

# Optical oxygen sensing based on luminescence quenching of platinum porphyrin dyes doped in ormosil coatings

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## Abstract

Organically modified sol–gel films (ormosils) doped with platinum porphyrin dyes were prepared by using acid-catalyzed hydrolysis and condensation of methyl triethoxysilane (MTEOS) as precursor. The process variables like water to precursor molar ratio, acid concentration and aging time of the acid-catalyzed MTEOS-based sol were controlled to obtain ormosil coatings with good sensor properties. The effect of dopant concentration on the oxygen sensitivity was studied. The photophysical properties and decay kinetics of the coatings were studied and compared. Stern–Volmer plots for both PtOEP- and PtTFPP-doped sensor coatings were linear. The oxygen sensitivities ( $I_0/I_{100}$ ) of these sensor coatings were found to be about 28 and 50 for PtTFPP and PtOEP, respectively. The ormosil coatings doped with porphyrin dyes exhibited higher oxygen sensitivity and better photostability compared to other silicone-based sensor coatings. Hence they may have good potential for surface pressure measurements in aerodynamic applications.

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**Keywords:** Oxygen sensor; Ormosil; Platinum porphyrin dyes; Luminescence quenching

## 1. Introduction

In the last decade there has been a growing interest in the development of optical oxygen sensors based on luminescent quenching of dyes by oxygen [1–33]. These sensors find application not only in the determination of oxygen in biomedical and environmental samples but also for surface pressure measurements on wind tunnel models in aerodynamics [26–32]. The oxygen sensor films and coatings are prepared by dispersing luminophore dye molecules in an oxygen permeable binder material. Different types of luminophores, such as polyaromatic hydrocarbons [1–3], metalloporphyrins [3–17] and transition metal complexes [3,18–27] have been employed as oxygen probes. Generally, silicone resins are used as binders due to their high oxygen permeability. In recent times, sol–gel process has been utilized for the production of thin silica sensor films [15–27]. Sol–gel films have certain advantages over polymer films for oxygen sensor applications. The sol–gel films have superior optical quality and mechanical properties as well

as ability to tailor the film properties. When a polymer matrix is used for sensor fabrication, the organic dye in the excited state may undergo photochemical reactions with the polymer or the dye may get leached out of the polymer film. Hence it is worthwhile to replace the polymer by the highly porous and transparent sol–gel matrix for the fabrication of optical oxygen sensors.

Sol–gel derived silica films are generally prepared by the room temperature hydrolysis and condensation of a silicon alkoxide sol. In most of the sol–gel oxygen sensors reported in literature, ruthenium dyes are often used as dopants because of their high oxygen sensitivity, good photostability and solubility in polar solvents [18–27]. Jiang et al. have prepared a sol–gel based pressure sensitive paint (PSP) coating using ruthenium complexes and studied their properties [26]. This coating gave a linear Stern–Volmer calibration graph with a pressure sensitivity of 75% but the sol was applied by spin coating and hence can be useful only to study planar surfaces. A sol–gel based PSP containing a temperature sensitive phosphor in addition to ruthenium complex has also been reported [27].

Platinum porphyrin dyes like platinum octaethyl porphyrin (PtOEP) and platinum *meso*-tetra (pentfluorophenyl) porphyrin

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(PtTFPP) in various polymer matrices have been widely used for oxygen sensing owing to their strong phosphorescence, long excited state lifetime, visible light absorption and large Stokes' shift [3–14]. Papkovsky has reported the applications of phosphorescent platinum porphyrins as highly efficient oxygen probes [4,5]. They have used polystyrene as the matrix and found that silicone polymers were not suitable as matrix due to undesirably high quenching. The response characteristics and sensing performance of PtOEP incorporated in various polymer matrices like ethyl cellulose, polyvinyl chloride, polystyrene and silicone polymer has been compared [3,7,8]. The oxygen sensitivity of three metalloporphyrins in suitable polymeric matrices has been studied and compared [9]. Amao et al. and Gillanders et al. have carried out studies on metalloporphyrins immobilized in fluoropolymers [10–12].

In the first PSP developed in the University of Washington, PtOEP was dispersed in a commercial silicone resin binder [28]. The disadvantages of this paint include rapid photodegradation and high temperature sensitivity. Subsequently, an improved paint was developed using PtTFPP as probe and a fluoropolymer (FIB) as binder [29]. But there are only few references on sol–gel based oxygen sensors and sol–gel PSP doped with platinum porphyrin dyes. Lee and Okura have prepared a sol–gel glass film doped with PtOEP for the first time and studied the optical properties of this sensor [15,16]. These authors have loaded PtOEP in sol–gel matrix prepared by slow hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in the presence of Triton X-100. Even though the sensor exhibited high degree of oxygen quenching, the prolonged time of about 4 weeks for gelation and drying of the sol–gel glass was a disadvantage of this method. Very recently, Yeh et al. have reported a highly sensitive optical fiber sensor using Pt(II) complexes embedded in sol–gel matrix prepared with a mixture of TEOS and *n*-octyltriethoxysilane [17]. The authors have reported high sensitivity and stability for the sensor. The sensor was prepared by dip-coating method and hence the coating thickness must be  $<1\ \mu\text{m}$ . The present work describes the method of preparation and photophysical properties of improved metalloporphyrin doped MTEOS-based ormosil oxygen sensor coatings with high sensitivity and good photostability.

## 2. Experimental

### 2.1. Materials required

TEOS and methyl triethoxy silane (MTEOS) were purchased from Sigma–Aldrich. Platinum porphyrin dyes, PtOEP and PtTFPP were purchased from Porphyrin Products Inc., USA. The molecular structure of porphyrin dyes are well known and shown elsewhere [4,7,17]. Ethanol was procured from Merck and chloroform from Ranbaxy Fine Chemicals. Since PtOEP is sparingly soluble in ethanol, a solution of PtOEP in chloroform (1.0 mg/ml) was prepared. PtTFPP solutions (1.0 mg/ml) were prepared using both ethanol and chloroform as solvents for the comparative study. HCl (0.1 M) was used for acid catalysis of the sol.

