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## Studies on the Fabrication and Characterization of Optical Sensor Coatings for Aerodynamic Applications

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**Abstract:** Optical sensor coatings for measurement of surface pressure on aircraft models are based on the principle of oxygen quenching of luminescence. Such luminescent sensor coatings were fabricated by immobilizing luminescent dyes in a suitable polymer matrix. The pressure sensitivity of the sensor coatings depends on the parameters associated with the Stern-Volmer constant,  $K_{sv}$ . These factors include the luminescence lifetime,  $\tau_0$  of the luminophore and the oxygen quenching rate constant,  $k_q$  of the luminophore in the polymer matrix. In the present study, two platinum porphyrin complexes, namely, platinum octaethylporphyrin (PtOEP) and platinum tetrakis (pentafluorophenyl) porphyrin (PtTFPP) were used as the luminescent dyes for the pressure sensor coatings owing to their strong luminescence, long excited state lifetimes, visible light absorption and large Stokes' shifts. The sensor coatings were prepared by doping PtOEP and PtTFPP in polystyrene (PS). The effect of luminophore concentration on photophysical characteristics and oxygen sensitivity was studied. The oxygen sensitivity of PtOEP/PS and PtTFPP/PS coatings were found to be 84 and 71%, respectively. The stability of the coatings was assessed by normal aging and thermal aging tests. The oxygen sensing of the coatings were also studied using lifetime measurements and discussed. The results suggest that these coatings were found to have good potential for the measurement of surface pressure distribution on aircraft models in wind tunnel studies.

**Key words:** Optical sensor, luminescence quenching, platinum porphyrin complexes

### INTRODUCTION

Optical sensor coatings using photoluminescent molecules have received considerable attention in recent years because of their potential applications in various fields, such as environmental monitoring, clinical analysis and aerodynamics (Wolfbeis, 2005; Narayanaswamy and Wolfbeis, 2004; Takeuchi and Amao, 2005; Liu and Sullivan, 2005; Lee and Okura, 1997a, b; Stich and Wolfbeis, 2008; Bell *et al.*, 2001; Gouterman, 1997; Basu *et al.*, 2009; Amao *et al.*, 2000a, b). Platinum octaethylporphyrin (PtOEP) and platinum tetrakis (pentafluorophenyl) porphyrin (PtTFPP) have widely been used as probes for oxygen sensor films (Lee and Okura, 1997a; Stich and Wolfbeis, 2008; Bell *et al.*, 2001; Gouterman, 1997). The platinum porphyrin complexes exhibit strong luminescence, high quantum yield, large Stokes' shifts, visible light absorption, long excited state lifetimes and high oxygen quenching sensitivity. The oxygen sensor coatings are used for measurement of surface pressure distribution on aircraft models in wind tunnel studies

(Stich and Wolfbeis, 2008; Bell *et al.*, 2001; Gouterman, 1997; Basu *et al.*, 2009). Such coatings are prepared by embedding luminescent molecules in suitable polymer binder and are generally known as Pressure Sensitive Paint (PSP) coatings in aerodynamic applications. The oxygen sensitivity is directly related to pressure sensitivity and is dependent on the luminescence lifetime of the sensor molecule and the oxygen permeability of the binder polymer. In order to obtain a sensor coating with high sensitivity, the luminophore dye should have long unquenched excited state lifetime and the polymer matrix should have high oxygen permeability.

The objective of the present study is to fabricate optical sensor coatings using PtOEP and PtTFPP as luminescent dyes and polystyrene (PS) as matrix and to compare their photophysical characteristics. The effect of dye concentration on luminescent intensity and oxygen sensitivity of the sensor coatings was studied. The stability of the sensor coatings was assessed by normal aging and thermal aging tests. The effect of oxygen concentration on luminescence lifetime was also investigated.

