for measuring temperatures in regions that are not normally directly accessible such as underwater or marine environments, underground geochemical sites, and internal parts of civil infrastructure systems require specialized temperature sensing designs that can best be realized by means of fiber optics and optical temperature sensors [4–7]. There have been several optical sensor techniques employing a wide range of chemical species for the desired temperature range. The design of optical temperature sensors typically relies on temperature-dependent modulation of optical properties and

consequent variations in parameters such as frequency or intensity of absorption or emission [8–11]. In this context, modulation of frequency (or wavelength) provides a direct means of correlating color with temperature and can be employed for both qualitative assessment via visual inspection or quantitative measurement through recording of optical absorption spectrum.

Thermochromic materials are characterized by temperature controlled optical properties, and therefore, have been used widely in design of temperature sensors [10–12]. While typical thermochromic response of materials constitutes a temperature-modulated change in equilibrium between two colored forms (or between colored and colorless forms), the thermochromic responses of pyridinium *N*-phenoxide betaine dyes constitute a temperature-dependent change in absorption maxima [13]. As such, these dyes provide a means for fabrication of optical color sensors for temperature.

Sol–gel glasses have attracted much attention in recent times as encapsulation matrices for molecular entities [14]. These materials have been used in many applications related

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to the development of different sensors through encapsulation of response-active molecules. Herein, we demonstrate the feasibility of a strategy for transduction of a thermal signal to an optical response by using a sol–gel-derived materials system that responds to changes in temperature by undergoing a color transition. The temperature sensing system comprises of a porous organosilica sol–gel with encapsulated pyridinium *N*-phenoxide betaine dye [13]. The pyridinium *N*-phenoxide betaine dye used is [2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate] (DTP) which is encapsulated in an organic–inorganic sol–gel network. The sol–gel encapsulated dye exhibits reversible changes in absorption as a function of temperature and this feature can be exploited for the design of a temperature sensing material. The sol–gel system is used to form thin films on a glass slide, which can be effectively employed for temperature sensing purposes. The results show that these glass-based materials may have potential applications as devices for sensing ambient temperature.

## 2. Experimental

### 2.1. Chemicals

Reichardt's dye [2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate] (DTP) was purchased from Aldrich Chemical Co., Milwaukee, WI. The sol–gel precursors methyltrimethoxysilane (MTMOS), and bis(trimethoxysilylpropyl)amine (ATMOS) were purchased from Gelest, Inc. Tullytown, PA.

### 2.2. Temperature sensing sol–gel system

#### 2.2.1. Sample preparation

Solution of DTP was prepared by dissolving the dye in methanol. For the evaluation of optical changes in solution, 10 mM solution of DTP in methanol was used. The sol–gels were prepared by mixing the DTP solution with silica precursor compositions. Sol–gel materials with ATMOS precursors were prepared by hydrolysis of the precursor in the presence of the dye. In order to provide improved mechanical stability to the gels, small amount of MTMOS precursor was also used in these preparations. For the preparation of ATMOS-derived sol–gels, 0.025 mL of ATMOS precursor was mixed in with 0.045 mL of methanol, 0.03 mL of water, 0.03 mL of MTMOS precursor along with 0.03 mL of DTP solution (10 mM in methanol). The resulting sol is stable and films of the sol were deposited onto a clean glass slide (approximately 1 cm × 3 cm) through dip-coating method to form uniform, homogenous, and optically transparent coatings of the sol–gels. The films were kept at room temperature for about 30 min for the gelation to take place. These glass-coated optical quality sol–gel samples were used for optical absorption measurements.

#### 2.2.2. Optical measurements

Optical characterization of the sensor element was done using optical absorbance measurements. The optical spectra of the sol–gel samples were recorded by placing the glass slides (coated with DTP–sol–gel mixture) in a cuvette containing water. The samples were kept at controlled temperature using an external water-circulating bath equipped with a temperature controller attached to the sample holder. The precise temperature of the samples was measured and recorded using a digital thermometer from Fisher Scientific. Absorption spectra were taken at different temperature with a UV–vis Hewlett-Packard model 8453 spectrophotometer.

## 3. Results and discussion

### 3.1. Design of temperature sensing sol–gel system

The optical properties of DTP arise due to an intramolecular charge transfer (CT) transition [13]. Due to a substantial change in polarity between the ground and charge transfer excited state, the dye molecule undergoes rather large shifts in absorption wavelength ( $\lambda_{\max}$ ) depending upon changes in its immediate environment. In contrast, most thermochromic systems are characterized by temperature-dependent shift in equilibrium between a colored and non-colored species. The thermochromic response of these materials is typically measured as a function of the intensity of the absorption. The thermochromism of DTP, on the other hand, is characterized by reversible change in wavelength of absorption. The thermochromism of DTP is attractive for its use in temperature sensing mechanisms since it provides a direct correlation with color or wavelength of absorption.