### 2.2. Instrumentation

A Fiber Optic Spectrometer, model S2000 from Ocean Optics, Inc., USA was used for recording absorbance and luminescence emission spectra as well as for intensity measurements. The excitation source used was a 300 W Xenon arc lamp, model 66901 from ORIEL Instruments. An interference filter (Melles Griot cat. No. FIV 111) was used to transmit radiation from the source in the wavelength region of 532 nm to excite the sensor films and coatings. Infrared radiation from the source was filtered by means of a water filter. The coating specimens were mounted in a sample chamber so that emission was measured by the front face technique. Nitrogen and oxygen were passed through the sample chamber to record the luminescent emission spectra in 100% nitrogen and 100% oxygen, respectively. Dry nitrogen, air and oxygen were mixed to obtain calibration gas mixtures containing different oxygen percentages using gas flow meters. All the luminescence spectra were recorded at room temperature.

Luminescence decay kinetics of the coatings was studied by using time-correlated single photon counting (TCSPC) based fluorescence lifetime measurement system from M/s Horiba Jobin Yvon IBH Ltd., UK and a pulsed SpectraLED with peak wavelength 377 nm (SpectraLED-03) as the excitation source. An inverted metallurgical microscope, LEICA DMIRM was used to examine the surface of the coatings. A dry film thickness gauge, QuaNix Keyless was used for measurement of thickness of the coatings.

### 2.3. Preparation of sensor coatings

The sol was prepared by adding required amounts of 0.1 M HCl and distilled water in drops while stirring to a mixture of 2 ml MTEOS and 1.14 ml ethanol in molar ratio 1:2. The water to silane molar ratio (*R*) in the sol was adjusted by adding calculated volumes of HCl and water. The sol was stirred at room temperature for 6 h followed by aging for 22 h under ambient conditions. Platinum porphyrin dye solution was added to the aged sol and the sol was stirred for 15 min. The sol was transferred to a spray gun and sprayed on microscopic glass slides and aluminum coupons coated with a white base-coat. The white base-coat was found to be helpful in enhancing the luminescent intensity from the sensor coating. The coatings were allowed to dry at room temperature and cured completely in 24 h. The coatings were hard and smooth and had good adhesion. Typical coating thickness was  $20\ \mu\text{m}$  but films and coatings thickness ranging from 5 to  $40\ \mu\text{m}$  could be prepared by this procedure. Coatings were prepared by changing the parameters like *R*, HCl concentration, aging time, and dye concentrations to study their effect on the sensor properties.

## 3. Results and discussion

### 3.1. Surface properties of the sensor coatings

TEOS and tetramethoxysilane (TMOS) are the most frequently used sol–gel precursors for the preparation of sensor

films. Organically modified silicates (ormosils) are also used as matrix to improve film adhesion to its support and reduce the concentration of surface silanol groups [19,20,25]. In the sol–gel process, organically modified surfaces can be produced by incorporation of alkoxy silane monomers with the desired functional groups in the starting mixture. Lavin et al. has shown that ormosil films fabricated from organically modified precursors produce better sensor performance for some specific applications compared to films prepared from conventional sol–gel precursors like TEOS [25].

We compared the properties of sol–gel coatings prepared by spraying acid-catalyzed sols of TEOS and MTEOS and found that smooth coatings could be obtained with acid-catalyzed MTEOS whereas the TEOS-based coatings developed cracks and peeled easily. It is well known that a serious problem in the preparation of sol–gel films is the occurrence of cracks. During the gelation and drying stages, the volume of sol–gel matrix shrinks due to evaporation of water and solvents from the pores [15]. Cracks and peeling of film occur for TEOS-based coating when the coating thickness exceeds  $0.3\text{ }\mu\text{m}$ . The problem of cracking was observed even after addition of certain drying control chemical additives. Comparatively, the surface smoothness and adhesion of MTEOS-based coatings were found to be good for films with thickness in the range of  $5\text{--}40\text{ }\mu\text{m}$ . Further, there is a difference in the thickness stabilization behaviour of TEOS and MTEOS films. It has been established that TEOS films stabilize after some weeks (due to continuing hydrolysis facilitated by atmospheric moisture) whereas MTEOS have a fast stabilization time (due to larger hydrolysis and condensation rates) [25]. MTEOS-based ormosil coatings also displayed good oxygen sensing properties and storage stability under ambient conditions. Therefore, MTEOS was chosen as the precursor for the sensor coatings in the present study.

Oxygen sensors based on MTEOS-based ormosil films doped with ruthenium dyes have been reported earlier [23–25,27]. Even though platinum porphyrin dyes have high oxygen quenching efficiency, they have not been used as dopants for ormosil films probably due to the poor solubility of PtOEP in ethanol and other polar solvents. In the case of PtTFPP, the dye was soluble in ethanol and completely miscible with the MTEOS-based sol. When a chloroform solution of PtOEP was used for doping, the sol turned slightly turbid. But the coatings were smooth and uniformly pink in both cases. Fig. 1 shows the photomicrographs of the sensor coatings with and without the luminophore dyes. Coatings doped with chloroform solution of PtOEP (containing 2 mg dye) displayed some micro particles of dye aggregates whereas coatings doped with ethanolic solution of PtTFPP (2 mg) did not show any dye particles (Fig. 1b and c). Thus, homogeneous distribution of dye molecules is seen only for PtTFPP coating because of the higher solubility of PtTFPP in ethanol and also in the sol. When coatings of PtTFPP were prepared with a chloroform solution of the dye, it was found that homogeneous coatings were obtained only at lower dye concentrations (1.0 mg PtTFPP in the sol containing 2 ml MTEOS and 1.14 ml ethanol as given in Section 2.3) as shown in Fig. 2a. At higher dye concentrations (2–4 mg PtTFPP), there was heterogeneity in dye distribution as shown in the photomicrographs