## MATERIALS AND METHODS

**Preparation of sensor coatings:** Polystyrene ( $M_w = 250,000$ ) was purchased from Sigma-Aldrich Corporation, USA. PtOEP and PtTFPP were purchased from Porphyrin Products Inc., USA. 0.1% of PtOEP and PtTFPP dye solutions were prepared by dissolving 0.01 g of PtOEP and PtTFPP in 10 mL of toluene ( $1 \text{ mg mL}^{-1}$ ). PS solution was made by dissolving 0.4 g PS in 10 mL toluene.

Different concentrations of PtOEP (0.10, 0.20, 0.40, 0.60, 0.80, 1.0 and 1.2 mg) were mixed with 10 mL PS solution (containing 0.40 g PS) for about 10 min and the mixture was spray coated on aluminium coupons with a white basecoat. Similarly, PtTFPP sensor coatings were prepared by mixing PtTFPP solutions containing 0.10, 0.20, 0.40, 0.60, 0.80, 1.0 and 1.2 mg PtTFPP with PS solution (containing 0.40 g PS) and spraying the mixture. The coupons were cured at room temperature for 24 h prior to measurements. The thickness of the sensor coatings was measured using a micrometer and was found to be about 10-12  $\mu\text{m}$ .

The absorption and luminescence emission spectra were recorded using a Fiber Optic Spectrometer, model S2000 from Ocean Optics, Inc., USA. A 150W Xenon arc lamp, model no. 6258 from ORIEL Instruments was used as the source. Excitation wavelength of 400 nm was used for the measurement of emission of sensor coatings. The luminescence spectra of the coatings were recorded in the presence of air and nitrogen. The lifetime measurements and analysis were carried out using a Time-correlated Single Photon Counting (TCSPC) Fluorescence lifetime measurement system, Fluorocube, model 5000U-14 from M/s Horiba Jobin Yvon IBH Ltd, UK with spectra LED (377 nm) in the MCS mode. Decay curves were recorded in presence of air and nitrogen.

## RESULTS AND DISCUSSION

### Photoluminescence studies of the sensor coatings:

Figure 1 shows the phosphorescence spectra of PtOEP/PS and PtTFPP/PS sensor coatings upon excitation with 400 nm radiation. The emission spectra exhibited a maximum peak at 645 nm. It was observed that the luminescent intensity of PtOEP/PS in the absence of oxygen ( $I_0$ ) was eight-fold than that in the presence of air ( $I$ ) whereas  $I_0$  of PtTFPP/PS was 3.6-fold than that in the presence of air. The decrease in intensity in the presence of oxygen was due to the oxygen quenching of luminescence. The oxygen molecules, permeating through the film collide with these excited dye molecules and quenched their excess energy. The quenching rate constant ( $K_{sv}$ ) of the PtOEP/PS and PtTFPP/PS sensor coatings was evaluated and found to be 0.25 and 0.12 %, respectively.

