

Oxygen pressure measurement using singlet oxygen emission

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Pressure sensitive paint (PSP) provides a visualization of two-dimensional pressure distributions on airfoil and model automobile surfaces. One type of PSP utilizes platinum tetra(pentafluorophenyl)porphine (PtTFPP) dissolved in a fluoro-polymer film. Since the intense 650 nm triplet emission of PtTFPP is quenched by ground state oxygen, it is possible to measure two-dimensional oxygen concentration from the 650 nm emission intensity using a Stern–Volmer-type relationship. This article reports an alternative luminescence method to measure oxygen concentration based on the porphyrin-sensitized 1270 nm singlet oxygen emission, which can be imaged with an InGaAs near infrared camera. This direct measurement of oxygen emission complements and further validates the oxygen measurement based on PtTFPP phosphorescence quenching. Initial success at obtaining a negative correlation between the 650 nm PtTFPP emission and the 1270 nm O₂ emission in solution led us to additional two-dimensional film studies using surfaces coated with PtTFPP, MgTFPP, and H₂TFPP in polymers in a pressure and temperature controlled chamber. © 2005 American Institute of Physics. [DOI: 10.1063/1.1896623]

I. INTRODUCTION

The phosphorescence originating from the ³T₁ excited state of platinum (II) porphyrin [PtP] is well known to have a short lifetime (~100 μs) and a high quantum yield (~90%).^{1–6} The high phosphorescent yield results from the near unity triplet quantum yield due to the mixing between the platinum filled d_π orbital and the porphyrin empty e_g(π*) molecular orbital, which brings strong spin coupling into the ³T₁(π, π*) transition.^{1,2,6} An alternative to phosphorescence for deactivation of PtP [³T₁] is quenching by energy transfer of PtP [³T₁] to O₂ [³Σ_g⁻] resulting in O₂ [¹Δ_g], which has an emission at 1270 nm. The quenching of PtP emission by oxygen gives rise to changes in PtP phosphorescence intensity and lifetime, and this response is the operating mechanism of pressure sensitive paint (PSP), a pressure measurement method that provides real time continuous two-dimensional surface pressure data with high spatial resolution.^{4,7–9}

An energy diagram corresponding to the interaction of PtP and oxygen under optical excitation is presented in Fig. 1. The following are the processes of interest for PSP:

- (i) PtP [¹S₀] + hν_{exc} → PtP [¹S_n]: Photoexcitation to a higher excited singlet;
- (ii) PtP [¹S_n] → PtP [³T₁] + heat: Intersystem crossing to the lowest triplet;
- (iii) PtP [³T₁] → PtP [¹S₀] + hν [650 nm]: Triplet phosphorescence;
- (iv) PtP [³T₁] → PtP [¹S₀] + heat: Intersystem crossing to ground state; and

- (v) PtP [³T₁] + O₂ [³Σ_g⁻] → O₂ [¹Δ_g] + PtP [¹S₀]: Triplet quenching with formation of singlet oxygen.

Process (ii) is so fast that the quantum yield of PtP [³T₁] is near unity. Processes (iii) and (iv) are intrinsic properties of PtP, where (iii) is much faster than (iv) as seen by a phosphorescence efficiency of ~90% when no alternative triplet PtP relaxation mechanisms such as (v) are available. Competition between (iii) and (v) provides the mechanism for oxygen sensing. As oxygen concentration increases, more PtP [³T₁] relaxes via (v) vs (iii), hence phosphorescence is quenched. Pressure sensitive paint (PSP) utilizes this indirect measurement of oxygen concentration by examining phosphorescence of PtP and agents other than O₂ [³Σ_g⁻]. In this article, we propose to measure oxygen concentration directly by looking at oxygen emission and use the comparison between the indirect and direct methods to validate and improve PSP performance.

The ground state of molecular oxygen is a triplet, ³Σ_g⁻. Its two lowest excited states are ¹Δ_g and ¹Σ_g⁺, known as singlet molecular oxygen, which lie 7882 cm⁻¹ (~1270 nm) and 13121 cm⁻¹ (~760 nm) above the ground state, respectively. In free molecular oxygen, the absorptions, ³Σ_g⁻ → ¹Δ_g and ³Σ_g⁻ → ¹Σ_g⁺, are very weak since these transitions are both electric dipole and spin forbidden. Thus singlet oxygen production by absorption of radiation is a very inefficient process. However, the process of oxygen quenching excited photosensitizers such as PtP [³T₁] produces singlet oxygen very effectively via bimolecular energy transfer. The radiative lifetimes of unperturbed singlet oxygen are 45 min for ¹Δ_g and 11 s for ¹Σ_g⁺. The observed lifetimes for ¹Δ_g range from milliseconds in gaseous phase to microseconds in aqueous media, whereas the lifetime of ¹Σ_g⁺ is much shorter

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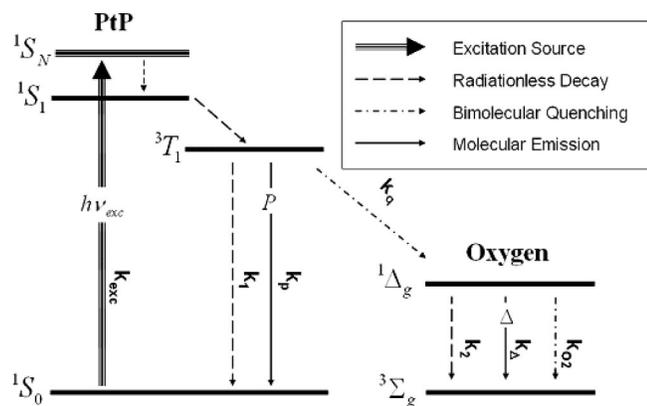