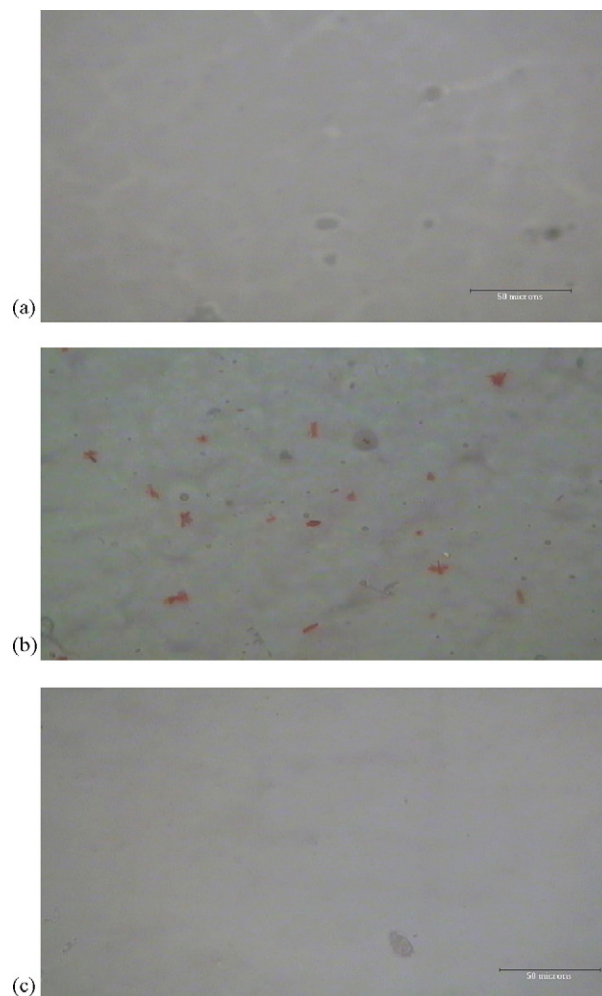


Fig. 1. Photomicrographs of ormosil coatings (a) blank coating without dye, (b) sensor coating doped with chloroform solution of PtOEP and (c) sensor coating doped with ethanolic solution of PtTFPP; magnification, 200.

(Fig. 2b and c). From these results, it is evident that sensor coatings with homogeneous dye distribution could be obtained only with ethanolic solutions of PtTFPP. However, we found that all the coatings displayed good oxygen sensitivity irrespective of whether they are homogeneous or contain micro-aggregates of dye.

### 3.2. Photophysical properties of the sensor coatings

The absorption and phosphorescence spectra of PtOEP in organic solvents like toluene and dimethyl formamide have been recorded earlier by several authors [4,7,15]. A comparison of the absorption spectra of the dye solutions in chloroform and the ormosil coatings doped with the dyes are shown in Figs. 3 and 4. PtOEP solution absorbs very strongly at 381 nm and less strongly at 502 and 537 nm. A broadening of absorption bands was observed for PtOEP-doped ormosil coating and the peak maxima were at 381, 505 and 540 nm. There was no shift in absorption maxima for peak 1 whereas there was only a minor shift of 2–3 nm for peak 3. In the case of PtTFPP, it was found that there was a slight shift in the absorption maximum for peak



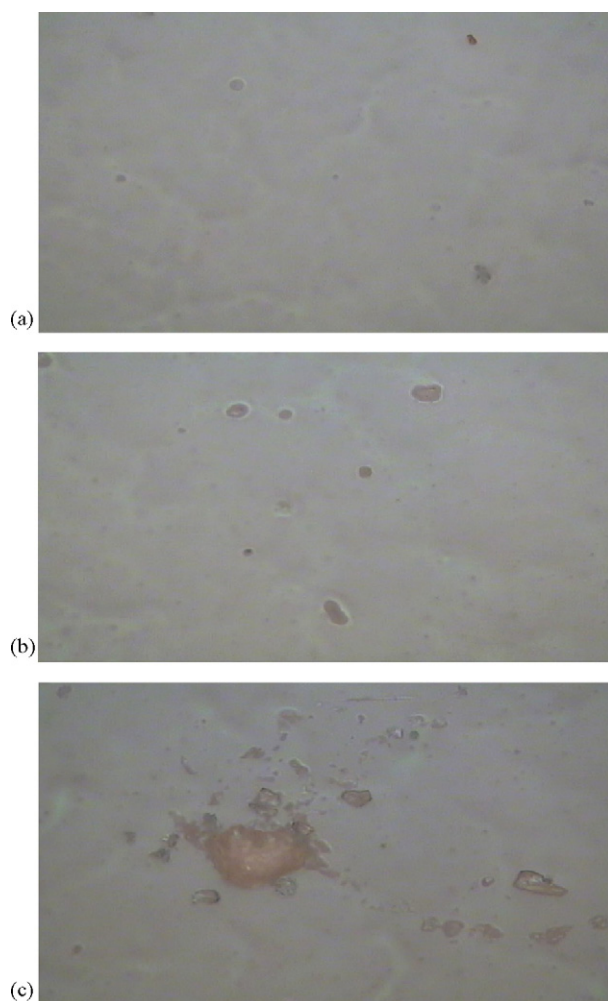


Fig. 2. Photomicrographs of ormosil sensor coatings doped with chloroform solutions of PtTFPP containing (a) 1 mg, (b) 2 mg and (c) 4 mg PtTFPP; magnification, 200.

1 from 393 to 396 nm in the ormosil coating. Lee and Okura had reported that the absorption bands of PtOEP-doped TEOS-based sol–gel glass were red shifted to 400, 550 and 586 nm compared to that of the PtOEP solution [15]. But we found that the shift in absorption peaks was negligible for the dye-doped ormosil coatings. It was also observed that the absorbance values of the two Q-bands (at 502 and 535 nm) of both ormosil coatings doped with PtOEP and PtTFPP were enhanced compared to that in solution as shown in Figs. 3b and 4b. A decrease in absorbance of the Soret band at 380–390 nm in the coating was also noticed. The difference in absorption spectra may be attributed to the change in environment of the dye molecules in the ormosil coating.

The steady state phosphorescence spectra of the dye-doped ormosil coatings in air and in the presence of nitrogen are shown in Fig. 5. Both coatings contain 1.0 mg dye per 2 ml MTEOS. The emission maximum was at about 645 nm for both coatings. The spectra could be obtained by excitation either at 390 nm or at 532 nm using interference filters. The luminescent intensity increased about 10- and 6-fold for PtOEP and PtTFPP, respectively, on changing from air to nitrogen. This indicates that the

