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by

Joanne M. Bedlek-Anslow
ACKNOWLEDGEMENTS

As I approach the completion of nearly 21 years of education, it becomes challenging to properly thank the numerous people that have helped me along the way. Foremost, my parents deserve my sincerest gratitude and appreciation for always being there for ups and downs of my life. As a young child, they encouraged my interests and helped me to realize that any dream is possible. One of their greatest lessons was that life is about decisions and choices. I am solely responsible for my happiness and must always be my greatest ally. The significance of this advice continues to grow with each passing year.

Only recently, have I begun to realize the extent of their sacrifices and support of my successes. Their examples as parents, companions and genuine people are constant reminders of the person I am trying to become.

I must also thank my sister, Jazmine, for her love and faith and exquisitely example as a witness of compassion and conviction. My appreciation also extends to my small but dedicated family for their love and support: Uncle Jim and Aunt Pat, Aunt Pim and Uncle Ken. Alyssa and Chris, Arianne, Kevin and Rosanne, Shary and Angie, Godmother Helen, Russ and Dee, Matt and “little” Grandma. Unfortunately, my grandfather did not live to see me finish my doctorate, yet I am positive he is rejoicing in my successes.

I am also fortunate to be the beneficiary of a large extended family of people who if not through ties of blood but rather ties of friendship have blessed me with guidance, love, and praise for longer than I can remember. This nucleus of people includes my dear...
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As I approach the completion of nearly 21 years of education, it becomes challenging to properly thank the numerous people that have helped me along the way. Foremost, my parents deserve my sincerest love and appreciation for always being there for me with constant and unconditional love, encouragement, and praise throughout the ups and downs of my life. As a young child, they encouraged my interests and helped me to realize that any dream is possible. One of their greatest lessons was that life is about decisions and choices. I am solely responsible for my happiness and must always be my greatest ally. The significance of this advice continues to grow with each passing year. Only recently, have I begun to realize the extent of their sacrifices and support of my successes. Their examples as parents, companions and genuine people are constant reminders of the person I am trying to become.

I must also thank my sister, Jeanne, for her love and faith and exquisite example as a woman of compassion and conviction. My appreciation also extends to my small but boisterous family for their love and support: Uncle Jim and Aunt Pat, Aunt Pam and Uncle Ken, Alyssa and Chris, Arianna, Kevin and Roxann, Shay and Angie, Godmother Helen, Russ and Dee, Matt and “little” Grandma. Unfortunately, my grandfather did not live to see me finish my doctorate, yet I am positive he is rejoicing in my successes.

I am also fortunate to be the beneficiary of a large extended family of people who if not through ties of blood but rather ties of friendship have blessed me with guidance, love, and praise for longer than I can remember. This nucleus of people includes my dear
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DEVELOPMENT AND CHARACTERIZATION OF LUMINESCENT OXYGEN SENSING COATINGS

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Traditional aerodynamic model systems monitor surface pressure at discrete points along a model surface. Models must be designed sufficiently large to accommodate placement of small electronic pressure transducers along the model surface and placement of the corresponding wiring through the model's hull. This process is time-consuming, expensive, and detection is limited to the point of sensor placement. Conversely, CCD (charge-coupled device) camera technology surveys the entire model's surface pressure by monitoring oxygen concentration induced intensity variations of a luminescent pressure-sensitive coating. However unfavorable intensity variations originating from surface temperature fluctuations can disrupt accurate pressure determination.

The research presented in this dissertation focuses on the development of several dual-luminophore coatings. These systems simultaneously determine surface pressure (oxygen concentration) and surface temperature. Therefore correction of the
temperature-induced intensity fluctuations of the pressure sensing luminophore is accomplished by determining the run-time temperature field across the model surface. Spectral resolution, compatibility with polymer binder and surface primer, and chemical inertness with respect to one another indicate successful integration of the two luminophores into one binder matrix. These systems are primarily evaluated using fluorescence spectroscopy to ascertain variations in luminescent intensity with respect to the degree of oxygen quenching. Experiments utilizing continuous illumination monitored photodegradation and luminescence quenching studies conducted at various temperatures evaluated the temperature-dependence of the pressure and temperature components and binder matrix. Studies conducted in a calibration cell determined application readiness.

Non-linear luminescent response to oxygen concentration prompted development of a new fluorescence microscopy technique. The technique interrogates several regions of a coating’s surface analyzing its microscopic luminescent pressure-sensitive response. It is believed that deviations from linearity are due to heterogeneity of the polymer matrix or the luminophore distribution. Successful quantitative measurement of the degree of oxygen quenching at the pixel level with micrometer spatial resolution is presented for several mono- and dual-luminophore sensing coatings utilizing various luminophores in a polymer binder. Characterization, evaluation, and discussion of the systems’ attributes provide insight for the enhanced design of future luminescent oxygen sensing coatings.
CHAPTER 1
INTRODUCTION

Background

The quest to quantitatively measure oxygen concentration in the gas phase, dissolved in the liquid phase or in solid gas permeable polymers with reproducible, accurate and precise results, has garnered considerable research interest throughout the past four decades. The beginnings of oxygen measurement are rooted in electrochemical sensors such as the amperometric Clark cell\(^1\) or the galvanic Mancy cell.\(^2\) These cells are robust and reliable measurement tools, when properly used; however, reliable measurements are often prohibited by electrical interferences, and reproducibility is hindered by consumption of the oxygen analyte during analysis. The systems also suffer from a bulky instrument size, which is difficult to miniaturize. Therefore the focus of oxygen detection shifted from these traditional invasive measurement methods to the development of noninvasive optical oxygen sensors.

As a detection system, optical sensors are advantageous, since they are robust, cost-effective, disposable, and easily scaled to suit their desired application. Optical sensors have been employed in numerous detection systems for such analytes as H\(^+\),\(^3\)-\(^6\) CO\(_2\),\(^7\),\(^8\) vapors of explosives,\(^9\) and biochemical compounds.\(^10\)-\(^12\) However, the analysis of oxygen concentration in blood and biological systems,\(^13\),\(^14\) combustion analysis,\(^15\) and pressure-sensitive paint (PSP) development\(^16\)-\(^20\) has been at the
forefront of optical sensor research. In particular, development in the area of pressure-sensitive paints (PSP) has grown considerably in the last fifteen years.

PSP's fundamentally consist of a luminescent molecular probe (a luminophore) dispersed or dissolved in an oxygen permeable polymer binder. The beginnings of this technology are seen as early as 1980, when Peterson and Fitzgerald demonstrated the quenching of a luminophore's photoluminescence emission by oxygen. They employed Fluorescein Yellow dye as the luminophore, and adsorbed it onto a silica gel chromatography plate. This initial experiment of flow visualization demonstrated the possibility of oxygen concentration measurement across a surface as a determination of overall surface pressure.

**Luminescence Quenching**

The composite mixture of luminophore in polymer binder described above is typically applied as an aerosol to substrate material such as aluminum, steel, polymer, or composite as a film of thickness less than 50 μm. Under UV or blue light illumination (\(\lambda \leq 450\) nm), the sensor coating emits light (photoluminescence) in the green, orange or red region of the visible spectrum (\(\lambda \geq 500\) nm). The photoluminescence intensity of the sensor film is inversely proportional to the partial pressure of \(O_2\) (\(pO_2\)) in the gas phase that is in equilibrium with the surface of the coated substrate. Moreover, since under normal conditions and assuming Henry's Law holds, \(pO_2\) is then proportional to the total air pressure (i.e., \(pO_2 = cP_{air}\)). The following processes thus define the kinetic scheme for the Stern-Volmer (SV) bimolecular quenching of the luminophore's photoluminescence intensity by oxygen:
\[ L + h\nu \rightarrow \ast L \quad \text{photon absorption} \quad (1-1) \]
\[ \ast L \rightarrow L + h\nu \quad \text{luminescence, } k_r \quad (1-2) \]
\[ \ast L \rightarrow L + \Delta \quad \text{non-radiative decay, } k_{nr} \quad (1-3) \]
\[ \ast L + Q \rightarrow L + \ast Q \quad \text{dynamic quenching, } k_q \quad (1-4) \]

The term L is the luminophore, and Q is the quencher molecule, O\textsubscript{2}. Therefore, by reference to the SV calibration in equation (1-5) it is possible to quantitatively relate the photoluminescence intensity to P\text{air},\textsuperscript{18}

\[
I(\lambda_{em}^P, P_{air} = 0) / I(\lambda_{em}^P, P_{air}) = 1 + K_{SV} P_{air} \quad (1-5)
\]

\[
K_{SV} = k_q \tau_0 = k_q (k_r + k_{nr})^{-1} \quad (1-6)
\]

where I is the photoluminescence intensity at emission wavelength \(\lambda_{em}^P\), and \(K_{SV}\) is the SV coefficient. Therefore the photoluminescence intensity is inversely proportional to P\text{air}.

In many applications it is impractical to use \(P_{air} = 0\) as a reference condition, and consequently the SV equation is re-cast as equation (1-7),

\[
I(\lambda_{em}^P, P_{air} = 1 \text{ atm}) / I(\lambda_{em}^P, P_{air}) = A + BP_{air} \quad (1-7)
\]

where the reference condition is taken as \(P_{air} = 1 \text{ atm}\),\textsuperscript{24} and the non-zero coefficients A and B are a function of temperature and reference conditions (\(B/A = K_{SV}\)).

**Modeling Non-linear Stern-Volmer Response**

Some luminescent O\textsubscript{2} sensor films feature linear SV calibrations in accord with equations (1-5) or (1-7); however, many sensors exhibit non-linear calibrations that are curved downward such as those displayed in Figure 1-1.\textsuperscript{25-27}
Figure 1-1: Stern-Volmer plots of \( \frac{I_0}{I} \) versus \( pO_2 \) for the following optical oxygen sensors: \([\text{Ru(phen)}_3]^{2+}\) in silicone rubber, GE RTV 118 (▲), and \([\text{Ru(bpy)}_3]^{2+}\) in silicone rubber, GE RTV 118 (●).

Although a number of studies have attempted to identify the basis for this non-ideal SV response, the fundamental process(es) responsible are still not well understood.\(^{25,28}\) Several mathematical models have been developed to fit the non-linear SV correlations. These mathematical models are formulated based on the physical hypothesis that the sensor film is inhomogeneous, possibly due to nano- or meso-scale irregularities in the polymer morphology or the environment surrounding the luminescent sensor molecules. Several models have received considerable attention.

The two quenching site model in (1-8),\(^{25,29,30}\) explains the complex quenching behavior exhibited by a microheterogeneous system. The two-site equation is

\[
\frac{I_0}{I} = \frac{1}{f_{01} + \frac{f_{02}}{1 + K_{SV1}^{p}P_{O_2} + 1 + K_{SV2}^{p}P_{O_2}}}
\]

where \( f_{0j} \) is the fraction of each of the two sites contributing to the unquenched intensity, and the \( K_{SV} \) values are the quenching constants for the two sites. The model works well...
for quantitatively fitting intensity quenching data; however, it should be cautioned that while it is able to fit more complex systems, the fitting parameters should be judiciously chosen to avoid mechanistic misinterpretations. In other words, the fact that the response of a specific sensor can be modeled by equation (1-8) does not necessarily mean that the sensor has two specific quenchable sites.

The Gaussian or log-Gaussian distributions represent another set of models which give predictive values for the non-linear response exhibited by SV plots. The log-Gaussian distribution in the natural luminescent lifetime of the luminophore \( \tau_0 \) and the quenching rate constant \( k_{q}' \) generates theoretical model parameter values which are physically plausible and consistent at all partial pressures of oxygen, \( pO_2 \). The log-Gaussian distribution in \( \tau_0 \) and \( k_{q}' \) with respect to \( x \) is

\[
\frac{I_0}{I} = \frac{\int_{-\infty}^{\infty} \exp(\rho_1 x) \exp(-x^2) dx}{\int_{-\infty}^{\infty} \{ \exp(\rho_1 x) \exp(-x^2)} [1 + \theta \exp(\{\rho_1 + \rho_2 \}x)] \} dx
\]

where

\[
\rho_1 x = \ln(\tau_{0,i}/\tau_{0,mdl})
\]

\[
\rho_2 x = \ln(k_{q,i}/k_{q,mdl})
\]

\[
\theta = K_{SV,mdl} pO_2 = t_{0,mdl} k_{q,mdl} pO_2
\]

and where \( \rho_1 \) is a measure of the breadth of the distribution with respect to \( \tau_{0,i} \), and \( \tau_{0,mdl} \) is the natural lifetime associated with the modal number of sites; \( \rho_2 \) is a measure of the breadth of the distribution with respect to \( k_{q,i} \), and \( k_{q,mdl} \) is the quenching rate constant by oxygen of the modal number of sites; \( \rho_2 \) can be of the same sign or opposite to \( \rho_1 \). The
model is capable of providing physical rationale for disparate response features in typical optical oxygen sensors; however, it fails to explain physical phenomena associated with bi-phasic material.\textsuperscript{33}

Finally, first-, second-, and third-order polynomials applied to non-linear SV response data\textsuperscript{20} tend to fit the data sets in a limited pressure region, but they fail when predicting extended pressure regions or an extrapolation of the data set.\textsuperscript{24} Therefore the dual sorption model has been applied to the SV relationship (1-5) producing the intensity-pressure relationship in (1-13),\textsuperscript{24}

\[
\frac{I_{\text{ref}}}{I} = A + \frac{B}{P_{\text{ref}}} + C \frac{D(P/P_{\text{ref}})}{1 + D(P/P_{\text{ref}})}
\]  

(1-13)

where the non-zero coefficients A, B, C, and D are a function of temperature and reference conditions. The model works well with cases where pressure ranges are large or extrapolated regions are needed; however, due to the non-linearity of such data, it requires an iterative technique for determining the calibration coefficients. Therefore, for high pressures and limited pressure regions, a first- or second-order polynomial is recommended.\textsuperscript{24}

\textbf{Luminophores and Polymers}

The luminescent molecular probe dispersed in a PSP is generally a luminescent transition metal complex (TMC). TMC's are more advantageous than fluorescent organic luminophores because of their long excited state lifetimes ($\tau_0$) and high luminescence quantum yields ($\Phi_L$).\textsuperscript{34} Most often, these metal complexes are either Ru(II) $\alpha$-diimine\textsuperscript{31,35} complexes or Pt(II)/Pd(II) porphyrin macrocycles.\textsuperscript{16,36-38}
oxygen permeable polymer binder most commonly used is silicone; however, other polymers such as cellulose acetate (CA), \(^{39}\) polymethylmethacrylate (PMMA), \(^{40}\) polyvinylchloride (PVC), \(^{41}\) polystyrene (PS), \(^{42}\) and sol-gels \(^{43,44}\) all with or without plasticizers have also been employed.

**Ru(II) α-Diimine Complexes**

The Ru(II) α-diimine complexes have been investigated extensively as oxygen-quenchable species both in the liquid \(^{45,46}\) and solid phases; \(^{47}\) tris(2,2’-bipyridyl)ruthenium(II), [Ru(bpy)\(_3\)]\(^{2+}\); tris(1,10-phenanthroline)ruthenium(II), [Ru(phen)\(_3\)]\(^{2+}\); and tris(4,7-diphenyl-1,10-phenanthroline)-ruthenium(II), [Ru(dpp)\(_3\)]\(^{2+}\). Their extensive use is due to several factors: (1) their ability to be excited in the visible region; (2) their long emission lifetimes (\(\tau_0\)), which are generally hundreds of nanoseconds to tens of microseconds, allow the excited state to be easily quenched by oxygen; (3) they exhibit high luminescence quantum yields (\(\Phi_L\)); (4) large Stokes shifts in the emission spectra minimize excitation source interferences; and (5) they possess excellent photostability. \(^{25,48,49}\) Several examples of Ru(II) α-diimine complexes are shown in Figure 1-2. \(^{50}\)
Figure 1-2: Structures of the major Ru(II) α-diimine luminophores used in optical oxygen sensors. ([Ru(bpy)]$_3^{2+}$, [Ru(phen)]$_3^{2+}$, and [Ru(dpp)]$_3^{2+}$).

