

## A composite sol–gel/fluoropolymer matrix for dissolved oxygen optical sensing

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### Abstract

A thin film dissolved oxygen optical sensor was fabricated by encapsulating the phosphorescent dye erythrosin B in a sol–gel/fluoropolymer composite matrix. Strong phosphorescence, which was efficiently quenched by dissolved oxygen, was observed. The sensor was stable, optically transparent, resistant to contamination, with good mechanical properties. Fast response, coupled with good sensitivity and resistance to leaching, were also exhibited by this system. The Stern–Volmer (SV) plot was linear at low dissolved oxygen concentrations, but exhibited marked upward turning at higher concentrations due to combined dynamic and static quenching processes.

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### 1. Introduction

An ideal chemical sensor should possess adequate sensitivity, selectivity and detection limits for the particular analyte under consideration. It should also be robust, easy to calibrate and possess long term stability. Dissolved oxygen (DO) sensors which will operate for prolonged periods in hostile and corrosive environments are in considerable demand for industrial and environmental applications. Conventional electrochemical (Clark electrode) detectors are not suitable for such environments since they are easily poisoned by sample constituents such as metal ions, proteins, oxidants and reductants. Consequently, considerable effort has been expended in the development of robust optical sensors based on oxygen sensitive luminescent dyes encapsulated in chemically resistant sol–gels or polymers. Besides being inert, suitable matrices must be able to dissolve the dye, be permeable to oxygen and impermeable to liquid water, and dissolved species which interfere with the operation of the sensor.

Luminescent quenching of organic fluorophores can form the basis of DO detectors due to their fast response, high sensitivity and specificity [1–6]. Unlike electrochemical detectors, they are less easily poisoned. Most of these sensors

have been based on transition-metal complexes trapped in polymer or sol–gel matrices [7–12].

The xanthene dye erythrosin B has shown promise as a suitable probe dye for the detection of both gaseous and dissolved oxygen [13–18]. Previous work has shown that in pure silica sol–gel matrices, erythrosin B phosphorescence is highly quenched by liquid water [18]. Erythrosin B doped sol–gels have been recently evaluated as phosphorescent dissolved oxygen sensors, but only in the form of monoliths containing a relatively high concentration of dye to compensate for excited triplet quenching by water hydroxyl vibrations [17]. Recently, studies of erythrosin B/sol–gel thin films found no detectable phosphorescence, but weak fluorescence which was very efficiently quenched by dissolved oxygen was observed. These results were interpreted on the basis of a singlet oxygen feedback mechanism [18].

In many respects, highly fluorinated polymers are ideal matrices for organic fluorophores. They are chemically inert, permeable to oxygen and since they are highly hydrophobic offer protection from many charged species which may poison the dye. Unfortunately, many highly fluorinated organic polymers are insoluble in common solvents rendering them unsuitable for fabricating thin film sensors. One fluorinated polymer, an amorphous copolymer of tetrafluoroethylene, vinylidene fluoride and propylene, is a colourless rubbery material soluble in ketones and esters. This polymer has recently been investigated as a host material for erythrosin

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B, with a view to constructing a sensitive, robust DO sensor suitable for aggressive aqueous environments. Although promising, this polymer suffered from two problems. Since it is relatively soft, it cannot withstand abrasive aqueous environments for extended periods. Also, due to its low glass transition temperature, the dye molecules tend to form aggregates at elevated temperatures and during the film deposition process. Since the phosphorescence arising from these dye aggregates was not quenched by dissolved oxygen, the sensor showed a large background optical signal. To address these problems sol–gel/fluoropolymer composite films were investigated as possible dye hosts. It was also hoped that these composites would reduce or eliminate some of the problems frequently encountered with pure silica sol–gels such as cracking and loss of transparency, at the same time retaining some of the key advantages of the fluoropolymer matrix. In this paper, the suitability of fluoropolymer/sol–gel composites as hosts for DO sensitive dyes was evaluated. Erythrosin B was chosen as the probe dye since it had already been characterised in both thin film sol–gel and fluoropolymer matrices [18,19].