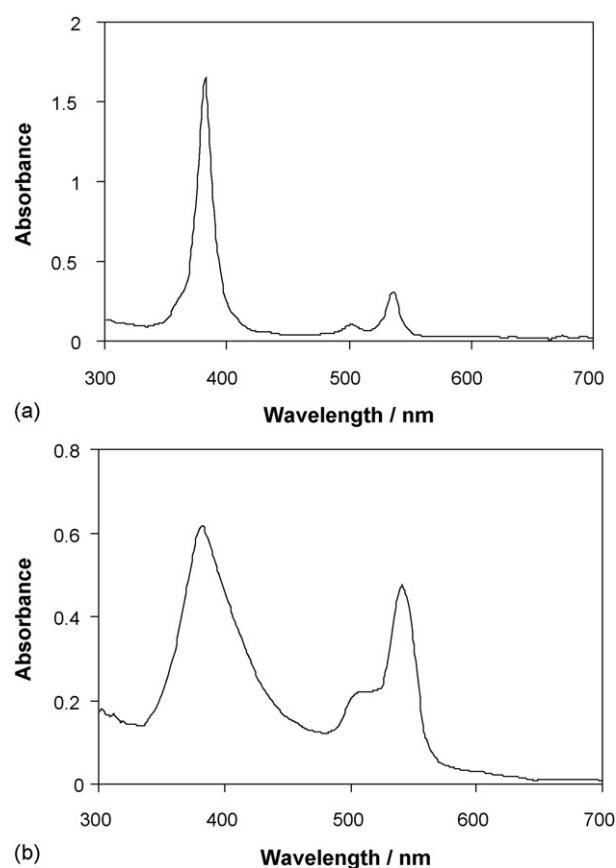


Fig. 3. Absorption spectra of PtOEP (a) dissolved in chloroform and (b) doped in ormosil coating.

phosphorescent intensity is strongly quenched by oxygen for both coatings.

The luminescence quenching is described by Stern–Volmer equation,

$$\frac{I_0}{I} = 1 + K_{SV}[O_2] \quad (1)$$

where  $I_0$  and  $I$  are the luminescence intensities in the absence of oxygen and in the presence of oxygen concentration,  $[O_2]$ , respectively, and  $K_{SV}$  is the Stern–Volmer quenching constant.

Fig. 6 shows the Stern–Volmer plots of both sensor coatings. It can be seen that the plots for both PtOEP- and PtTFPP-doped ormosil coatings are linear (Fig. 6a). The oxygen sensitivity of a sensor is generally defined as  $I_0/I_{100}$  where  $I_0$  and  $I_{100}$  are the luminescence intensities at 0 and 100% oxygen, respectively. From Fig. 6a, the oxygen sensitivities ( $I_0/I_{100}$ ) of these sensor coatings were found to be about 28 and 50 for PtTFPP and PtOEP, respectively. The Stern–Volmer plots for 1-year-old coatings are shown in Fig. 6b. The plot for PtTFPP-doped sensor coating is still linear whereas the PtOEP-doped sensor coating shows non-linear calibration with decreased  $I_0/I_{100}$  on aging. These results indicate the long term stability of PtTFPP-doped sensor coating.

For aerodynamic applications, a modified form of Stern–Volmer equation is generally used since it is impossible to evacuate the wind tunnel and acquire intensity image of the PSP-

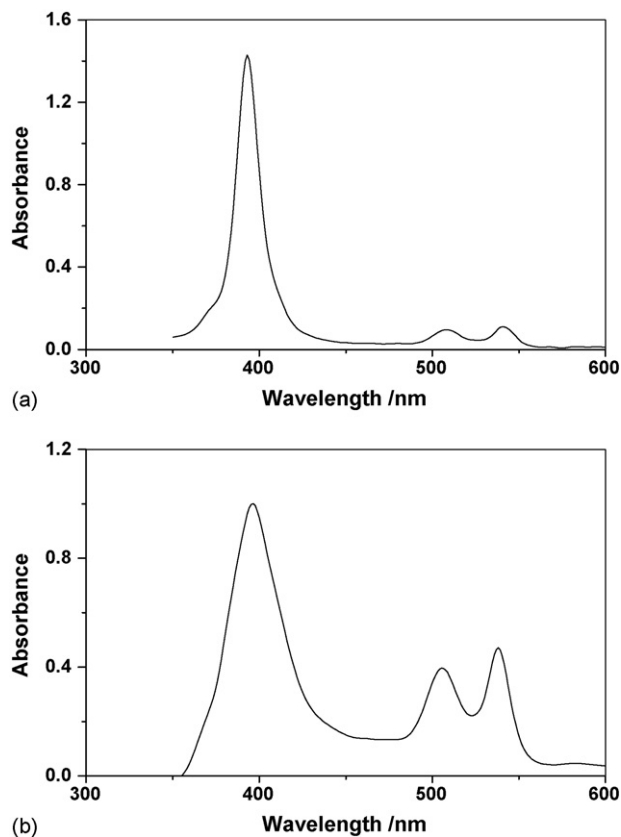


Fig. 4. Absorption spectra of PtTFPP (a) dissolved in chloroform and (b) doped in ormosil coating.

coated model in the absence of oxygen. The modified equation is as follows:

$$\frac{I_{\text{ref}}}{I} = A + B \left( \frac{P}{P_{\text{ref}}} \right) \quad (2)$$

where  $I_{\text{ref}}$  and  $I$  are the luminescence intensities at the reference pressure,  $P_{\text{ref}}$  and at air pressure,  $P$ , respectively, and  $A$  and  $B$  are constants so that  $A + B = 1$  for linear plots [28–32]. Air pressure (1 atm) is normally taken as the reference pressure. Pressure sensitivity of the sensor coating can be obtained from the slope of the linear calibration plot of  $I_{\text{ref}}/I$  versus  $P/P_{\text{ref}}$ . Since we have developed these sensor coatings with an aim to study their usefulness as PSP coatings for aerodynamic applications, our focus is on the sensor performance in the oxygen concentration range of 0–21% (nearly equivalent to a pressure range of 0–1 bar). Therefore, oxygen sensitivity of the sensor coatings in this range of oxygen concentration was determined using the equation,  $S = [(I_{\text{N}_2} - I_{\text{Air}})/I_{\text{N}_2}] \times 100$  where  $I_{\text{Air}}$  and  $I_{\text{N}_2}$  were the emission intensities of the coating in the presence of air and nitrogen, respectively. The intensities and oxygen sensitivities of the coatings are given in Table 1. The intensity of PtTFPP-based coating was higher compared to the intensity of PtOEP-based sensor because of the higher quantum yield of PtTFPP. The sensitivity values for PtOEP- and PtTFPP-doped sensor coatings were 89.0 and 83.0%, respectively.

