

A Novel Luminescence-Based Colorimetric Oxygen Sensor with a “Traffic Light” Response

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We report a novel dual-lumophore oxygen sensor incorporating two lumophores: (1) the platinum(II) cyclometalated complex of the N[^]C[^]N-coordinating ligand 1,3,5-tri-(2-pyridyl)benzene and (2) Platinum octaethylporphyrin, which differ in both their emission colours and oxygen sensitivities. Sensor response is given by a dramatic change in emission colour, from red to green at different oxygen concentrations, due to the complete or partial luminescence quenching of one or both of the sensing elements. This approach enables the simple and rapid evaluation of the O₂ concentration present, making it applicable to commercial technologies such as modified atmosphere packaging.

KEY WORDS: Luminescence; oxygen quenching; oxygen sensor; Stern–Volmer; dual-lumophore; colorimetric.

INTRODUCTION

Recent years have seen a growing interest in thin film optical sensors for the sensing of both gaseous and dissolved oxygen [1–10]. Sensor response is characterised by a change in some optical property, such as absorbance or luminescence, as a function of oxygen concentration. The relative advantages of these two approaches with regard to a variety of applications have already been discussed [11–15]. In the development of sensors for food packaging, a visual O₂ indicator is generally favoured [15]. Absorbance-based devices are particularly suited to this application, as sensor response is typically indicated by a colour change enabling qualitative and in some cases semi-quantitative oxygen detection, without the need for expensive spectroscopic equipment [10, 16–19]. Luminescence-based sensors offer an alternative to purely visual O₂ indicators. They provide a non-destructive means of quantitative

O₂ detection, but they do require an external detector [20–22].

To date, most studies of luminescence sensors have concentrated on single lumophore with emphasis on the accurate measurement of oxygen concentration via Stern–Volmer analysis which requires some scientific expertise. In contrast, most work using absorbance sensors has relied on colour-change technology, which gives less accurate measurement but has the advantage of easy operator use. In this work, we report a novel luminescence-based colorimetric sensor for oxygen detection in modified atmosphere packaging (MAP), which combines the advantages of both luminescence and absorbance-based devices. The sensor is prepared by incorporating two lumophores with different oxygen sensitivities and emission colours in the same device, namely (i) a cyclometalated platinum(II) complex of the N[^]C[^]N-coordinating ligand 1,3,5-tri-(2-pyridyl)benzene (PtLCl) and (ii) Pt octaethylporphyrin (PtOEP) (Fig. 1). In degassed dichloromethane solution, PtLCl exhibits intense luminescence in the green spectral region ($\lambda_{em}^{max} = 506 \text{ nm}$, $\Phi_p = 0.57$, $\tau = 9.2 \mu\text{s}$) [23], whereas PtOEP displays a broad, longer-lived emission band in the red ($\lambda_{em}^{max} = 646 \text{ nm}$, $\Phi_p \sim 0.5$, $\tau \sim 100 \mu\text{s}$) [24].

The response of this sensor is characterised by a series of red–orange–green “traffic light” colour changes. We

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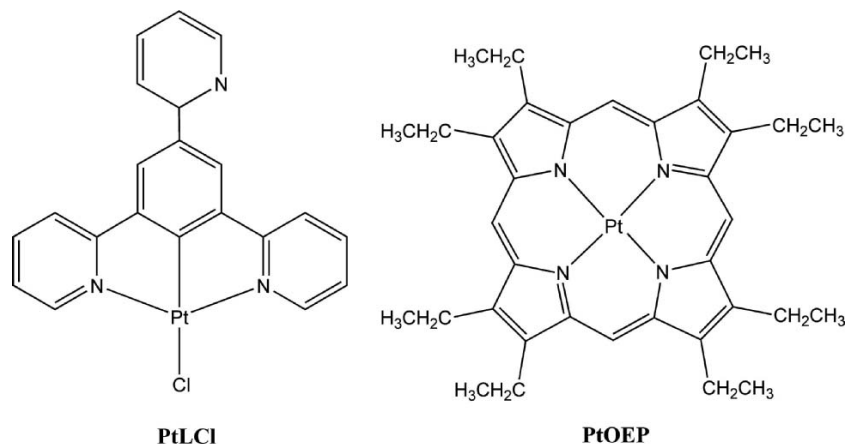