As a result of the desirable properties shown in Table 1-1, the design of Ru(II) α-diimine complexes has been extensively investigated.

Table 1-1: Photochemical Characteristics of the Ru(II) α-diimine Complexes in Water.

<table>
<thead>
<tr>
<th>Luminophore</th>
<th>$\tau_0$, µs</th>
<th>$\lambda_{\text{max}}$, nm (absorption)</th>
<th>$\varepsilon$, $10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$ (emission)</th>
<th>$\lambda_{\text{max}}$, nm (emission)</th>
<th>$\Phi_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)]$_3^{2+}$</td>
<td>0.60</td>
<td>(423)$_{sh}$, 452</td>
<td>1.46</td>
<td>613, 627</td>
<td>0.042</td>
</tr>
<tr>
<td>[Ru(phen)]$_3^{2+}$</td>
<td>0.92</td>
<td>447, 421</td>
<td>1.83, 1.90</td>
<td>605, 625</td>
<td>0.080$^b$</td>
</tr>
<tr>
<td>[Ru(dpp)]$_3^{2+}$</td>
<td>5.34$^a$</td>
<td>460</td>
<td>2.95</td>
<td>613, 627</td>
<td>~0.30$^c$</td>
</tr>
</tbody>
</table>

$^a$ in methanol, $^b$ in 2-butanol, $^c$ in water/ethanol, sh = shoulder
Pt(II)/Pd(II) Porphyrin Macrocycles

Pt(II)/Pd(II) porphyrin macrocycles have received considerable recent research interest because of their ability to be more sensitive to oxygen quenching than the Ru(II) α-diimine complexes. Several examples of Pt(II)/Pd(II) porphyrin macrocycles are shown in Figure 1-3.50

![Tetr phenyl porphyrin (TPP) and Octaethyl porphyrin (OEP)](image)

![Porphyarin and Octaethyl porphyrin ketone (OEPK)](image)

Figure 1-3: Structures of the major platinum and palladium porphyrins used in optical oxygen sensors. (M = Pt(II) or Pd(II)).

Their high oxygen sensitivity results from long excited state lifetimes, generally tens to hundreds of microseconds, due in part to π-π* transitions centered on the porphyrin ring. A strong spin-orbit coupling exists resulting from significant interaction between the Pt(II) or Pd(II) metal d-orbitals and the anti-bonding π* orbitals of the porphyrin ring which induces intersystem crossing to the triplet state. This
effect significantly decreases the triplet lifetime and increases the phosphorescence yield; therefore, surrounding oxygen molecules effectively quench the luminophores’ photoluminescence.

In addition to their enhanced ability to be quenched by oxygen, Pt(II)/Pd(II) complexes also possess the same desired excitation and emission characteristics as the Ru(II) α-diimine complexes: (1) they are easily excited in the visible region; (2) they possess high luminescence quantum yields (ΦL); and (3) they exhibit large Stokes shifts and excellent photostability.16,50 A listing of several optical sensor characteristics for Pt(II)/Pd(II) porphyrins disbursed in polymer binders are displayed in Table 1-2.50

| Pt-TDCPP | 0.082 | 620 | 0.16 | Silicone rubber RTV 113(GE) |
| Pt-TFMP | 0.039 | 646 | 0.08 |
| Pt-BuTDP | 0.023 | 721 | 0.02 |
| Pt-CEP | 0.095 | 740 | 0.2 |
| Pt-QEP | 0.091 | 944 | 0.5 |
| Pt-DQEP | 0.090 | 944 | 0.5 |

CPP: coproporphyrin; OEPK: octaethyl porphyrin ketone; TPF: tetraphenylporphyrin; TSP: tetrakis(4-sulfonatophenyl)porphyrin; TDCPP: meso-tetra(2.6-dichlorophenyl)porphyrin; TFMP: meso-tetra(3.5-dinitrobenzoyl)porphyrin; Bu2TDP: meso-tetraoctamethyl-β-norhexadecanol porphyrin; OEP: octaethyl porphyrin

Silicone

Silicone is the most widely used polymer binder matrix employed in optical oxygen sensors due to its high permeability (62 x 10⁻⁹ (cm² · cm)/(cmHg) at 25°C) and solubility (0.31 ml·g⁻¹ at 25°C) to oxygen associated with a low glass transition temperature, Tg (~ 27°C), high chemical and mechanical durability, and benign physiological effects beneficial to in vivo measurement applications.54,55 However, silicone as a binder matrix is incredibly hydrophobic in nature due to its extended
Table 1-2: Platinum and Palladium Porphyrin Based Optical Oxygen Sensors.

<table>
<thead>
<tr>
<th>Luminophore</th>
<th>( \tau_0 ), ms</th>
<th>( \lambda_{\text{max}, \text{nm}} ) (emission)</th>
<th>( \Phi_L )</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-CPP</td>
<td>0.40</td>
<td>667</td>
<td>0.2</td>
<td>Water</td>
</tr>
<tr>
<td>Pd-CPP</td>
<td>0.80</td>
<td>667</td>
<td>0.2</td>
<td>Silicone rubber RTV 118(GE)</td>
</tr>
<tr>
<td>Pd-CPP</td>
<td>1.06</td>
<td>667</td>
<td>0.2</td>
<td>PS</td>
</tr>
<tr>
<td>Pd-CPP</td>
<td>0.91</td>
<td>667</td>
<td>0.2</td>
<td>PMMA</td>
</tr>
<tr>
<td>Pt-OEPK</td>
<td>0.061</td>
<td>760</td>
<td>0.1</td>
<td>PS</td>
</tr>
<tr>
<td>Pt-OEPK</td>
<td>0.061</td>
<td>759</td>
<td>0.12</td>
<td>PS</td>
</tr>
<tr>
<td>Pt-OEPK</td>
<td>0.058</td>
<td>759</td>
<td>0.12</td>
<td>PS</td>
</tr>
<tr>
<td>Pd-OEPK</td>
<td>0.46</td>
<td>790</td>
<td>0.01</td>
<td>PS</td>
</tr>
<tr>
<td>Pd-OEPK</td>
<td>0.064</td>
<td>759</td>
<td>0.12</td>
<td>PVC</td>
</tr>
<tr>
<td>Pd-OEPK</td>
<td>0.44</td>
<td>790</td>
<td>0.01</td>
<td>PVC</td>
</tr>
<tr>
<td>Pd-TPP</td>
<td>-</td>
<td>690</td>
<td>-</td>
<td>Arachidic acid L-B film</td>
</tr>
<tr>
<td>Pd-TSPP</td>
<td>1.0</td>
<td>702, 763</td>
<td>-</td>
<td>Water</td>
</tr>
<tr>
<td>Pd-TSPP</td>
<td>0.5</td>
<td>698,685</td>
<td>-</td>
<td>Water</td>
</tr>
<tr>
<td>Pd-CPP</td>
<td>0.53</td>
<td>667</td>
<td>-</td>
<td>Water</td>
</tr>
<tr>
<td>Pt-TDCPP</td>
<td>0.082</td>
<td>650</td>
<td>0.16</td>
<td>Silicone Rubber RTV 118(GE)</td>
</tr>
<tr>
<td>Pt-TFMPP</td>
<td>0.030</td>
<td>646</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Pt-Br₈TMP</td>
<td>0.023</td>
<td>721</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Pd-OEP</td>
<td>0.99</td>
<td>670</td>
<td>0.2</td>
<td>PS</td>
</tr>
<tr>
<td>Pt-OEP</td>
<td>0.091</td>
<td>644</td>
<td>0.5</td>
<td>PS</td>
</tr>
<tr>
<td>Pt-OEP</td>
<td>0.091</td>
<td>644</td>
<td>0.5</td>
<td>PS</td>
</tr>
</tbody>
</table>

CPP: coproporphyrin; OEPK: octaethyl porphyrin ketone; TPP: tetraphenylporphyrin; TSPP: tetrakis(4-sulfonatophenyl)porphyrin; TDCPP: meso-tetra(2,6-dichlorophenyl)porphyrin; TFMPP: meso-tetra(3,5-bis(trifluoromethyl)phenyl)porphyrin; Br₈TMP: meso-tetramesityl-β-octabromoporphyrin; OEP: octaethyl porphyrin

Silicone

Silicone is the most widely used polymer binder matrix employed in optical oxygen sensors due to its high permeability (62 x 10⁻⁹ (cm³ cm)/cm² s cm Hg) at 28° C and solubility (0.31 ml·g⁻¹ at 28° C) to oxygen associated with a low glass transition temperature, \( T_g \), (-127° C), high chemical and mechanical durability, and benign physiological effects beneficial to in vivo measurement applications. However, silicone as a binder matrix is incredibly hydrophobic in nature due to its extended
nonpolar Si-O-Si backbone which forms during polymerization.\textsuperscript{25} Adequate homogeneous distribution of the hydrophilic Ru(II) $\alpha$-diimine complexes in the polymer binder then becomes a challenge in avoiding aggregation or microcrystallization effects which lead to inefficient oxygen quenching.\textsuperscript{31} Therefore, several researchers have investigated the addition of Ru(II) $\alpha$-diimine adsorbed silica gel to the polymer binder. The addition of silica gel aids luminescence oxygen quenching by lessening the negative quenching effects due to formation of metal complex aggregates and microcrystallites.\textsuperscript{25,56}

**Plasticizers**

Other polymers such as cellulose acetate (CA),\textsuperscript{39} polymethylmethacrylate (PMMA),\textsuperscript{40} polyvinylchloride (PVC),\textsuperscript{41} polystyrene (PS),\textsuperscript{42} and sol-gels\textsuperscript{43,44} have been employed as oxygen permeable polymer binders. These polymers are not as permeable to oxygen as the elastomeric silicone polymer binders and slow and inaccurate oxygen concentration measurements result. When a plasticizer such as tetrabutyl borate or dodecyl sulfate is incorporated into the given polymer, it lowers the $T_g$ and improves the parent polymer’s permeability to oxygen.\textsuperscript{8,37} However, a plasticizer can leach from the polymer binder and adversely affect the polymer’s ability to adsorb oxygen.\textsuperscript{27}

**Modified Polymers**

One way to avoid incorporating additives such as silica gel or plasticizers into the polymer binder is to design synthetically modified polymers. These polymers are designed to possess similar oxygen permeability as the silicone polymers yet not suffer from the same inaccurate sensing affects arising from inadequate luminophore
distribution or impurity leaching. Several alternative polymer binders have been
developed recently.

Puklin et al. have developed a fluoroacrylic copolymer (FIB),
(fluoro/isopropyl/butyl)acrylic polymer displayed in Figure 1-4.\textsuperscript{57} When Pt(II)
tetra(pentafluorophenyl)porphyrin (PtTFPP) is distributed through the polymer, the
coating displays a Stern-Volmer dynamic range of \( \sim 0.9 \) [defined as \( \frac{(I_{\text{vac}} - I_{\text{atm}})}{I_{\text{vac}}} \)],
where \( I \) is luminescence intensity and the subscripts vac and atm refer to vacuum and
atmospheric pressure, respectively. Other attributes include a response time of less than
1 s to an increase in pressure from near vacuum to 1 atm, good photostability, and low
temperature dependence (\( \sim 0.6 \% \cdot ^\circ C^{-1} \)).

\[
\text{Figure 1-4: Repeat unit of (fluoro/isopropyl/butyl)acrylic polymer.}
\]

Amao et al. have developed a different fluorocopolymer [copoly(styrene/PFS)],
poly(styrene-\textit{co}-pentafluorostyrene) illustrated in Figure 1-5.\textsuperscript{51} When Pt(II)
octaethylporphyrin (PtOEP) is distributed through the polymer, the coating displays a
\( I_0/I_{100} = 18.0 \) response as compared to \( I_0/I_{100} = 4.5 \) for a simple polystyrene coating,
where \( I_0 \) and \( I_{100} \) represent the detected phosphorescence intensity from a coating exposed
to 100 \% argon and 100 \% oxygen, respectively. The photoluminescence response times
are 5.66 s for polymer exposure to argon then oxygen and 30.0 s for polymer exposure to oxygen then argon.

**Figure 1-5:** Repeat unit of poly(styrene-co-pentafluorostyrene) copolymer.

The preceding research groups are working from the basis that fluoropolymer coatings possess an increased permeability to oxygen\(^5\) and a higher stability towards photo-oxidation compared to polymers lacking highly electronegative groups. The C-F bonds possess a large bonding energy (116 kcal-mol\(^{-1}\)) and short bond lengths (1.381 Å) which enhance the bonds' stability towards photo-oxidation and increases their affinity towards oxygen sorption when incorporated into a polymer binder backbone.\(^5\)

Ruffolo et al. have developed another type of block copolymer poly(aminothionylphosphazene)-\(b\)-poly(tetrahydrofuran) (PATP\(_y\)-PTHF\(_x\)) displayed in Figure 1-6.\(^6\) When [Ru(dpp)\(_3\)]Cl\(_2\) is distributed through the block copolymer, the coating displays good quenching sensitivity and linear Stern-Volmer response compared to earlier poly(butylaminothionylphosphazene) (PBATP\(_y\)) and PBATP\(_y\)/PTHF\(_x\) blends.
This particular design idea stems from the often-impractical necessity for silicone coating polymers to cross-link prior to formation of a solid stable coating. The cross-linking is not a controlled physical process and can change in degree and directionality from coating to coating leading to irreproducible SV response.\textsuperscript{25,50,61} This lack of cross-linking continuity can be one source of problems associated with poor luminophore distribution. Therefore the (PATPy-PTHFx) design benefits from production of a dimensionally stable coating without the need for cross-linking. Moreover, such a design leads to a better understanding of the polymer coating's structure-function relationship.\textsuperscript{60} It will be interesting to see how future polymer designs will compare to the above modified polymers, to one another, and to the more traditional elastomeric silicone binder systems; what current morphological questions will be answered; and how will knowing such answers lead to the development of other luminophore/polymer binder systems.

**Wind-Tunnel Application**

In a typical application of aerodynamic engineering, a sensor coating is composed of a luminophore dispersed in a polymer binder which is dissolved in a volatile thinning solvent and sprayed onto an aerodynamic model. The coating forms upon evaporation of the volatile solvent. The model is installed in a wind-tunnel, and the photoluminescence
from the sensor coating at $\lambda^p_{\text{em}}$ is imaged with a camera (digital or film-based) that is fitted with appropriate filters that pass light of wavelength $\lambda^p_{\text{em}}$. By using appropriate computer algorithms, it is possible to apply the Stern-Volmer calibration (1-5) to convert the photoluminescence intensity map generated by the camera into a full-field map of air pressure ($P_{\text{air}}$) over the surface of the model displayed in Figure 1-7.

![Pressure Sensitive Paint measurement system](image)

**Figure 1-7:** Pressure Sensitive Paint measurement system for testing of air pressure profiles on an airplane model in a wind-tunnel.

Pressure maps obtained from the set-up in Figure 1-7 would show luminescence characteristics similar to Figure 1-8. Figure 1-8 displays an intensity pressure map for a nitrogen jet protruding out of the plane of a PSP coating. The direction of the tunnel air-flow travels from behind the nitrogen injection jet forward (bottom to top of image). A pressure field of high and low pressures develop. The oval shape preceding the nitrogen jet indicates an area of high pressure or high oxygen concentration, and the cone shape directly preceding the nitrogen jet indicates an area of low pressure or low oxygen concentration due to air-flow disruption. Colors would then be assigned to the gradients.
of gray in the image to enhance and discriminate among the pressure changes by making them more discernable to the viewer’s eye.

Figure 1-8: Gray-scale pressure distribution map for a nitrogen jet protruding from a PSP coating.