FIG. 1. Energy diagram for PtP and of oxygen. The relevant low energy states for PtP are the ground state 1S_0 , excited state 3T_1 , and higher excited states 1S_n , and those for oxygen are ground state $^3\Sigma_g^-$ and lowest energy excited state $^1\Delta_g$. Excitation, $h\nu_{exc}$, is with 400 nm laser light. The solid lines with labels P and Δ are, respectively, the phosphorescence of PtP at 650 nm and the 1270 nm oxygen emission; k_p and k_Δ are the radiative rate constants corresponding to each emission. The dashed lines are radiationless transitions that do not involve emission; they are labeled with rate constants k_1 and k_2 . The dot-dashed lines are bimolecular process; k_q is $^3\Sigma_g^-$ quenching 3T_1 rate constant, and k_{O_2} is $^1\Delta_g$ - $^3\Sigma_g^-$ self-quenching rate constant.

since the excited state $^1\Sigma_g^+$ quickly decays into either the excited state $^1\Delta_g$ or the ground state $^3\Sigma_g^-$.¹⁰⁻¹² The recent review by Schweitzer and Schmidt provides an excellent discussion of schemes for generation and detection of singlet oxygen.¹³ Several photosensitizer candidates were reported to have 100% $^1\Delta_g$ generation efficiency,^{14,15} and work in the field of photodynamic therapy has produced many excellent photosensitizers for singlet oxygen generation.^{16,17} With these and the availability of InGaAs near infrared (NIR) detectors, detection of $^1\Delta_g$ emission becomes much more feasible even though quantum efficiency is low.¹⁸ We believe $^1\Delta_g$ emission can be a probe for direct oxygen concentration measurement and surface pressure mapping, which we shall demonstrate in this article.

Figure 1 outlines the energy transfer diagram between PtP and oxygen. In addition to processes (i)–(v), the further processes related to oxygen emission are as follows:

- (vi) $O_2[{}^1\Delta_g] \rightarrow O_2[{}^3\Sigma_g^-] + h\nu[1270 \text{ nm}]$: Singlet oxygen emission;
- (vii) $O_2[{}^1\Delta_g] \rightarrow O_2[{}^3\Sigma_g^-] + \text{heat}$: Intersystem crossing of oxygen to its ground state; and
- (viii) $O_2[{}^1\Delta_g] + O_2[{}^3\Sigma_g^-] \rightarrow 2O_2[{}^3\Sigma_g^-] + \text{heat}$: Quenching of $O_2[{}^1\Delta_g]$ by $O_2[{}^3\Sigma_g^-]$.

Process (vi) is the 1270 nm emission of interest for this article. Process (vii) is the radiationless intersystem crossing process, and (viii) is the radiationless quenching mechanism of singlet oxygen by ground state oxygen.

In this article we present results for three photosensitizers from the tetra(pentafluorophenyl)porphyrin family, namely PtTFPP, MgTFPP, and H₂TFPP. PtTFPP is frequently used in PSP as it has strong phosphorescence yield and no detectable fluorescence. MgTFPP and H₂TFPP, on the other hand, both show moderate fluorescence and very weak phosphorescence.² All three are known to photogenerate singlet oxygen.

II. EXPERIMENT

A. Materials

PtTFPP [platinum tetra(pentafluorophenyl)porphine], MgTFPP [(magnesium tetra(pentafluorophenyl)porphine), and H₂TFPP [(free base tetra(pentafluorophenyl)porphine), were purchased from Frontier Scientific (formerly Porphyrin Products) in Logan, UT. Both PtTFPP and MgTFPP were made by standard porphyrin metallation procedures. Three polymers were used: Polystyrene (PS) beads were purchased from Polysciences, Inc., Warrington, PA. Poly(Bisphenol A-carbonate) polymer (PC) was purchased from Aldrich Chemical Company, Milwaukee, WI. Fluoroacrylic polymer (FIB) was purchased from ISSI, Dayton, OH. Four solvents were used: Dichloromethane CAS 75-09-2 and toluene were purchased from Fisher Scientific Chemicals, Fairlawn, NJ, α , α -trifluorotoluene (TFT) CAS 98-08-8 was purchased from Acros Chemicals, NJ, and chloropentafluorobenzene [C₆F₅Cl], from PCR.

B. Sample preparation

A solution sample was prepared by dissolving 0.3 mg of PtTFPP in 30 ml of C₆F₅Cl. The solvent was chosen for its high solubility for oxygen and high yield of singlet oxygen. Thin film samples were made by spin coating a dye-polymer solution onto an aluminum plate. Three stock polymer solutions were prepared in advance of dye-polymer solution. We choose an optimum solvent for each polymer: TFT for FIB, toluene for PS, and dichloromethane for PC. First, 15% by weight polymer solutions for our respective polymers were prepared by dissolving 3.00 g of polymer into 20.00 g of solvent. After a homogeneous polymer solution was obtained, we dissolved an appropriate amount of porphyrin into a small amount of polymer solution to obtain dye-polymer solutions of pre-selected concentration.

The dye-polymer solutions prepared for concentration effect study were 1:50, 1:100, and 1:200 PtTFPP to FIB, where 6.0 mg of PtTFPP was dissolved in 2 g of the FIB polymer solution for the 1:50, and then by subsequent dilution with the polymer stock solution. Thus 1:100 was made from 1:50, and 1:200 was made from 1:100. For polymer effect study, 1:100 PtTFPP/FIB, 1:200 PtTFPP/PC, and 1:200 PtTFPP/PS were used. The 1:100 PtTFPP/FIB solution was the same sample from concentration study, and the 1:200 PtTFPP/PC and PtTFPP/PS were prepared in similar fashion such that 3.0 mg of PtTFPP was dissolved in 4 mg of the PC or PS polymer stock solution. To make these dye polymer solutions into thin films, we applied 0.5 ml of each solution on to a 1 × 1 in.² aluminum plate separately. The solution was allowed to stand for 1 min to adhere to the aluminum plate, and the plate was spun at 1400 rpm to dry for another minute. The resulting films were of approximately equal thickness after this process, and they were annealed in an oven at 70 °C.

Another thin film sample was prepared by spray painting a 1:200 PtTFPP/FIB 10% polymer solution on polycarbonate film. This sample was then cut in the shape of “UW” for imaging.

