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Extruded polymer films pigmented with a *heterogeneous* ion-pair based lumophore for O_2 sensing

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A novel approach to polymeric Ru(II)–diimine luminescent O_2 sensors is described. The Ru(II)–diimine, tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) dichloride ($[Ru(dpp)_3]^{2+}$), is first ion-paired to the surface of *heterogeneous* TiO_2 particles, rendered negatively charged due to the alkali nature of the aqueous solution, to produce an O_2 sensitive pigment with a strikingly high oxygen sensitivity (*i.e.* PO_2 ($S = 1/2$) = 0.002 atm, where PO_2 ($S = 1/2$) 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_2 sensing plastic film, with an O_2 sensitivity (PO_2 ($S = 1/2$) = 0.84 atm) comparable to the more traditional *homogeneous* lumophore ion-pair based O_2 sensor ink films reported in the literature.

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.[1–3] Research into O_2 detection has increasingly moved away from the more traditional Clark electrode[4] 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_2 sensors, two main dye groups have been studied as the O_2 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,[5] although the former have generally higher sensitivities (especially the Pd porphyrins).[6] These complexes are quenched by molecular oxygen and so, upon exposure to O_2 the lifetime and luminescence intensity of the lumophore decreases, *i.e.*

$$D + h\nu \rightarrow D^* \tag{1a}$$

$$D^* + O_2 \rightarrow D + O_2^* \tag{1b}$$

In homogeneous media, such as aqueous solution, this quenching is found to obey the linear Stern–Volmer equation, eqn (2), where I_0 (and τ_0) and I (and τ) are the luminescence intensities (and lifetimes) in the absence and presence of oxygen, respectively, and K_{SV} is the Stern–Volmer constant.

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

Usually, when these Ru(II)–diimine complexes are used in O_2 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.[7] 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,[8,9] 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_{01} and f_{02} are the fractions of the dye molecules in the two different microdomains, the sum of which is unity, and K_{SV1} and K_{SV2} are the Stern–Volmer constants of the lumophore in these two microdomains. Although the model is based on two different O_2-quenching microdomains, it is recognised as a likely gross oversimplification of the true nature of the system.[8] However, eqn (3) does provide a good fit to most data sets generated by lumophores in polymer based O_2 sensors.

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

One of the earliest O_2 sensors based on $[Ru(dpp)_3]^{2+}$, was reported by Wolfbeis *et al.*, in 1986,[10] and incorporates the lumophore into silica gel beads (5 microns diameter with 30 nm pores), which were then dried, homogenously mixed with a silicone prepolymer, cured for 12 h at 40 °C, and the volume

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

Ion-pair	Encapsulating polymer	f_{01}	K_{SV1} (atm^{-1})	K_{SV2} (atm^{-1})	PO_2 ($S = 1/2$) (atm)	Ref.
$[Ru(dpp)_3Cl_2]$ in silica beads	Silicone, E43	0.83	9.13	0.17	0.16	10
$[Ru(dpp)_3ClO_4)_2]$	Silicone, RTV-118	0.88	53.65	4.67	0.02	12
$[Ru(dpp)_3(DS)_2]$	Silicone, E4	0.35	11.55	0.55	0.73	11
$[Ru(dpp)_3(TSPS)_2]$	Silicone, E4	0.28	15.69	0.60	0.83	11
$[Ru(dpp)_3(Ph_4B)_2]$	Cellulose acetate	0.7	20.44	1.76	0.09	13
$[Ru(dpp)_3(ClO_4)_2]$	Silicone, RTV-118	0.98	29.25	1.22	0.04	14
$[Ru(dpp)_3(ClO)_4)_2]$	Polystyrene	0.88	2.02	0.05	0.64	15
$[Ru(dpp)_3(ClO)_4)_2]$	PVC	0.54	8.66	3.29	0.18	16
$[Ru(dpp)_3(Ph_4B)_2]$	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 $[Ru(dpp)_3]^{2+}$ 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.[11]