As demonstrated, PSP technology has revolutionized traditional wind-tunnel testing which monitors discrete surface pressure measurements at localized pressure taps across a test model. The transducers are connected to multitudes of electronic wiring and hardware, and the assembly of such a model takes 9 - 12 months to design and construct. As compared to the complexity of the transducer system, PSP coatings are easily applied to a model surface and ready to use within a few hours. The noninvasive approach offered is essential to prototype aerodynamic model testing; therefore, luminescence imaging has generated significant research interest in the aerodynamic engineering community.\textsuperscript{16,27}
**Temperature Effects**

Under ideal conditions, the photoluminescence intensity of a sensor coating would respond only to changes in $pO_2$; other environmental parameters such as temperature (T) would not interfere with the measurement. Unfortunately, it is well known that at constant air pressure, the photoluminescence intensity of most oxygen sensor coatings varies inversely with T as does the Stern-Volmer coefficient ($K_{SV}$). For many sensor coatings, $K_{SV}$ varies linearly with T over a narrow range of temperatures demonstrated by equation (1-14):

$$K_{SV}(T) = K_{SV}^{ref} + bT$$  \hspace{1cm} (1-14)

Because of the temperature dependence of $K_{SV}$, when a sensor coating is applied under non-isothermal conditions (most often the case in a wind-tunnel), the global map of $P_{air}$ that is created will be in error. On the other hand, since $K_{SV}$ is a well-behaved function of temperature as in equation (1-14), if one knows the temperature distribution over the surface of the aerodynamic model, it is possible to apply computer algorithms to correct for the temperature dependence of $K_{SV}$ and obtain an accurate global surface pressure distribution. Several data reduction methods have been developed, which convert the processed wind tunnel image into false-color image representations of the quantitative pressure distribution across the model surface. The intensity-ratios obtained at each pixel are converted into pressures using a modified Henry's law relation, which accounts for the non-ideal porous nature of the polymer binder in equation (1-15),

$$\frac{P}{P_{ref}} = C_1 + C_2(I_{ref}(T_{ref})/I_{run}(T_{run})) + C_3(I_{ref}(T_{ref})/I_{run}(T_{run}))^2$$  \hspace{1cm} (1-15)
where $C_1$, $C_2$, and $C_3$ are the reduction method coefficients, and $I_{\text{ref}}(T_{\text{ref}})/I_{\text{run}}(T_{\text{run}})$ is the intensity-ratio obtained at each pixel.

**Isothermal Calibration**

An isothermal calibration assumes that the wind-tunnel surface is spatially and temporally isothermal during the run of the flow. An initial static calibration is taken at a reference temperature over a given pressure range, and a least-squares fit is employed to obtain the resulting calibration curve. The pressure values obtained from pressure taps fashioned along the model surface are compared to the intensity-ratio images obtained. As is expected, the method does not account for the temperature drop that occurs across the model during airflow that results in a prediction of pressure values lower than measured. Therefore, it is best that this method only be used for qualitative evaluations of coatings.

**In-situ Calibration**

An in-situ calibration accounts for the change in surface temperature across a model surface during wind-tunnel operation. For this reduction method, a limited number of pressure taps are placed across the surface of the model. These taps should be placed in the regions of highest and lowest pressures as well as several intermediate regions for the best results. However, a priori knowledge of the pressure distribution is difficult to know and a disadvantage for this reduction method.

The intensity of the paint around the taps is evaluated and used in conjunction with the pressure values obtained at the taps to develop a calibration curve. A least-squares fit is applied to equation (1-15), and the pressure tap and intensity values are used
to determine the values for $C_1$, $C_2$, and $C_3$. The pressure values across the model surface are then obtained through interpolation of the data.

**K-fit Calibration**

The K-fit calibration is a hybrid of the isothermal and in-situ calibration methods. It was found that equation (1-15) will coalesce if $T_{run} = T_{ref}$, therefore, equation (1-15) can be re-cast as equation (1-16),

$$\frac{P}{P_{ref}} = C_1' + C_2'(I_{ref}(T_1)/I_{run}(T_1)) + C_3'(I_{ref}(T_1)/I_{run}(T_1))^2$$

(1-16)

where $T_1$ is an arbitrary number, and the coefficients $C_1'$, $C_2'$, and $C_3'$ do not vary with temperature. A scaling process, function $K$ in equation (1-17), is applied to rescale the reference image ($I_{ref}(T_1)$), so it then emulates a reference image taken at $T_2$.

$$K = \frac{I_{ref}(T_1)}{I_{ref}(T_2)} = f(T_1,T_2)$$

(1-17)

Equation (1-16) is recast as (1-18),

$$\frac{P}{P_{ref}} = C_1' + C_2'(KI_{ref}(T_2)/I_{run}(T_1)) + C_3'(KI_{ref}(T_2)/I_{run}(T_1))^2$$

(1-18)

where $T_1$, $T_2$, and $K$ are constant over the model surface. If $T_1 = T_{run}$ and $T_2 = T_{ref}$, then a least-squares fit of equation (1-18) will result in $K$. This reduction method is superior to the isothermal method but less accurate than the in-situ method, since this model under-predicts the pressure values in the low-pressure region. A possible explanation for this is that it may not be physically reasonable to assume that there exists a separation in the pressure-dependent ($C_1'$, $C_2'$, and $C_3'$) and the temperature-dependent ($K$) relationships of the coating. Therefore, the $K$ value in equation (1-17) may be pressure-sensitive, and the equation should be recast as equation (1-19).

$$K = f(T_1,T_2,P)$$

(1-19)
Temperature-corrected Pressure Calibration

This method accounts for the change in surface temperature across the model surface between the reference image and the wind-tunnel images. It utilizes a pixel-by-pixel correction method by employing the image information of a temperature-sensitive coating to correct for the temperature-dependence of a pressure-sensitive coating. By knowing the intensity-ratio and temperature values at each pixel, a pressure value can be determined by equation (1-20).64

\[ \frac{I_{\text{ref}}}{I_{\text{cal}}} = f(P,T) \]  

(1-20)

The pressure values at each pixel are calculated through a linear interpolation between isothermal calibration curves generated from in-situ taps and the temperature-sensitive coating’s temperature values. The advantages of this method allow for knowledge of the slightest temperature gradient across the surface with no need for pressure taps to calculate the final pressure values. However, there can be problems associated with photodegradation of the coating materials; an inconsistent use of substrate material for calibration samples and wind tunnel fixtures accounts for inaccurate comparisons of pressure-sensitivities in calibration curve generations; and the temperature values obtained from the temperature-sensitive coating may not be the exact values experienced by the pressure-sensitive coating.64

Physical Manifestations of the Temperature Effect

The temperature effects experienced by the pressure-sensing coatings are due to the two major components of the PSP: the luminophore and the polymer binder. First, it is known that in degassed solution experiments that the temperature dependence of a luminophore is dependent on the non-radiative decay pathways, since the radiative decay
rates are only weakly temperature dependent. Luminophores such as the Ru(II) \( \alpha \)-diimine complexes experience temperature dependence of non-radiative decay processes because of the coupling of the excited state with vibrational levels of the metal ground state and the solvent or polymer matrix. More specifically, for the Ru(II) \( \alpha \)-diimine complexes, temperature dependent excited state decay arises due to increased coupling of the emissive MLCT (metal-to-ligand charge-transfer) state to a nearby dd manifold.

Temperature dependent quenching can arise due to the temperature-dependence of the diffusivity and solubility of the quencher molecule (O\(_2\)) in the polymer matrix. The permeability (\( P_{O_2} \)) of oxygen in the binder is a product of the solubility (\( S_{O_2} \)), and diffusivity (\( D_{O_2} \)). The rate constant for quenching (\( k_q \)) is proportional to \( D_{O_2} \), and the concentration of oxygen [O\(_2\)] in the polymer is affected by \( S_{O_2} \). However, since it is known that the solubility of diatomic gases in polymers is only weakly dependent on temperature, temperature dependent quenching then arises primarily due to the temperature dependence of \( D_{O_2} \). Gas diffusivity in polymers depends on the polymer total free volume, which increases with increased temperatures. Polymer segments undergo thermal expansion creating free sites accessible to oxygen molecules.

According to Schanze et al., \( k_q[O_2] = A_q\exp(-E_q/RT) \), where \( A_q \) and \( E_q \) are the frequency factor and activation energy for oxygen quenching, respectively. Since \( k_q \) is proportional to \( D_{O_2} \), it can be assumed that the \( E_q \) is related to the activation energy of diffusion (\( E_a \)). Therefore, by the relations outlined above, PSP coatings should be developed which have the lowest possible activation energy for oxygen diffusion.
Advances in PSP Design

A convenient method for obtaining the necessary information regarding the temperature distribution over the aerodynamic model is to incorporate into the sensor coating a second “temperature sensitive” luminophore that has the following properties: (1) it is sufficiently excited at the same wavelength as the oxygen sensing luminophore; (2) photoluminescence occurs in a different region of the visible spectrum ($\lambda_{em}^T$) than the photoluminescence of the oxygen sensing luminophore (i.e., $\lambda_{em}^T \neq \lambda_{em}^P$); (3) photoluminescence intensity is independent of pressure; (4) the luminophore is photostable or deteriorates at a rate similar to that of the oxygen sensing luminophore; and (5) photoluminescence intensity varies strongly and monotonically with temperature.

With such a dual-luminophore sensor system, one would be able to obtain a global map of the temperature of the surface of an aerodynamic model by imaging the photoluminescence from the temperature-sensitive luminophore with a camera fitted with filters that pass light only at wavelength $\lambda_{em}^T$. The resulting temperature map could then be used in an algorithm to correct for the temperature-dependence of the photoluminescence intensity from the pressure-sensitive luminophore.

The Gouterman research group has worked extensively in developing luminophores and polymer binders which correct for temperature-dependence. They reported in 1998 the incorporation of a second luminophore to a polymer binder: a pressure-insensitive but temperature-sensitive inorganic phosphor to correct for the temperature-dependence of the PSP coating. However this coating experienced some problems with competitive absorption of the excitation light by PtTFPP, absorption of the emission light from the phosphor ($\text{BaMg}_2\text{Al}_{16}\text{O}_{27}::\text{Eu}^{2+}$) by PtTFPP, and a heterogeneous
distribution of the phosphor particles. Expanding on earlier work with platinum porphyrins, the Gouterman group investigated the use of silicon octaethylporphine (SiOEP) as a new pressure-insensitive, temperature-sensitive luminophore. The silicon porphine complex suffers from an increase in fluorescence intensity as the temperature rises due to repopulation of the singlet excited state via the triplet state; moreover, the rise in fluorescence can cause confusion in calibration runs at vacuum. Fortunately, the temperature-dependence is only at vacuum conditions - not a standard wind-tunnel condition.65

Gouterman’s group has also researched the development of a polymer possessing a low activation energy to oxygen diffusion. A temperature sensitivity of \(-0.6\%\cdot{^\circ}\text{C}^{-1}\) for PtTFPP dispersed in the fluoroacrylic polymer FIB (Figure 1-4) has been reported. This number is significantly better than a temperature sensitivity of \(-1.7\%\cdot{^\circ}\text{C}^{-1}\) reported for PtOEP in the silicone polymer binder Genesee GP-197.57

**Monitoring Methods**

There exist three monitoring methods for the analysis of PSP coatings: luminescence intensity method, pulsed lifetime method, and phase-shift method.

**Luminescence Intensity**

The luminescence intensity method measures the emission intensity produced by the luminophore(s) in the sensor coating. It is the most widely used method, since the equipment is relatively inexpensive to assemble and small enough to be portable. The pressure profile experienced by the coating is then determined from a calibration curve. However, an accurate analysis by the method is directly affected by changes in the excitation source intensity, variations in efficiency of the system equipment to collect the
emission signal(s), and the photostability of sensing coatings. Fortunately, collecting a reference signal and limiting the exposure time of the sensor coatings can help alleviate the effects of these problems.

**Pulsed Lifetime**

The pulsed lifetime method utilizes an excitation source with a pulse termination time that is shorter than the lifetime of the emission lifetime(s) being evaluated. This method is employed less frequently due to the problem of reducing the complex decay curves obtained by the traditional least-squares method; however, the simpler technique of rapid lifetime determination (RLD) is being employed to reduce the complex decays to a single parameter.\(^6^8\) The RLD technique allows for direct integration of various regions under the integration curve resulting in reduction to a single parameter.

**Phase-shift**

The phase-shift method employs a sinusoidally modulated excitation source combined with phase-sensitive detection.\(^2^3\) The modulated emission is delayed in phase by an angle \(\phi\), relative to the excitation demonstrated by equation (1-21).

\[
\phi = \arctan(\omega t) \tag{1-21}
\]

where

\[
\omega = 2\pi f \tag{1-22},
\]

and \(f\) is the linear modulation frequency. The phase shifts are easy to measure, since the phase shift varies monotonically with oxygen concentration.\(^6^9\) The equipment required for this method is relatively inexpensive. This method like the RLD method does not provide an a priori knowledge of the complexity of the decay(s) measured; however, the frequency can be varied for optimization of accuracy at a known concentration of oxygen.\(^2^7\)
Scope of This Work

Initial research has focused on development of a “temperature-sensitive” luminophore, which is temperature-sensitive and pressure-insensitive. This system configuration corrects for the temperature dependency of the pressure component by determining the run-time temperature field. Dual-luminophore sensor coatings were developed where the temperature sensing luminophore, encapsulated in polystyrene microspheres, and the pressure sensing luminophore are conjointly distributed through a polydimethylsiloxane polymer binder. Extensive studies were conducted to evaluate the photo, thermal-, and temporal-stability of the luminophore/binder coatings, and fluorescence microscopy, SEM and TEM analytical techniques were employed to evaluate the molecular distribution of the luminophores in the coatings. Finally the coatings were subjected to static calibration cell imaging to evaluate their overall application performance.

Fluorescence microscopy has also been employed to analyze the variable nonlinear Stern-Volmer response exhibited by several Ru(II) α-diimine based coatings and the linear Stern-Volmer response exhibited by several Pt(II) tetra(pentafluorophenyl)porphyrin based coatings. It is believed that deviations from linearity are due to heterogeneity of the polymer matrix or the luminophore distribution. By quantitatively measuring the oxygen quenching efficiency at the pixel level with micrometer spatial resolution, we have been able to provide experimental evidence to explain the linear and non-linear SV responses exhibited by such coatings.
CHAPTER 2  
DUAL-LUMINOPHORE OXYGEN SENSING COATINGS

Introduction

As outlined in Chapter One, ideal oxygen sensing conditions produce photoluminescence intensity which responds only to changes in $pO_2$; however, other environmental parameters such as temperature ($T$) interfere with this measurement. For many sensors, the $K_{SV}$ value varies linearly with temperature over a narrow range of temperatures as indicated by equation (2-1).

$$K_{SV}(T) = K_{SV}^{ref} + bT$$  \hspace{1cm} (2-1)

When a sensor coating is evaluated under non-isothermal conditions (most often the case in a wind-tunnel), the global map of $P_{air}$ that is created will be in error, because of the temperature dependence of $K_{SV}$. Since $K_{SV}$ is a well-behaved function of temperature as in (2-1), if one knows the temperature distribution over the surface of the aerodynamic model, it is then possible to apply computer algorithms to correct for the temperature-dependence of $K_{SV}$ and obtain an accurate global surface pressure distribution.\textsuperscript{63-65}

A convenient method for obtaining the necessary information regarding the temperature distribution over the aerodynamic model is to incorporate into the sensor coating a second “temperature-sensitive” luminophore that exhibits similar properties\textsuperscript{65} to those outlined in Chapter One under PSP Advances. Therefore a dual-luminophore sensor system would provide a global temperature map for the surface of an aerodynamic model by imaging the photoluminescence from the temperature-sensitive luminophore.
The global temperature map would then be used to correct for the temperature-dependence of the photoluminescence intensity imaged from the pressure-sensitive luminophore, and a corrected global surface pressure distribution would result.

When incorporated separately (i.e., one at a time, but not together) into a polymer binder, many photoluminescent probe molecules display desirable emission characteristics for oxygen or temperature sensing. However, when two or more probe molecules are mixed into the same binder, they typically do not display the desired oxygen and/or temperature sensing photoluminescence properties. This non-ideal behavior arises from both physical and chemical molecular interactions, and often yields unpredictable results with respect to the overall photoluminescence properties of the sensor coating.\textsuperscript{65} One solution to this problem is to design nanometer to micrometer sized “molecular cages” or “compartments” that separate the luminophores in the polymer binder at the molecular level yet provide a coating that is spatially homogeneous on the millimeter scale (i.e., camera spatial resolution). In this manner, it is possible to produce a sensor coating system incorporating two or more photoluminescent probe molecules which display separate and well-defined photoluminescence intensity variations due to temperature and oxygen sensing.

