

# Extruded polymer films pigmented with a heterogeneous ion-pair based lumophore for O<sub>2</sub> sensing

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Andrew Mills\* and Ashleigh Graham

A novel approach to polymeric Ru(II)–diimine luminescent O<sub>2</sub> sensors is described. The Ru(II)–diimine, tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) dichloride ([Ru(dpp)<sub>3</sub>]<sup>2+</sup>), is first ion-paired to the surface of *heterogeneous* TiO<sub>2</sub> particles, rendered negatively charged due to the alkali nature of the aqueous solution, to produce an O<sub>2</sub> sensitive pigment with a strikingly high oxygen sensitivity (*i.e.* PO<sub>2</sub> (*S* = 1/2) = 0.002 atm, where PO<sub>2</sub> (*S* = 1/2) is defined as the amount of oxygen required to reduce the initial, oxygen free luminescence by 50%), and a rapid response to oxygen. The pigment is extruded in low density polyethylene (LDPE) to produce a thin (60 μm), flexible, O<sub>2</sub> sensing plastic film, with an O<sub>2</sub> sensitivity (PO<sub>2</sub> (*S* = 1/2) = 0.84 atm) comparable to the more traditional *homogeneous* lumophore ion-pair based O<sub>2</sub> sensor ink films reported in the literature.

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## 1. Introduction

The detection and quantification of oxygen is of great importance in many industries and practical applications, not least environmental monitoring, medical applications, and more recently, food packaging.<sup>1–3</sup> Research into O<sub>2</sub> detection has increasingly moved away from the more traditional Clark electrode<sup>4</sup> and GC analysis, which is limited by its expense and bulkiness, towards optical detection. Most optical sensors for oxygen are based on luminescence quenching, and within the area of such luminescence-based O<sub>2</sub> sensors, two main dye groups have been studied as the O<sub>2</sub> quenchable lumophores, namely: platinum and palladium metal porphyrins, and ruthenium α-diimines. The latter are favoured because of their large Stokes shift, high quantum yield of luminescence, and high photostability,<sup>5</sup> although the former have generally higher sensitivities (especially the Pd porphyrins).<sup>6</sup> These complexes are quenched by molecular oxygen and so, upon exposure to O<sub>2</sub> the lifetime and luminescence intensity of the lumophore decreases, *i.e.*



In homogeneous media, such as aqueous solution, this quenching is found to obey the linear Stern–Volmer equation, eqn (2), where *I*<sub>0</sub> (and τ<sub>0</sub>) and *I* (and τ) are the luminescence intensities (and lifetimes) in the absence and presence of oxygen, respectively, and *K*<sub>SV</sub> is the Stern–Volmer constant.

$$I_0/I = \tau_0/\tau - (1 = K_{SV}[O_2]) \quad (2)$$

Usually, when these Ru(II)–diimine complexes are used in O<sub>2</sub> sensors, they are immobilized as a *homogeneous* ion-pair with a lipophilic anion, such as tetraphenyl borate, in a hydrophobic encapsulating medium, such as a polymer.<sup>7</sup> More often than not, upon encapsulation, the quenching behaviour of these complexes no longer obeys the linear Stern–Volmer relationship, but instead exhibits a negative deviation from linearity and a new kinetic model is required to fit the quenching data. Probably the most commonly accepted and widely used model to fit such data is the two-site model,<sup>8,9</sup> reported by Demas and co-workers, in which it is assumed that the lumophore exists in two different microdomains within the encapsulating medium, with each microdomain associated with a different quenching response by the lumophore contained therein. The modified Stern–Volmer equation for this system is given in eqn (3), where *f*<sub>01</sub> and *f*<sub>02</sub> are the fractions of the dye molecules in the two different microdomains, the sum of which is unity, and *K*<sub>SV1</sub> and *K*<sub>SV2</sub> are the Stern–Volmer constants of the lumophore in these two microdomains. Although the model is based on two different O<sub>2</sub>-quenching microdomains, it is recognised as a likely gross oversimplification of the true nature of the system.<sup>8</sup> However, eqn (3) does provide a good fit to most data sets generated by lumophores in polymer based O<sub>2</sub> sensors.

$$I/I_0 = f_{01}/(1 + K_{SV1}[O_2]) + f_{02}/(1 + K_{SV2}[O_2]) \quad (3)$$

One of the earliest O<sub>2</sub> sensors based on [Ru(dpp)<sub>3</sub>]<sup>2+</sup>, was reported by Wolfbeis *et al.*, in 1986,<sup>10</sup> and incorporates the lumophore into silica gel beads (5 microns diameter with 30 nm pores), which were then dried, homogeneously mixed with a silicone prepolymer, cured for 12 h at 40 °C, and the volume