Fig. 1. Structures of lumophores.

selected the *ca.* 500–650 nm spectral region as the human eye exhibits the maximum sensitivity to colour changes across these wavelengths [25]. Colour is a very subjective phenomenon, causing description of colour differences to be quite challenging. The CIE (Commission Internationale de L’Eclairage) system of colorimetry provides a numerical description of colour, known as *xy* colour coordinates, which is based on the human eye’s sensitivity to light across the visible region [26]. We show how the CIE *xy* coordinates may be used to describe the sensor response both qualitatively and semi-quantitatively for rapid oxygen measurements.

EXPERIMENTAL

Materials

PtLCl was synthesised using the previously reported method [23,27]. Cellulose acetate butyrate (CAB) (MW 30000) and ethyl cellulose (EC) (46% ethoxy content) were purchased from Aldrich. PtOEP was obtained from Porphyrin Products Ltd. (Logan, UT, USA). O₂ and N₂ were BOC “high purity” gases and were used as received.

Oxygen sensors were prepared by dissolving 2 mg of lumophore in 2 ml THF and adding 0.4 ml of this solution to 1.0 g of a polymer solution, prepared by dissolving the polymer in an appropriate solvent to give solutions of similar viscosity as follows: EC in 10% (w/v) 80:20 toluene:ethanol and CAB in 20% (w/v) acetone. Sensor films were prepared by spin coating these solutions on glass slides. The dual lumophore sensor was prepared by casting PtOEP-EC and PtLCl-EC as separate layers on the same glass support. The PtOEP-EC layer was allowed to dry completely before casting the PtLCl-EC layer above it.

Methods

Gas mixtures from 0–100% O₂ were generated using a gas blender (model no. 852 V1-B, Signal Instruments Co., UK) with N₂ as the diluent gas. Purging was performed between each measurement to allow equilibration between the gas stream and the film. Films were held in a 1 cm quartz cuvette, the lid of which carried two needles suspended on either side of the film within the cell. This allowed the gas stream of known composition into the cell and onto the film.

Steady-state luminescence measurements were carried out using a Jobin-Yvon JY3D fluorimeter with a continuous Xenon lamp as the excitation source. Time-resolved nanosecond (ns) laser studies were made using a Nd/YAG Spectron laser with an Applied Photophysics laser kinetic spectrometer. The third harmonic pulse (355 nm) was used for excitation and the average trace from 32 kinetic decays was collected on a Gould OS4072 digital storage oscilloscope and transferred to a PC for analysis.

Table I. Unquenched Lifetimes (τ_0), Stern–Volmer Constants (K_{SV}) and Sensitivities ($1/S_{50}$) Calculated for Oxygen Quenching of Sensor Films Using Steady-State and Emission Decay Data

Sensor	τ_0 (μ s)	K_{SV} (Torr ⁻¹)	$1/S_{50}$ (Torr ⁻¹)
PtLCl/EC	5.77	0.0070	0.0070
PtLCl/CAB	6.70	0.0050	0.0040
PtOEP/EC	81	–	0.0625
PtOEP/EC- PtLCl/EC	–	0.060 (PtOEP) 0.0030 (PtLCl)	–