Recent work by Gouterman et al. has yielded two types of dual-luminophore sensor coatings. In one coating, they have incorporated a second luminophore: a pressure-insensitive but temperature-sensitive inorganic phosphor to correct for the temperature-dependence of the PSP coating.\textsuperscript{70} Expanding on their earlier work with platinum porphyrins, the Gouterman group has also investigated the use of silicon octaethylporphine (SiOEP) as a new pressure-insensitive, temperature-sensitive luminophore.\textsuperscript{65}
In the work presented in this chapter, two dual-luminophore coatings were developed and characterized. These coatings contain a temperature-sensitive luminophore adsorbed onto polystyrene microspheres and an oxygen-sensitive luminophore. The dyed-microspheres and the oxygen sensing luminophore were distributed in a gas-permeable polymer binder. Detailed schemes for the preparation of the dyed-microspheres and resulting dual-luminophore coatings are outlined in Figures 2-1, 2-2, and 2-3.

Figure 2-1: Scheme for preparation of DOCl highly cross-linked polymer microspheres (DOClµsp). A) 5 vol % DVB relative to total volume, AIBN 2 wt. % relative to monomer, Δ 70° C for 24 h., EtOH wash, dry in vacuo at 50° C for 12 h. B) 1 mL MeOH, sonicate 1 h., soak in dark for 7 d., MeOH and CH₂Cl₂ wash, dry in vacuo at 30° C for 12 h.
Figure 2-2: Scheme for preparation of DOCI sulfonated polymer microspheres (DOCI-Ssmusp). A) 45 vol % DVB relative to total volume, DI H₂O:porogen = 25:1 v/v, porogen:monomer = 1:1.4 v/v, porogen = 1:1 1-dodecanol:toluene, sodium laurylsulfate 0.3 mol % relative to monomer, Δ 26° - 70° C 7 h. at 250 rpm, DI H₂O and acetone wash, THF Soxhlet extraction, dry in vacuo 48° C 12 h. B) 40 mL CH₂Cl₂, 0° C, 0.5 mL CISO₃H in 40 mL CH₂Cl₂ dropwise, warm to 25° C, stir 24 h. 25° C, CH₂Cl₂ wash, air dry. C) 150 mL DI H₂O, 50 mL NaOH (150 mM), stir 100 min. 25° C, 3x100 mL DI H₂O wash, 100 mL acetone wash, dry in vacuo 53° C 40 h. D) 4 mL MeOH, 2 mL DI H₂O, sonicate for 20 min., MeOH and acetone wash.
Figure 2-3: Scheme for preparation of dual-luminophore oxygen sensing coatings. PtDOCIμsp/VPDMS and PtDOCI-Sσsp/VPDMS.

Extensive studies were conducted to evaluate the photo, thermal-, and temporal-stability of the dual-luminophore coatings, and SEM, TEM, and fluorescence
microscopic analytical techniques were employed to evaluate the size and distribution of the luminophores in the coatings. Finally the coatings were subjected to static calibration imaging to evaluate their overall application performance. The results and discussion of this work are presented in the following chapter.

Results

Dual-luminophore Coatings

Two dual-luminophore coatings were developed incorporating an oxygen sensing luminophore and a temperature sensing luminophore adsorbed onto a polystyrene microsphere dispersed in a polydimethylsiloxane (PDMS) polymer binder.

PtDOCIµsp/VPDMS Coating

The first coating consists of Pt(II) meso-tetrakis(pentafluorophenyl)porphine (PtTFPP) as the oxygen sensing luminophore and DOCI-adsorbed microspheres and a weaker band, T(0,1), centered at 710 nm. The emission bands are due to produced via precipitation polymerization (DOCIµsp)(3,3'-diethyloxacarbocyanine iodide = DOCI) as the temperature sensing luminophore dispersed in a vinyl polydimethylsiloxanes (VPDMS) polymer binder. The preparation of the coating is schematically represented in Figure 2-3.

A typical emission spectrum of the coating is shown in Figure 2-4.
Figure 2-4: Emission intensity spectra for PtTFPP and DOClpμsp dispersed in VPDMS polymer on primed glass.

Two emission bands are detected when the coating is excited with 450 nm light. The PtTFPP emission consists of two bands: an intense band, T(0,0), centered at 645 nm and a weaker band, T(0,1), centered at 710 nm. The emission bands are due to phosphorescence from the $^3T_1(\pi,\pi^*)$ state of the porphyrin macrocycle. Back bonding between the $d_{xz}$ and $d_{yz}$ orbitals of the Pt with the empty $e_g(\pi^*)$ orbitals of the porphyrin produce a strong spin-orbit coupling. This leads to singlet-triplet mixing which increases the radiative decay rate from $^3T_1(\pi,\pi^*) \rightarrow ^1S_0$. The increase in phosphorescence facilitates efficient oxygen quenching. Therefore, a decrease in emission intensity is observed as the oxygen concentration above the coating sample is increased.

The DOClpμsp temperature-sensing luminophore exhibits two weak emission bands centered at 510 nm and 550 nm, respectively. This is fluorescence from the $\pi-\pi^*$ transitions centered along the conjugated chromophore backbone. The fluorescence is split at 540 nm due to absorption by PtTFPP.
The PtTFPP porphyrin is a d^8 phosphorescent hypso porphyrin possessing absorption features blue-shifted relative to normal porphyrins. PtTFPP exhibits several absorption bands. The first band is an intense near-UV band termed the Soret band at 395 nm, $^1S_0 \rightarrow ^1S_2(\pi,\pi^*)$. The second two bands appear in the visible region between 505 to 540 nm and are referred to as the Q bands. The first Q band, Q(0,0), represents the excitation from the lowest vibrational level of the ground-state singlet to the lowest vibrational level of the first singlet excited state, and the second Q band, Q(1,0), has one quantum of vibration in the first singlet excited state, $^1S_0 \rightarrow ^1S_1(\pi,\pi^*)$. For square planar metalloporphyrins, such as PtTFPP, the Q bands are due to degenerate excited states with x and y polarization.72

For a d^8 metalloporphyrin, the filled d_z orbitals, d_xz or d_yz, are located between the occupied a_1u(\pi), a_2u(\pi) orbitals and the empty degenerate LUMO e_g(\pi^*) of the porphyrin ring. The metal d_z electrons can then interact with the empty e_g(\pi^*) orbitals inducing a mixing between the empty e_g(\pi^*) orbital and the filled e_g(d\pi) orbital. Stabilization of the filled e_g(d\pi) orbital raises the energy of the e_g(\pi^*) orbital and results in a blue-shift of the absorption bands.52,73

The fluorescence emission of the DOCIp\mu\textit{sp} is centered at 510 nm due to $\pi-\pi^*$ transitions, and the Q bands of the PtTFPP overlap well with the DOCI fluorescence. Therefore, the PtTFPP luminophore can absorb some of the DOCIp\mu\textit{sp} emission, and the DOCI emission band experiences an emission bleach around 535 nm. The effect is clearly seen in Figure 2-4.
PtDOI-Sssp/VPDMS Coating

The second coating is a modification of the first. The formulation still contains Pt(II) meso-tetrakis(pentafluorophenyl)porphine (PtTFPP) as the oxygen sensing luminophore; however the DOI-adsorbed microspheres were produced via a suspension polymerization, sulfonated, and negatively charged prior to dye adsorption. The luminophores are dispersed in a vinyl polydimethylsiloxanes (VPDMS) polymer binder. A typical emission spectrum of the coating is displayed in Figure 2-5.

![Emission intensity spectra for PtTFPP and DOI-Sssp dispersed in VPDMS polymer on primed glass.](image)

**Figure 2-5:** Emission intensity spectra for PtTFPP and DOI-Sssp dispersed in VPDMS polymer on primed glass.

Under 450 nm excitation light, the coating exhibits two emission bands that are similar to the previous coating. The $I_{\text{max}}$ of PtTFPP is only slightly less intense than in Figure 2-4. However, the intensity of the DOI-Sssp is less than half intense as the previous DOI$pssp$ emission in Figure 2-4. Adding twice as much dyed-microspheres (DOI-Sssp) to the coating formulation did not significantly increase the emission intensity either. The impact of the different microsphere preparation methods to the
overall performance of the PtDOClµsp/VPDMS and PtDOCl-Sµsp/VPDMS coatings will become clearer when the quantity and distribution of the PtTFPP, DOClµsp, and DOCl-Sµsp luminophores in relation to imaging of the coatings with CCD camera technology is discussed later in the chapter.

**Temperature Dependence and Thermal-stability**

The temperature dependence and thermal-stability of the PtDOClµsp/VPDMS and PtDOCl-Sµsp/VPDMS coatings were assessed over a 40 K temperature range from 273 - 313 K. The temperature dependence of the PtTFPP pressure probe’s photoluminescence response to oxygen quenching for the emission region 630 - 670 nm was established, and the stability of the probe’s emission response to cyclic variations of temperature from 273 → 313 → 273 K was evaluated. The temperature dependence and thermal-stability of the photoluminescence between 530 - 570 nm for the DOClµsp and DOCl-Sµsp temperature probes were evaluated in the same manner as the photoluminescence of the pressure probe.

Specimens were prepared by air-brushing four layers of each coating onto borosilicate microscope slides primed with a TiO₂/SPDMS (SPDMS = silanol polydimethylsiloxanes with methyltriacetoxysilane cross-linker) coating and storing the specimens in the dark at room temperature and 33 % relative humidity until analysis. Exact details of the coating preparations can be found in the Experimental section. The specimens were evaluated 24 h. after coating application using the pressure cell attachment on the fluorimeter. The samples were illuminated with 450 nm light, and the emission was evaluated at predetermined wavelength areas. This procedure was followed to maintain consistency in coating characterization. The samples evaluated using the fluorimeter were also evaluated using a calibration cell with CCD detection (as described...
in the Experimental section). The calibration cell set-up monitors photoluminescence utilizing a series of bandpass filters with an optical bandwidth of 40 nm FWHM. Therefore in keeping with consistency, emission values obtained utilizing the fluorimeter were calculated for areas rather than discrete wavelengths.

PtTFPP

The temperature dependence of PtTFPP photoluminescence was analyzed. The luminescence intensity decreases moderately with increasing temperature at all pressures from 0.1 - 14.7 psi. This is a typical behavior for many pressure probes.\textsuperscript{16,57} Stern-Volmer (SV) analysis of the solid coatings were conducted utilizing equation (2-2),

$$\frac{I(\lambda_{em}, P_{air} = 1 \text{ atm})}{I(\lambda_{em}, P_{air})} = A + BP_{air} \quad (2-2)$$

and \((B/A) = K_{SV}\). The pressure probe’s response to oxygen quenching at different temperatures yields linear SV plots with excellent correlation and high \(K_{SV}\) values. The coatings are strongly pressure sensitive, as the total light intensity decreases by nearly a factor of 10 when the pressure above the film increases from 0.1 – 14.7 psi. A SV plot for each temperature is displayed in Figures 2-6 and 2-7 for the two coatings on primed glass. The temperature dependence of the coatings’ emission is evidenced by the “fan-out” of the regression lines at higher pressure. Comparison of Figures 2-6 and 2-7 reveals that the pressure probe in the PtDOCI-Sμsp/VPDMS coating is more temperature-dependent than the PtDOClpμsp/VPDMS coating.
Figure 2-6: SV plot PtDOClµsp/VPDMS coating on primed glass for temperatures between 273 – 313 K. \( A_{\text{REF}} \): area between 630 - 670 nm at 14.7 psi and 313 K.

Figure 2-7: SV plot PtDOCl-Sµsp/VPDMS coating on primed glass for temperatures between 273 – 313 K. \( A_{\text{REF}} \): area between 630 - 670 nm at 14.7 psi and 313 K.

For the SV analysis, the data for the percent decrease in PtTFPP emission area at each pressure as a function of oxygen concentration for a change in temperature are listed in Tables 2-1 and 2-2 for the two coatings on primed glass. At all pressures, the corresponding percent change in emission is consistent and provides evidence for a well-behaved oxygen sensing coating. These numbers are consistent with ones obtained by...
Puklin et al. for PtTFPP dispersed in fluoroacrylic polymer (FIB) and poly(methylmethacrylate) (PMMA) polymers.57

Table 2-1: Percent change in PtTFPP emission area at seven pressures over a 40 K range for PtDOClµsp/VPDMS coating on primed glass.

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>ΔA %·K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>273 - 313 K</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>- 1.05</td>
</tr>
<tr>
<td>2</td>
<td>- 0.78</td>
</tr>
<tr>
<td>4</td>
<td>- 0.55</td>
</tr>
<tr>
<td>6</td>
<td>- 0.77</td>
</tr>
<tr>
<td>8</td>
<td>- 0.57</td>
</tr>
<tr>
<td>10</td>
<td>- 0.77</td>
</tr>
<tr>
<td>14.7</td>
<td>- 0.80</td>
</tr>
</tbody>
</table>

Table 2-2: Percent change in PtTFPP emission area at seven pressures over a 40 K range for PtDOCI-Ssµsp/VPDMS coating on primed glass.

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>ΔA %·K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>273 - 313 K</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>- 1.30</td>
</tr>
<tr>
<td>2</td>
<td>- 0.73</td>
</tr>
<tr>
<td>4</td>
<td>- 0.78</td>
</tr>
<tr>
<td>6</td>
<td>- 0.78</td>
</tr>
<tr>
<td>8</td>
<td>- 0.76</td>
</tr>
<tr>
<td>10</td>
<td>- 0.87</td>
</tr>
<tr>
<td>14.7</td>
<td>- 0.88</td>
</tr>
</tbody>
</table>

The thermal-stability of the pressure probe’s photoluminescence was evaluated by subjecting the samples to various pressures between 0.1 – 14.7 psi at specific temperatures during a cyclic run from 273 → 313 → 273 → 313 → 273 K. Analysis of the pressure probe’s response to oxygen at each temperature reveals a consistent SV response at all temperatures, and no indication of hysteresis or change in the coatings
morphology. The SV data at each temperature evaluated for the PtDOClµsp/VPDMS and PtDOCl-Sµsp/VPDMS coatings are presented in Tables 2-3 and 2-4, respectively.

As can be seen in Tables 2-3 and 2-4, $K_{SV}$ increases with temperature. This is not surprising, since the diffusion of oxygen in a polymer is a thermally activated phenomenon. Raising the temperature increases the diffusion rate of oxygen thereby enhancing the efficiency of luminescence quenching. Even though small changes in
the intercept value can greatly affect the calculated $K_{SV}$ value. The $K_{SV}$ values in Tables 2-3 and 2-4 do not differ significantly and indicate that the coating is stable with respect to repeated thermal cycling over the 273 – 313 K range.

**DOCIµsp and DOCI-Sµsp**

The temperature dependence of the photoluminescence from the DOCIµsp and DOCI-Sµsp temperature probes was evaluated. The luminescence intensity of either temperature probes did not vary significantly with change in pressure at a constant temperature; however, it did decrease with increasing temperature.

The emission spectra for both coatings at 0.1 psi and five temperatures between 273 – 313 K are displayed in Figures 2-8 and 2-9 for the PtDOCIµsp/VPDMS and PtDOCI-Sµsp/VPDMS coatings on primed glass, respectively.

![Figure 2-8: Emission intensity spectra for DOClµsp in PtDOClµsp/VPDMS coating on primed glass at 0.1 psi for five temperatures between 273 – 313 K.](image-url)
Figure 2-9: Emission intensity spectra for DOCI-S\(\text{S}_\mu\text{sp}\) in PtDOCl-S\(\text{S}_\mu\text{sp}\)/VPDMS coating on primed glass at 0.1 psi for five temperatures between 273 – 313 K.