School of Chemistry and Chemical Engineering, Queen's University, Stranmillis Road, Belfast, BT9 5AG, UK. E-mail: andrew.mills@qub.ac.uk; Fax: +44 (0)28 9097 6524; Tel: +44 (0)28 9097 4339



**Table 1** Examples of oxygen sensors based on  $[\text{Ru}(\text{dpp})_3]^{2+}$ 

Ion-pair	Encapsulating polymer	$f_{01}$	$K_{\text{SV}1}$ ( $\text{atm}^{-1}$ )	$K_{\text{SV}2}$ ( $\text{atm}^{-1}$ )	$\text{PO}_2$ ( $S = 1/2$ ) (atm)	Ref.
$[\text{Ru}(\text{dpp})_3\text{Cl}_2]$ in silica beads	Silicone, E43	0.83	9.13	0.17	0.16	10
$[\text{Ru}(\text{dpp})_3\text{ClO}_4]_2$	Silicone, RTV-118	0.88	53.65	4.67	0.02	12
$[\text{Ru}(\text{dpp})_3(\text{DS})_2]$	Silicone, E4	0.35	11.55	0.55	0.73	11
$[\text{Ru}(\text{dpp})_3(\text{TSPS})_2]$	Silicone, E4	0.28	15.69	0.60	0.83	11
$[\text{Ru}(\text{dpp})_3(\text{Ph}_4\text{B})_2]$	Cellulose acetate	0.7	20.44	1.76	0.09	13
$[\text{Ru}(\text{dpp})_3(\text{ClO}_4)_2]$	Silicone, RTV-118	0.98	29.25	1.22	0.04	14
$[\text{Ru}(\text{dpp})_3(\text{ClO}_4)_2]$	Polystyrene	0.88	2.02	0.05	0.64	15
$[\text{Ru}(\text{dpp})_3(\text{ClO}_4)_2]$	PVC	0.54	8.66	3.29	0.18	16
$[\text{Ru}(\text{dpp})_3(\text{Ph}_4\text{B})_2]$	PMMA	0.98	23.53	0.001	0.04	7

inside the silica beads – now in a cured silicone membrane – then filled with water by dipping the sensor membrane in boiled water. It is possible in this work that the silica initially binds the  $[\text{Ru}(\text{dpp})_3]^{2+}$  electrostatically, although the authors note the silica has ‘a low ion-exchanging capacity’ and the need for a film hydration step and to store the film in an aqueous or moist environment, suggests that the dye might be instead simply adsorbed as the dichloride salt onto the internal surfaces of the silica beads. Whatever the binding, these films suffer problems of low luminescence and a tendency for the lumophore to undergo self-quenching of luminescence when its concentration exceeds a critical value.<sup>11</sup>

Given these difficulties, other means of encapsulating  $[\text{Ru}(\text{dpp})_3]^{2+}$  into a lipophilic polymer, such as silicone, were investigated subsequently, and now most  $\text{O}_2$  sensors utilise this lumophore in a form in which it is electrostatically bound as an ion-pair to a lipophilic anion, such as perchlorate, dodecyl sulphate ( $\text{DS}^-$ ), tetramethylsilylpropansulfonate ( $\text{TSPS}^-$ ) or tetraphenyl borate ( $\text{Ph}_4\text{B}^-$ ). These are *homogeneous* ion-pair lumophores, many examples of which are given in Table 1 (ref. 7 and 10–16) and, not surprisingly, these ion-pair, lipophilic lumophores are a major feature of most commercial  $\text{O}_2$  optical sensors (e.g. OxySense<sup>17</sup>) and pressure sensitive paints.<sup>18</sup>

Two of the examples in Table 1 utilise the one component, acetic acid releasing, prepolymer, E4 from Wacker (Burhausen, Germany) to encapsulate the  $[\text{Ru}(\text{dpp})_3]^{2+}$  homogeneous ion-pair. This prepolymer, as with many silicone prepolymers, contains a hydrophobic silica gel as a filler.<sup>11</sup> The latter is prepared from hydrophilic silica *via* a reaction of the surface silanol groups with an organosilane, to generate Si–R surface groups, so rendering the material hydrophobic. Klimant and Wolfbeis note that with their numerous *homogeneous*  $[\text{Ru}(\text{dpp})_3]^{2+}$  ion-pair sensors based on E4, ‘the lumophore doesn’t accumulate at the filler/silicone interface’, presumably based on the observation that the ‘quenching constants are similar for sensor membranes based on silicones containing either silica gel as filler or no filler’.<sup>9</sup> Thus, in  $\text{O}_2$  sensors containing hydrophobic silica as a filler, there is no evidence that the lumophore is in anything but its *homogeneous* ion-pair form.