Given these difficulties, other means of encapsulating $[Ru(dpp)_3]^{2+}$ into a lipophilic polymer, such as silicone, were investigated subsequently, and now most 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 (DS^-), tetramethylsilypropansulfonate ($TSPS^-$) or tetraphenyl borate (Ph_4B^-). 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 O_2 optical sensors (*e.g.* OxySense[17]) and pressure sensitive paints.[18]

Two of the examples in Table 1 utilise the one component, acetic acid releasing, prepolymer, E4 from Wacker (Burhausen, Germany) to encapsulate the $[Ru(dpp)_3]^{2+}$ homogeneous ion-pair. This prepolymer, as with many silicone prepolymers, contains a hydrophobic silica gel as a filler.[11] 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* $[Ru(dpp)_3]^{2+}$ 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'.[9] Thus, in 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 O_2 concentration. As a consequence the data is often fitted to eqn (3), values for which (*i.e.* f_{01}, K_{SV1} and K_{SV2}) are given in Table 1 for the various $[Ru(dpp)_3]^{2+}$-based 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.[19] Thus, with regard to O_2 sensors, others[20] have used the ratio, $R = I_0/I_{100}$, as a measure of sensitivity, where I_{100} is the luminescence signal in 100% O_2. Here, as elsewhere,[7] we use the parameter, PO_2 ($S = 1/2$) as a rough measure of sensitivity of 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 $[Ru(dpp)_3]^{2+}$/silicone rubber O_2-sensor of Bacon and Demas,[12] with a PO_2 ($S = 1/2$) = 0.02 atm, to be one of the most sensitive of all the O_2 sensitive inks based on $[Ru(dpp)_3]^{2+}$ 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 O_2 sensor fabrication, in which the cationic, lumophoric dye, $[Ru(dpp)_3]^{2+}$, is ion-paired to the surface of *heterogeneous* TiO_2 nanoparticles in aqueous solution, which have been rendered anionic through the exploitation of the pzc (point of zero charge) of the TiO_2 (~pH 6). After filtering, the result is a pigment, which can then be extruded in LDPE to produce a thin (60 μm), highly flexible, luminescence-based O_2 sensitive plastic film. Such *heterogeneous* O_2 sensors overcome the problems associated with the more traditional, *homogeneous* ion-pair lumophore O_2-sensitive inks, such as film curling[12] and the need for a solid, largely inflexible support (such as glass or Mylar).[11,12,15,16]

2. Experimental

2.1 Materials and instrumentation

The $[Ru(dpp)_3]^{2+}$, in its dichloride salt form, was purchased from GFS Chemicals, and used as received. The P25 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.[21] Titania was chosen as the inorganic support, over silica (pzc ~ 3) due to its higher surface density of ionisable protons (12.5 *cf.* 5.9 sites per nm^2 based on surface crystal structure calculations).[22] 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_2 lumophore encapsulating material before.[23] In this, and other examples,[12] the O_2-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_2 sensing lumophoric systems. One problem with such systems is the tendency for the lumophore to crystallise over time.[11]

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 $[Ru(dpp)_3]^{2+}$ dye and the point of zero charge (pzc) of the TiO_2 (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_2 forms surface $\equiv$Ti–O$^-$ groups, (the latter is a common representation[24] 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.*

$$2{\equiv}\text{Ti–O}^- + [\text{Ru(dpp)}_3]^{2+} \rightarrow [({\equiv}\text{Ti–O}^-)_2(\text{Ru(dpp)}_3] \quad (4)$$

Hence, typically, to 100 ml of a 10^{-4} M solution of the dye in 10^{-3} M NaOH (*i.e.* at pH 11) were added 5 g of P25 TiO_2, the mixture was stirred for 2 hours, filtered, air dried, and the resulting solid washed with three 10 ml aliquots of a 10^{-3} 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_2.