In a homogeneous solution, when only dynamic quenching is present, the emission intensity of a lumophore, which decays naturally by a first order process, and which is quenched bimolecularly by oxygen (often at a diffusion controlled rate), is given by the Stern–Volmer equation:

$$\frac{I_0}{I} = 1 + \tau_0 k_q [\text{O}_2] \quad (1)$$

where  $I_0$  is the emission intensity of a lumophore which decays naturally in the absence of oxygen,  $I$  the emission intensity in the presence of oxygen,  $\tau_0$  the lifetime of the fluorescing state in the absence of oxygen, and  $k_q$  the bimolecular rate constant for quenching by oxygen. The equivalent kinetic equation is

$$\frac{\tau_0}{\tau} = 1 + \tau_0 k_q [\text{O}_2] \quad (2)$$

where  $\tau$  is the lifetime in the presence of oxygen concentration  $[\text{O}_2]$ . In both cases the dynamic Stern–Volmer constant  $K_{sv}$  is  $\tau_0 k_q$ . The two equations are equivalent when no static quenching is involved.

Frequently, optical sensors based on matrix encapsulated luminescent dyes, deviate from the Stern–Volmer equation at higher oxygen concentrations. Usually, a downward turning curve is found, which is often attributed to dynamic quenching of the triplet state combined with a heterogeneous environment for the immobilised dye molecules. This behaviour can generally be fitted by a two-site model [20]. An alternative model combines both dynamic and static quenching and predicts a quadratic dependence of luminescence intensity on quencher concentration, and a Stern–Volmer plot which turns upward at higher quencher concentration [20].

## 2. Experimental

### 2.1. Chemicals and materials

Erythrosin B (95% pure) and tetraethoxysilane (TEOS) were obtained from Aldrich and used as received. The fluorinated polymer, an amorphous random copolymer of tetrafluoroethylene (~56 wt.%), vinylidene fluoride (~27 wt.%), and propylene (~17 wt.%), was obtained from Aldrich and used without further treatment or purification. Glass microscope slides were obtained from Fischer and cut to dimensions 12 mm × 25 mm were used as substrates for the sensor films. All other chemicals and solvents were reagent grade and used without further purification. De-ionised water was used throughout.

### 2.2. Procedures

The sol–gel/fluoropolymer composite was prepared by mixing a TEOS sol with a 5% solution of the polymer in MEK. In a typical preparation, 4.5 ml of TEOS was mixed with 1 ml 0.1 M HCl and 0.4 ml of deionised water. The mixture was stirred at room temperature for 2 h when a clear homogeneous solution of TEOS sol was formed. After standing at room temperature for 24 h, 1 ml of the TEOS sol was then mixed with 1 ml of a 5% solution of the fluoropolymer in MEK containing erythrosin B at a concentration of  $10^{-4}$  M. After standing overnight, a clear slightly pink solution was obtained which was used immediately to coat the slides.

The substrates were cleaned by soaking in an alkaline detergent, followed by immersion in a solution of ammonium persulphate in 98% sulphuric acid for at least 12 h. This was followed by thorough washing in room temperature de-ionised water, after which the slides were oven dried at 110 °C. The sensors were prepared by dip-coating using cleaned glass substrates. The film thickness was found to be about 600 nm on each side of the glass substrate. The coated slides were cured at room temperature in the dark, for 2 weeks, when transparent, optically clear films were obtained which were not affected by prolonged immersion in water. The films appeared to be unchanged after standing in the dark, at room temperature, for more than 12 weeks.