It has been reported that oxygen sensitivity of sensor films depends on the matrix used [7–17]. For PtOEP immobilized in

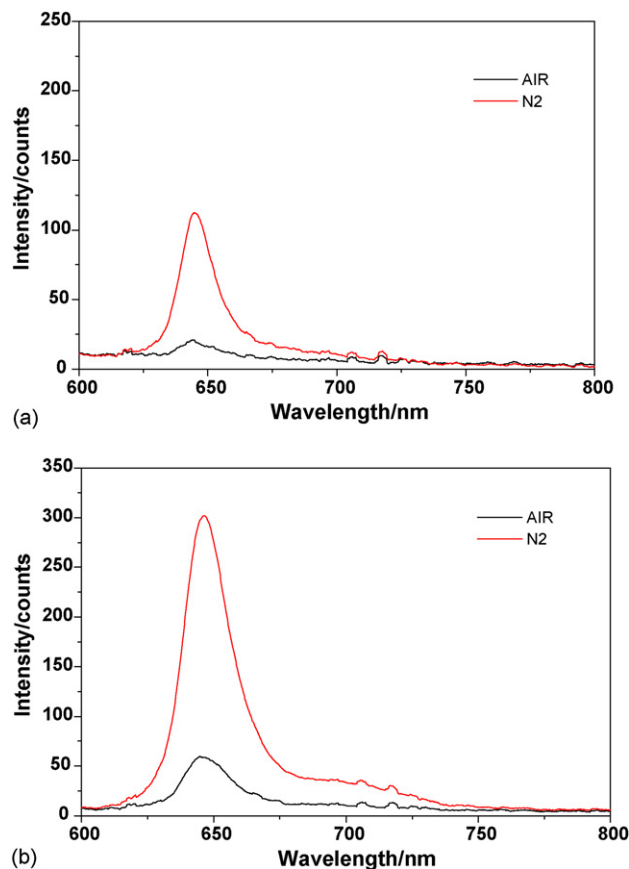


Fig. 5. Phosphorescence spectra of ormosil sensor coatings doped with (a) PtOEP and (b) PtTFPP in air and nitrogen.

polymer matrices such as polystyrene, poly (dimethylsiloxane) and PVC, the oxygen sensitivity ( $I_0/I_{100}$ ) was less than 5 [7]. It has also been reported that the plots for PtOEP immobilized in these polymer matrices are linear only at lower oxygen concentrations and show a downward curvature at higher oxygen concentrations. On the other hand, plots of PtOEP immobilized in methacrylate co-polymers and fluoropolymers are reported to exhibit good linearity and high oxygen sensitivity [10–12]. Such sensor coatings with high oxygen sensitivity are not likely to be useful for PSP since the intensity in air would be completely quenched by oxygen leading to a poor intensity signal under ambient conditions. A comparison of the photophysical properties of our ormosil sensors shows that PtTFPP-doped sensor would be suitable for PSP applications because of its optimal pressure sensitivity, higher quantum efficiency and good stability.

The luminescence decay curves for both coatings were examined under ambient conditions of pressure and temperature as well as in the presence of nitrogen. The emission decays provide valuable information regarding the excited state decay kinetics of the luminophores. The decay behaviour of ormosil coatings with different dye concentrations was studied and the results are shown in Table 2. The coatings PtOEP-1 and PtOEP-2 (as well as PtTFPP-1 and PtTFPP-2) contain 1 and 2 mg dye, respectively, in the ormosil matrix prepared as described in Section 2.3. Typical phosphorescence emission decay curves of an ormosil

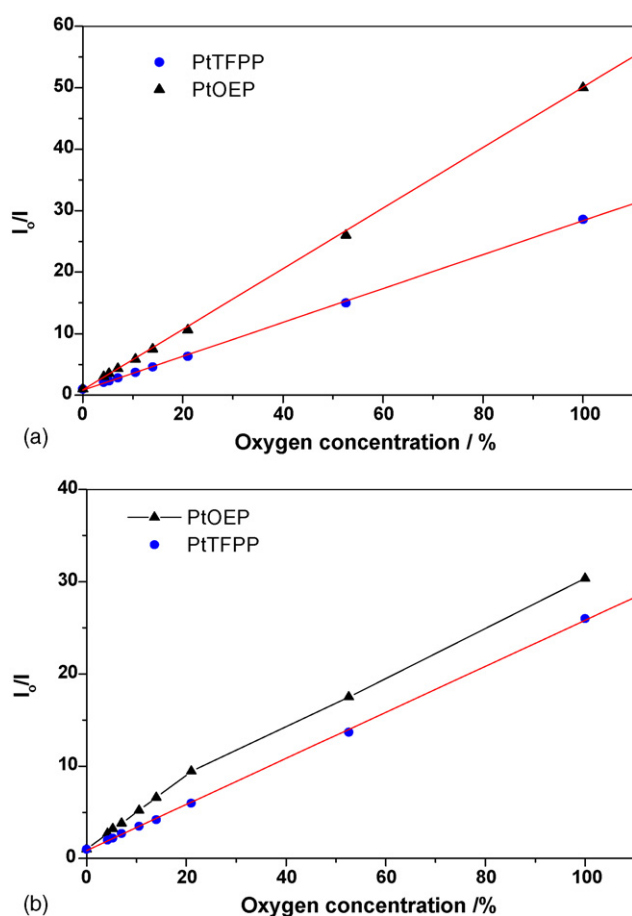


Fig. 6. Stern–Volmer plots for ormosil sensor coatings doped with PtOEP and PtTFPP (2 mg dye in a sol containing 2 ml MTEOS) (a) for freshly prepared coatings and (b) for 1-year-old coatings.

coating doped with PtOEP in air and in the presence of nitrogen are shown in Fig. 7a and b, respectively ( $\lambda_{em} = 645$  nm). The luminescence decay kinetics of both PtOEP- and PtTFPP-doped sensor coatings in the presence of nitrogen obeyed a single exponential equation,

$$I(t) = \alpha \exp\left(\frac{-t}{\tau}\right) \quad (2)$$

where  $\alpha$  and  $\tau$  represents the amplitude and lifetime of the decay components, respectively. The phosphorescence lifetime ( $\tau_0$ ) of PtOEP sensor coating in nitrogen was about 110  $\mu$ s whereas the lifetime ( $\tau_0$ ) of PtTFPP in sensor was 80–82  $\mu$ s (Table 2). The  $\chi^2$  values in all the cases were near unity. It has been reported earlier that the decay curves of porphyrin dyes are single exponential decays in the absence of oxygen [8,14,33]. On the other hand,

Table 2

Luminescence decay lifetimes of ormosil coatings doped with PtOEP and PtTFPP in the presence of air and nitrogen