2.3 Preparation of O_2-sensitive plastic films

The O_2-sensitive plastic films were fabricated by the extrusion of the TiO_2–$[Ru(dpp)_3]^{2+}$ 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^{-1}. These pellets were then diluted by 50% w/w with virgin LDPE pellets (MFI 4) and 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^{-1}. The average, central thickness of the O_2-sensitive LDPE film was measured by micrometry to be 60 μm. The TiO_2–$[Ru(dpp)_3]^{2+}$ pigmented extruded LDPE film was a pale yellow colour and luminesced brightly under UV light even in air, as illustrated in Fig. 1.

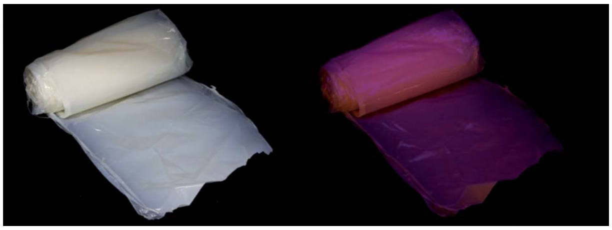

Fig. 1 Photographs of the TiO_2–$[Ru(dpp)_3]^{2+}$ pigmented extruded LDPE film in air under room light, and under UV light.

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 $\lambda_{\text{excitation}}$ always set at 430 nm. The desired O_2/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_2. 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 Continuim 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 TiO_2–$[Ru(dpp)_3]^{2+}$ pigment as an O_2 indicator

Upon excitation at 430 nm, the emission maximum of the 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 O_2, 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 O_2 sensors reported in Table 1; indeed, the calculated 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[12] silicone-based sensor (see Table 1). This is not too surprising given the O_2-sensitive lumophoric dye is bound on the surface of the TiO_2 pigment particles and so much more easily quenched by oxygen than when the *homogeneous* ion-paired dye 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.

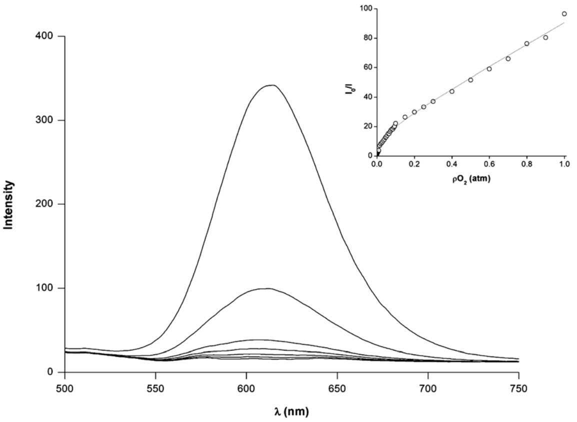

Fig. 2 Emission spectra of $[Ru(dpp)_3]^{2+}$–TiO_2 pigment upon exposure to (from top to bottom) 0, 0.01, 0.05, 0.3, 0.6 and 1 atm O_2; inset is Stern–Volmer plot ○ = experimental data, solid line is 2-site model fit to data.

Table 2 Quenching parameters of the $[Ru(dpp)_3]^{2+}$ pigment and LDPE film (determined from luminescence intensity *vs.* PO_2 studies)

Indicator type	f_{01}	K_{SV1} (atm^{-1})	K_{SV2} (atm^{-1})	PO_2 ($S = 1/2$) (atm)
TiO_2 pigment	0.959 ± 0.004	459.7 ± 44.2	3.6 ± 0.4	0.002
LDPE film	0.24 ± 0.01	30.7 ± 3.5	0.65 ± 0.02	0.84

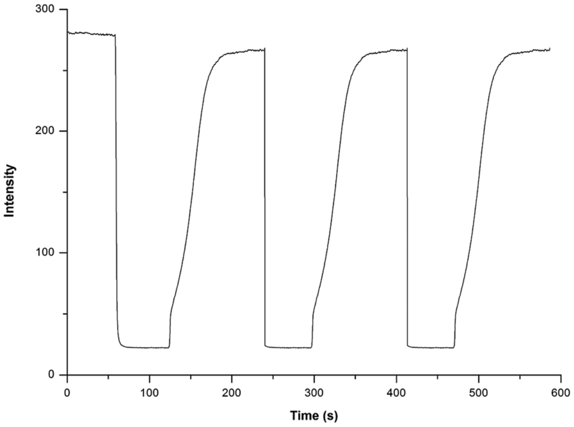

Fig. 3 Repeat response and recovery of TiO_2–$[Ru(dpp)_3]^{2+}$ pigment to alternating streams of 0 and 1 atm O_2.