Analysis of the response of the temperature probes’ emission at specific temperatures from 273 - 313 K are displayed in Figures 2-10 and 2-11 for the PtDOCl-p\(\mu\)sp/VPDMS and PtDOCl-S\(\mu\)sp/VPDMS coatings, respectively. The origins of the probes’ temperature dependence and pressure independence will be discussed later in the chapter.
Figure 2-10: Temperature dependence of emission for DOClµsp in PtDOClµsp/VPDMS coating on primed glass for a series of pressures between 0.1 - 14.7 psi. $A_{REF}$: area between 530 - 570 nm at 273 K and 0.1 psi.

Figure 2-11: Temperature dependence of emission for DOCl-Sµsp in PtDOCl-Sµsp/VPDMS coating on primed glass for a series of pressures between 0.1 - 14.7 psi. $A_{REF}$: area between 530 - 570 nm at 273 K and 0.1 psi.

The temperature dependence was nearly linear over the temperature range 273 – 310 K with a slope of the linear correlation of approximately - 0.80 %-K$^{-1}$ for Figure 2-10 and - 0.54 %-K$^{-1}$ for Figure 2-11. For the PtDOClµsp/VPDMS coating, 0.80 %-K$^{-1}$ correlates well with the percent change in emission area as a function of temperature for
each pressure displayed for Run 1 of Table 2-5. The temperature dependence at assorted pressures varied between -0.69 to -0.80 %-K\(^{-1}\) for the temperature range 273 \(\rightarrow\) 313 K. For the PtDOCI-S\(\mu\)sp/VPDMS coating, the -0.54 %-K\(^{-1}\) value agrees with the percent change in emission area as a function of temperature for each pressure displayed for Run 1 of Table 2-6. The temperature dependence varied between -0.33 to -0.66 %-K\(^{-1}\).

Compared to DOCI\(\mu\)sp emission variation in Table 2-5, DOCI-S\(\mu\)sp exhibit less temperature dependence at each pressure with greater breadth in the distribution of percent change from pressure to pressure. These are both undesirable features and provide evidence for DOCI\(\mu\)sp as the better temperature-sensitive probe.

Table 2-5: Percent change in DOCI\(\mu\)sp emission area at seven pressures over a cyclic temperature run of 40 K for PtDOCI\(\mu\)sp/VPDMS coating on primed glass.

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>(\Delta A) %-K(^{-1}) 273 - 313 K</th>
<th>(\Delta A) %-K(^{-1}) 313 - 273 K</th>
<th>(\Delta A) %-K(^{-1}) 273 - 313 K</th>
<th>(\Delta A) %-K(^{-1}) 313 - 273 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>0.74</td>
<td>0.60</td>
<td>0.75</td>
<td>0.63</td>
</tr>
<tr>
<td>Run 2</td>
<td>0.69</td>
<td>0.60</td>
<td>0.73</td>
<td>0.54</td>
</tr>
<tr>
<td>Run 3</td>
<td>0.78</td>
<td>0.64</td>
<td>0.80</td>
<td>0.62</td>
</tr>
<tr>
<td>Run 4</td>
<td>0.76</td>
<td>0.60</td>
<td>0.70</td>
<td>0.59</td>
</tr>
<tr>
<td>Run 5</td>
<td>0.75</td>
<td>0.64</td>
<td>0.73</td>
<td>0.56</td>
</tr>
<tr>
<td>Run 6</td>
<td>0.79</td>
<td>0.55</td>
<td>0.70</td>
<td>0.57</td>
</tr>
<tr>
<td>Run 7</td>
<td>0.80</td>
<td>0.62</td>
<td>0.63</td>
<td>0.52</td>
</tr>
</tbody>
</table>
Table 2-6: Percent change in DOCl-Ssµsp emission area at seven pressures over a cyclic temperature run of 40 K for PtDOCl-Ssµsp/VPDMS coating on primed glass.

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>ΔA %·K⁻¹</th>
<th>ΔA %·K⁻¹</th>
<th>ΔA %·K⁻¹</th>
<th>ΔA %·K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>Run 2</td>
<td>Run 3</td>
<td>Run 4</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>-0.63</td>
<td>0.60</td>
<td>-0.47</td>
<td>0.52</td>
</tr>
<tr>
<td>2</td>
<td>-0.44</td>
<td>0.44</td>
<td>-0.40</td>
<td>0.47</td>
</tr>
<tr>
<td>4</td>
<td>-0.48</td>
<td>0.41</td>
<td>-0.43</td>
<td>0.51</td>
</tr>
<tr>
<td>6</td>
<td>-0.33</td>
<td>0.25</td>
<td>-0.40</td>
<td>0.55</td>
</tr>
<tr>
<td>8</td>
<td>-0.41</td>
<td>0.49</td>
<td>-0.62</td>
<td>0.61</td>
</tr>
<tr>
<td>10</td>
<td>-0.34</td>
<td>0.40</td>
<td>-0.44</td>
<td>0.45</td>
</tr>
<tr>
<td>14.7</td>
<td>-0.40</td>
<td>0.53</td>
<td>-0.61</td>
<td>0.48</td>
</tr>
</tbody>
</table>

The data for the thermal-stability of the temperature probes’ emission obtained by subjecting the samples to cyclic temperature changes from 273 → 313 → 273 → 313 → 273 K is outlined in Tables 2-5 and 2-6. Three trends from these tables should be noted. (1) The DOClpµsp exhibit greater temperature dependence when the coating is heated then when it is cooled. (2) The DOCI-Ssµsp display a consistent temperature-dependence when the coating is heated or cooled. (3) Both probes’ emission intensity response is appreciable with changes in temperature yet reproducible and thermally stable throughout the cyclic run of temperatures. This last characteristic will allow for correction of the photoluminescence temperature dependence exhibited by the PtTFPP pressure probe.63-65

**Emission Intensity**

Throughout the thermal cycling experiments, the stability of not only the probes’ responses to oxygen pressure and temperature changes were monitored but the stability of the probes’ overall intensity was monitored as well. The magnitude of the emission intensity data for both the pressure and temperature probes did not change during the thermal cycling. This is an indication that the photoluminescence of both coatings is not
only responsive to repeated pressure and temperature changes but the magnitude of the probes’ luminescence intensity is stable as well.

**Temporal-stability**

The stability of photoluminescence emission intensity over time was analyzed for the PtDOCI-[μsp/VPDMS and PtDOCI-S-[μsp/VPDMS coatings. To better understand possible influences one luminophore might impart on the other over time, the individual luminophores in VPDMS polymer were separately analyzed. The coatings, dual- and mono-luminophore, were applied to plain and primed (TiO2/SPDMS) borosilicate microscope slides and stored in the dark at room temperature and 33% relative humidity. For each spectroscopic analysis, the specimen slides were scored and a fresh piece broken-off for evaluation of the photoluminescence properties. The specimen was excited with 450 nm light, and emission was monitored from 475 - 800 nm. Particular emphasis was placed on evaluating the areas under the emission curve between 530 - 570 nm for the temperature probes and 630 - 670 nm for the pressure probe at seven distinct pressures in the range of 0.1 and 14.7 psi. All spectroscopic evaluations were conducted at room temperature.

**PtTFPP**

The area of emission for the PtTFPP pressure probe (λ = 630 - 670 nm) in the PtDOCI-[μsp/VPDMS, PtDOCI-S-[μsp/VPDMS and PtTFPP/VPDMS coatings was evaluated for its response to oxygen pressure. The coatings were analyzed at weekly intervals for the first month after application and then at monthly intervals for a total period of four or eight months. Stern-Volmer (SV) analysis of the pressure probe’s response to quenching at seven different pressures was performed for each analysis, and
the data are displayed in Tables 2-7, 2-8, and 2-9 for the coatings on bare glass and Table 2-10, 2-11, and 2-12 for the coatings on primer.

Table 2-7: SV Analysis of PtTFPP emission quenching in PtDOCIpmosp/VPDMS coating on bare glass.

<table>
<thead>
<tr>
<th>Time Interval</th>
<th>Intercept</th>
<th>Slope (psi⁻¹)</th>
<th>r²</th>
<th>Ksv (psi⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 h</td>
<td>0.046</td>
<td>0.065</td>
<td>0.994</td>
<td>1.43</td>
</tr>
<tr>
<td>1 wk</td>
<td>0.031</td>
<td>0.066</td>
<td>0.998</td>
<td>2.16</td>
</tr>
<tr>
<td>2 wk</td>
<td>0.020</td>
<td>0.066</td>
<td>0.999</td>
<td>3.23</td>
</tr>
<tr>
<td>3 wk</td>
<td>0.030</td>
<td>0.068</td>
<td>0.998</td>
<td>2.28</td>
</tr>
<tr>
<td>4 wk</td>
<td>0.011</td>
<td>0.067</td>
<td>0.999</td>
<td>5.96</td>
</tr>
<tr>
<td>4 mo</td>
<td>0.015</td>
<td>0.069</td>
<td>0.985</td>
<td>4.56</td>
</tr>
<tr>
<td>8 mo</td>
<td>0.045</td>
<td>0.068</td>
<td>0.986</td>
<td>1.51</td>
</tr>
</tbody>
</table>

*fresh sample used for each SV measurement, intercept = A in equation (2-2), slope = B in equation (2-2), Ksv = B/A*

Table 2-8: SV Analysis of PtTFPP emission quenching in PtDOCI-Ssosp/VPDMS coating on bare glass.

<table>
<thead>
<tr>
<th>Time Interval</th>
<th>Intercept</th>
<th>Slope (psi⁻¹)</th>
<th>r²</th>
<th>Ksv (psi⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 h</td>
<td>0.048</td>
<td>0.067</td>
<td>0.995</td>
<td>1.40</td>
</tr>
<tr>
<td>1 wk</td>
<td>0.023</td>
<td>0.068</td>
<td>0.999</td>
<td>2.96</td>
</tr>
<tr>
<td>2 wk</td>
<td>0.031</td>
<td>0.066</td>
<td>0.999</td>
<td>2.13</td>
</tr>
<tr>
<td>3 wk</td>
<td>0.055</td>
<td>0.067</td>
<td>0.992</td>
<td>1.22</td>
</tr>
<tr>
<td>4 wk</td>
<td>0.018</td>
<td>0.068</td>
<td>0.995</td>
<td>3.78</td>
</tr>
<tr>
<td>2 mo</td>
<td>0.047</td>
<td>0.063</td>
<td>0.992</td>
<td>1.34</td>
</tr>
<tr>
<td>4 mo</td>
<td>0.018</td>
<td>0.065</td>
<td>0.998</td>
<td>3.61</td>
</tr>
</tbody>
</table>

*fresh sample used for each SV measurement, intercept = A in equation (2-2), slope = B in equation (2-2), Ksv = B/A*
Table 2-9: SV Analysis of PtTFPP emission quenching in VPDMS polymer on bare glass.

<table>
<thead>
<tr>
<th>Time Interval</th>
<th>Intercept</th>
<th>Slope (psi⁻¹)</th>
<th>r²</th>
<th>Ksv (psi⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 h</td>
<td>0.100</td>
<td>0.067</td>
<td>0.969</td>
<td>0.670</td>
</tr>
<tr>
<td>1 wk</td>
<td>0.054</td>
<td>0.068</td>
<td>0.986</td>
<td>1.26</td>
</tr>
<tr>
<td>2 wk</td>
<td>0.110</td>
<td>0.061</td>
<td>0.995</td>
<td>0.555</td>
</tr>
<tr>
<td>3 wk</td>
<td>0.047</td>
<td>0.067</td>
<td>0.995</td>
<td>1.43</td>
</tr>
<tr>
<td>4 wk</td>
<td>0.083</td>
<td>0.063</td>
<td>0.981</td>
<td>0.759</td>
</tr>
<tr>
<td>2 mo</td>
<td>0.135</td>
<td>0.065</td>
<td>0.965</td>
<td>0.481</td>
</tr>
<tr>
<td>4 mo</td>
<td>0.111</td>
<td>0.068</td>
<td>0.946</td>
<td>0.613</td>
</tr>
<tr>
<td>8 mo</td>
<td>0.072</td>
<td>0.064</td>
<td>0.979</td>
<td>0.889</td>
</tr>
</tbody>
</table>

a fresh sample used for each SV measurement, b intercept = A in equation (2-2), c slope = B in equation (2-2), d Ksv = B/A

Table 2-10: SV Analysis of PtTFPP emission quenching in PtDOClµsp/VPDMS coating on primed glass.

<table>
<thead>
<tr>
<th>Time Interval</th>
<th>Intercept</th>
<th>Slope (psi⁻¹)</th>
<th>r²</th>
<th>Ksv (psi⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 h</td>
<td>0.005</td>
<td>0.068</td>
<td>0.999</td>
<td>14.4</td>
</tr>
<tr>
<td>1 wk</td>
<td>0.011</td>
<td>0.067</td>
<td>0.999</td>
<td>5.96</td>
</tr>
<tr>
<td>2 wk</td>
<td>0.013</td>
<td>0.068</td>
<td>0.999</td>
<td>5.14</td>
</tr>
<tr>
<td>3 wk</td>
<td>0.016</td>
<td>0.065</td>
<td>0.997</td>
<td>4.09</td>
</tr>
<tr>
<td>5 wk</td>
<td>0.017</td>
<td>0.067</td>
<td>0.999</td>
<td>4.01</td>
</tr>
<tr>
<td>4 mo</td>
<td>0.042</td>
<td>0.066</td>
<td>0.999</td>
<td>1.56</td>
</tr>
<tr>
<td>8 mo</td>
<td>0.018</td>
<td>0.065</td>
<td>0.996</td>
<td>3.70</td>
</tr>
</tbody>
</table>

a fresh sample used for each SV measurement, b intercept = A in equation (2-2), c slope = B in equation (2-2), d Ksv = B/A

Table 2-11: SV Analysis of PtTFPP emission quenching in PtDOCl-Ssµsp/VPDMS coating on primed glass.

<table>
<thead>
<tr>
<th>Time Interval</th>
<th>Intercept</th>
<th>Slope (psi⁻¹)</th>
<th>r²</th>
<th>Ksv (psi⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 h</td>
<td>0.020</td>
<td>0.067</td>
<td>0.999</td>
<td>3.35</td>
</tr>
<tr>
<td>1 wk</td>
<td>0.024</td>
<td>0.068</td>
<td>0.999</td>
<td>2.83</td>
</tr>
<tr>
<td>2 wk</td>
<td>0.017</td>
<td>0.067</td>
<td>0.999</td>
<td>3.94</td>
</tr>
<tr>
<td>3 wk</td>
<td>0.047</td>
<td>0.068</td>
<td>0.993</td>
<td>1.45</td>
</tr>
<tr>
<td>4 wk</td>
<td>0.030</td>
<td>0.067</td>
<td>0.998</td>
<td>2.23</td>
</tr>
<tr>
<td>2 mo</td>
<td>0.042</td>
<td>0.066</td>
<td>0.999</td>
<td>1.57</td>
</tr>
<tr>
<td>3 mo</td>
<td>0.061</td>
<td>0.066</td>
<td>0.996</td>
<td>1.08</td>
</tr>
<tr>
<td>4 mo</td>
<td>0.045</td>
<td>0.066</td>
<td>0.998</td>
<td>1.47</td>
</tr>
</tbody>
</table>

a fresh sample used for each SV measurement, b intercept = A in equation (2-2), c slope = B in equation (2-2), d Ksv = B/A
Table 2-12: SV Analysis of PtTFPP emission quenching in VPDMS polymer on primed glass.