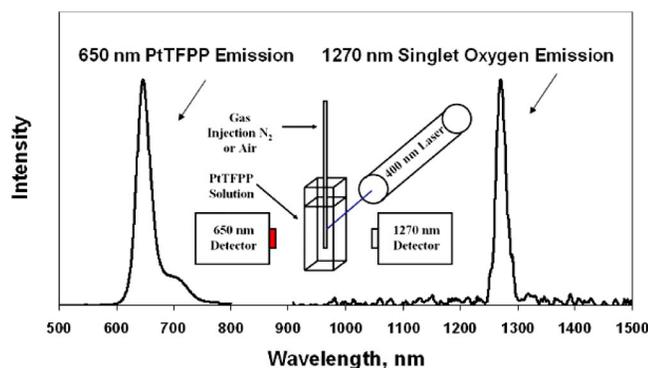


FIG. 2. The normalized emission spectra of PtTFPP and singlet oxygen with experimental setup of solution system in search for cross correlation between 650 nm emission from PtTFPP phosphorescence and 1270 nm singlet oxygen emission. The solution system includes PtTFPP dissolved in C_6F_5Cl and contained in a cuvette. Dissolved oxygen concentration may be reduced by N_2 injection by needle to purge oxygen out. A 400 nm laser is used to excite PtP, where 650 and 1270 nm detectors are placed perpendicular to laser path to emission without direct impact of laser.

C. Instrumentation

1. Singlet oxygen lifetime measurement

Singlet oxygen luminescence lifetimes were measured using the pulses (532 nm, 10 ns, ca. 5 mJ/pulse) from a Spectra Physics Nd: yttrium–aluminum–garnet laser (GCR-150-30), which excited the polymer film on an Al plate which was inserted into a 10×10 mm empty quartz cell. The singlet oxygen phosphorescence at 1270 nm was collected and isolated using a lens and filter system (Interference filter; NB-170-010-B; Spectrogon) and focused into a NIR sensitive photomultiplier tube (PMT) (H9170-45; Hamamatsu). The photocurrent from the PMT was amplified (SR 560, Stanford Research Systems) and stored on a digital oscilloscope (TDS 360, Tektronix). To achieve different oxygen concentrations, the sample cell containing the polymer film was flushed with oxygen/nitrogen mixtures of different ratios for at least 20 min prior to the measurements. The phosphorescence lifetimes of PtTFPP at 650 nm were measured using the same instrumentation as described above for singlet oxygen lifetime measurements, except a R928 Hamamatsu photomultiplier tube in conjunction with a monochromator (H10; Jobin-Yvon Inc.) was used as detector.

2. Solution study

The experimental setup for the solution correlation study is outlined in Fig. 2. An InGaAs detector, New Focus' Model 2153 IR femtowatt photoreceiver, was used to collect point intensity 1270 nm emission, and a standard S-20 photomultiplier tube (PMT) was used for the detection of 650 nm emission intensity; both detectors were fitted with the appropriate bandpass filters. The PtTFPP solution was placed in the cuvette and excited with 400 nm laser, where both the 1270 and 650 nm detectors were placed next to the sample. Injecting nitrogen gas to sample to purge ambient oxygen and then allowing O_2 to diffuse back into the N_2 gas purged solution allowed the oxygen concentration to vary slowly. Data acquisition is achieved using LabVIEW to acquire intensity output under continuous excitation. Figure 2 also displays the emission spectra of the PtTFPP triplet and of the

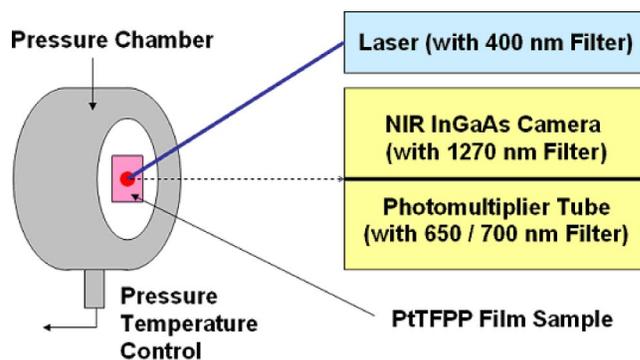


FIG. 3. Experimental setup for Stern–Volmer analysis in pressure chamber: The airfoils of PtTFPP, MgTFPP, and H_2 TFPP in different polymers or concentration are placed within a pressure chamber. The chamber has pressure and temperature controls to modulate oxygen concentration and temperature. Porphyrin emissions at 650, 700 nm and singlet oxygen 1270 nm emissions are recorded while 400 nm laser excites the film.

oxygen [$^1\Delta_g$] phosphorescences, which are centered at 650 and 1270 nm, respectively. The singlet oxygen emission spectrum was collected by a NIR spectrometer of Control Development, Model NIR-256L-1.7t and a luminescence Spectrometer LS-50 B from Perkin-Elmer was used to generate the visible emission spectra. Both emissions were stimulated with 400 nm excitation.

3. NIR film pressure and temperature measurements

The apparatus used for evaluating the pressure sensitive paint is shown in Fig. 3, which can measure intensity as function of pressure and temperature. This instrument has a sample chamber that is temperature and pressure controlled. The sample was excited either by a 400 nm laser Power Technology, LDCU12/5373 or with a 10×10 array of 395 nm light emitting diodes (LEDs) (ETG, Inc., Los Angeles, CA, ETG-5UV395-30). The 1270 nm singlet oxygen emission was imaged with a InGaAs detector, FLIR System's Alpha NIR camera. The camera was fitted with 1280 nm bandpass filter with 20 nm full width at half maximum. The instrument allows the operator to choose up to 50 pressure steps. The pressure is set to vacuum and then to atmospheric for initial calibration. A computer controlled valve mechanism sets the desired pressure value. Temperature dependence study was controlled by computer using a thermoelectric module. The module can add or subtract heat and set temperature to the desired value, where temperature is measured by an integrated circuit with $0.1^\circ C$ resolution. Measurement is made from 5 to $45^\circ C$ in $5^\circ C$ increments. Instrumentation for measuring visible signals was discussed in detail previously.¹⁹ A qualitative pressure experiment was first conducted using the UW PSP film with 400 nm LED array excitation prior to quantitative pressure and temperature experiments with PSP films.