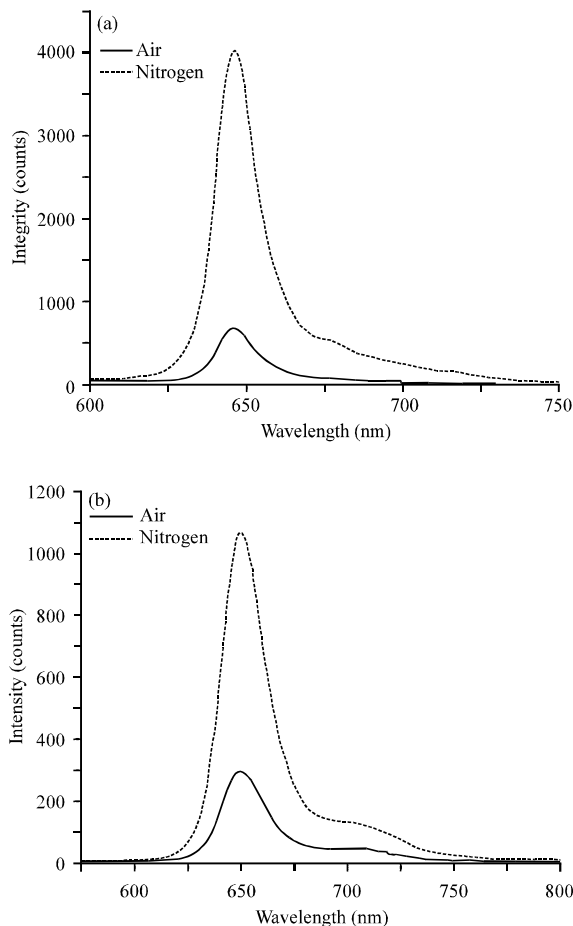


Fig. 1 (a-b): Phosphorescence spectrum of (a) PtOEP/PS and (b) PtTFPP/PS sensor ( $1 \text{ mg g}^{-1}$ ) film in presence of air and nitrogen, ( $\lambda_{\text{ex}} = 400 \text{ nm}$ )

respectively. The mechanism of this quenching process was the exchange energy transfer from the lowest triplet excited state of PtOEP to molecular oxygen, which was accompanied by the formation of singlet oxygen.

The oxygen sensitivity of the PtOEP/PS and PtTFPP/PS sensor coatings were evaluated using the equation:

$$\frac{I_0 - I}{I_0} \times 100$$

where,  $I_0$  and  $I$  were the intensity values of the coating in nitrogen and air respectively. It was found that the oxygen sensitivity of PtOEP/PS and PtTFPP/PS coatings were 84 and 72%, respectively. It is also observed that the oxygen sensitivity remained constant and was independent of the porphyrin dye concentration.

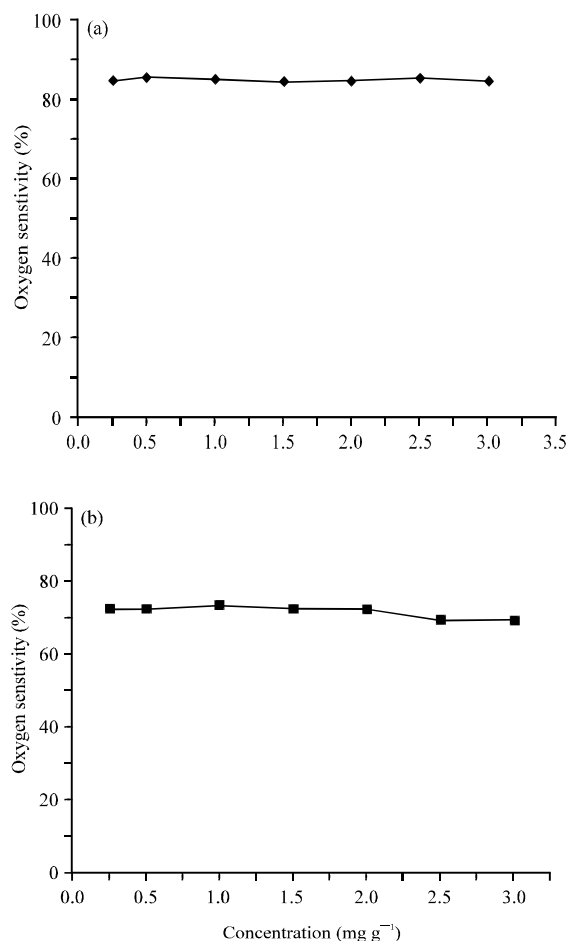


Fig. 2 (a-b): Variation of oxygen sensitivity with concentration of (a) PtOEP/PS and (b) PtTFPP/PS sensor coatings