<table>
<thead>
<tr>
<th>Time Interval&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Intercept&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Slope (psi&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>r&lt;sup&gt;2&lt;/sup&gt;</th>
<th>K&lt;sub&gt;SV&lt;/sub&gt; (psi&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 h</td>
<td>0.025</td>
<td>0.067</td>
<td>0.999</td>
<td>2.68</td>
</tr>
<tr>
<td>1 wk</td>
<td>0.033</td>
<td>0.067</td>
<td>0.999</td>
<td>2.03</td>
</tr>
<tr>
<td>2 wk</td>
<td>0.028</td>
<td>0.067</td>
<td>0.999</td>
<td>2.39</td>
</tr>
<tr>
<td>4 wk</td>
<td>0.019</td>
<td>0.067</td>
<td>0.999</td>
<td>3.53</td>
</tr>
<tr>
<td>8 mo</td>
<td>0.028</td>
<td>0.066</td>
<td>0.998</td>
<td>2.36</td>
</tr>
</tbody>
</table>

<sup>a</sup> fresh sample used for each SV measurement, <sup>b</sup> intercept = A in equation (2-2), <sup>c</sup> slope = B in equation (2-2), <sup>d</sup> K<sub>SV</sub> = B/A

Over a four- or eight-month period, the coatings retained an excellent response to variation in P<sub>air</sub> as evidenced by the high K<sub>SV</sub> values in Tables 2-7 to 2-12. At all time intervals, SV evaluation results in steep linear plots with minimal fluctuations in the intercept values – a small intercept value indicates excellent coating sensitivity to oxygen concentration. The small variations in intercept however translate into large overall variations in K<sub>SV</sub> values. The most noticeable variation in K<sub>SV</sub> is for the PtDOCIP<sub>µ</sub>sp/VPDMS coating on primed glass 24 h. after application. The K<sub>SV</sub> value of 14.4 psi<sup>-1</sup> is 3.5 times larger than the average K<sub>SV</sub> value, 4.08 psi<sup>-1</sup>, for subsequent time intervals. The increased K<sub>SV</sub> value is possibly due to photolysis of the coating and not necessarily a consequence of oxygen pressure.

Comparison of the intercept and K<sub>SV</sub> values from Tables 2-7, 2-8, 2-10, and 2-11 to those in Tables 2-9 and 2-12, makes it is clear that the sensitivity of PtTFPP emission to oxygen pressure is more sensitive in the dual-luminophore coatings than in the monoluminophore coating. Enhancement of PtTFPP’s emission sensitivity in the dual-luminophore coatings is a beneficial finding which counters negative effects seen in other dual-luminophore coatings.
**DOCI_{µsp} and DOCI-S_{µsp}**

Analysis of the area of the photoluminescence spectrum for the DOCI_{µsp} and DOCI-S_{µsp} (λ = 530 – 570 nm) temperature probes resulted in fairly consistent emission intensity that was unaffected by oxygen pressure. The emission intensity areas for each pressure were averaged (this is assuming that the emission intensity does not fluctuate greatly with variation in P_{air}), and the coefficient of variation (CV %) (the standard deviation of average emission intensity area divided by the average emission intensity area) was determined for each time interval analysis. The CV % statistically describes the degree of variance in the emission intensity areas of seven spectral emission scans for pressures between 0.1 – 14.7 psi. Since the temperature probe is ideally pressure insensitive, a low CV % is expected. The CV % data at different time intervals for the temperature probes are presented in Tables 2-13 and 2-14 for the PtDOCI_{µsp}/VPDMS and PtDOCI-S_{µsp}/VPDMS coatings on bare and primed glass.

Table 2-13: Analysis of the area under the emission curve for DOCI_{µsp} in PtDOCI_{µsp}/VPDMS coating on bare and primed glass.

<table>
<thead>
<tr>
<th>Time Intervala</th>
<th>CV % for glassb</th>
<th>Time Intervala</th>
<th>CV % for primerb</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 h</td>
<td>3.26</td>
<td>24 hr</td>
<td>1.23</td>
</tr>
<tr>
<td>1 wk</td>
<td>6.14</td>
<td>1 wk</td>
<td>4.87</td>
</tr>
<tr>
<td>2 wk</td>
<td>5.06</td>
<td>2 wk</td>
<td>3.64</td>
</tr>
<tr>
<td>3 wk</td>
<td>7.25</td>
<td>3 wk</td>
<td>2.98</td>
</tr>
<tr>
<td>4 wk</td>
<td>3.76</td>
<td>2 mo</td>
<td>4.92</td>
</tr>
<tr>
<td>4 mo</td>
<td>2.97</td>
<td>4 mo</td>
<td>4.45</td>
</tr>
<tr>
<td>8 mo</td>
<td>1.41</td>
<td>8 mo</td>
<td>6.47</td>
</tr>
</tbody>
</table>

*a* fresh sample used for each SV measurement, *b* CV % for seven emission scans of the sample obtained at pressures between 0.1 – 14.7 psi.
Table 2-14: Analysis of the area under the emission curve for DOCI-Ssμsp in PtDOCI-Ssμsp/VPDMS coating on bare and primed glass.

<table>
<thead>
<tr>
<th>Time Interval</th>
<th>CV % for glass</th>
<th>Time Interval</th>
<th>CV % for primer</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 h</td>
<td>3.75</td>
<td>24 h</td>
<td>2.94</td>
</tr>
<tr>
<td>1 wk</td>
<td>3.29</td>
<td>1 wk</td>
<td>3.33</td>
</tr>
<tr>
<td>2 wk</td>
<td>4.06</td>
<td>2 wk</td>
<td>5.95</td>
</tr>
<tr>
<td>3 wk</td>
<td>5.82</td>
<td>3 wk</td>
<td>9.24</td>
</tr>
<tr>
<td>4 wk</td>
<td>3.31</td>
<td>4 wk</td>
<td>4.82</td>
</tr>
<tr>
<td>2 mo</td>
<td>9.15</td>
<td>2 mo</td>
<td>2.99</td>
</tr>
<tr>
<td>4 mo</td>
<td>3.65</td>
<td>3 mo</td>
<td>6.81</td>
</tr>
<tr>
<td>8 mo</td>
<td>7.74</td>
<td>4 mo</td>
<td>1.26</td>
</tr>
</tbody>
</table>

*a fresh sample used for each SV measurement,  
b CV % for seven emission scans of the sample obtained at pressures between 0.1 – 14.7 psi.

The DOCIμsp and DOCI-Sμsp temperature probes were also analyzed separately in the VPDMS polymer binder. This was done to prove that the emission of the dyed-microspheres is not quenched by oxygen, regardless if the microspheres were dispersed in VPDMS with or without the PtTFPP oxygen sensing probe. The CV % data for dyed-microspheres in VPDMS on bare and primed glass are presented in Tables 2-15 and 2-16.

Table 2-15: Analysis of the area under the emission curve for DOCIμsp in VPDMS polymer on bare and primed glass.

<table>
<thead>
<tr>
<th>Time Interval</th>
<th>CV % for glass</th>
<th>Time Interval</th>
<th>CV % for primer</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 h</td>
<td>8.36</td>
<td>24 h</td>
<td>6.82</td>
</tr>
<tr>
<td>1 wk</td>
<td>11.5</td>
<td>1 wk</td>
<td>6.92</td>
</tr>
<tr>
<td>2 wk</td>
<td>12.7</td>
<td>2 wk</td>
<td>3.96</td>
</tr>
<tr>
<td>3 wk</td>
<td>11.8</td>
<td>3 wk</td>
<td>6.95</td>
</tr>
<tr>
<td>4 wk</td>
<td>9.04</td>
<td>5 wk</td>
<td>7.01</td>
</tr>
<tr>
<td>4 mo</td>
<td>4.48</td>
<td>4 mo</td>
<td>4.32</td>
</tr>
<tr>
<td>8 mo</td>
<td>7.04</td>
<td>8 mo</td>
<td>9.29</td>
</tr>
</tbody>
</table>

*a fresh sample used for each SV measurement,  
b CV % for seven emission scans of the sample obtained at pressures between 0.1 – 14.7 psi.
Table 2-16: Analysis of the area under the emission curve for DOCI-Ssp in VPDM polymer on bare and primed glass.

<table>
<thead>
<tr>
<th>Time Interval&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CV % for glass&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Time Interval&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CV % for primer&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 h</td>
<td>10.2</td>
<td>24 h</td>
<td>10.2</td>
</tr>
<tr>
<td>1 wk</td>
<td>8.78</td>
<td>1 wk</td>
<td>16.1</td>
</tr>
<tr>
<td>3 wk</td>
<td>11.8</td>
<td>2 wk</td>
<td>13.3</td>
</tr>
<tr>
<td>4 wk</td>
<td>12.3</td>
<td>3 wk</td>
<td>15.3</td>
</tr>
<tr>
<td>2 mo</td>
<td>16.9</td>
<td>4 wk</td>
<td>8.95</td>
</tr>
<tr>
<td>4 mo</td>
<td>6.78</td>
<td>2 mo</td>
<td>4.57</td>
</tr>
<tr>
<td>8 mo</td>
<td>6.21</td>
<td>4 mo</td>
<td>17.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> fresh sample used for each SV measurement,  <sup>b</sup> CV % for seven emission scans of the sample obtained at pressures between 0.1 – 14.7 psi.

Inspection of Tables 2-13 to 2-16 reveals that the data are similar. The variance in the emission response for the dyed-microspheres is characteristic to the spheres and is not influenced by dual-luminophore interactions.

**Emission Intensity**

Throughout the temporal-stability experiments, the magnitude of emission intensity for the pressure and temperature probes' responses to oxygen pressure was monitored. The emission intensity data for both probe types decreased by an order of magnitude between their respective first to last and final interval emission scans. This effect was consistent for the coatings on glass but not for the coatings on primer. Only the emission intensity of the PtTFPP, DOClµsp, and PtDOClµsp in VPMDS on primer decreased by an order of magnitude between their first to last and final interval emission scans. The emission intensity of the DOCl-Sµsp and PtDOCl-Sµsp in VPDMS on primer were stable throughout the interval emission scans. The decrease in emission intensity is not detrimental to the coatings, since the decrease in emission intensity did not hinder the SV response of the pressure probe. Nor did it increase the small variance in emission intensity exhibited by the temperature probes to variation in $P_{air}$. 
Photostability

The stability of the photoluminescence intensity to continuous illumination for a period of four hours was examined for the PtDOClµsp/VPDMS and PtDOCl-Sµsp/VPDMS coatings. To better understand possible influences one luminophore might impart on the other over time, the individual luminophores were also analyzed separately. The coatings, dual- and mono-luminophore, were air-brushed onto plain and primed (TiO₂/SPDMS) borosilicate microscope slides. After application, the coatings were stored in the dark at room temperature and 33 % relative humidity. The coating samples were illuminated with 450 nm light with a 50-W arc-bulb, and emission was monitored from 475 - 800 nm. A fresh specimen piece was broken-off the respective prepared slide for each photostability experiment. Illumination was initiated at time equals zero and an emission scan was obtained every 30 min. These experiments were carried out in the fluorimeter. Particular emphasis was placed on evaluating the area under the emission curve between 530 - 570 nm for the temperature probes and 630 - 630 nm for the pressure probe at two pressures, 5 and 14.7 psi, and room temperature.

PtTFPP

The photostability of the photoluminescence of the PtTFPP pressure probe (λ = 630 - 670 nm) in PtDOClµsp/VPDMS and PtDOCl-Sµsp coatings was evaluated at 5 and 14.7 psi. Analysis of the relative PtTFPP emission intensity versus time is displayed in Figure 2-12 for the PtDOClµsp/VPDMS coating on bare and primed glass, in Figure 2-13 for the PtDOCl-Sµsp/VPDMS coating on bare and primed glass, and in Figure 2-14 for PtTFPP in VPDMS polymer coating on bare and primed glass as a comparison.
Figure 2-12: Photostability of PtTFPP emission in PtDOC1pµSp/VPDMS coating on bare and primed glass at 5 and 14.7 psi and RT. $A_{\text{REF}}$: area between 630 – 670 nm at 240 min.

Figure 2-13: Photostability of PtTFPP emission in PtDOC1-SµSp/VPDMS coating on bare and primed glass at 5 and 14.7 psi and RT. $A_{\text{REF}}$: area between 630 – 670 nm at 240 min.
Figure 2-14: Photostability of PtTFPP emission in VPDMS polymer coating on bare and primed glass at 5 and 14.7 psi and RT. $A_{\text{REF}}$: area between 630 – 670 nm at 240 min.

The photostability of the photoluminescence of the PtTFPP pressure probe in the PtDOClμsp/VPDMS and PtDOCl-Sμsp/VPDMS coatings exhibits minimal random fluctuations in intensity ratio over the four-hour period. These results are within a standard deviation of error for each scan point and similar to photostability experiments conducted by Lee and Okura for PtTFPP in polystyrene. The PtDOCl-Sμsp/VPDMS coating on primed glass at 14.7 psi experiences a decline in photoluminescence emission intensity over the first 60 – 90 minutes of illumination. This “photolysis period”, only exhibited for one pressure condition of the photostability experiments, is not uncommon, and has been observed by other groups not only for the PtTFPP luminophore but for other Pt(II) porphyrin macrocycles.

The photostability of the photoluminescence of the PtTFPP pressure probe in VPDMS polymer without incorporation of the dyed-microspheres behaves similarly to the PtDOClμsp/VPDMS coating. Therefore, the PtTFPP ratioed emission intensity
exhibits minor fluctuations over the time period that are not dependent on chemical or physical interactions with the temperature probes.

**DOClpμsp and DOCl-Sμsp**

The photostability of the photoluminescence of the DOClpμsp and DOCl-Sμsp temperature probes ($\lambda = 530 - 570$ nm) in PtDOClpμsp/VPDMS and PtDOCl-Sμsp coatings were evaluated at 5 and 14.7 psi. Analysis of the relative DOClpμsp emission intensity versus time is displayed in Figure 2-15 for the PtDOClpμsp/VPDMS coating on bare and primed glass. The relative DOCl-Sμsp emission intensity versus time is depicted in Figure 2-16 for the PtDOCl-Sμsp/VPDMS coating on bare and primed glass, and the relative emission intensities of the DOClpμsp and DOCl-Sμsp temperature probes, dispersed separately in VPDMS polymer coating without incorporation of the PtTFPP pressure probe, versus time are illustrated in Figures 2-17 and 2-18, respectively, as a comparison.

![Figure 2-15: Photostability of DOClpμsp relative emission intensity in PtDOClpμsp/VPDMS coating on bare and primed glass at 5 and 14.7 psi and RT. $A_{REF}$: area between 530 – 570 nm at 240 min.](image-url)
Figure 2-16: Photostability of DOCl-Ssusp relative emission intensity in PtDOCl-Ssusp/VPDMS coating on bare and primed glass at 5 and 14.7 psi and RT. $A_{\text{REF}}$: area between 530 – 570 nm at 240 min.

Figure 2-17: Photostability of DOClpusp relative emission intensity in VPDMS polymer coating on bare and primed glass at 5 and 14.7 psi and RT. $A_{\text{REF}}$: area between 530 – 570 nm at 240 min.
The photoluminescence of the temperature probes in PtDOClµsp/VPDMS and PtDOCl-Sµsp coatings is less photostable than that of the PtTFPP pressure probe in the same coatings. The DOClµsp temperature probe in the PtDOClµsp/VPDMS coating on bare and primed glass exhibits a decrease in relative emission intensity over the 240 min. time period at both pressures. The results for the percent photodegradation are listed in Table 2-17.

Table 2-17: Percent photodegradation of the relative emission intensity for DOClµsp in PtDOClµsp/VPDMS coating on bare and primed glass.

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>Glass</th>
<th>Primer</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.119 %-min⁻¹</td>
<td>0.77 %-min⁻¹</td>
</tr>
<tr>
<td>14.7</td>
<td>0.094 %-min⁻¹</td>
<td>0.179 %-min⁻¹</td>
</tr>
</tbody>
</table>

The DOCl-Sµsp temperature probe in the PtDOCl-Sµsp coating on bare glass experiences minor fluctuations in relative emission intensity over the four-hour time period. However, the intensity decreases over the 240 min. period, as shown in Figure 2-18. A REF: area between 530 – 570 nm at 240 min.
period. However, the relative emission intensity decreases over the 240 min. time period for the coating on primed glass. The results for the percent photodegradation of the coating on primed glass are listed in Table 2-18.

Table 2-18: Percent photodegradation of the relative emission intensity for DOCI-Sµsp in PtDOI-Sµsp/VPDMS coating on primed glass.