III. MODEL

We here develop a Stern–Volmer-type equation for the use of 1270 nm singlet oxygen emission to measure oxygen pressure in analogy to the Kavandi equation for using 650 nm PtP emission to measure oxygen pressure.⁴ The observed phosphorescence intensity, I , is directly proportional

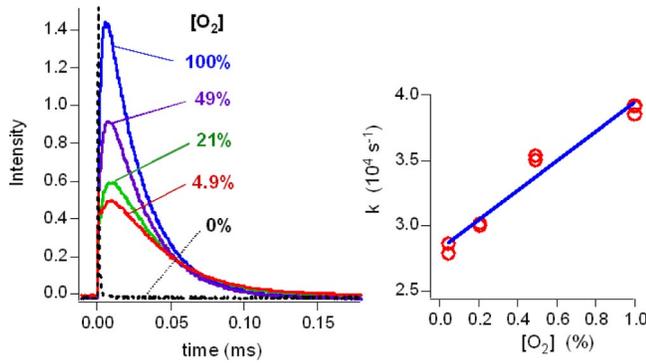


FIG. 4. Left: Kinetic traces of the phosphorescence of singlet oxygen (1270 nm) generated by excitation of PtTFPP in FIB films with laser pulses at 532 nm in oxygen-nitrogen mixtures of different ratios at 1 atm. Right: First order rate constant of the decay of the singlet oxygen phosphorescence vs the percentage of oxygen in an oxygen-nitrogen mixture.

to the quantum yield. The ratio I_0/I is obtained from the ratio of the intensity at 1 atm (21% oxygen) $[I_0]$ to the measured intensity at any other pressure (or oxygen concentration) $[I]$. This intensity ratio corresponds to the quantum yield Φ_0 divided by the quantum yield Φ . The quantum yield of an emission is defined as the number of photons emitted divided by the number of photons absorbed. The quantum yield is also given by the rate of radiative decay (k_p) divided by the total rate of decay of the excited triplet PtP molecule.

From Fig. 1 and the definition of quantum yield Φ , we first derive the Kavandi equation for the PtP phosphorescence emission intensity. Here the subscript 0 refers to atmospheric pressure.

$$\Phi|_{650 \text{ nm}} = \frac{k_p}{k_p + k_1 + k_q[\text{O}_2]},$$

$$\frac{I_0}{I} \Big|_{650 \text{ nm}} = \frac{\Phi_0}{\Phi} \Big|_{650 \text{ nm}} = \frac{k_p + k_1 + k_q[\text{O}_2]}{k_p + k_1 + k_q[\text{O}_2]_0},$$

$$\frac{I_0}{I} \Big|_{650 \text{ nm}} = \left(\frac{k_p + k_1}{k_p + k_1 + k_q[\text{O}_2]_0} \right) + \left(\frac{k_q[\text{O}_2]_0}{k_p + k_1 + k_q[\text{O}_2]_0} \right) \times \left(\frac{[\text{O}_2]}{[\text{O}_2]_0} \right),$$

$$\frac{I_0}{I} \Big|_{650 \text{ nm}} = A + B \left(\frac{[\text{O}_2]}{[\text{O}_2]_0} \right), \quad (1)$$

$$\text{where } A = \frac{k_p + k_1}{k_p + k_1 + k_q[\text{O}_2]_0} \text{ and } B = \frac{k_q[\text{O}_2]_0}{k_p + k_1 + k_q[\text{O}_2]_0}.$$

The Stern-Volmer-type equation for singlet oxygen emission from $^1\Delta_g$ state can be derived in a similar manner from the yield definition, $\Phi|_{1270 \text{ nm}} = k_\Delta / (k_\Delta + k_2 + k_{\text{O}_2}[\text{O}_2]) \times \Phi_\Delta \times \Phi_T$, where Φ_Δ is the $^1\Delta_g$ state yield of oxygen, and Φ_T is the 3T_1 state yield of PtP. Note that Φ_T is essentially unity for PtP, and Φ_Δ is $k_q[\text{O}_2] / (k_p + k_1 + k_q[\text{O}_2])$.

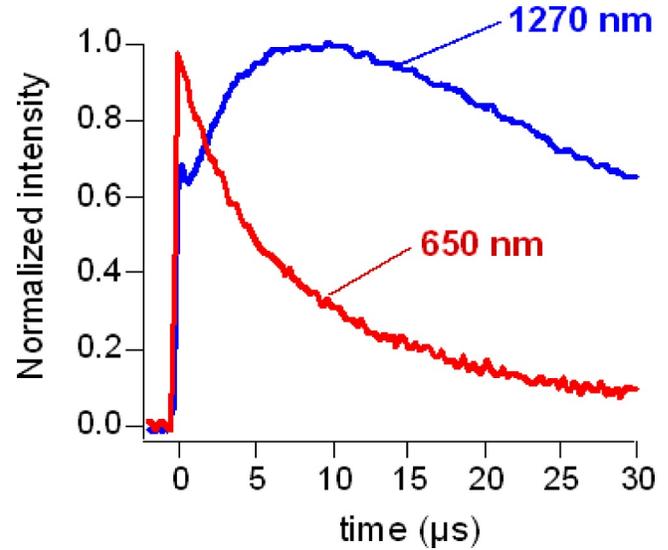


FIG. 5. Kinetic traces of the phosphorescence of PtTFPP (observed at 650 nm) and singlet oxygen (observed at 1270 nm) generated by excitation of PtTFPP in FIB films with laser pulses at 532 nm in an air atmosphere (1 atm).