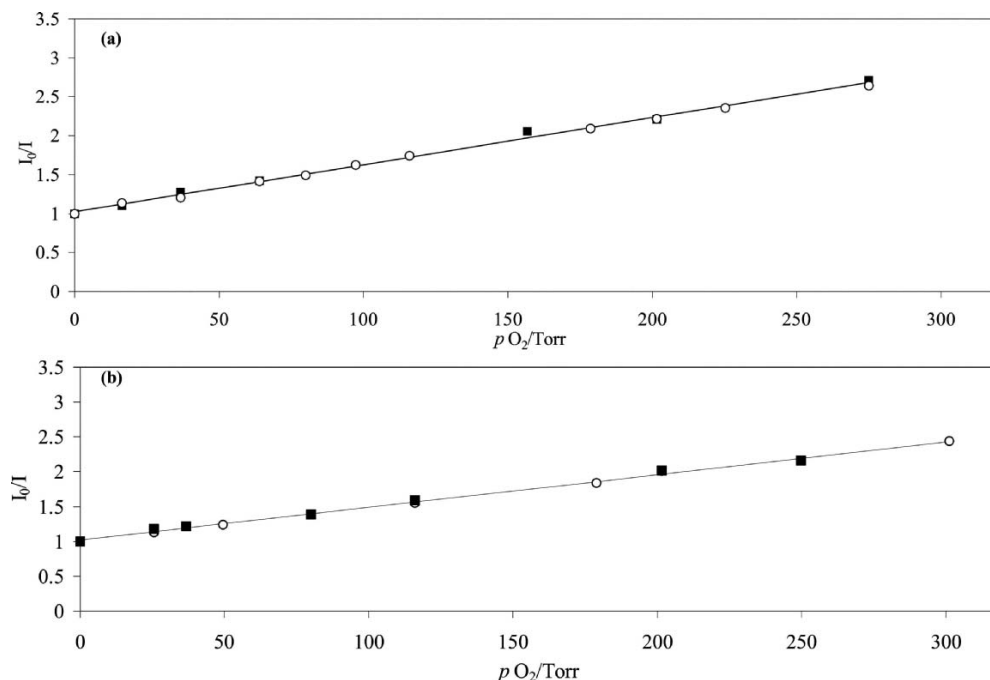


Fig. 2. Stern–Volmer plots for oxygen quenching of PtLCl in (a) EC and (b) CAB polymer films. Data from laser studies (■) and steady-state fluorimetry (●). Curve fits from linear regression

RESULTS AND DISCUSSION

In solution, luminescence from PtLCl is quenched efficiently by O_2 with a quenching rate constant in the order of $10^9 \text{ M}^{-1} \text{ s}^{-1}$. Emission decay curves measured in the absence and in the presence of O_2 are well described by a single-exponential fit, which is as expected for a single species which decays naturally by a first-order process in a homogeneous environment. As the concentration of complex is increased, self-quenching accompanied by excimer formation is observed, with an emission band centered at 680 nm [23]. In EC and CAB polymer films, the luminescence decay curves are also good fits to single exponential decays in the absence of oxygen. The lifetimes (τ_0) measured from these decay curves are shown in Table I. At the concentrations of complex used in the films, there is no evidence of excimer emission, and the observed lifetime is close to the limiting lifetime in solution. It seems probable that in these films the polymer matrix inhibits the bimolecular interaction responsible for excimer formation. In the presence of oxygen the decay curves exhibit more complex kinetics, attributed to lumophore heterogeneity within the polymer matrix [4–6].

Stern–Volmer data for oxygen quenching of PtLCl in EC and CAB films, obtained from steady-state experiments and from the integrated emission decay curves, are shown in Fig. 2. It has previously been shown that

identical results should be obtained by these two experimental methods, provided that excitation intensity is not a significant factor in determining relative emission intensities [5,9]. Here both sets of experimental data are in excellent agreement, indicating that this is true in this instance. CAB films show decreased sensitivity compared with the

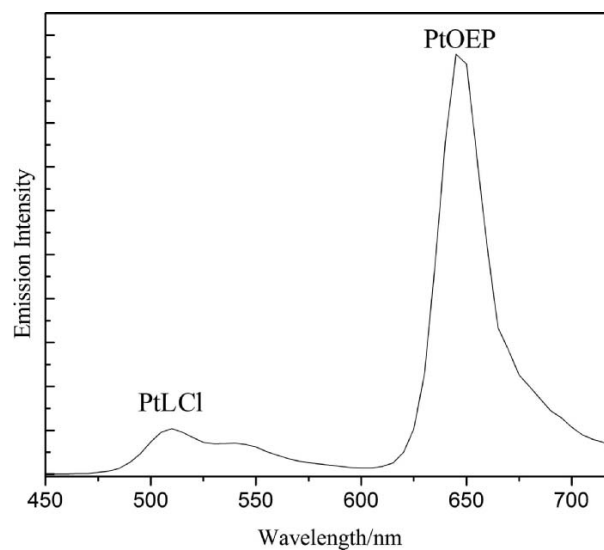


Fig. 3. Emission spectrum of PtOEP/EC-PtLCl/EC dual-lumophore sensors in the absence of oxygen at 295 K. $\lambda_{\text{ex}} = 380 \text{ nm}$.