**Effect of PtOEP and PtTFPP concentration on luminescent intensity and oxygen sensitivity of sensor coatings:** The effect of concentration of PtOEP and PtTFPP on the photophysical characteristics of the sensor was studied at constant concentration of polystyrene. In the case of PtOEP/PS coatings, the PL intensity increased with increasing concentration of PtOEP up to 1.5 mg g<sup>-1</sup> and thereafter the saturation occurred. The PL intensity of PtTFPP/PS coating showed an increase in increase intensity with PtTFPP concentration in the range of 0.25-2.0 mg g<sup>-1</sup>. But no shift in wavelength was observed. Figure 2a and b shows the variation of oxygen sensitivity with PtOEP and PtTFPP concentration in polystyrene sensor coatings. It was found that oxygen sensitivity of PtOEP/PS was independent of the concentration of PtOEP concentration whereas oxygen sensitivity of PtTFPP/PS remained constant in the range of 0.25-2.0 mg g<sup>-1</sup> and decreased slightly at higher concentrations.

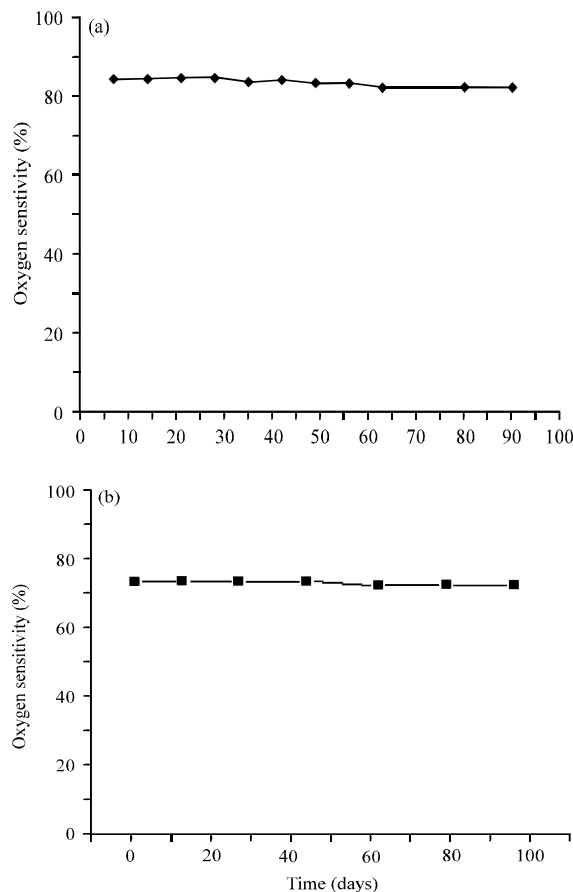


Fig. 3 (a-b): Oxygen sensitivity vs. time (a) PtOEP/PS (2 mg g<sup>-1</sup>) and (b) PtTFPP/PS (2 mg g<sup>-1</sup>) sensor film for 90 days

The ratio,  $I_{N_2}/I_{Air}$  had been used as an indicator of the oxygen sensitivity of the sensor coating, where  $I_{N_2}$  and  $I_{Air}$  were the luminescence intensities in the presence of nitrogen and air, respectively. A sensor having  $I_0/I_{100} > 3.0$  is considered suitable for oxygen sensing device (Amao *et al.*, 2000c) which indicates that both PtOEP/PS and PtTFPP/PS coatings of the present study have fulfilled this criterion and are suitable for oxygen sensing.  $I_{N_2}/I_{Air}$  of PtOEP/PS coating was 8 which was greater than the value ( $I_0/I_{100} = 4.5$ ) for PtOEP/PS reported by (Amao *et al.*, 2000a). High quenching ratios would be the result of good quenching which in turn occurred when the dye molecules were easily accessible to oxygen. This suggests that, a uniform distribution of dye molecules in the polymer matrix is essential to get better oxygen sensitivity.