$$\text{Therefore, } \Phi|_{1270 \text{ nm}} = \left(\frac{k_\Delta}{k_\Delta + k_2 + k_{\text{O}_2}[\text{O}_2]} \right) \times \left(\frac{k_q[\text{O}_2]}{k_p + k_1 + k_q[\text{O}_2]} \right) \text{ and}$$

$$\frac{I_0}{I} \Big|_{1270 \text{ nm}} = \frac{\Phi_0}{\Phi} \Big|_{1270 \text{ nm}} = \left\{ \frac{(k_\Delta + k_2) + (k_{\text{O}_2}[\text{O}_2])}{k_\Delta + k_2 + k_{\text{O}_2}[\text{O}_2]_0} \right\} \times \left(\frac{[\text{O}_2]_0}{[\text{O}_2]} \right) \left(\frac{k_p + k_1 + k_q[\text{O}_2]}{k_p + k_1 + k_q[\text{O}_2]_0} \right).$$

Note that the third term of this equation is identical to Kavandi equation. After reducing the first two terms of the equation and substituting for the third, we obtained

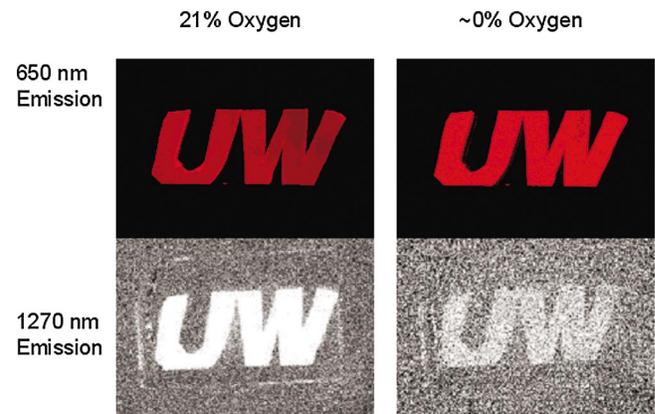


FIG. 6. (Color) Images of 1270 and 650 nm emissions of UW logo: PSP foil imaged at 21% oxygen and at ~0% oxygen, all excited at 400 nm.

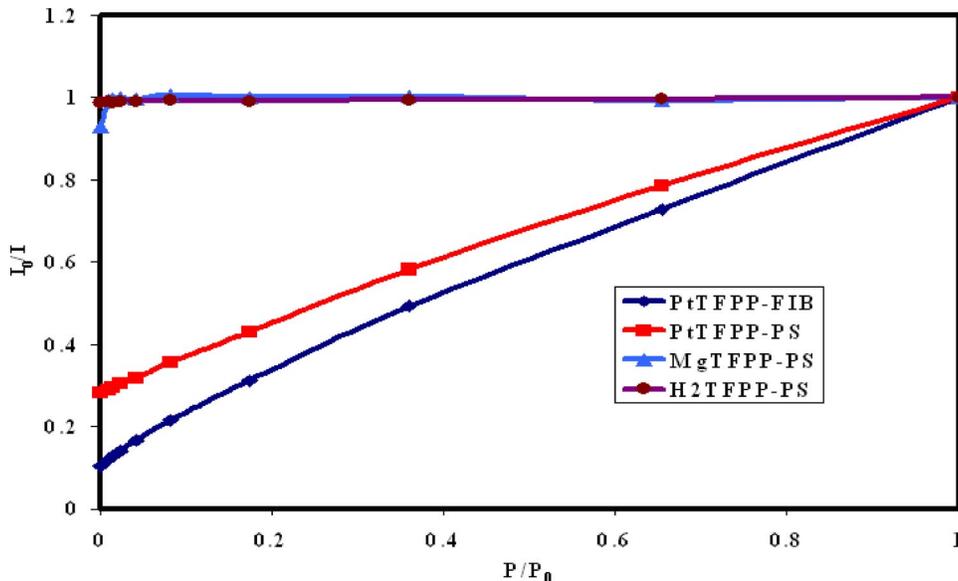


FIG. 7. I_0/I vs P/P_0 Stern–Volmer (Kavandi) plots for PtTFPP in polystyrene (PS) and in FIB polymers measured at 650 nm, H₂TFPP in PS measured at 700 nm and MgTFPP in PS measured at 650 nm, all excited at 400 nm.

$$\frac{I_0}{I} \Big|_{1270 \text{ nm}} = \frac{\Phi_0}{\Phi} \Big|_{1270 \text{ nm}} = \left\{ \left(\frac{k_{\Delta} + k_2}{k_{\Delta} + k_2 + k_{O_2}[O_2]_0} \right) \left(\frac{[O_2]_0}{[O_2]} \right) + \left(\frac{k_{O_2}[O_2]_0}{k_{\Delta} + k_2 + k_{O_2}[O_2]_0} \right) \right\} \times \left(A + B \frac{[O_2]}{[O_2]_0} \right)$$

$$\frac{I_0}{I} \Big|_{1270 \text{ nm}} = C \frac{[O_2]_0}{[O_2]} + D, \tag{3}$$

$$\frac{I_0}{I} \Big|_{650 \text{ nm}}$$

where $C = k_{\Delta} + k_2 / k_{\Delta} + k_2 + k_{O_2}[O_2]_0$ and $D = k_{O_2}[O_2]_0 / k_{\Delta} + k_2 + k_{O_2}[O_2]_0$. Note that $C + D = 1$.