Most oxygen sensors based on the ruthenium diimine lumophores, with and without filler, exhibit a negative deviation from linearity in the Stern–Volmer plots of the observed luminescence data as a function of  $\text{O}_2$  concentration. As a consequence the data is often fitted to eqn (3), values for which

(i.e.  $f_{01}$ ,  $K_{\text{SV}1}$  and  $K_{\text{SV}2}$ ) are given in Table 1 for the various  $[\text{Ru}(\text{dpp})_3]^{2+}$ -based  $\text{O}_2$  sensors. Although formally sensitivity is defined as signal change/concentration, in systems in which a non-linear response curve is generated this formal definition is not considered particularly useful.<sup>19</sup> Thus, with regard to  $\text{O}_2$  sensors, others<sup>20</sup> have used the ratio,  $R = I_0/I_{100}$ , as a measure of sensitivity, where  $I_{100}$  is the luminescence signal in 100%  $\text{O}_2$ . Here, as elsewhere,<sup>7</sup> we use the parameter,  $\text{PO}_2$  ( $S = 1/2$ ) as a rough measure of sensitivity of  $\text{O}_2$  sensors, which is defined as: the level of oxygen required for a 50% reduction in luminescence intensity. A brief examination of Table 1 reveals the  $[\text{Ru}(\text{dpp})_3]^{2+}$ /silicone rubber  $\text{O}_2$ -sensor of Bacon and Demas,<sup>12</sup> with a  $\text{PO}_2$  ( $S = 1/2$ ) = 0.02 atm, to be one of the most sensitive of all the  $\text{O}_2$  sensitive inks based on  $[\text{Ru}(\text{dpp})_3]^{2+}$  that have been reported to date.

In contrast to most of the examples in Table 1, in this paper we present a novel method of luminescent, Ru(II)-diimine-based  $\text{O}_2$  sensor fabrication, in which the cationic, lumiphoric dye,  $[\text{Ru}(\text{dpp})_3]^{2+}$ , is ion-paired to the surface of *heterogeneous*  $\text{TiO}_2$  nanoparticles in aqueous solution, which have been rendered anionic through the exploitation of the pzc (point of zero charge) of the  $\text{TiO}_2$  ( $\sim\text{pH } 6$ ). After filtering, the result is a pigment, which can then be extruded in LDPE to produce a thin ( $60 \mu\text{m}$ ), highly flexible, luminescence-based  $\text{O}_2$  sensitive plastic film. Such *heterogeneous*  $\text{O}_2$  sensors overcome the problems associated with the more traditional, *homogeneous* ion-pair lumophore  $\text{O}_2$ -sensitive inks, such as film curling<sup>12</sup> and the need for a solid, largely inflexible support (such as glass or Mylar).<sup>11,12,15,16</sup>

## 2. Experimental

### 2.1 Materials and instrumentation

The  $[\text{Ru}(\text{dpp})_3]^{2+}$ , in its dichloride salt form, was purchased from GFS Chemicals, and used as received. The P25  $\text{TiO}_2$  powder was a gift from Evonik Industries, and comprised particles with a primary size of 21 nm, in turn comprised of an intimate mixture of 75% anatase and 25% rutile crystalline phases.<sup>21</sup> Titania was chosen as the inorganic support, over silica (pzc  $\sim 3$ ) due to its higher surface density of ionisable protons (12.5 *cf.* 5.9 sites per  $\text{nm}^2$  based on surface crystal structure calculations).<sup>22</sup> The low density polyethylene, LDPE, powder (for masterbatch work) had a melt flow index (MFI) of 20 was supplied by PW Hall UK and the LDPE for film preparation



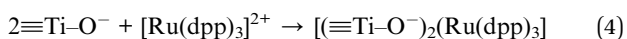
had an MFI of 4 (lupolen 3020 K) and was supplied as pellets by Ultrapolymers UK.

LDPE has been used as an O<sub>2</sub> lumophore encapsulating material before.<sup>23</sup> In this, and other examples,<sup>12</sup> the O<sub>2</sub>-sensitive lumophore (ref. 23 used fluoranthene) is incorporated into the polymer film by soaking the film in a volatile organic solvent, such as cyclohexane, in which the lumophore is dissolved. The solvent causes the polymer film to swell and adsorb some of the solution and rapid drying then leaves some of the dye entrapped in the polymer. Since this approach requires the lumophore to be lipophilic, it follows that such indicators are examples of *homogeneous* O<sub>2</sub> sensing lumophoric systems. One problem with such systems is the tendency for the lumophore to crystallise over time.<sup>11</sup>

All gases were purchased from BOC gases and blended using a Cole Parmer gas blender. All fluorescence work was carried out using a PerkinElmer LS45 Fluorescence Spectrometer. The pigmented polymer film was extruded using a Rondol Microlab Twin Screw extruder.