#### Stability of oxygen sensor coatings

**Normal aging:** The aging effect on oxygen sensitivity of the prepared sensor coatings was studied at regular intervals and the results are shown in Fig. 3a and b. It

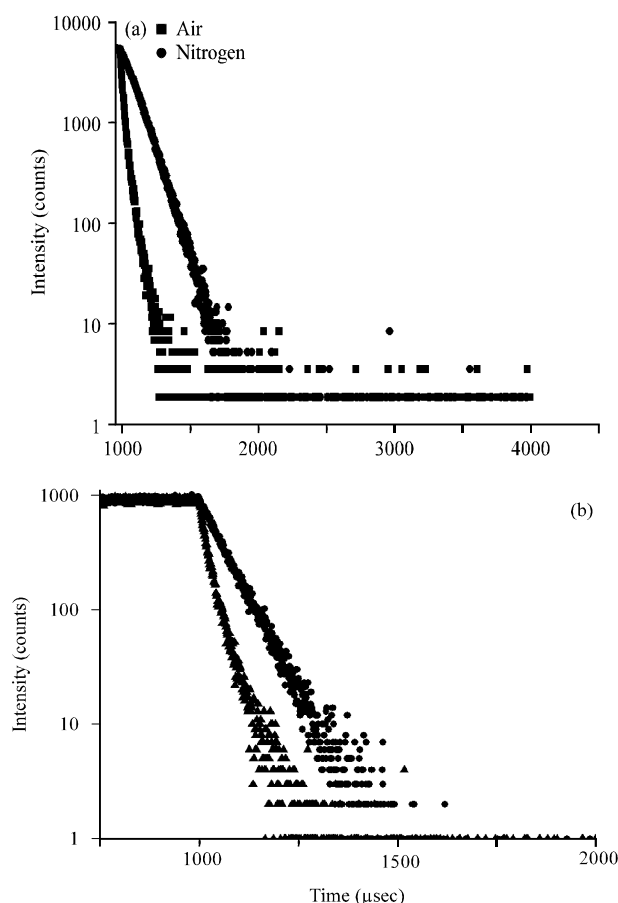


Fig. 4 (a-b): Typical phosphorescence decay curve of (a) PtOEP/PS and (b) PtTFPP/PS sensor film with  $\lambda_{ex} = 377$  nm

was found that the intensity did not change with time. The oxygen sensitivity also remained constant at  $84 \pm 1\%$  for PtOEP/PS and  $71 \pm 1\%$  for PtTFPP/PS, respectively for 90 days. Both sensor coatings were stable up to 90 days as confirmed by the aging studies indicating that there was no degradation of intensity with time.

**Thermal aging:** The PtOEP/PS and PtTFPP/PS sensor films were subjected to thermal aging at  $60^\circ\text{C}$  for 1 h. The luminescent intensity was measured before and after thermal aging. With PtOEP/PS the sensitivity of the films remained  $84 \pm 1\%$  and with PtTFPP/PS the sensitivity of the films remained  $71 \pm 1\%$  before and after thermal aging. These studies suggest that for oxygen sensing applications the PtOEP/PS and PtTFPP/PS are good candidates for sensor films as it exhibited all requirements like high oxygen sensitivity, optimum quantum efficiency and good stability.

**Luminescence decay analysis:** The oxygen sensing of PtOEP/PS also could be performed by lifetime

Table 1: Luminescent lifetimes ( $\tau$ ) for PtOEP/PS in the presence of air and nitrogen

	Lifetime ( $\mu\text{sec}$ )		Amplitude		$\chi^2$	$\langle\tau\rangle(\mu\text{sec})$
	$\tau_1$	$\tau_2$	$\alpha_1$	$\alpha_2$		
Air	2.69	28.13	2.11	97.9	1.05	27.59
N <sub>2</sub>	305.7	102.4	-1.69	101.7	1.00	98.96

Table 2: Luminescent lifetimes ( $\tau$ ) for PtTFPP/PS in the presence of air and nitrogen