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>Primer</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.028 %-min⁻¹</td>
</tr>
<tr>
<td>14.7</td>
<td>0.079 %-min⁻¹</td>
</tr>
</tbody>
</table>

DOCIµsp and DOCI-Sµsp, dispersed separately in VPDMS polymer without PtTFPP incorporation, display relative emission intensity plots versus time which are scattered from point to point, however, the scatter from point to point is within the one standard deviation error bars. Therefore the emission intensity for the temperature probes in the VPDMS polymer coating is stable over the four-hour illumination period and unaffected by chemical or physical interactions with the PtTFPP luminophore.

Scanning and Transmission Electron Microscopy

**Scanning electron microscopy (SEM)**

SEM was used to image the two types of microspheres used in this work. Images were obtained on the undyed samples as well as on the dyed samples that were used in the coating preparations. The method used to prepare the SEM specimens is discussed in the Experimental section.

**DOIpµsp.** The poly(divinylbenzene) microspheres were prepared by precipitation polymerization. A typical image of the microspheres prior to DOCI (3,3'-diethyloxacarbocyanine iodide) adsorption is illustrated in Figure 2-19. All images display the microspheres as aggregates of large and small particles.
Figure 2-19: Scanning electron micrograph of precipitation microspheres (pμsp)(5 vol % of DVB55; acetonitrile). The scale bar consists of 11 white vertical lines and is 5 μm long from the first line to the last line.

The larger particles are 3 to 5 μm in size while the smaller particles are as tiny as 0.5 μm. The polymer particles possess a nonspherical shape and no evidence of pore formation. It appears that in some instances the particles are fused together. This fusion is most likely a consequence of an earlier stage in their growth.75

Placing carbon tape on an aluminum stud and pressing it against the above-prepared sample fractured the polymer particles. The fractured microspheres were transferred to the carbon tape and sputter-coated with 15 nm of gold. As a result of fracturing the polymer particles, a closer look of their interior morphology was obtained and imaged in Figure 2-20.
Figure 2-20: Scanning electron micrograph of fractured precipitation microspheres (pμsp)(5 vol % of DVB55; acetonitrile). The scale bar consists of 11 white vertical lines and is 1.5 μm long from the first line to the last line.

Magnification of the microspheres depicts the fusion of the smaller particles to the larger particles as seen in the upper half and left side of the figure. The sphere in the center of the figure exhibits jagged incisions due to the crushing process. Closer analysis of the exterior and interior morphologies reveals a cauliflower-like surface. This effect is most likely due to pore formation at the sub-micron level.75

When 3,3’-diethyloxacarbocyanine iodide (DOCI) was adsorbed onto the microspheres, the particles possess a more spherical swollen shape with no evidence of pore formation. Figure 2-21 displays a typical cluster of swollen 7.27 wt. % DOCI adsorbed microspheres (DOCIpμsp).
Figure 2-21: Scanning electron micrograph of precipitation microspheres (5 vol % of DVB55; acetonitrile) with 7.27 wt. % adsorbed DOCI (DOClµsp). The scale bar consists of 11 white vertical lines and is 2.31 µm long from the first line to the last line.

Again, the particles were fractured to display the interior morphology imaged in Figure 2-22. Magnification of the polymer particles reveals that the interior and exterior morphologies are tightly polymerized spheres creating small pores.

Figure 2-22: Scanning electron micrograph of fractured precipitation microspheres (5 vol % of DVB55; acetonitrile) with 7.27 wt. % DOCI (DOClµsp). The scale bar consists of 11 white vertical lines and is 750 nm long from the first line to the last line.
DOCI-S\textsuperscript{S}\textit{S}. The poly(divinylbenzene) microspheres were also prepared via suspension polymerization, sulfonated, and negatively charged. A typical image of the microspheres prior to dye adsorption is displayed in Figure 2-23.

![Figure 2-23: Scanning electron micrograph of negatively charged, sulfonated, suspension microspheres (S\textit{S}\textsuperscript{S}) (45 vol \% of DVB55; 1-dodecanol:toluene = 1:1). The scale bar consists of 11 white vertical lines and is 10 \( \mu \text{m} \) long from the first line to the last line.](image)

Polymerization produced a variety of microsphere sizes. The majority are 3 \( \mu \text{m} \) and smaller; although, some are as large as 8 to 10 \( \mu \text{m} \). The microspheres exhibit a porous structure due to the use of a porogen 1-dodecanol nonsolvent.\textsuperscript{76} The larger 8 to 10 \( \mu \text{m} \) polymer particles possess larger pores but are also more agglomerated and less spherical than the smaller microspheres. Stöver reported similar character in porosity, shape, and size distribution of poly(divinylbenzene) microspheres polymerized with increased percentages of porogen nonsolvent.\textsuperscript{76}

The interior morphology was revealed upon fracturing the microspheres. Figure 2-24 illustrates how the porous nature of the exterior surface is channeled throughout the interior morphology.
Figure 2-24: Scanning electron micrograph of fractured negatively charged, sulfonated, suspension microspheres (Ssµp') (45 vol% of DVB55; 1-dodecanol:toluene = 1:1). The scale bar consists of 11 white vertical lines and is 750 nm long from the first line to the last line.

DOCI was adsorbed onto the charged, sulfonated, suspension microspheres (Ssµp') replacing the Na⁺ counter ion. Figure 2-25 reveals that some of the microspheres are spherical while others are fractured from the preparation procedure. The most noticeable feature of these spheres is the appearance of a “sticky film” connecting and covering the spheres.
Figure 2-25: Scanning electron micrograph of fractured negatively charged, sulfonated, suspension microspheres (45 vol % of DVB55; 1-dodecanol:toluene = 1:1) with 3.83 wt. % adsorbed DOCl (DOCl-S$_{\text{sp}}$). The scale bar consists of 11 white vertical lines and is 2.73 $\mu$m long from the first line to the last line.

The film forms an incomplete coating across the spheres in the left side of the figure and a bridge connecting a larger particle and its nearest neighbors in the image right of center. The film appears to be less than 1 $\mu$m thick, and its origins are unknown. However, its existence was reproducible in additional SEM preparations.

**SPDMS and VPDMS incorporating DOCl$_{\text{sp}}$ or DOCl-S$_{\text{sp}}$.** Clusters of microspheres penetrating the surface of the coating are observed when a thin film of SPDMS (silanol polydimethylsiloxanes and methyltriacetoxy silane cross-linker) containing DOCl$_{\text{sp}}$ (7.27 wt. % DOCl) (prepared by air-brush; approximately 10 $\mu$m thick) was imaged by SEM. The randomness and irregularity of the microspheres’ distribution and size can be clearly seen in Figure 2-26. This image compliments findings presented later in the chapter which utilize fluorescence microscopy to describe the distribution of the microspheres in the polymer binder, Figure 2-30.
Figure 2-26: Scanning electron micrograph of the surface of a thin film (~10 μm) of SPDMS containing DOClµsp (7.27 wt. % DOCl)(5 vol % of DVB55; acetonitrile). The scale bar consists of 11 white vertical lines and is 5.02 μm long from the first line to the last line.

A thin film of VPDMS (vinyl polydimethylsiloxanes) containing DOClµsp (7.27 wt. % DOCl) was more difficult to image than the DOClµsp in SPDMS polymer binder. The surface of DOClµsp in the VPDMS film did not produce characteristic clusters of microspheres. Only random indentations and crevices are found which are due to either the morphology of the polymer cure, dust particles or embedded microspheres. However upon fracturing the sample and imaging the interior film morphology, clusters of microspheres are found and imaged in Figure 2-27.
Figure 2-27: Scanning electron micrograph of the interior morphology of a thin film (~10 μm) of VPDMS containing DOClpμsp (7.27 wt. % DOCl)(5 vol % of DVB55; acetonitrile). The scale bar consists of 11 white vertical lines and is 33.3 μm long from the first line to the last line.

Magnification of the microsphere cluster is displayed in Figure 2-28. This image further confirms scanning electron microscopy and fluorescence microscopy results which indicate that the microspheres are not homogeneously distributed within the polymer film.

Figure 2-28: Scanning electron micrograph of the interior morphology of a thin film (~10 μm) of VPDMS containing DOClpμsp (7.27 wt. % DOCl)(5 vol % of DVB55; acetonitrile) (27X magnification of Figure 2-27). The scale bar consists of 11 white vertical lines and is 1.20 μm long from the first line to the last line.
DOCI-Ssµp dispersed in VPDMS polymer could not be imaged with SEM. The surface of the DOCI-Ssµsp/VPDMS film did not reveal a globular texture as seen with the DOCIpµsp in SPDMS polymer (Figure 2-26). Fracturing of the DOCI-Ssµsp/VPDMS sample did not reveal microspherical clusters of distinct microsphere regions either. Two factors could be affecting the imaging. (1) It is possible that due to the elastic nature of the VPDMS, the fractured specimen polymer binder closes over the exposed interior region masking the microspheres. (2) The DOCI-Ssµsp are smaller than the DOCIpµsp and more difficult to image, since, as will be seen in the fluorescence microscopy data, the DOCI-Ssµsp are more evenly distributed and less clustered than the DOCIpµsp in the VPDMS polymer binder.

One solution to the problem of imaging is cooling the sample to 77 K, fractioning, and using a cryostat-stage for the SEM imaging thereby precluding any negative effects exhibited by the polymer’s tendency to resume its shape at room temperature. This option was not available at the time of the imaging. Regardless, it still does not guarantee that the microsphere particles will be revealed and successfully imaged.

**Transmission electron microscopy**

Due to the elastomeric nature of the polydimethylsiloxane (PDMS) polymer binders utilized in PSP/TSP coatings, the coatings exhibit rather poor mechanical properties and were therefore difficult to microtome and analyze. However, after a three month storage period at 50 % relative humidity, tris-(4,7-diphenyl-1,10-phenanthroline)ruthenium (II) dichloride ([Ru(dpp)₃]Cl₂) dispersed SPDMS polymer was sufficiently cured making it possible to microtome slices that were less than a 100 nm thick. Visual and physical inspection of the SPDMS coating showed that cured SPDMS was not as soft and pliable and easier to cleanly microtome than cured VPDMS polymer.
TEM images of the microtomed $[\text{Ru(dpp)}_3]\text{Cl}_2$ thin film are shown in Figure 2-29. Due to the spraying application of the film, the SPDMS polymer is visualized as droplets. Dark gray areas are indicative of increased electron density either from a single heavy atom, Ru, or a high concentration of a low atomic weight atom, C, Si, O. The dark black areas are the formvar resin used in sample preparation. The $[\text{Ru(dpp)}_3]\text{Cl}_2$ complex was not discernable as discrete microcrystals, possibly due to the fact that its concentration was low (i.e. 0.2 wt. % relative to polymer weight, 500 mg).

Figure 2-29: Transmission electron micrographs of a <100 nm slice of $[\text{Ru(dpp)}_3]\text{Cl}_2$ dispersed in SPDMS polymer. (A) X4500 magnification of polymer, white scale bar is 3.0 μm long and (B) X70000 magnification of polymer, white scale bar is 0.4 μm long.

**Energy dispersive spectroscopy (EDS)**

Energy dispersive spectroscopy coupled with TEM was utilized to determine the elemental composition of the darker droplet areas in Figure 2-29. The $[\text{Ru(dpp)}_3]\text{Cl}_2$ complex could not be identified, since its concentration at any one point was less than 1 wt. % (the limit of detection for this method). However the atoms along the exterior of the droplets (the darker areas of Figure 2-29 B) were identified as Si. The abundance of silicon atoms along the exterior surface of the droplets is 3.29 times greater than the abundance of interior droplet Si concentration. The ratio of Si was calculated by
determining the electron count from Si in the sample and Cu from the copper mesh disk on which the polymer slice was attached. Ratio of Si = Edge/Interior = (722/794)/(253/914) = 3.29.

**Fluorescence Microscopy**

Fluorescence microscopy techniques were employed to better understand the size and distribution of [Ru(dpp)$_3$]Cl$_2$, PtTFPP, DOCI$_\mu$sp, and DOCI-S$_\mu$sp in the VPDMS and SPDMS polymer binders. First, DOCI$_\mu$sp and DOCI-S$_\mu$sp are analyzed for size (length of particle major axis) and distribution (number of particles per region analyzed). Second, the PtDOCI$_\mu$sp/VPDMS and PtDOCI-S$_\mu$sp/VPDMS film coatings are analyzed for determination of the relative position of PtTFPP to the dyed-microspheres. Third, the spatial distribution of the PtTFPP probe’s luminescence response to oxygen quenching in the PtDOCI$_\mu$sp/VPDMS and PtDOCI-S$_\mu$sp/VPDMS films are evaluated. Fourth, the evaluation of [Ru(dpp)$_3$]Cl$_2$ distribution in SPDMS binder.

**Size and distribution of DOCI$_\mu$sp and DOCI-S$_\mu$sp**

The DOCI$_\mu$sp (0.6 wt. %, relative to polymer weight, 500 mg) and DOCI-S$_\mu$sp (0.2 wt. %, relative to polymer weight, 500 mg) were distributed separately in VPDMS polymer binder. Two layers of each coating were air-brushed onto clean borosilicate microscope slides. The DOCI-S$_\mu$sp/VPDMS film was approximately 5 μm thick, and the DOCI$_\mu$sp/VPDMS film was approximately 10 μm thick, as measured by profilometry. The slides were analyzed using the inverted fluorescence microscope. A detailed explanation for the system set-up is found in the Experimental section. For this experiment, an IR filter, $\sim$ 50 % neutral density filter, and a 425 nm 40 nm, bandpass filter were used in front of the 100-W mercury-bulb excitation source. The DOCI$_\mu$sp/VPDMS film was imaged with the 40X objective and the DOCI-
Ssµsp/VPDMS film was imaged with the 40X objective set at 60X magnification by the microscope’s 1.5X magnification knob. The emission light was filtered through a 475 nm long-pass filter, and the side of the slide that was coated with the polymer film faced the objective. Five regions of each coating were analyzed at an exposure time of 150 msec for the DOCIµsp/VPDMS film and 200 msec for the DOCI-Ssµsp/VPDMS film.

Fluorescence microscope images of the DOCIµsp/VPDMS and DOCI-Ssµsp/VPDMS films are displayed in Figure 2-30. Image A is 218 µm x 173 µm (1300 x 1030 pixels; calibration 0.168 µm-pixel⁻¹). Image B is 146 µm x 115 µm (1300 x 1030 pixels; calibration 0.112 µm-pixel⁻¹). The images are representative of each film. Within each image the white clusters and solo particles are defined by the DOCI fluorescence emission detected from the microspheres.

Figure 2-30: Fluorescence microscope image of A) DOCIµsp/VPDMS film and B) DOCI-Ssµsp/VPDMS film obtained with a CCD camera through a 40X and 60X objective, respectively. White scale bar is 26.5 µm and 17.8 µm long, respectively.

Five regions were imaged for each film. White clusters were considered one microsphere object rather than counting the individual microsphere components. The
number of objects in each region for the DOCI-μsp/VPDMS and DOCI-Sμsp/VPDMS films is given in Tables 2-19 and 2-20, respectively.

Table 2-19: Number of microsphere objects for five regions of the DOCI-μsp/VPDMS film.

<table>
<thead>
<tr>
<th>Region</th>
<th>Number of DOCI-μsp Objects</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>56</td>
</tr>
<tr>
<td>3</td>
<td>61</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>62</td>
</tr>
<tr>
<td>Average</td>
<td>69.6 ± 13.7</td>
</tr>
</tbody>
</table>

Table 2-20: Number of microsphere objects for five regions of the DOCI-Sμsp/VPDMS film.

<table>
<thead>
<tr>
<th>Region</th>
<th>Number of DOCI-Sμsp Objects</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>84</td>
</tr>
<tr>
<td>Average</td>
<td>78.6 ± 8.57</td>
</tr>
</tbody>
</table>

For all of the microsphere objects counted, the objects’ major axis lengths were determined using a statistical imaging program, Sigma Scan Pro (SPSS Inc.). The average and the standard deviation for the microsphere objects’ lengths for each region analyzed are given in Tables 2-21 and 2-22.
Table 2-21: Average and standard deviation of the microsphere objects’ lengths for each region of the DOCI-psp/VPDMS film.