## 2.2 Preparation of intelligent pigments

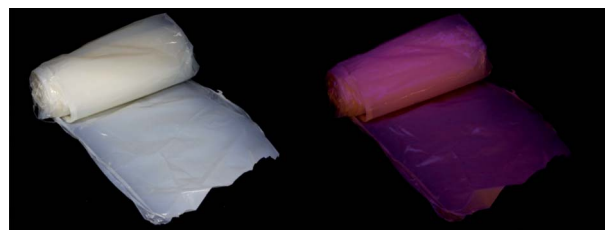
The cationic nature of the [Ru(dpp)<sub>3</sub>]<sup>2+</sup> dye and the point of zero charge (pzc) of the TiO<sub>2</sub> (pH 6.6) were exploited in order to ion-pair the dye to the surface of the titania particles. Thus, at pH 11, the TiO<sub>2</sub> forms surface ≡Ti–O<sup>−</sup> groups, (the latter is a common representation<sup>24</sup> of such surface groups, in this case with the Ti forming 3 bonds to three different atoms in the bulk and one to a surface oxygen) to which the cationic dye can bind *via* ion-pairing, *i.e.*



Hence, typically, to 100 ml of a 10<sup>−4</sup> M solution of the dye in 10<sup>−3</sup> M NaOH (*i.e.* at pH 11) were added 5 g of P25 TiO<sub>2</sub>, the mixture was stirred for 2 hours, filtered, air dried, and the resulting solid washed with three 10 ml aliquots of a 10<sup>−3</sup> M NaOH aqueous solution. The pale yellow/orange powdered solid product was allowed to air dry for a few hours before being transferred to an oven (50 °C) for 1 hour, ground with a mortar and pestle, and sieved through a 250 μm sieve. The final, fine, evenly coated, yellow powder luminesced brightly under UV light in the absence of O<sub>2</sub>.

## 2.3 Preparation of O<sub>2</sub>-sensitive plastic films

The O<sub>2</sub>-sensitive plastic films were fabricated by the extrusion of the TiO<sub>2</sub>–[Ru(dpp)<sub>3</sub>]<sup>2+</sup> pigment powder in low density polyethylene (LDPE), with a final pigment loading of 5 wt%, using a Rondol Microlab 10 mm twin screw extruder (barrel L/D 25/1). The pigment was first dispersed through LDPE powder (melt flow index, MFI, 20) to produce a masterbatch of pigmented pellets with 10 wt% pigmentation, using the extruder to create masterbatch pellets at processing temperatures ramped gradually from 90 °C at the feed zone, to 140 °C at the die, using a feed hopper rate of 41 rpm, extruder screw speed of 80 rpm and a pelletizer speed of 0.5 m min<sup>−1</sup>. These pellets were then diluted by 50% w/w with virgin LDPE pellets (MFI 4) and



**Fig. 1** Photographs of the TiO<sub>2</sub>–[Ru(dpp)<sub>3</sub>]<sup>2+</sup> pigmented extruded LDPE film in air under room light, and under UV light.

extruded to produce a cast film at the following processing conditions: temperatures starting at 90 °C (at the feed zone) then increasing to: 110–125–135 °C (across the barrel) and finally 140 °C (at the die), at a feed hopper rate of 41 rpm, extruder screw speed of 100 rpm, and take-off speed of 1.5 m min<sup>−1</sup>. The average, central thickness of the O<sub>2</sub>-sensitive LDPE film was measured by micrometry to be 60 μm. The TiO<sub>2</sub>–[Ru(dpp)<sub>3</sub>]<sup>2+</sup> pigmented extruded LDPE film was a pale yellow colour and luminesced brightly under UV light even in air, as illustrated in Fig. 1.

## 2.4 Characterization

For luminescence intensity measurements, the pigment and plastic film were both mounted on a microscope slide using double-sided tape, which in turn was cut to fit the diagonal of a typical 1 cm quartz fluorescence cell. In order to maximise the measured luminescence intensity of these solid-state polymer film samples, the slide was placed in the cuvette, and positioned so that the edge of the sensor films was directly in line with the emission detector of the fluorimeter and so square on to the excitation beam, allowing the luminescence, which was mostly gathered by total internal reflection, and exits from the edge of the film, to be more easily measured.