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 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 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 → 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 TiO_2 particle pigment upon exposure to O_2 (≤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 O_2 to the quenchable, surface-bound lumophore. Note that in this work, the relative humidity sensitivity of the pigment was not evaluated and may alter the PO_2 ($S = ½$) value reported in Table 2.

3.2 TiO_2–$[Ru(dpp)_3]^{2+}$ – pigmented LDPE film as an O_2 indicator

3.2.1 Luminescence intensity studies. Upon extrusion of the 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 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 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

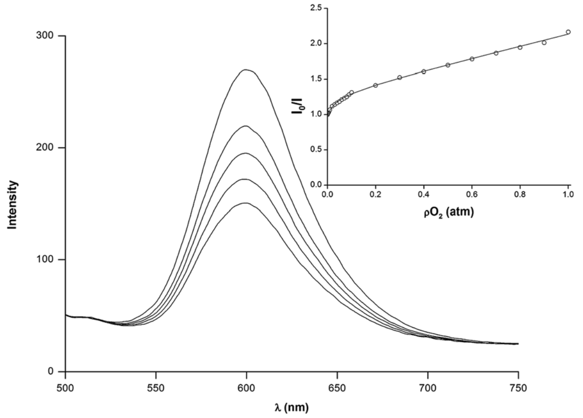

Fig. 4 Emission spectra of $[Ru(dpp)_3]^{2+}$ LDPE film upon exposure to (from top to bottom) 0, 0.1, 0.3, 0.6 and 1 atm O_2; inset is Stern–Volmer plot ○ = experimental data, solid line is 2-site model fit to data.

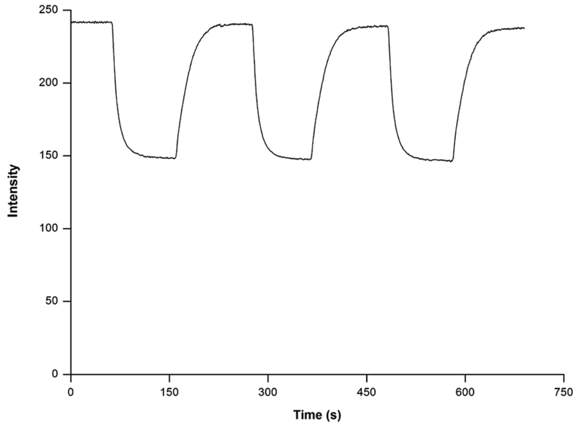

Fig. 5 Repeat response and recovery of TiO_2–$[Ru(dpp)_3]^{2+}$ pigmented LDPE film to alternating streams of 0 and 1 atm O_2.

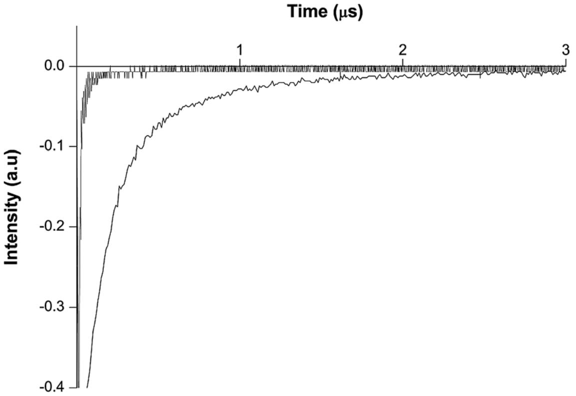

Fig. 6 Typical decay curves of the TiO_2–$[Ru(dpp)_3]^{2+}$ pigmented LDPE film in the absence and presence of O_2.