Steady state luminescence measurements on the coated substrates were made using a Perkin Elmer LS 45B fluorimeter with 530 nm excitation and 10 nm slit widths. The coated slide was placed diagonally in a standard polymethylmethacrylate 1 cm × 1 cm cuvette and the phosphorescence collected at 90° to the exciting radiation beam. Water samples containing different concentrations of dissolved oxygen were obtained by bubbling pure oxygen, air and argon slowly through distilled water, at room temperature for at least 15 min. Other oxygen intermediate dissolved oxygen concentrations were obtained by bubbling appropriate gas mixtures through the water until equilibrium was reached. Oxygen concentrations up to  $20 \text{ mg l}^{-1}$  (the limit of the

meter) were checked using a calibrated Oakton dissolved oxygen meter.

### 3. Results and discussion

#### 3.1. Luminescence emission

The structure of erythrosin B, a xanthene dye, is shown in Fig. 1 together with the molecular structure for the fluoropolymer. The absorption spectrum of a solution of the dye in MEK is shown in Fig. 2. The excitation spectrum of a typical dip-coated slide is shown in Fig. 3. Both spectra shown a strong absorption near 530 nm with a high frequency shoulder. The encapsulated dye absorption however, at 524 nm is blue shifted with respect to the solution absorption at 531 nm, and is also much broader indicating a heterogeneous environment for the dye molecules. With excitation at 530 nm, strong phosphorescent emission at 680 nm was observed when the slide was immersed in air saturated de-ionised water at room temperature.

#### 3.2. Dissolved oxygen sensing

The strong phosphorescence from erythrosin B in the composite matrix decreased in intensity as the dissolved oxygen concentration increased as shown for example in Fig. 4. Typical Stern–Volmer plots (e.g. Fig. 5) all approximately follow first order kinetics (i.e. are fairly linear) up to about  $10 \text{ mg l}^{-1}$  of DO. At higher DO concentrations, the plots all exhibit a very marked upward curvature. A maximum Stern–Volmer ratio  $I_0/I$  of about 82 was observed, corresponding to the ratio of fluorescence emission in de-oxygenated to that in oxygen saturated water at  $20^\circ\text{C}$ . The

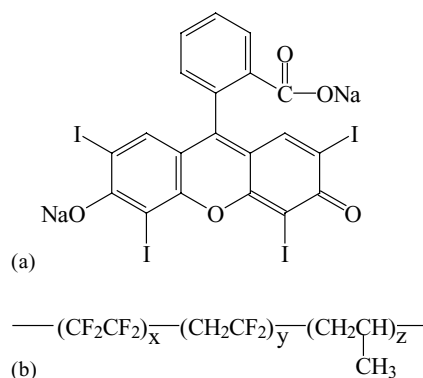


Fig. 1. (a) Structure of erythrosin B. (b) Structure of fluoropolymer ( $x \sim 56 \text{ wt.}\%$ ;  $y \sim 27 \text{ wt.}\%$ ;  $z \sim 17 \text{ wt.}\%$ ).

Stern–Volmer plots can be well fitted by an exponential function facilitating calibration of the sensor.

From Fig. 4, it can be seen that phosphorescence that is not quenched by DO is small, in marked contrast to the pure fluoropolymer based sensors which exhibited a large residual (unquenched) phosphorescence. This suggests, that dye aggregation does not occur to a significant extent in the composite matrix, at least during the coating procedure and at relatively short cure times, and that triplet dye quenching by DO is very efficient. Thus oxygen must diffuse readily through this composite matrix and the dye molecules must largely reside in oxygen accessible sites. The excitation and phosphorescence spectra of the composite encapsulated dye are also somewhat sharper than those found in the pure fluoropolymer matrix [19], indicative of a narrower distribution of local molecular environments in this matrix for the erythrosin B dye.