**2.4.1 Oxygen sensitivity.** The emission spectrum of a typical sample (pigment or film) on a microscope slide was recorded after 1 minute purging of a rubber septum sealed fluorescence cell with gas blends containing different, known, levels of argon and oxygen; with λ<sub>excitation</sub> always set at 430 nm. The desired O<sub>2</sub>/Ar mixtures/blends were generated using a Cole-Parmer gas blender fitted with 150 mm flow tubes, and fed by separate streams of pure Ar and O<sub>2</sub>. The cycles of response–recovery curves were generated by using the fluorimeter in the timedrive mode, which allows the luminescence intensity at one wavelength (typically 615 nm for the pigment, and 600 nm for the extruded film) to be recorded as a function of time.

**2.4.2 Lifetime measurements.** The lifetime measurements were carried out using an in-house built nanosecond flash photolysis system. Briefly, the system comprised a Continuum Surelite I-10 Nd–YAG laser connected to a Surelite Separator Package (SSP), as the excitation source used to excite the sample film in the sample chamber. The luminescence produced by laser excitation of the sample was detected using a system comprising a monochromator coupled to a photomultiplier tube (PMT) detector. The laser was used at a power of ~5 mW,



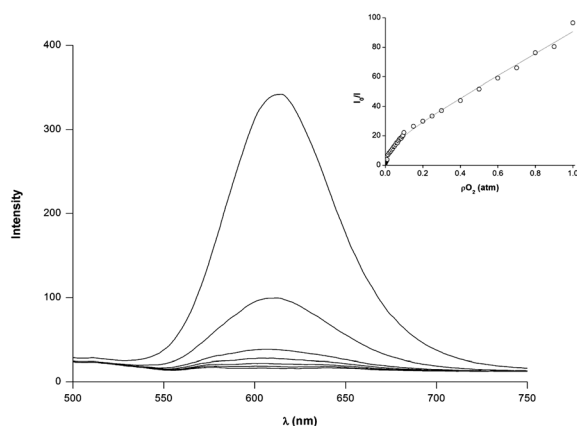
with a 355 nm dichroic mirror in place, and the monochromator set at 600 nm (the maximum wavelength of emission for most of the indicator films). The pulse had an energy of 5 mJ, and a pulse width of 4–6 ns, and the samples were positioned as per the fluorimetry work, *i.e.* approximately perpendicular to the excitation light.

### 3. Results and discussion

#### 3.1 $\text{TiO}_2$ -[Ru(dpp) $_3$ ] $^{2+}$ pigment as an $\text{O}_2$ indicator

Upon excitation at 430 nm, the emission maximum of the  $\text{TiO}_2$ -[Ru(dpp) $_3$ ] $^{2+}$  pigment (adhered to a microscope slide using double-sided tape) was observed at 615 nm. Quenching of this luminescence was monitored as a function of partial pressure of  $\text{O}_2$ ,  $\text{PO}_2$ , and the resulting recorded emission spectra are shown in Fig. 2, with the corresponding Stern–Volmer plot shown as the inset diagram. As expected, a negative deviation from linearity was observed in this plot, so eqn (3) was used to model the data, and the resulting calculated optimum fit parameters are presented in Table 2.

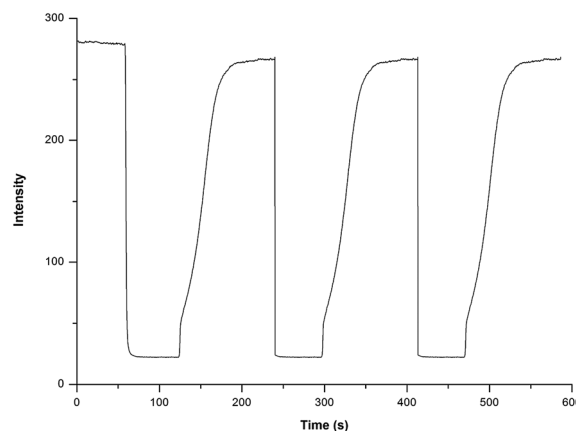
These quenching parameters reveal the pigment to be extremely sensitive to oxygen, more so than the *homogeneous*, ion-pair, ink-based  $\text{O}_2$  sensors reported in Table 1; indeed, the calculated  $\text{PO}_2$  ( $S = 1/2$ ) (0.002 atm) for the pigment (see Table 2) is ten times less than that of the Bacon and Demas<sup>12</sup> silicone-based sensor (see Table 1). This is not too surprising given the  $\text{O}_2$ -sensitive lumophoric dye is bound on the surface of the  $\text{TiO}_2$  pigment particles and so much more easily quenched by oxygen than when the *homogeneous* ion-paired dye



**Fig. 2** Emission spectra of [Ru(dpp) $_3$ ] $^{2+}$ - $\text{TiO}_2$  pigment upon exposure to (from top to bottom) 0, 0.01, 0.05, 0.3, 0.6 and 1 atm  $\text{O}_2$ ; inset is Stern–Volmer plot  $\bigcirc$  = experimental data, solid line is 2-site model fit to data.