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 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 O_2 sensitive film has a much (*ca.* 420 times) reduced O_2 sensitivity compared to the pigment alone most probably due to the low O_2 permeability in LDPE (2.3×10^{10} cm^3 cm cm^{-2} s^{-1} cm Hg^{-1} (ref. 25)). However, despite this, the extruded TiO_2–$[Ru(dpp)_3]^{2+}$ pigmented LDPE film reported here is of comparable O_2 sensitivity to the $[Ru(dpp)_3]^{2+}$–silicone sensors previously reported and listed in Table 2, which is possibly not too surprising given the similarity in O_2 permeability, *i.e.* P_M (silicone) = 6.2×10^{10} cm^3 cm cm^{-2} s^{-1} cm Hg^{-1}.[26]

Finally, the luminescence responses of the TiO_2–$[Ru(dpp)_3]^{2+}$ pigmented extruded LDPE film to 0, 0.21 and 1 atm O_2 in the presence (100%) and absence (0%) of relative humidity (RH) were measured, and the results indicated little, if any, change in the O_2 sensitivity of the indicator to changes in RH. This is most likely due to the low permeability of water in polyethylene (0.05×10^{10} cm^3 cm cm^{-2} s^{-1} cm Hg^{-1}), which is in striking contrast to silicone rubber (51.8×10^{10} cm^3 cm cm^{-2} s^{-1} cm Hg^{-1}).[27]

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 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,[28] for a two quenching domain, heterogeneous system:

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

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

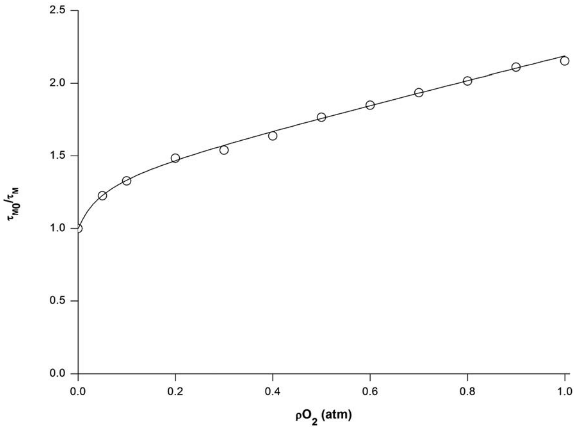

Fig. 7 Lifetime Stern–Volmer plot of TiO_2–$[Ru(dpp)_3]^{2+}$ pigmented extruded LDPE film: ○ experimental data, solid line is two-site model fit to the data; $f_{01} = 0.29 \pm 0.02$, $K_{SV1} = 26.4 \pm 7.3$ atm^{-1}, $K_{SV2} = 0.59 \pm 0.05$ atm^{-1}, PO_2 ($S = 1/2$) = 0.78 atm.

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

$$\tau_{\mathrm{m}} \equiv \frac{\sum \alpha_i \tau_i}{\sum \alpha_i} \qquad (6)$$

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_2 ($S = 1/2$) 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_2 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 –$[Ru(dpp)_3]^{2+}$ is ion-paired to the surface of TiO_2 nanoparticles to produce a *heterogeneous* O_2 sensing pigment, with a strikingly high O_2 sensitivity, most likely due to the ready access afforded to the ambient O_2 to the quenchable luminescent dye, $[Ru(dpp)_3]^{2+}$. This pigment was extruded in LDPE to form a thin, flexible, plastic film which was readily quenched by O_2. 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_2 sensing.[11,12,15,16] In contrast, extrusion of polymer films containing the O_2 sensitive lumophore (in this case in pigment form) produces a fully flexible and self-supporting, ready to use, O_2 sensitive film. Other reported problems with the traditional O_2 sensors include: dye leaching in solvents which cause the polymer to swell, such as acetone,[12] and water,[11] film curling,[12] water condensation on the film surface,[12] and a reduction of sensitivity at high RH.[11] 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_2 sensitive, flexible, polymer films.

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