Curvature in the Stern–Volmer plots at higher oxygen concentrations has been explained on the basis of two

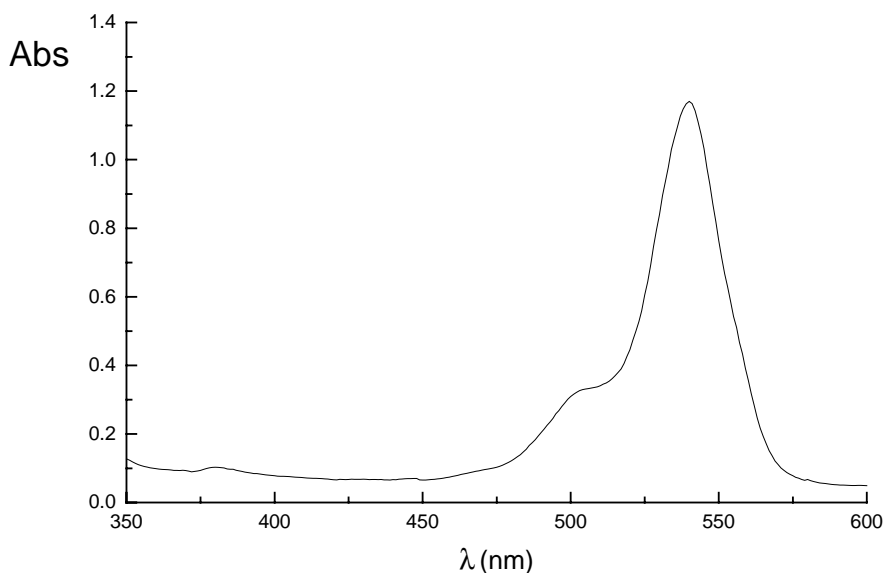


Fig. 2. Absorption spectrum of erythrosin B in air saturated methyl ethyl ketone solution.

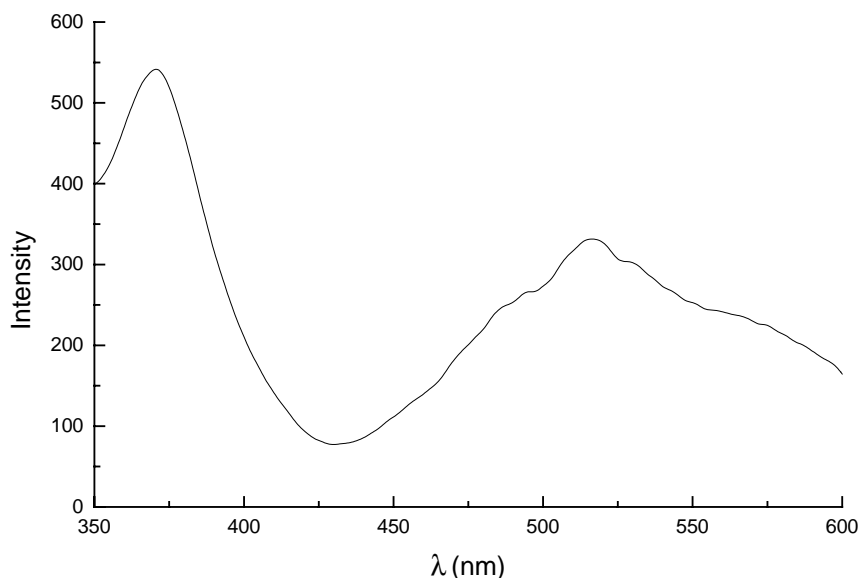


Fig. 3. Excitation spectrum of a dip-coated film of erythrosin B in a sol-gel/fluoropolymer matrix on glass in air.

different theories [20]. The first assumes the presence of two simultaneous quenching processes, dynamic and static in nature with or without a heterogeneous environment for the dye. The second theory assumes dynamic quenching only is present, but the probe molecules are considered to reside in different sites in the matrix with differing accessibility to oxygen molecules.

If the first mechanism is operative, the probe dye is quenched both by excited state collisions, and by ground state complex formation with the quencher. The relative intensity ratio  $I_0/I$  is thus given by the product of both dynamic and static quenching processes.

This assumption leads to the relationship

$$\frac{I_0}{I} = (1 + K_D[Q])(1 + K_S[Q]) = 1 + K_1[Q] + K_2[Q]^2 \quad (3)$$

where  $K_D$  and  $K_S$  are the dynamic and static quenching constants respectively and  $K_1 = K_D + K_S$  and  $K_2 = K_D K_S$ .