**Table 2** Quenching parameters of the [Ru(dpp) $_3$ ] $^{2+}$  pigment and LDPE film (determined from luminescence intensity vs.  $\text{PO}_2$  studies)

Indicator type	$f_{01}$	$K_{\text{SV}1}$ (atm $^{-1}$ )	$K_{\text{SV}2}$ (atm $^{-1}$ )	$\text{PO}_2$ ( $S = 1/2$ ) (atm)
$\text{TiO}_2$ pigment	$0.959 \pm 0.004$	$459.7 \pm 44.2$	$3.6 \pm 0.4$	0.002
LDPE film	$0.24 \pm 0.01$	$30.7 \pm 3.5$	$0.65 \pm 0.02$	0.84



**Fig. 3** Repeat response and recovery of  $\text{TiO}_2$ -[Ru(dpp) $_3$ ] $^{2+}$  pigment to alternating streams of 0 and 1 atm  $\text{O}_2$ .

is embedded in the polymer of a dried ink film, since in the latter case the oxygen must first dissolve and then diffuse through the polymer in order to quench the homogeneously dispersed lumophore.

In a separate experiment, the luminescence intensity response of the titania-[Ru(dpp) $_3$ ] $^{2+}$  pigment towards repeated alternating streams of 0 atm and 1 atm  $\text{O}_2$ , and its response and recovery times, were measured by measuring the luminescence intensity as a function of time at 615 nm, and switching the gas stream between pure Ar and  $\text{O}_2$  (Fig. 3). From this data, it was possible to determine the 50% response and recovery times,  $t_{\downarrow 50}$  and  $t_{\uparrow 50}$ , defined as the time taken for the luminescence intensity to decrease/recover by 50% on switching from Ar  $\rightarrow$   $\text{O}_2$ , and back again, which were 2 s and 25 s, respectively.

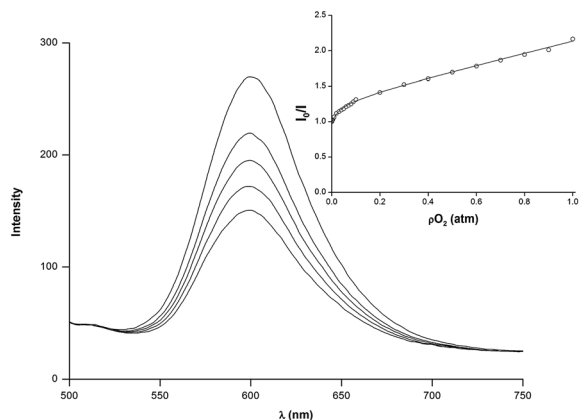
The extremely rapid change in luminescence of the [Ru(dpp) $_3$ ] $^{2+}$  bound to the surface of the  $\text{TiO}_2$  particle pigment upon exposure to  $\text{O}_2$  ( $\leq 2$  s) is also likely due to the large surface area of the pigment (*ca.* 50 m $^2$  g $^{-1}$ ) which provides much greater access for the  $\text{O}_2$  to the quencheable, surface-bound lumophore. Note that in this work, the relative humidity sensitivity of the pigment was not evaluated and may alter the  $\text{PO}_2$  ( $S = 1/2$ ) value reported in Table 2.

#### 3.2 $\text{TiO}_2$ -[Ru(dpp) $_3$ ] $^{2+}$ - pigmented LDPE film as an $\text{O}_2$ indicator

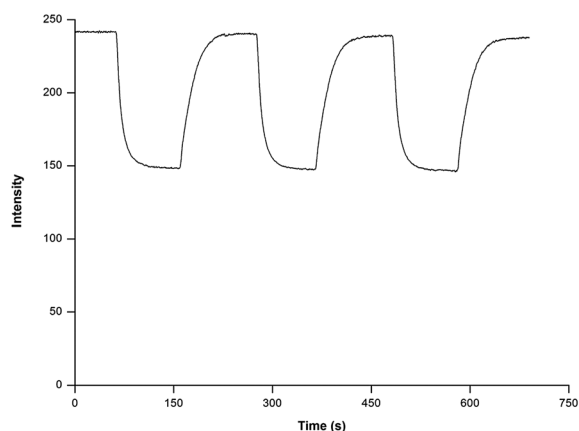
**3.2.1 Luminescence intensity studies.** Upon extrusion of the  $\text{TiO}_2$ -[Ru(dpp) $_3$ ] $^{2+}$  lumophore in LDPE, the luminescence properties of the polymer film were studied and the emission maximum of the film observed at 600 nm, *i.e.* slightly blue-shifted, but otherwise similar in shape, to that of the lumophore ion-pair on the naked pigment (compare the data in Fig. 2 and 4). The intensity of this luminescence was measured as a function of  $\text{PO}_2$ , the results of which are shown in Fig. 4, and a corresponding Stern–Volmer plot generated from the data (inset, Fig. 4). As expected, and as seen for the  $\text{TiO}_2$ -[Ru(dpp) $_3$ ] $^{2+}$  pigment, the Stern–Volmer plot showed negative deviation from linearity, and as such was analysed using the 2 site model and