Coating <sup>a</sup>	In air			In nitrogen		
	$\tau$ ( $\mu$ s)	$\alpha$	$\chi^2$	$\tau$ ( $\mu$ s)	$\alpha$	$\chi^2$
PtOEP-1	69.90	0.700	0.996	108.8	1.0	1.0019
	11.04	0.275				
	290.47	0.025				
PtOEP-2	71.24	0.692	1.006	110.3	1.0	1.0037
	12.28	0.292				
	290.56	0.016				
PtTFPP-1	34.98	0.605	1.0037	80.0	1.0	1.010
	10.82	0.382				
	292.80	0.013				
PtTFPP-2	34.65	0.594	1.0007	82.3	1.0	1.0022
	11.34	0.383				
	287.00	0.023				

<sup>a</sup> PtOEP-1 and PtOEP-2 (as well as PtTFPP-1 and PtTFPP-2) contain 1 and 2 mg dye, respectively, in the ormosil matrix prepared with 2 ml MTEOS.

the decay kinetics of both coatings followed a three exponential equation in the presence of oxygen in air,

$$I(t) = \alpha_1 \exp\left(\frac{-t}{\tau_1}\right) + \alpha_2 \exp\left(\frac{-t}{\tau_2}\right) + \alpha_3 \exp\left(\frac{-t}{\tau_3}\right) \quad (3)$$

with three lifetime values,  $\tau_1$ ,  $\tau_2$  and  $\tau_3$ . When the decay curves of the coatings in air were fitted with single and double exponential equations, the  $\chi^2$  values were high indicating complex decay behaviour. The emission decays in air are characterized by a long lifetime of negligibly low amplitude and shorter lifetimes of higher amplitudes. This might probably be due to spatial variations in the oxygen concentration in the different regions of the ormosil matrix [33]. The sol–gel environment is complex with different regions like pores, pore wall, interface region and silicate matrix [34]. It is probable that the dye molecules exist in different micro-environments within the sol–gel matrix, and these may have different accessibility to oxygen due to difference in oxygen concentration and its diffusion coefficient. Since Stern–Volmer plots are linear, it can be assumed that dye molecules existing in different sites have the same unquenched lifetimes.

Lu and Winnik have described the factors that affect the interaction of excited dyes in sensor systems with oxygen [33]. Oxygen can adsorb reversibly onto certain regions and then diffuse along the surface until it encounters and quenches an excited dye molecule. This may lead to a higher rate of quenching for the dye molecules located in those regions compared to certain

Table 1

Comparison of emission intensity, oxygen sensitivity, and photodegradation of sensor coatings prepared with ormosil and silicone matrices doped with PtOEP and PtTFPP

Coating	Intensity in air	Intensity in nitrogen	Oxygen sensitivity (%)	Photodegradation (% min <sup>-1</sup> )
PtOEP/silicone	3.44	10.4	66.9	−1.32
PtOEP/ormosil	14.1	128.2	89.0	−0.23
PtTFPP/silicone	29.6	179.4	83.5	−2.90
PtTFPP/ormosil	68.6	418.4	83.6	−0.08

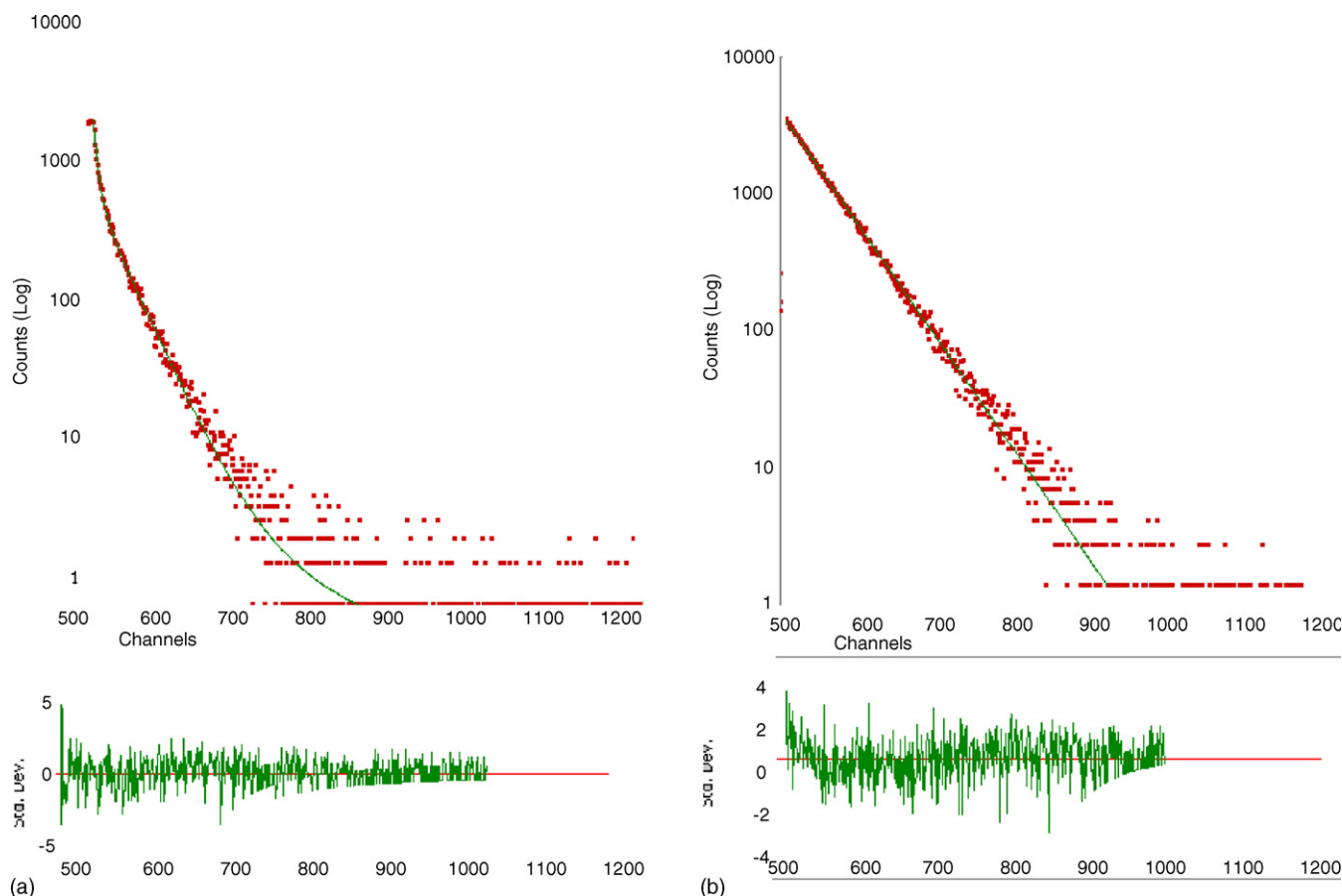


Fig. 7. (a) Typical phosphorescence emission decay curve of an ormosil coating doped with PtOEP in air ( $\lambda_{\text{em}} = 645$  nm). The three exponential fit to the data is superimposed as full line; the residuals are also shown;  $\chi^2 = 0.996$ . (b) Typical emission decay curve of an ormosil coating doped with PtOEP in the presence of nitrogen ( $\lambda_{\text{em}} = 645$  nm) including the single exponential fit to the data superimposed as full line and the residuals;  $\chi^2 = 1.0019$ .