The hydrophobic nature of DTP necessitates use of non-polar media. Recently DTP was encapsulated in a polymeric gel network. However, in these PVA hydrogels, DTP dye was solubilized through addition of a surfactant [15]. Given the hydrophobic nature of the dye, in general, it is poorly soluble in aqueous hydrophilic media. As a result, it precipitates in purely inorganic silica sol–gels derived from tetramethoxysilane (TMOS) when the gels are dried. Furthermore, the dye also has a tendency to lose its optical properties due to protonation of the phenolate group in an acidic environment. Consequently, TMOS-derived sol–gels slowly turn colorless upon drying and cannot be used for optical applications. This problem is further compounded by the acid-catalyzed synthesis conditions normally used for preparation of sol–gel glasses, which cause enhanced protonation of the dye.

In order to overcome these issues, the chemical composition of the porous sol–gel matrix as well as the internal pH within the pores are critical. In order to stabilize the dye we used an organosilica precursor, ATMOS, whose structure is given as



The overall design strategy for selecting the ATMOS precursor was based on several factors that offer unique advantages

to facilitate stabilization of dye in the gel and preserve its optical properties. First, the use of alkoxodisilane precursor with a long-chain spacer unit that contains both hydrophobic and hydrophilic groups provides a balance of polar and non-polar environment and effectively stabilizes both the ground and the excited state of the dye. As a result, the dye is effectively solubilized in the matrix and precipitation does not occur. Additionally, the hydrophobic nature of the gel provides suitable non-covalent interactions with the dye and prevents leaching of the dye even when the gels are placed in water for extended periods. Second, the use of an amino-containing precursor provides a basic internal pore environment ( $\text{pH} \sim 9$ ) that prevents protonation of the phenol group. As a result, the dye is able to retain its optical properties. Finally, the use of organosilane precursors yields sol–gel compositions that are mechanically stable and excellent optical quality thin films can be formed.

The porous glasses with a combination of hydrophobic and hydrophilic groups are characterized by optical transparency and long-term mechanical stability due to increased elasticity provided by the long chain spacer unit. As a result, the films are uniform, homogeneous, and crack-free even when subjected to cyclical variations in temperature. In contrast, films made from TMOS-derived purely inorganic glasses have a tendency to crack extensively and the films peel off from the substrate. Additionally, the hydrophobic nature of the gels prevents release and the dye is fully trapped in the sol–gel matrix and does not leach out when placed in water.

### 3.2. Evaluation of system response

The thermochromic response of DTP dye constitutes a change in wavelength of absorption ( $\lambda_{\text{max}}$ ) as a result of differential stabilization of the ground and excited states of the molecule at different temperatures [13]. The changes in absorption maxima as a function of temperature of DTP (dissolved in methanol) are shown in Fig. 1(b). As can be seen, the dye shows an increase in  $\lambda_{\text{max}}$  as the temperature is increased from 20 to 80 °C. Lowering the temperature restores the  $\lambda_{\text{max}}$  to its original value. As a result of these changes, the

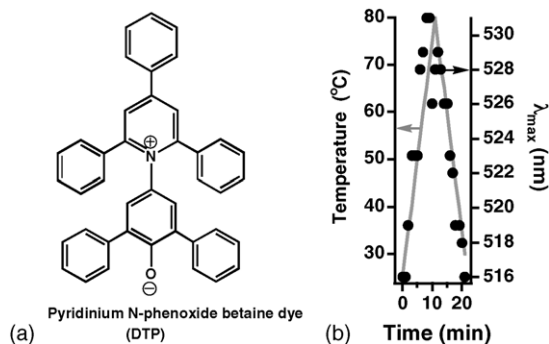


Fig. 1. (a) Chemical structure of DTP, (b) reversible changes in absorption wavelength ( $\lambda_{\text{max}}$ ) of a solution of DTP in methanol as a function of cyclical change in temperature from 20 to 80 °C and back.

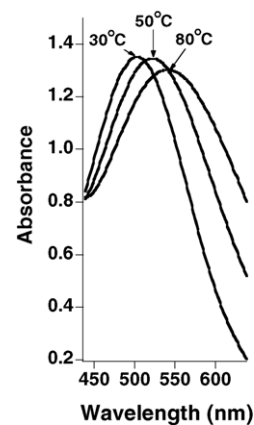


Fig. 2. Optical absorption spectra of DTP-ATMOS sol–gel system at 30, 50, and 80 °C showing shifts in absorption maxima as a result of temperature changes.

dye solution is red colored at room temperature and purple-violet at high temperature. Thus, overall a reversible change in  $\lambda_{\text{max}}$  of about 15 nm is observed in the temperature range of 20–80 °C for methanolic solutions of DTP. Furthermore, a direct correlation between the optical properties of DTP and temperature can be observed in this practically relevant region.