**Fig. 4** Emission spectra of  $[\text{Ru}(\text{dpp})_3]^{2+}$  LDPE film upon exposure to (from top to bottom) 0, 0.1, 0.3, 0.6 and 1 atm  $\text{O}_2$ ; inset is Stern-Volmer plot  $\bigcirc$  = experimental data, solid line is 2-site model fit to data.

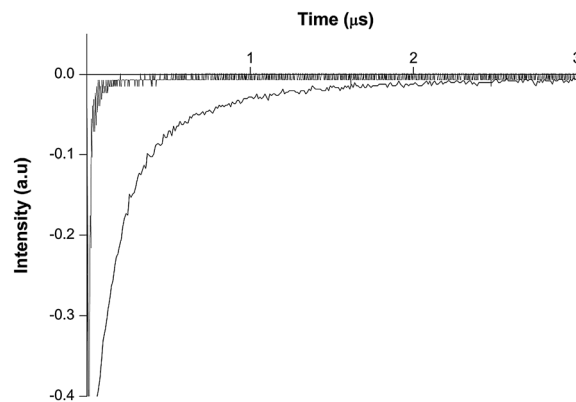


**Fig. 5** Repeat response and recovery of  $\text{TiO}_2$ - $[\text{Ru}(\text{dpp})_3]^{2+}$  pigmented LDPE film to alternating streams of 0 and 1 atm  $\text{O}_2$ .

eqn (3); the calculated optimum fit quenching parameters for which are presented in Table 2.

A study of the variation in luminescence intensity upon switching the gas stream alternately from  $\text{O}_2$  to Ar was carried out and the results are illustrated in Fig. 5, from which values for  $t_{\downarrow 50}$  and  $t_{\uparrow 50}$  were calculated to be 6 s and 14 s, respectively. These results show that the *heterogeneous* lumophore ion-pair  $\text{O}_2$  sensitive film has a much (*ca.* 420 times) reduced  $\text{O}_2$  sensitivity compared to the pigment alone most probably due to the low  $\text{O}_2$  permeability in LDPE ( $2.3 \times 10^{10} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cm Hg}^{-1}$  (ref. 25)). However, despite this, the extruded  $\text{TiO}_2$ - $[\text{Ru}(\text{dpp})_3]^{2+}$  pigmented LDPE film reported here is of comparable  $\text{O}_2$  sensitivity to the  $[\text{Ru}(\text{dpp})_3]^{2+}$ -silicone sensors previously reported and listed in Table 2, which is possibly not too surprising given the similarity in  $\text{O}_2$  permeability, *i.e.*  $P_{\text{M}}$  (silicone) =  $6.2 \times 10^{10} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cm Hg}^{-1}$ .<sup>26</sup>

Finally, the luminescence responses of the  $\text{TiO}_2$ - $[\text{Ru}(\text{dpp})_3]^{2+}$  pigmented extruded LDPE film to 0, 0.21 and 1 atm  $\text{O}_2$  in the presence (100%) and absence (0%) of relative humidity (RH) were measured, and the results indicated little, if any, change in



**Fig. 6** Typical decay curves of the  $\text{TiO}_2$ - $[\text{Ru}(\text{dpp})_3]^{2+}$  pigmented LDPE film in the absence and presence of  $\text{O}_2$ .

the  $\text{O}_2$  sensitivity of the indicator to changes in RH. This is most likely due to the low permeability of water in polyethylene ( $0.05 \times 10^{10} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cm Hg}^{-1}$ ), which is in striking contrast to silicone rubber ( $51.8 \times 10^{10} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cm Hg}^{-1}$ ).<sup>27</sup>