other regions where the oxygen diffusivity is low. The issues are complex and a complete understanding remains a challenge. The main issues are location of the dye and its state of aggregation and location of oxygen in the system. Depending on structure of the dye and the matrix, the dye may remain dissolved or as dimers or aggregates in the sol–gel matrix. Similarly oxygen may remain dispersed in the system or adsorbed preferentially in certain regions. Therefore, it is difficult to explain the complex decay behaviour with our present knowledge.

### 3.3. Photostability and response time of ormosil sensor coatings

Photostability was tested by exposing the porphyrin dye-doped ormosil sensor coatings continuously with excitation radiation from the Xenon lamp under ambient conditions and measuring the emission intensity at periodic intervals. For comparison, the photostability of dye-immobilized silicone coatings was also determined under the same conditions. The degree of photodegradation depends on the luminous flux and the distance of the excitation source from the coating. It also depends on the thickness of the coating and hence the dye-doped ormosil and silicone coatings of same thickness were used for compar-

ison. The photodegradation of dye-doped ormosil and silicone coatings are given in Table 1. The ormosil sensor coatings are found to have better photostability than silicone-based coatings. Even though both silicone and ormosil coatings with PtTFPP have same oxygen sensitivity, the ormosil coatings had higher quantum yield and lower photodegradation. The ormosil coatings also were found to have longer shelf-life. There was no significant change in luminescent intensity and sensitivity after being stored in dark under ambient conditions for a period of 1 year. The coatings also have good mechanical properties like hardness and adhesion. There was no interference from moisture and small amounts of carbon dioxide as present in air.

The change in relative intensity of a dye-doped ormosil coating (of 25  $\mu\text{m}$  thickness) on switching between 100% nitrogen and 100% oxygen for repeated cycles was recorded and is shown in Fig. 8. The response times of the coating were 15 s on switching from nitrogen to oxygen and 60 s on switching from oxygen to nitrogen. This is comparable to the response times obtained for silicone-based sensor films and better than that of polystyrene based sensor films [9–11]. The response times could be further decreased by reducing the thickness of the coating and using an experimental set up to achieve faster switching between the two gases.

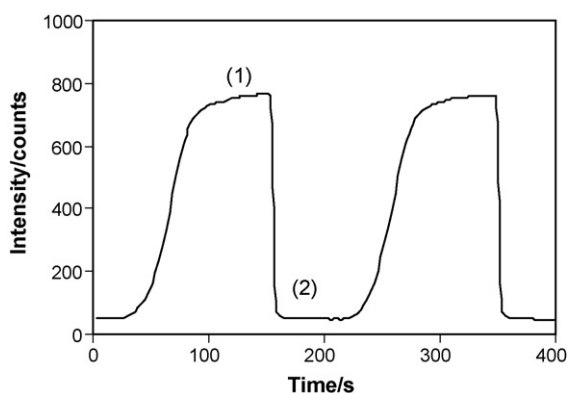


Fig. 8. Response times and intensity change for PtOEP-doped ormosil film on switching between (1) 100% nitrogen and (2) 100% oxygen for 400 s.

### 3.4. Effect of sol–gel process variables on the sensor properties

The porosity of the matrix plays an important role in determining both the sensitivity and response time of optical sensors [19,20,25]. Different process parameters such as water to precursor molar ratio ( $R$ ), pH and aging time influence the rates of hydrolysis and condensation of sol–gel process. It has been reported that  $R$  is an important parameter that controls microstructure and porosity of sol–gel films [20,25]. For oxygen sensors, the diffusion coefficient of oxygen in the matrix increases with porosity of the coating. This in turn increases oxygen sensitivity of the sensor since oxygen sensitivity is dependent on the oxygen permeability of the matrix [33].

The effect of  $R$  on the oxygen sensitivity of PtOEP-doped sol–gel PSP coatings was studied. The sols were prepared as described in Section 2.3. HCl content of the sol was kept constant. Coatings were prepared by adding 0.36 ml 0.1 M HCl to each sol containing 2 ml MTEOS and 1.14 ml ethanol (molar ratio of silane to ethanol was 1:2).  $R$ -values were adjusted to 2, 4 and 6 by adding 0.0, 0.36 and 0.72 ml water, respectively, to the sols. The sols were doped with 1.0 mg dye after stirring for 6 h and then aging for 22 h and coatings were prepared. All coatings were smooth and had good adhesion. Oxygen sensitivity was nearly same for all the different  $R$ -values of the coatings. Further, the effect of  $R$  on sensitivity was studied by keeping the molarity of HCl in the sols constant at 0.1 M.  $R$ -values were adjusted to 2, 4, 6 and 8 by adding, respectively, 0.36, 0.72, 1.08 and 1.44 ml 0.1 M HCl to each sol containing 2 ml MTEOS and 1.14 ml ethanol and the sols were doped with 1.0 mg dye after stirring and aging. Coatings of sol with  $R=2$  were smooth with good adhesion to the substrate while coatings at  $R$ -values of 6 and

Table 4

Effect of HCl concentration of the sol on the oxygen sensitivity of the sensor coating;  $R=2$ ; [dye] = 1.0 mg; aging time = 22 h; thickness of the coating = 20–25  $\mu\text{m}$

HCl added to the sol (M)	Oxygen sensitivity (%)	
	PtOEP	PtTFPP
0.050	86.7	80.1
0.063	86.8	81.3
0.10	89.1	83.5
0.125	90.2	84.1
0.15	88.4	83.7

8 were rough with poor adhesion. Coatings of sol with  $R=4$  had matt finish with intermediate adhesion. The oxygen sensitivity of these coatings were calculated and compared (Table 3). Even though oxygen sensitivity was higher for coatings at  $R=4$ , surface smoothness and adhesion were better for coatings at  $R=2$ . These results indicate that the sensitivity and surface properties of the coating can be controlled by proper adjustment of  $R$  and HCl concentration of the sol.