A more useful parameter is the intensity ratio between the oxygen $^1\Delta_g$ 1270 nm emission and the porphyrin 3T_1 650 nm emission. Using the yield definitions we can derive the following:

or in short $\frac{I_0}{I} \Big|_{1270 \text{ nm}} = \frac{\Phi_0}{\Phi} \Big|_{1270 \text{ nm}} = \left(C \frac{[O_2]_0}{[O_2]} + D \right) \left(A + B \frac{[O_2]}{[O_2]_0} \right).$ (2)

$$\frac{I_{1270 \text{ nm}}}{I_{650 \text{ nm}}} = \frac{\Phi|_{1270 \text{ nm}}}{\Phi|_{650 \text{ nm}}} = \frac{\left(\frac{k_{\Delta}}{k_{\Delta} + k_2 + k_{O_2}[O_2]} \right) \left(\frac{k_q[O_2]}{k_p + k_1 + k_q[O_2]} \right)}{\left(\frac{k_p}{k_p + k_1 + k_q[O_2]} \right)},$$

To modify this relationship to be more Kavandi like, we can take this 1270 nm ratio and divide it by the Kavandi 650 nm ratio

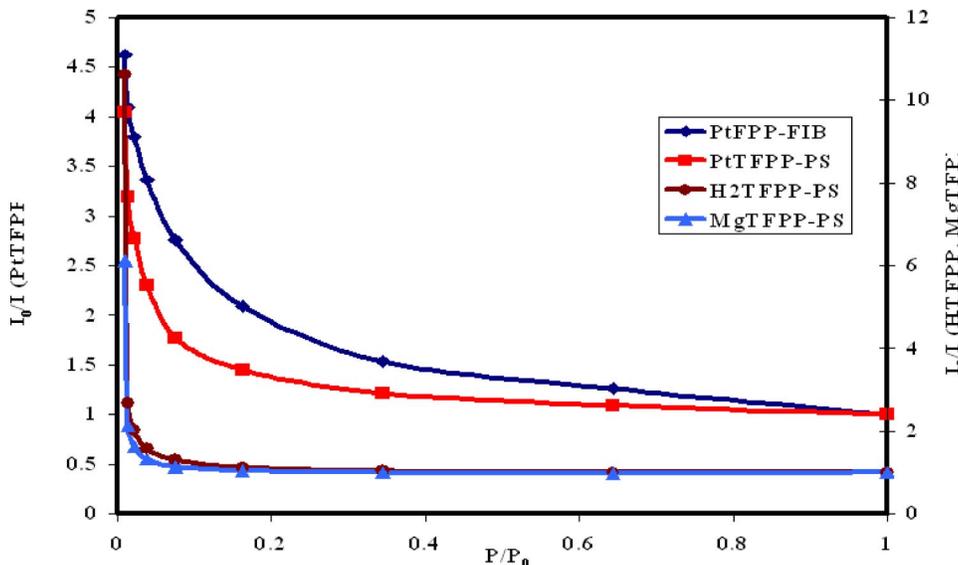


FIG. 8. I_0/I vs P/P_0 Stern–Volmer (Kavandi) plots for PtTFPP in polystyrene (PS) and in FIB polymers, H₂TFPP in PS and MgTFPP in PS, spin-coated at 25 °C, all measured at 1270 nm all excited at 400 nm. The PtTFPP I_0/I data are plotted on the left Y axis, The MgTFPP and H₂TFPP I_0/I data are plotted on right Y axis.

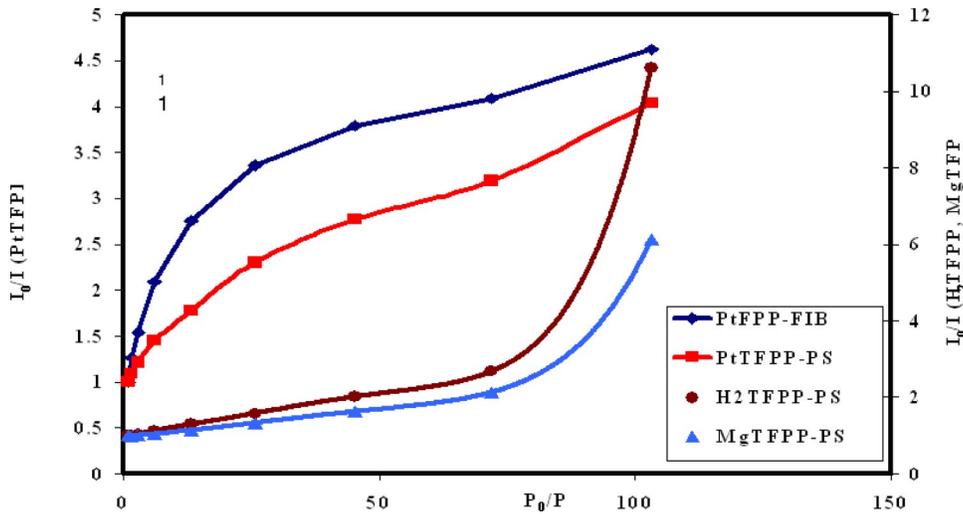


FIG. 9. I_0/I vs P_0/P Stern-Volmer plots for PtTFPP in polystyrene (PS) and in FIB polymers, H_2 TFPP in PS and MgTFPP in PS, spin-coated at 25 °C, all measured at 1270 nm all excited at 400 nm. The PtTFPP I_0/I data are plotted on the left Y axis, The MgTFPP and H_2 TFPP I_0/I data are plotted on right Y axis.

$$\frac{I_{1270 \text{ nm}}}{I_{650 \text{ nm}}} = \frac{\Phi|_{1270 \text{ nm}}}{\Phi|_{650 \text{ nm}}} = \frac{(k_{\Delta}\tau_{\Delta}) \times (k_q[\text{O}_2])}{(k_p)},$$

$$\frac{I_{1270 \text{ nm}}}{I_{650 \text{ nm}}} = \frac{\Phi|_{1270 \text{ nm}}}{\Phi|_{650 \text{ nm}}} = \frac{k_{\Delta}k_q\tau_{\Delta}}{k_p}[\text{O}_2]. \quad (4)$$