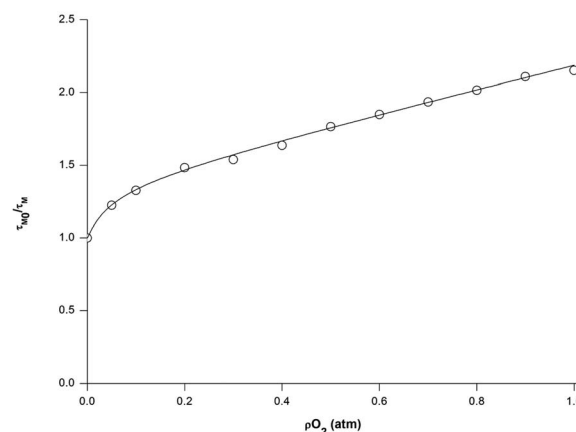
### 3.2.2 Luminescence lifetime studies

Quenching analysis of the extruded film was additionally carried out *via* lifetime measurements, and typical nanosecond flash photolysis luminescence decay curves of the lumophore in the extruded film in the presence and absence of  $\text{O}_2$  are shown in Fig. 6.

As expected, these decays were not described by simple first order kinetics, as expected for homogeneous solutions, but rather a multi-exponential decay was observed. Such decays fit eqn (5), as proposed by Demas,<sup>28</sup> for a two quenching domain, heterogeneous system:

$$i(t) = \sum_i \alpha_i e^{-t/\tau_i} \quad (5)$$

where  $i(t)$  is the response of the system,  $\alpha_i$  is the pre-exponential weighting factor for the  $i$  domains, and  $\tau$  is the lifetime. From



**Fig. 7** Lifetime Stern-Volmer plot of  $\text{TiO}_2$ - $[\text{Ru}(\text{dpp})_3]^{2+}$  pigmented extruded LDPE film:  $\bigcirc$  experimental data, solid line is two-site model fit to the data;  $f_{01} = 0.29 \pm 0.02$ ,  $K_{SV1} = 26.4 \pm 7.3 \text{ atm}^{-1}$ ,  $K_{SV2} = 0.59 \pm 0.05 \text{ atm}^{-1}$ ,  $\text{PO}_2$  ( $S = 1/2$ ) = 0.78 atm.



the decay data fitted to eqn (5), it is possible to calculate the preexponentially weighted mean lifetime,  $\tau_m$ , from eqn (6).

$$\tau_m \equiv \frac{\sum \alpha_i \tau_i}{\sum \alpha_i} \quad (6)$$

These weighted lifetimes can be compared directly to the intensity values gained from the fluorimetry work, *via* a corresponding Stern–Volmer (lifetime) plot, the results of which are illustrated in Fig. 7. The calculated quenching parameters derived from fitting the data in Fig. 7 to eqn (3) are in extremely good agreement with those calculated from the intensity data illustrated in Fig. 4, notably a value for PO<sub>2</sub> ( $S = 1/2$ ) of 0.78 atm can be calculated from the lifetime study that compares well with that from the luminescence intensity study (see Fig. 4), of 0.84 atm.

## 4. Conclusions

Most previous work on O<sub>2</sub> sensors involving Ru(II) diimine complexes as the lumophores have combined the cationic lumophores with a lipophilic anion, rendering the *homogeneous* dye-anion ion-pair lipophilic, and so soluble in a solvent containing a polymer such as polystyrene or silicone. In contrast, in this work  $[\text{Ru}(\text{dpp})_3]^{2+}$  is ion-paired to the surface of TiO<sub>2</sub> nanoparticles to produce a *heterogeneous* O<sub>2</sub> sensing pigment, with a strikingly high O<sub>2</sub> sensitivity, most likely due to the ready access afforded to the ambient O<sub>2</sub> to the quenchable luminescent dye,  $[\text{Ru}(\text{dpp})_3]^{2+}$ . This pigment was extruded in LDPE to form a thin, flexible, plastic film which was readily quenched by O<sub>2</sub>. A major drawback of using a *homogeneous* ion-pair polymer ink is the need for a largely inflexible, support on which the ink must be cast and dried prior to O<sub>2</sub> sensing.<sup>11,12,15,16</sup> In contrast, extrusion of polymer films containing the O<sub>2</sub> sensitive lumophore (in this case in pigment form) produces a fully flexible and self-supporting, ready to use, O<sub>2</sub> sensitive film. Other reported problems with the traditional O<sub>2</sub> sensors include: dye leaching in solvents which cause the polymer to swell, such as acetone,<sup>12</sup> and water,<sup>11</sup> film curling,<sup>12</sup> water condensation on the film surface,<sup>12</sup> and a reduction of sensitivity at high RH.<sup>11</sup> The LDPE film produced in this work shows none of these undesirable characteristics and from the results of this work, dye-pigment pairing followed by extrusion into a polymer appears a promising route to make O<sub>2</sub> sensitive, flexible, polymer films.

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