The effect of HCl concentration of the sol on the oxygen sensitivity of the sensor coatings was studied. Five sols with same composition of MTEOS and ethanol were prepared with same  $R$  ( $=2$ ) and different HCl concentrations. 0.36 ml of HCl with different concentrations varying from 0.01 to 0.25 M were added to the sols. The dye concentration in all the sols was 1.0 mg. The results are summarized in Table 4. It was found that the coatings prepared with sols with HCl concentration  $<0.06$  M did not cure. Coatings of sols with HCl concentrations of 0.10–0.125 M were smooth and had good adhesion to the substrate whereas the coatings of sols with  $>0.15$  M HCl were rough with poor adhesion. The rough coatings peeled due to poor adhesion. The coatings should be smooth and adherent for PSP applications in wind tunnel studies. Hence the optimum HCl concentration of sol should be 0.10–0.125 M. Oxygen sensitivity of coatings was 88–90% for PtOEP and 83–84% for PtTFPP (Table 4).

Aging time has great influence on porosity of sol–gel films [20–25]. During aging, hydrolysis and condensation reactions can cause aggregation and cross-linking. For most of the sols, aging is necessary to produce a sol suitable for spray coating. But aging for too long a period and higher temperature may cause gelation. The effect of aging time on the oxygen sensitivity of the sensor coatings was studied by varying stirring time and aging time. All the sols had the same composition of MTEOS and ethanol and 0.36 ml 0.1 M HCl ( $R=2$ ) but they were stirred and aged for different durations at room temperature. It was found that coatings prepared with sols that were stirred for 3 h and

Table 3

Effect of  $R$  on the oxygen sensitivity of coatings prepared from sols with HCl concentration of 0.10 M; dye concentration in the sol = 1 mg; aging time = 22 h; thickness of the coating = 20–25  $\mu\text{m}$

$R$	Nature of the coating	Oxygen sensitivity of PtOEP-doped sensor (%)	Oxygen sensitivity of PtTFPP-doped sensor (%)
2	Very smooth, good adhesion	90.0	83.5
4	Smooth	92.4	87.1
6	Rough, poor adhesion	$<80$	–
8	Rough, poor adhesion	$<80$	–



Table 5

Effect of dye concentration on the oxygen sensitivity of coatings prepared from sols with  $R=2$ ; HCl concentration = 0.10 M; aging time = 22 h; thickness of the coating = 20–25  $\mu\text{m}$

PtOEP		PtTFPP	
Dye concentration (mg)	Oxygen sensitivity (%)	Dye concentration (mg)	Oxygen sensitivity (%)
0.5	85.7	1.0	83.0
1.0	89.1	2.0	84.2
2.0	89.4	3.0	82.7
		4.0	83.1

aged for  $\leq 20$  h did not cure and were tacky. The tackiness of the coating may be due to incomplete hydrolysis and condensation of the sol. With sols stirred for 6 h and aged for  $\geq 20$  h, completely cured coatings were obtained in 18–20 h. Maximum oxygen sensitivity was obtained for coatings prepared with sols stirred for 6 h and aged for 22 h.

In order to optimize the dye concentration on the phosphorescent intensity and oxygen sensitivity, ormosil coatings with different concentrations of PtOEP and PtTFPP were prepared under the same process conditions and their oxygen sensing properties were studied. 0.36 ml 0.1 M HCl was added to the sols so that  $R=2$  and HCl concentration was constant. The sols were doped with different dye concentrations. The results are shown in Table 5. Phosphorescent intensity increased with increase in dye concentration. However, oxygen sensitivity was nearly constant for coatings with dye contents in the range of 1.0–2.0 mg for PtOEP and 1.0–4.0 mg for PtTFPP.

### 3.5. Effect of temperature on the emission intensity

It is well known that the phosphorescent emission of PSP coatings based on platinum porphyrin dyes are sensitive to temperature [28–32]. Hence the effect of temperature on the intensity was studied for both sensor coatings doped with PtOEP and PtTFPP in the temperature range of 25–50 °C. It was found that the phosphorescent intensity of both coatings decreased almost linearly with increase in temperature. The temperature coefficients of the ormosil coatings doped with PtOEP and PtTFPP were  $-1.6$  and  $-2.0\%/^{\circ}\text{C}$ , respectively. Hence temperature correction has to be applied to get accurate surface pressure measurements in wind tunnel studies. Further work on the incorporation of a temperature sensitive luminophore in the ormosil coating is being carried out.

## 4. Conclusions

The oxygen sensor coatings prepared by doping platinum porphyrin dyes in an ormosil matrix exhibited higher oxygen sensitivity and higher quantum yield compared to silicone-based sensor coatings reported earlier. The method of preparation was fast and curing occurred in  $<24$  h. The coatings could be applied on any planar or non-planar surface by spraying and any desired thickness in the range of 5–40  $\mu\text{m}$  could be obtained. The sensor properties could be optimized by adjusting the sol–gel process

variables like water to precursor molar ratio, acid concentration, dopant concentration and aging time of the sol. The oxygen sensitivities ( $I_0/I_{100}$ ) of these sensor coatings were found to be about 28 and 50 for PtTFPP and PtOEP, respectively, and the typical Stern–Volmer plots for both coatings showed good linearity. The other advantages of the ormosil sensor coatings are excellent surface smoothness, good shelf-life and photostability.

Both sensor coatings exhibited single exponential decay profiles in the absence of oxygen and multi-exponential decay in the presence of oxygen. This may be indicative of spatial variations in oxygen concentration in the ormosil matrix. Photomicrographs of the surface of the sensor coatings revealed that homogenous dye distribution could be obtained only with PtTFPP whereas dye aggregates were observed on the surface of PtOEP-doped sensor.

The results of this study indicate that the sensitivity of these coatings is in the optimum range for PSP applications, the method of preparation and application is simple and fast, quantum efficiency and photostability are better compared to the same dyes in silicone matrix. Even though PtOEP-based ormosil coatings have higher pressure sensitivity, PtTFPP-based coatings may be more suitable for PSP applications due to their higher intensity signal at atmospheric pressure, better photostability and long term stability.

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## Biography

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