Note that k_{Δ} , k_q , and k_p are constants for a given platinum porphyrin and polymer combination, and τ_{Δ} is the lifetime of singlet oxygen. Krasnovsky and his group observed that τ_{Δ} remains constant when varying the oxygen pressure in a measurement in which $^1\Delta_g$ was produced through a sensitizer in aqueous solution.²⁰ We measured the $^1\Delta_g$ lifetime of PtTFPP in FIB polymer as function of oxygen concentration. Figure 4, left, shows kinetic plots of the singlet oxygen phosphorescence (1270 nm) at different oxygen concentrations. The observed total rate constant of the decay increases slightly with increasing oxygen concentration as illustrated in Fig. 4, right. The observed singlet oxygen lifetime ($\tau_{\Delta} = 1/k$) decreased by 10 μs from 0% to 100% oxygen and the change from 0% to 21% oxygen is only 15%. Therefore, the pressure range of our measurement τ_{Δ} can be considered constant. Equation (4) can be simplified to

$$\frac{I_{1270 \text{ nm}}}{I_{650 \text{ nm}}} = K \times [\text{O}_2], \quad (5)$$

where K is $k_{\text{O}} \times k_q \times \tau_{\Delta} / k_p$, with a dimension of $[\text{molar}]^{-1}$.

IV. RESULTS AND DISCUSSIONS

The time evolutions of the phosphorescence of PtTFPP (monitored at 650 nm) and the phosphorescence of singlet oxygen (monitored at 1270 nm) were studied in more detail using a pulsed laser excitation (532 nm, 10 ns) and a time resolved luminescence detection system. The decay of the PtTFPP phosphorescence at 650 nm is paralleled by a buildup of singlet oxygen emission at 1270 nm as illustrated in Fig. 5. The PtTFPP triplet states are quenched by molecular oxygen ($^3\Sigma_g^-$) resulting in singlet oxygen ($^1\Delta_g$). Figure 4 (left) shows the decay kinetics of the singlet oxygen phosphorescence at different oxygen concentrations. With increasing oxygen concentrations, the absolute intensity of singlet oxygen phosphorescence increases, because of increased efficiency of PtTFPP triplet quenching by molecular oxygen ($^3\Sigma_g^-$). The singlet oxygen phosphorescence decay fitted well to pseudo-first order kinetics and the plot of the decay rate

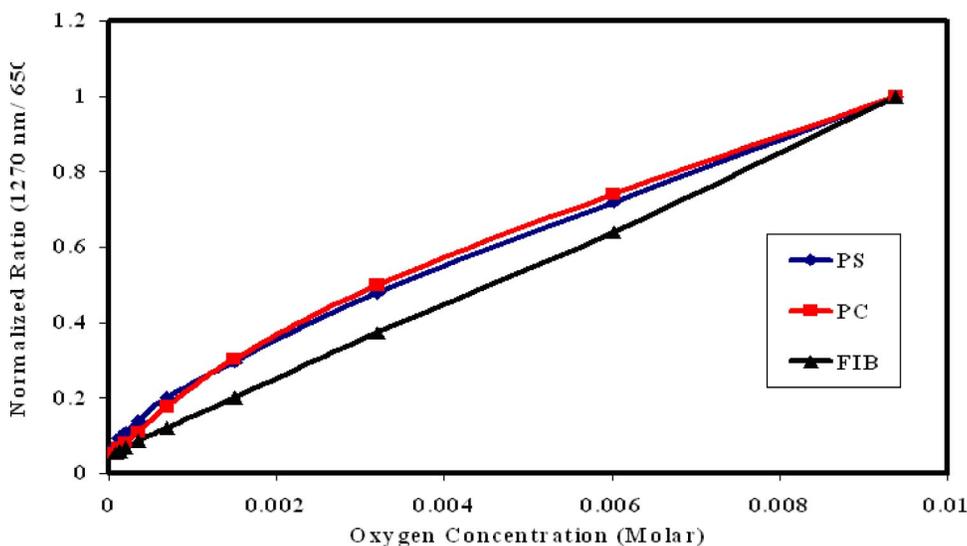


FIG. 10. Normalized intensity ratio plots of the singlet oxygen emission at 1270 nm to the PtTFPP triplet state phosphorescence at 650 nm as function of oxygen concentrations in molar. The ratio measured for three films of PtTFPP in FIB, polystyrene (PS) and polycarbonate (PC) all excited at 400 nm.

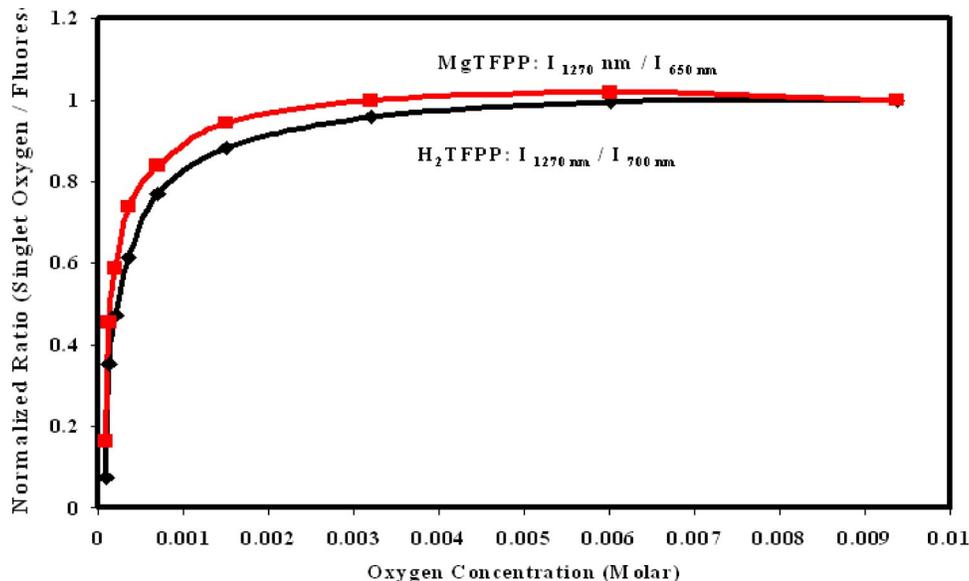


FIG. 11. Normalized intensity ratio plots of the singlet oxygen emission at 1270 nm to the MgTFPP and H₂TFPP singlet state fluorescence at 650 and 700 nm, respectively as function of oxygen concentrations in molar. The ratio measured for films of MgTFPP and H₂TFPP in polystyrene (PS) all excited at 400 nm.

constants versus the oxygen concentrations is shown in Fig. 4 (right). The plot shows that the decay rate constant ($1/\tau_{1\Delta_g}$) increases slightly with increasing oxygen concentrations. The faster decay of the singlet oxygen phosphorescence is attributed to quenching of singlet oxygen ($^1\Delta_g$) by molecular oxygen ($^3\Sigma_g^-$). However, this quenching is negligible at the low oxygen concentrations we used for the following experiments and therefore, $\tau_{1\Delta_g}$ can be considered constant.