Thus, this mechanism leads to a quadratic dependence of  $I_0/I$  on  $[Q]$ . Since  $K_2$  is positive however, the quadratic term can result in an upward curvature to the Stern–Volmer plot which agrees with the observed quenching behaviour in the present composite/dye system. The latter mechanism results

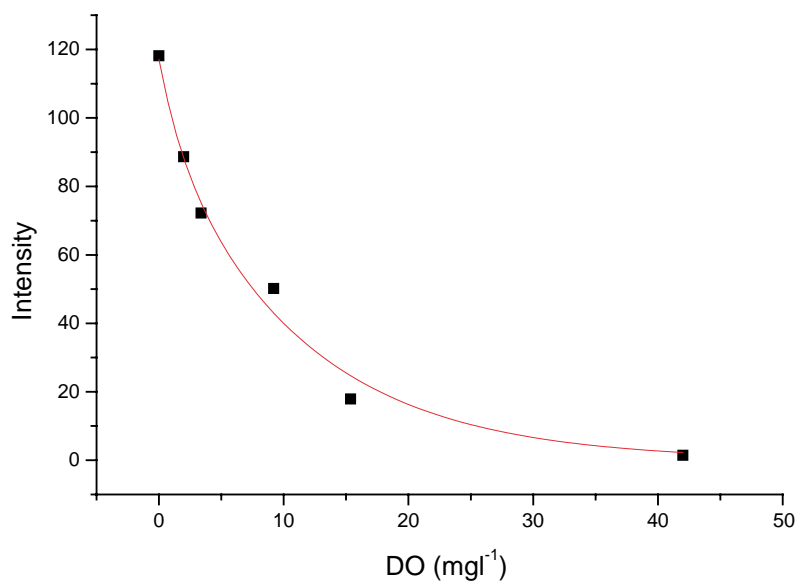


Fig. 4. Variation of phosphorescence intensity of erythrosin B in sol-gel/fluoropolymer matrix at 680 nm with dissolved oxygen concentration.

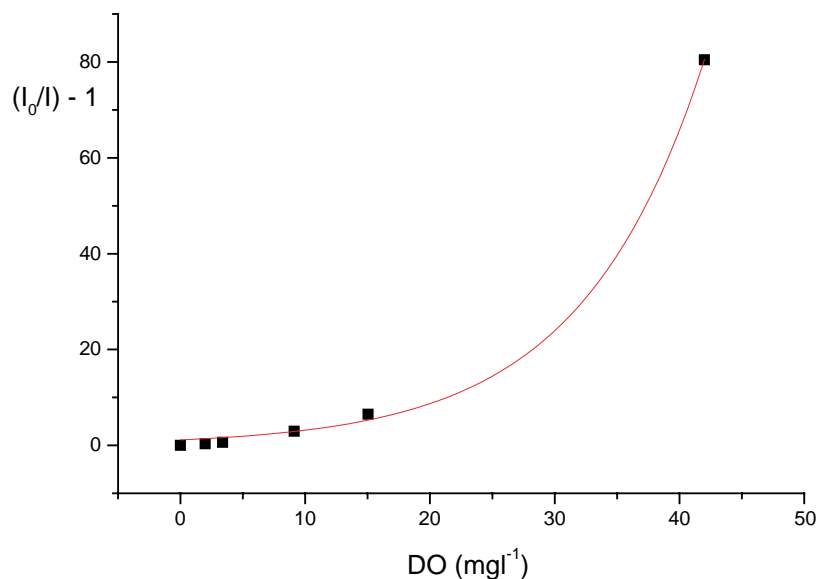


Fig. 5. Stern–Volmer plot for erythrosin B in sol–gel/fluoropolymer matrix. Data fitted by:  $y = \exp(a + bx)$  with  $a = 0.700$ ,  $b = 0.088$ .

in a downward turning Stern–Volmer plot a behaviour previously observed with the fluoropolymer system and which is much more common with oxygen sensors based on encapsulated luminescent dyes.