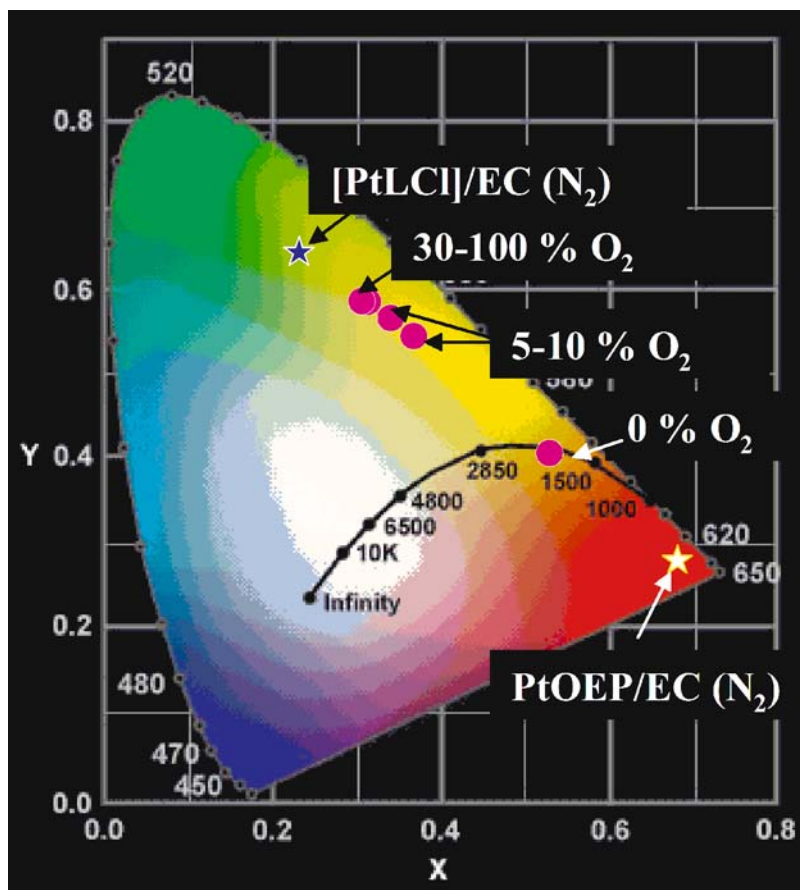


Fig. 4. CIE xy colour coordinates of the PtOEP/EC-PtLCl/EC dual-lumophore sensor response at different oxygen concentrations (in percentage) (○). Single lumophore sensor xy colour coordinates in the absence of O_2 and the xy coordinates of a black body emitter (black line) at temperatures between 1000 K and infinity are included for comparison.

corresponding EC films due to decreased O_2 permeability in the CAB matrix. Stern–Volmer constants (K_{SV}) are small in both polymer matrices as a consequence of the relatively short lifetime of the lumophore (Table I), indicating that these sensors are more suited to the detection of comparatively high oxygen concentrations.

There has been considerable interest in thin film sensors incorporating PtOEP as the sensing element as its long-lived luminescence is very efficiently quenched by oxygen, resulting in highly sensitive sensor films suited to the detection of relatively low oxygen concentrations [5–8]. A dual lumophore oxygen sensor incorporating both PtOEP and PtLCl therefore introduces the possibility of accurate detection over a wide O_2 concentration range. In our novel sensor, PtOEP and PtLCl are cast as two separate EC layers on the same glass substrate. We denote

this as PtOEP/EC-PtLCl/EC. Both lumophores can be excited in the near-UV-blue spectral region but exhibit very different molar extinction coefficients ($PtOEP \gg PtLCl$). In the absence of oxygen, independent luminescence from both species is observed indicating that there is no interaction between the lumophores in the two layers (Fig. 3).