Correlation between singlet oxygen and the porphyrin triplet phosphorescence emissions was determined using the experimental setup shown in Fig. 2. The intensities of 650 and 1270 nm are collected under identical conditions after first purging the solution with N₂ gas and then allowing oxygen to diffuse back in over time. The time courses for the two luminescence wavelengths complement each other: The 650 nm intensity decreases as oxygen concentration increases, while the 1270 nm intensity increases as oxygen concentration increases. Cross correlation of the two intensities was calculated to be (-0.997). This result motivated us to do further film studies.

Luminescence images of a PtTFPP film in the FIB polymer shaped in the form of “UW” taken at two oxygen concentrations are given in Fig. 6. In Fig. 6, the top shows the 650 nm emission of PtTFPP phosphorescence emission under air (21% oxygen) where the emission is low and under near 0% the luminescence is brighter. In Fig. 6, the bottom shows the 1270 nm singlet oxygen emission under air (21% oxygen) where the emission is bright and under near 0% oxygen the intensity is low. The four images illustrate the correlations between the quenching of the porphyrin triplet state and the production of oxygen singlet [$^1\Delta_g$] state. The images appear to be exchanged such that the 650 nm signal has the opposite effect of the 1270 nm signal as expected. This study shows qualitatively that the concentration of singlet oxygen over the surface of the film can be measured by the oxygen emission intensity as well as by the luminescence quenching of the PtTFPP.

Figure 7 is the standard Stern–Volmer (Kavandi) plot⁴ of

I_0/I vs P/P_0 [Eq. (1)] monitoring the 650 nm phosphorescence intensity of PtTFPP in films made from two different polymers, polystyrene and FIB. For comparison Fig. 7 also shows the Stern–Volmer plot monitoring the fluorescence intensity of MgTFPP at 650 nm and H₂TFPP at 700 nm in polystyrene polymer. All films were measured at ten pressure values and recorded at room temperature. Here the subscript o refers to atmospheric pressure of air (21% oxygen). Ideally the Stern–Volmer curves of PtTFPP are linear as predicted by Stern and Volmer, and in the case of FIB polymer this behavior is observed,⁵ whereas the Stern–Volmer of the MgTFPP and H₂TFPP shows a nearly flat response to pressure. The MgTFPP and H₂TFPP fluorescence has short lifetimes of 9.8 and 5.5 ns, respectively, and is the reason for little or no change of the intensity with pressure.^{2,15}

Figure 8 also shows a plot of I_0/I vs P/P_0 , but here we monitor the 1270 nm luminescence of oxygen instead. In this case, I_0/I decreases to the right as the intensity of the oxygen 1270 nm emission increases at higher oxygen pressure. As might be expected, the slopes and curvatures between Figs. 7 and 8 are quite different. It should be noted that the Stern–Volmer of 1270 nm for MgTFPP and H₂TFPP shows also a significant intensity change as function of oxygen pressure; their curves are fairly flat for most of the pressure range but changes by tenfold at low oxygen pressure. The results show that oxygen pressure measurements using the 1270 nm emission can be accomplished using a phosphorescent dye like PtTFPP or a fluorescent dye like MgTFPP and H₂TFPP. The difference in response between these two types of sensitizers can be attributed to the polymer film response time and the corresponding porphyrin triplet state lifetimes. The 90% response time for the FIB polymer was measured to be <1 ms.²¹ The phosphorescent lifetimes in the absence of oxygen for PtTFPP, MgTFPP, H₂TFPP are 0.12, 5.6, and 46 ms, respectively.^{1,2,22,23} Thus the long lived triplet state of MgTFPP and H₂TFPP is accessible to oxygen quenching and the production of $^1\Delta_g$ state is not diffusion limited, which can explain the Stern–Volmer response of the two dyes.

Figure 9 shows a plot of I_0/I vs P_0/P for the 1270 nm

luminescence of oxygen. In this case I_0/I increase to the right as the intensity of the oxygen 1270 nm emission decreases at lower oxygen pressure. Note that PtTFPP curves have wider dynamic range than H₂TFPP and MgTFPP curves. The plots similarly show that H₂TFPP and MgTFPP have greater response at low pressures.

Figure 10 shows a ratio plot of the 1270 nm singlet oxygen intensity to the 650 nm triplet porphyrin intensity for PtTFPP in three different polymers as function of oxygen concentration [Eq. (5)]. We note the PtTFPP plot for FIB shows a linear response over the oxygen concentration range and has slope (K) of 100 M⁻¹. The ratio of the two correlated signals $I_{1270\text{ nm}}$ and $I_{650\text{ nm}}$ produces an enhanced sensitivity measure. Moreover, since the two intensities are being generated from a single luminophor film, the ratio should compensate for illumination variation and angular sensitivity. We anticipate a ratio-metric measurement approach will produce a robust method for determining pressure/oxygen on two-dimensional surfaces.

Figure 11 shows a ratio plot of the 1270 nm singlet oxygen intensity to the 650 and to the 700 nm fluorescence intensities for MgTFPP and H₂TFPP. The ratio plots show only linear response at the low oxygen concentration range. Similarly, using MgTFPP and H₂TFPP fluorescence signal as intensity reference will produce reliable measurement especially low pressure/oxygen applications.

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