	$\tau$ ( $\mu\text{sec}$ )	$\chi^2$
Air	28.56	1.0001
Nitrogen	67.70	1.0010

measurements since they had luminescence lifetimes in the microsecond range and large change in lifetime with oxygen concentration (Amao *et al.*, 2000c). The location of the dye, the location of oxygen and its state of aggregation has the strong influence on the lifetime of luminophore. Figure 4 shows the typical decay curves of (A) PtOEP/PS and (B) PtTFPP/PS sensor coatings in air and in the presence of nitrogen. The excitation wavelength,  $\lambda_{ex}$  was 377 nm and emission wavelength,  $\lambda_{em}$  was 645 nm. The luminescence decay curves of the  $1 \text{ mg g}^{-1}$  of luminophore concentration coatings at  $25^\circ\text{C}$  were recorded in the multichannel scaler (MCS) mode. In a polymer matrix, the emission intensity of a luminophore which decays naturally by a first order process and which is quenched bimolecularly by oxygen is given by the Stern-Volmer equation (Gillanders *et al.*, 2004).

The luminescence decay of PtOEP/PS coatings showed two components (shorter and longer lifetimes) under nitrogen and air saturated conditions. The decay curves obeyed a double exponential behaviour and were analyzed using the expression (Lakowicz, 1999).

$$I(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) \quad (1)$$

where,  $I$  is the luminescence intensity at any time  $t$  after cutting off the excitation wavelength,  $\alpha_1$  and  $\alpha_2$  are constants and  $\tau_1$  and  $\tau_2$  are decay times for the exponential components. Table 1 lists the different components of the luminescent lifetimes ( $\tau_1$  and  $\tau_2$ ) along with their mean lifetime ( $\tau$ ) for PtOEP/PS in air and in the presence of nitrogen. The mean lifetime  $\langle\tau\rangle$  was calculated using the equation,

$$\langle\tau\rangle = \frac{(\tau_1 \alpha_1 + \tau_2 \alpha_2)}{100} \quad (2)$$

It is observed that in presence of air, the average lifetime of the coatings was about 28  $\mu\text{sec}$ . In the presence of nitrogen, the mean lifetime was found to be 100  $\mu\text{sec}$ . The luminescence decay curves of PtTFPP/PS coatings in the presence of air and nitrogen obeyed single exponential fit. The luminescent lifetimes for PtTFPP/PS sensor film in the presence of air and nitrogen are depicted in Table 2.

The decay of photoexcited triplet state of porphyrin dye under oxygen saturated condition was faster than that under nitrogen saturated condition suggest that the effective quenching of the excited triplet state of porphyrin by oxygen. The faster and slower components are attributed to oxygen-accessible sites on the surface and bulk PtOEP and PtTFPP coatings, respectively. The contribution of different oxygen accessible sites in PtOEP/PS and PtTFPP/PS for oxygen sensing is clarified by the above technique.

### CONCLUSIONS

Optical sensor coatings PtOEP/PS and PtTFPP/PS were prepared by spray coating and the performance of these coatings have been examined using photoluminescence and lifetime techniques. It was observed that the luminescent emission measured in absence of oxygen was 8-fold in the case of PtOEP/PS whereas it was 3.6-fold in the case of PtTFPP/PS coatings. The oxygen sensitivities of PtOEP/PS and PtTFPP/PS coatings were found to be  $84 \pm 1$  and  $71 \pm 1\%$ , respectively.

The stability of the coatings was assessed by normal aging and thermal aging tests. The photophysical properties of the coatings remained nearly constant for a period of about 90 days indicating the stability of these sensor coatings. There was no degradation in intensity after thermal aging test at  $60^\circ\text{C}$ . The decay curves of PtTFPP/PS in the presence of air and nitrogen obeyed single exponential fit whereas that of PtOEP/PS obeyed double exponential fit. The lifetime of PtOEP/PS coatings was about 28  $\mu\text{sec}$  in air and 100  $\mu\text{sec}$  in nitrogen. For PtTFPP/PS it was 28  $\mu\text{sec}$  in air and 67  $\mu\text{sec}$  in nitrogen. The faster and slower components are attributed to oxygen-accessible sites on the surface and bulk of the coating respectively. The prepared sensor coatings have high oxygen sensitivity, good quantum efficiency and good stability; hence they may have potential applications as PSP coatings in aerodynamic applications.

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