For the dual-lumophore sensor, both PtLCl and PtOEP are quenched to some degree at all oxygen concentrations, with Stern–Volmer constants comparable to those obtained in the corresponding single lumophore sensors (Table I). At low pO_2 the PtOEP layer is quenched preferentially due to its higher sensitivity, whereas the reduced sensitivity of PtLCl allows the complex to emit significantly even at higher oxygen pressures. This results in a gradual, but dramatic shift in the sensor emission

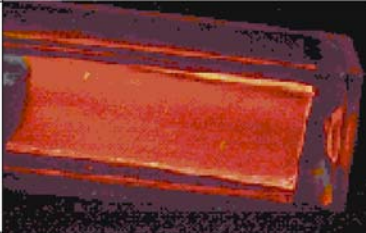
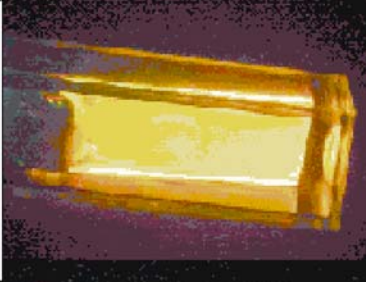
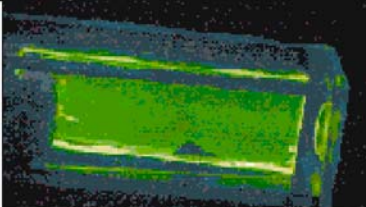
% O ₂	Sensor Colour
0	
5-10	
30-100	

Fig. 5. Observed sensor emission colour at different O₂ concentrations (in percentage). $\lambda_{\text{ex}} = 366$ nm (UV lamp). Photographs taken with a Nikon Coolpix 3700 digital camera.

colour across the red-green spectral region with increasing oxygen concentration.

CIE xy colour coordinates were calculated using the secondary standard observer data [25] for the PtOEP/EC-PtLCl/EC sensor response at a series of oxygen concentrations and are shown in the xy chromaticity diagram in Fig. 4. Significant changes in the xy coordinates correspond to dramatic changes in colour in the diagram. In the absence of O₂, emission from the PtOEP/EC layer is dominant due to its larger molar extinction coefficient at λ_{ex} in this sensor film and the xy coordinates lie in the red domain. With increasing $p\text{O}_2$, luminescence from the PtOEP layer becomes increasingly quenched, until eventually emission from the PtLCl layer is predominantly observed.

The xy chromaticity diagram illustrates the track of the sensor emission colour coordinates across the red-yellow-green spectral region with increasing oxygen concentration (Fig. 4). It is important to note that the CIE does not associate a specific colour with any point on the xy chromaticity diagram as it does not take into account *lightness*, which is very important in human perception

[25]. Figure 5 shows the observed sensor film emission colour in different O₂ concentrations, which is in good agreement with the hues predicted by the xy colour coordinates. This red-yellow-green “traffic light” response therefore provides a simple and rapid method for both the qualitative and semi-quantitative measurement of oxygen. Fully quantitative measurements are also possible by Stern–Volmer analysis of luminescence quenching of one or both of the emissive components. Measurement of both lumophores offers the additional advantage of internal referencing to minimise errors caused by fluctuations in excitation intensity.

Our “traffic light” sensor offers the potential for O₂ detection in many commercial technologies including modified atmosphere packaging. MAP increases product shelf-life by surrounding the foodstuff with a specific gas mixture designed to inhibit food deterioration by microbial or bacterial action [15,28]. The gas mixture is optimised for a specific food group, for example red meats are often maintained under a high oxygen pressure (60–85%) to prevent bacterial growth [28]. Incorporation of the “traffic light” sensor inside the food packaging would facilitate the rapid assessment of the approximate O₂ concentration, enabling the verification of package integrity.

CONCLUSIONS

We have shown that the incorporation of two lumophores with different sensitivities and different emission colours in a single sensor introduces the possibility of O₂ detection across a broad range of concentrations using a simple, easily detectable, visual colour indication. Our PtOEP/EC-(PtLCl)/EC sensor exhibits a red-yellow-green “traffic light” response which is suitable for oxygen sensing in technologies such as MAP. The sensor can be excited simply using a cheap, commercially available UV LED or lamp and requires no scientific expertise in use. With judicious selection of the lumophore sensitivity, emission colour, relative concentration and host matrix, it should be possible to design a series of multi-lumophore colorimetric sensors with the required spectral response for a very wide variety of applications.

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