The relative contributions of dynamic and static quenching processes can be estimated graphically. Eq. (3) can be rearranged to give:

$$\frac{\{I_0/I - 1\}}{[Q]} = (K_D + K_S) + K_D K_S [Q] \quad (4)$$

A plot of  $\{I_0/I - 1\}/[Q]$  against  $[Q]$  yields a straight line with a slope equal to  $K_D K_S$  and an intercept of  $K_D + K_S$ . This plot using the data in Fig. 5, is shown in

Fig. 6. The measured intercept is  $0.16 \pm 0.04 \text{ (mg l}^{-1}\text{)}^{-1}$  and the slope is  $0.01 \pm 0.002 \text{ (mg l}^{-1}\text{)}^{-2}$ . Using these quantities, calculated values for both  $K_D$  and  $K_S$  of about  $0.1 \text{ (mg l}^{-1}\text{)}^{-1}$  were obtained for this model. These equate to values of  $3.2 \times 10^5 \text{ M}^{-1}$  for both  $K_D$  and  $K_S$ . Assuming a phosphorescent triplet lifetime of  $446 \mu\text{s}$  for the dye [16], the corresponding bimolecular quenching constant  $k_q$  is  $7.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . Since the maximum dynamic bimolecular quenching constant for oxygen in aqueous solution is about  $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  these results imply that static quenching is relatively efficient in this system giving rise to the marked upturning Stern–Volmer plot.

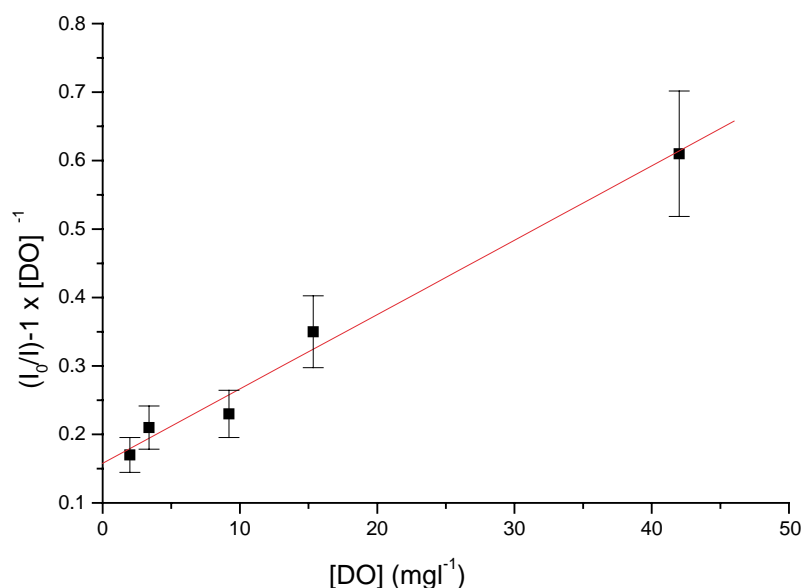


Fig. 6. Separation of the dynamic and static quenching constants for erythrosin B in a composite matrix quenched by dissolved oxygen.  $[Q]$  is the concentration of dissolved oxygen in  $\text{mg l}^{-1}$ .

The conventional interpretation of static quenching assumes the formation of a non-luminescent complex between the chromophore and quencher. In this case, the formation of a conventional ground state complex is improbable. It is more likely, that oxygen molecules in the vicinity of the chromophore during excitation (dark complexes) quench the luminescence of the dye. This type of apparent static quenching is usually interpreted in terms of a “sphere of action” within which the probability of quenching is unity. The modified form of the Stern–Volmer, which describes this situation, is [20]