Encapsulation of the dye in organosilica sol–gel matrices retains its optical properties. As shown in Fig. 2, the thermochromic responses of the dye are preserved upon encapsulation and temperature-regulated shifts in absorption maxima can be observed. The absorption maximum of the dye progressively shifts to longer wavelengths as the temperature is increased. It is important to note that the changes in optical properties of the dye in both the ATMOS sol–gel systems only involved a shift in peak frequency and the changes in intensity were minimal (ca. 5%) as compared to gels made from purely inorganic tetramethoxysilane (TMOS) precursor where the dye precipitated and the peak was lost upon drying the film. Similarly, for films made out of pure MTMOS gels, the intensity of the peak was lost by about 80–90% upon gelation and drying. It is important to note that no leaching of the dye was observed from the ATMOS sol–gels during the thermal cycling experiments as well as during ambient storage.

The thermochromic response of DTP-ATMOS sol–gel system is shown in Fig. 3. The response is analogous to that in solution. Subjecting the DTP-ATMOS system to temperature variation results in reversible shifts in  $\lambda_{\text{max}}$  such that a red shift accompanies increase in temperature followed by blue shift when the temperature is lowered. This effect is preserved for several cycles without any significant deterioration in optical properties. It is important to note that, as compared to methanolic solution of DTP, the  $\lambda_{\text{max}}$  of the dye is red shifted in ATMOS sol–gels at a given temperature. The increase in  $\lambda_{\text{max}}$  in the sol–gel matrices is possibly due to altered non-covalent interactions of the dye with sol–gel matrix. Since the intramolecular charge transfer transition of DTP is strongly

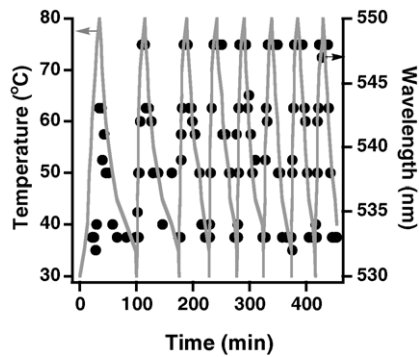


Fig. 3. Reversible changes in absorption wavelength maximum ( $\lambda_{\max}$ ) of DTP-ATMOS sol-gel system coated on a glass slide as a function of cyclical changes in temperature between 30 and 80 °C. The gray solid line corresponds the actual temperature (left axis) of the system and the solid points represent the wavelength maxima (right axis) of DTP.

influenced by non-covalent interactions responsible for solvation [13], environmental effects are expected to play a large role in optical properties and observed changes are consistent with influence of the hydrophobic sol-gel matrix. The red shift of  $\lambda_{\max}$  in ATMOS matrix compared with methanol suggests ATMOS matrix is less polar than methanol and agrees with the expected trend based on increased stabilization of the less polar excited state of DTP by the sol-gel matrix. While at present, the precise nature of interactions between DTP and the sol-gel matrix remains to be elucidated, from the perspective of the use of this system as a temperature sensor, the red shift in  $\lambda_{\max}$  is beneficial as it enhances the visual color contrast of the dye between the low temperature form (wine red) and high temperature form (blue-purple).

As shown in Fig. 3, the changes in  $\lambda_{\max}$  correlate directly with temperature and are fully reversible between the temperature range of 30–80 °C for several cycles. In this case, an overall change of about 15 nm in  $\lambda_{\max}$  is observed as a function of temperature change. The relationship between temperature and  $\lambda_{\max}$  of DTP-ATMOS materials systems is shown in Fig. 4. It is important to note that the data in Fig. 4 is on a single sensor element subjected to multiple variations of temperature. The direct correlation of  $\lambda_{\max}$  with temperature provides a potential means for design of optical sensor elements as well as chromogenic display or alert systems for visual inspection and detection.

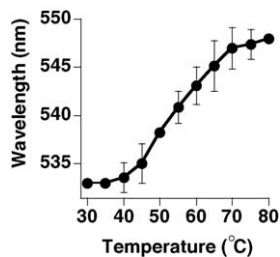


Fig. 4. Temperature-wavelength correlation profile for DTP-ATMOS sol-gel system.

## 4. Conclusions

In conclusion, we demonstrate preliminary feasibility of a sol-gel-derived system for temperature sensing based on encapsulation of a dye that exhibits changes in its color when subjected to variations in temperature. The use of an organosilica sol-gel with a combination of hydrophilic and hydrophobic groups effectively stabilizes both the polar ground state and the non-polar excited state of the dye as result the optical properties of the dye are preserved upon encapsulation. The sensor system exhibits reversible changes in wavelength as a function of changes in a practically relevant region of temperature. The thermochromic system can be used to translate a thermal signal to an optical response and, therefore, illustrates an example of a simple easy-to-use signal transducer which may find potential utility in several specialized areas such as designs of embedded fiber optics sensors in civil infrastructures as well as common uses related to low-cost display systems for visual estimation of temperature.

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