$$\frac{I_0}{I} = (1 + K_D[Q]) \exp\left(\frac{[Q]VN_A}{1000}\right) \quad (5)$$

where  $V$  is the volume of the sphere in  $\text{cm}^3$  and  $N_A$  the Avogadro’s number. In the present case, the data in Fig. 6 is consistent with a sphere of radius near 9 nm. This is much larger than the combined radii of dye and quencher, but it is probable that the concentration of quencher  $[Q]$  is larger than the experimental value used in the calculation. It is likely, that the matrix consists of microdomains of sol–gel and fluoropolymer. The polar dye would tend to reside in the sol–gel domains while the oxygen molecules would adsorb at the gas/solid interface of the fluoropolymer domains. This would result in a higher local concentration of oxygen in the vicinity of the fluorophore (Langmuir adsorption) resulting in a proportionally smaller calculated value of the active sphere radius. Langmuir adsorption isotherms have been found for gases adsorbed in amorphous polymers both above and below the glass transition of the polymer [19,21]. It is also probable that aggregation of the dye molecules will occur within the sol–gel microdomains leading to a larger radius than the monomolecular species.

Interestingly, a similar upward turning Stern–Volmer plot was also observed with erythrosin B in a pure TEOS sol–gel matrix [18] although in this case no phosphorescence but only weak delayed fluorescence at 590 nm was observed. A similar mechanism could also be operating in this case giving rise to the upward turning Stern–Volmer plots. However, the reduced access to water molecules in the composite matrix would result in less quenching of the phosphorescence. Thus the presence of significant static quenching of the triplet state of this dye seems to be associated particularly with the silica sol–gel matrix since the pure fluoropolymer matrix exhibits the opposite behaviour (i.e. downward turning Stern–Volmer) [19].

The observation of significant delayed fluorescence in the case of the pure sol–gel matrix [18], led to the proposal of a singlet oxygen feedback mechanism. This involves the generation of singlet oxygen  $^1\text{O}_2$  when the erythrosin triplets are quenched by oxygen, followed by activated energy transfer from  $^1\text{O}_2$  to a neighbouring triplet dye molecule producing excited singlet  $^1\text{S}$  states. This mechanism would also be second order in  $[Q]$  resulting in an upward turning

Stern–Volmer plot and may also contribute to the dynamic quenching constant in the present case.

### 3.3. Probe characteristics

Extended reproducible measurements over many weeks showed that photobleaching was not a significant problem with this sensor system at least on this time scale. The slides were however, stored in the dark in closed containers between experiments. No longer term curing or photostability measurements have as yet been carried out but are planned as part of future studies involving optical fibres as well as glass slides as the substrates. The sensors were mechanically stable, quite hard but not brittle. No cracking or chipping of the coatings was observed and the sensors appeared to be generally robust. They were not affected by prolonged immersion in water at room temperature and dye leaching was insignificant. Excellent signal/noise ratios were obtained under the experimental conditions used, and much thinner coatings or lower dye concentrations could be used in future devices incorporating, for example, optical fibre probes.

## 4. Conclusions

Thin film optical sensors, using a composite TEOS sol–gel/fluoropolymer matrix and erythrosin B dye, exhibited strong phosphorescence at 680 nm, which was efficiently quenched by DO in aqueous systems. There was very little residual phosphorescence, in oxygen saturated water. The sensor was linear in concentration at DO concentrations corresponding to air saturated water. At higher DO concentrations, the Stern–Volmer plot turned upwards probably due to the presence of static as well as dynamic quenching. This seems to arise from the formation of dark complexes on specific sites in the sol–gel matrix. Dye leaching, photobleaching, and light scattering were not significant over the time scales measured. This system shows promise as a relatively inexpensive, easily constructed sensor for the optical detection of dissolved oxygen in aggressive aqueous environments. The long phosphorescent lifetimes of the indicator dye also facilitates the use of phase-shift lifetime measurements as alternatives to the steady state intensity techniques used. The combination of attractive properties of the composite matrix should make it an encapsulant of choice for other DO sensitive phosphorescence dyes if long term studies are successful.

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