<table>
<thead>
<tr>
<th>Region</th>
<th>Objects’ Average Length (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.04 ± 5.97</td>
</tr>
<tr>
<td>2</td>
<td>2.46 ± 1.31</td>
</tr>
<tr>
<td>3</td>
<td>3.93 ± 3.20</td>
</tr>
<tr>
<td>4</td>
<td>4.24 ± 4.20</td>
</tr>
<tr>
<td>5</td>
<td>2.10 ± 0.46</td>
</tr>
</tbody>
</table>

Table 2-22: Average and standard deviation of the microsphere objects’ lengths for each region of the DOCI-Ssp/VPDMS film.

<table>
<thead>
<tr>
<th>Region</th>
<th>Objects’ Average Length (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.55 ± 0.51</td>
</tr>
<tr>
<td>2</td>
<td>1.52 ± 0.56</td>
</tr>
<tr>
<td>3</td>
<td>1.19 ± 0.26</td>
</tr>
<tr>
<td>4</td>
<td>1.22 ± 0.32</td>
</tr>
<tr>
<td>5</td>
<td>1.44 ± 0.48</td>
</tr>
</tbody>
</table>

The lengths of the objects’ major axes from the five regions analyzed for each film are represented by histograms in Figure 2-31. The number of objects for a given size range are plotted versus the length of the objects (0.5 µm bin increments).

Figure 2-31: Histogram of the microsphere objects’ major axis lengths for A) DOCI-psp/VPDMS film and B) DOCI-Ssp/VPDMS film. Vertical bars equal a 0.5 µm length increment.
For the DOCIpμsp/VPDMS film, the microsphere object lengths' are in the range of 0.5 to 30 μm with a substantial number of objects between 2 - 7 μm in length. For the DOCI-Ssμsp/VPDMS film, the microsphere object lengths' are in the range of < 0.5 to 7.5 μm with a substantial number of objects between 0.5 – 2.5 μm in length. Considering that the number of objects per region for each film is similar, the large number of objects (~ 140) for the DOCI-Ssμsp/VPDMS film proves that the microspheres are smaller and less aggregated than the microspheres of the DOCIpμsp/VPDMS film. The measured object lengths correlate well with the lengths determined from the SEM images, Figures 2-19 and 2-23.

The number and corresponding lengths of DOCIpμsp particles in Tables 2-19 and 2-21 and the objective depth of focus (DOF) were used to predict the density distribution of microspheres in the VPDMS polymer binder for any given region. In this analysis, the DOF is 4 μm at 40X. (The DOF is defined as the length along the optical axis of the microscope by which, for a constant level of the image, the focusing position of the objective can be varied without disturbing the sharpness of the image at the center of the field.) Since the numbers of objects for each region are within a standard deviation of one another as were the respective object lengths, then it can be derived that a certain number of microspheres of average length are distributed throughout the coating for a known region of predetermined size. This is not to say that the microspheres are evenly distributed throughout the coating; rather, for any region analyzed, an average number of spheres with average length are found. For example, the DOCIpμsp/VPDMS film average is (69.6 objects)/(4 μm x 218 μm x 173 μm) = 4.61x10^{-4} objects-μm^{-3}. 
For the DOCI-Sµsp/VPDMS film, the 60X objective DOF is not known, but a rough estimate using the fine focus adjustment of the microscope yields a 2 µm measurement for the DOF. By evaluating the microspheres’ quantity and length data in Tables 2-20 and 2-22, the numbers of objects for each region were within a standard deviation of one another as were the respective object lengths. Therefore, a certain number of microspheres of average length are distributed throughout the film for a known region of thickness and size. For example, the DOCI-Sµsp/VPDMS film average is $(78.6 \text{ objects})/(2 \mu m \times 146 \mu m \times 115 \mu m) = 2.34 \times 10^{-3} \text{ objects-} \mu m^{-3}$. Although the DOCI-Sµsp may not be evenly distributed throughout an analyzed region, an average number of microspheres with average lengths are found in any region.

**Relative distribution of PtTFPP, DOCIµsp, and DOCI-Sµsp**

The position of the PtTFPP probe relative to the microspheres in the PtDOCIµsp/VPDMS and PtDOCI-Sµsp/VPDMS films was determined using the fluorescence microscope. Two layers of each formulation coating were air-brushed onto clean borosilicate microscope slides, and the luminescence of the two luminophores (PtTFPP and DOCIµsp or DOCI-Sµsp) was detected. Three images from each coating were obtained using the 40X objective, IR filter, $\approx 50 \%$ neutral density filter, and a 425 nm 40 nm, bandpass filter in front of the excitation source. Three emission filters were used interchangeably: a 475 nm longpass filter for imaging PtTFPP and DOCIµsp or DOCI-Sµsp luminescence; a 525 nm 50 nm, bandpass filter for imaging DOCIµsp or DOCI-Sµsp luminescence; and a 630 nm 60 nm, bandpass filter for imaging the PtTFPP luminescence.
The PtDOCIpµsp/VPDMS film is imaged in Figure 2-32 at the three emission wavelengths. Each image is 218 µm x 173 µm (1300 x 1030 pixels; calibration 0.168 µm-pixel\(^{-1}\)). The filters were chosen such that the emission of the luminophore components could be selectively filtered and detected.

Figure 2-32: Fluorescence images of PtDOCIpµsp/VPDMS film obtained with a CCD camera through a 40X objective. White scale bars are 37.9 µm long. A) PtTFPP emission (ca. 630 nm), B) DOCIpµsp emission (ca. 525 nm), C) PtTFPP and DOCIpµsp emissions (>475 nm).

There is not much difference in the visual fields from one image to the other, yet this lack of differentiation accurately illustrates the distribution of the luminophores relative to one another. As a reference, image C of Figure 2-32 depicts the emission intensity of both the DOCIpµsp and the PtTFPP luminophores. In image B only the green emission intensity from the microspheres is detected and represented as white globules. The background field does not exhibit significant emission intensity. To illustrate this, several 30 µm line scans through the microsphere clusters were performed to determine the intensity counts for the microspheres versus the background. The emission intensity line scans are plotted in Figure 2-33, graph B. The microsphere clusters are very intense compared to the non-emissive background. In particular, a line
scan for cluster 1 bisects three microspheres, and an outline of the intense microsphere shapes is characterized by the corresponding line scan in graph B.

![Image A](A.png)

![Graph B](B.png)

Figure 2-33: Line scan analysis of the emission intensity of a fluorescence microscope image of PtDOClµsp/VPDMS film obtained with a CCD camera through a 40X objective with a 525 nm 50 nm, bandpass filter (DOCl emission response). A) Fluorescence microscope image of DOCIµsp emission and B) Emission line scans for three 30 µm lines through microsphere clusters in image A.

Image A in Figure 2-32 is striking; it only represents the detected emission intensity of the PtTFPP luminophore, yet “fuzzy” outlines of the microspheres are clearly seen. The background field of the image emits a homogeneous red photoluminescence. To illustrate this point, several 30 µm line scans through the white clusters were performed. Figure 2-34 depicts the line scan areas in image A and the corresponding emission intensity plots in image B. The intensities of the microspheres are much greater than the background intensity; however, in comparison to image B of Figure 2-33, the background intensity of image B in Figure 2-34 is rather intense. This is supporting evidence for the distribution of the PtTFPP not only on or near the microsphere clusters but also through the remainder of the polymer binder.
Figure 2-34: Line scan analysis of the emission intensity of a fluorescence microscope image of PtDOClµmsp/VPDMS film obtained with a CCD camera through a 40X objective with a 630 nm 60 nm, bandpass filter (PtTFPP emission response). A) Fluorescence microscope image of PtTFPP emission and B) Emission line scans for three 30 µm lines through microsphere clusters in image A.

There are three possibilities for this emission patterns in Figures 2-33 and 2-34:

1) Adsorption of PtTFPP onto the surface of the microspheres during the coating preparation generates areas of concentrated PtTFPP emission. 2) The photoluminescence from the DOClµmsp is “pumping” the photoluminescence of the PtTFPP through energy transfer or a trivial emission reabsorption mechanism.53 3) The photoluminescence of the background PtTFPP is internally reflected in the polymer illuminating the microspheres’ shape.

The PtDOCl-Sµmsp/VPDMS film exhibits the same emission tendencies as the PtTFPP and DOClµmsp luminophores when imaged with different emission filters.

**Microscopic Stern-Volmer analysis of PtDOClµmsp/VPDMS and PtDOCl-Sµmsp/VPDMS thin films**

A fluorescence microscopy technique was developed to explore the spatial distribution of the luminescence properties for oxygen sensing coatings within a spatial resolution of < 5 µm. Fluorescence microscopy coupled with CCD image analysis was employed to create spatially resolved “image maps” of the Stern-Volmer (SV) constant
(K_{SV}) for luminescent oxygen sensing films. The SV luminescence intensity response to variation in air pressure (P_{air}) for PtDOCIpμsp/VPDMS and PtDOCI-Ssμsp/VPDMS thin films was measured at the microscopic level. The details of the instrument set-up and sample preparation are found in the Experimental section, and a thorough explanation of the fluorescence image analysis is provided in the Experimental section of Chapter Three. A series of quantitative image maps of the PtTFPP probe's response to variation in P_{air} were generated using 10X and 40X objectives.

False-colored fluorescence microscope images for the PtDOClpμsp/VPDMS and PtDOCl-Ssμsp/VPDMS thin films obtained at P_{air} = 0.5 psi with a 10X objective and 630 nm 30 nm, bandpass filter are shown in Figures 2-35 and 2-36, respectively. The image size is 436 μm x 345 μm (650 x 515 pixels; calibration 0.67 μm-pixel^{-1}). For both luminescence intensity images (Figures 2-35 A and 2-36 A) there are several bright yellow and red spots, which correspond to the enhanced PtTFPP photoluminescence centered over the microsphere particles. The intense spots are superimposed on a background field of homogeneous luminescence intensity.
Figure 2-35: False-colored quantitative microscopic fluorescence intensity (0.5 psi, 10X) and $K_{SV}(x,y)$ image maps for PtDOClµsp/VPDMS thin film. White scale bars are 61.5 µm long. A) False-colored quantitative microscopic fluorescence intensity image, $I_{\text{max}} = 11081$ a.u., yellow color and B) Quantitative microscopic $K_{SV}(x,y)$ image map for the identical region, $K_{SV}^{\text{max}} = 0.870 \text{ psi}^{-1}$, yellow color.

Figure 2-36: False-colored quantitative microscopic fluorescence intensity (0.5 psi, 10X) and $K_{SV}(x,y)$ image maps for PtDOCl-Sµsp/VPDMS thin film. White scale bars are 61.5 µm long. A) False-colored quantitative microscopic fluorescence intensity image, $I_{\text{max}} = 16562$ a.u., yellow color and B) Quantitative microscopic $K_{SV}(x,y)$ image map for the identical region, $K_{SV}^{\text{max}} = 0.880 \text{ psi}^{-1}$, yellow color.

For each film, five regions were interrogated with each objective at seven $P_{\text{air}}$ values between 0.4 – 14.7 psi. A total of ten $K_{SV}(x,y)$ image maps were generated with accompanying statistical data listed in Tables 2-23 and 2-24. A $K_{SV}(x,y)$ image map for each coating is displayed in Figures 2-35B and 2-36B. A spatial correlation exists between the intensity and $K_{SV}(x,y)$ image maps: microscopic regions that feature bright
emission (yellow spots) tend to exhibit comparatively larger \( K_{SV} \) values (red and yellow spots). However, in image B of both Figures 2-34 and 2-35, the light blue ovals near the red spots are erroneous \( K_{SV} \) data due to image shifting during analysis. The bright red spots in the \( K_{SV}(x,y) \) image maps and the statistical data in Tables 2-23 and 2-24 demonstrate the inhomogeneous distribution of PtTFPP luminescence response to oxygen quenching.

Table 2-23: Microscopic SV analysis of five regions for PtDOCIpµsp/VPDMS thin film using the 10X and 40X objectives.

<table>
<thead>
<tr>
<th>Region</th>
<th>( K_{SV}^{avg} ) (psi(^{-1})) (10X)</th>
<th>( \sigma_{Ksv} ) %</th>
<th>( K_{SV}^{avg} ) (psi(^{-1})) (40X)</th>
<th>( \sigma_{Ksv} ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.278</td>
<td>33.5</td>
<td>1.84</td>
<td>26.8</td>
</tr>
<tr>
<td>2</td>
<td>0.287</td>
<td>9.41</td>
<td>0.470</td>
<td>7.02</td>
</tr>
<tr>
<td>3</td>
<td>0.275</td>
<td>13.8</td>
<td>0.643</td>
<td>3.89</td>
</tr>
<tr>
<td>4</td>
<td>0.293</td>
<td>34.1</td>
<td>0.644</td>
<td>34.3</td>
</tr>
<tr>
<td>5</td>
<td>0.266</td>
<td>13.5</td>
<td>0.799</td>
<td>22.0</td>
</tr>
<tr>
<td>Average</td>
<td>0.280</td>
<td>3.21</td>
<td>0.879</td>
<td>55.9</td>
</tr>
</tbody>
</table>

Table 2-24: Microscopic SV analysis of five regions for PtDOCl-Sµsp/VPDMS thin film using the 10X and 40X objectives.

<table>
<thead>
<tr>
<th>Region</th>
<th>( K_{SV}^{avg} ) (psi(^{-1})) (10X)</th>
<th>( \sigma_{Ksv} ) %</th>
<th>( K_{SV}^{avg} ) (psi(^{-1})) (40X)</th>
<th>( \sigma_{Ksv} ) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.218</td>
<td>30.7</td>
<td>1.06</td>
<td>12.1</td>
</tr>
<tr>
<td>2</td>
<td>0.243</td>
<td>7.00</td>
<td>2.12</td>
<td>27.4</td>
</tr>
<tr>
<td>3</td>
<td>0.210</td>
<td>9.05</td>
<td>1.89</td>
<td>12.9</td>
</tr>
<tr>
<td>4</td>
<td>0.225</td>
<td>13.8</td>
<td>0.928</td>
<td>10.0</td>
</tr>
<tr>
<td>5</td>
<td>0.241</td>
<td>10.4</td>
<td>1.30</td>
<td>9.08</td>
</tr>
<tr>
<td>Average</td>
<td>0.227</td>
<td>5.73</td>
<td>1.46</td>
<td>32.0</td>
</tr>
</tbody>
</table>

The 10X regions exhibit lower \( K_{SV}^{avg} \) values than the 40X regions. An explanation for this is the 40X images are 1/36 the size of the 10X images. The 40X intensity images capture a smaller more homogeneous region of the film such as a single bright spot; whereas the 10X intensity images capture a larger heterogeneous region of many intense
spots and background illumination. Therefore, the $K_{SV}^{avg}$ values of a 10X image are lower than the $K_{SV}^{avg}$ values of a 40X image. Remarkably, the heterogeneous distribution of $K_{SV}$ response at the microscopic level does not affect the macroscopic level response. Figures 2-37 and 2-38 represent the SV response to variation in $P_{air}$ for PtDOCImµsp/VPDMS and PtDOCIsµsp/VPDMS thin films when the samples are evaluated using the fluorimeter. The macroscopic SV data are listed in Table 2-25.

Figure 2-37: Macroscopic SV plot of PtDOCImµsp/VPDMS thin film on glass. $A_{REF}$: area between 630 - 670 nm at 14.7 psi and 298 K.
Figure 2-38: Macroscopic SV plot of PtDOCI-Sµsp/VPDMS thin film on glass. $A_{REF}$: area between 630 - 670 nm at 14.7 psi and 298 K.

Table 2-25: Macroscopic SV response data for PtDOCIµsp/VPDMS and PtDOCI-Sµsp/VPDMS films on glass.

<table>
<thead>
<tr>
<th>Luminophore</th>
<th>Slope (psi$^{-1}$)$^a$</th>
<th>Intercept$^b$</th>
<th>$K_{SV}$ (psi$^{-1}$)$^c$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtDOCIµsp</td>
<td>0.067</td>
<td>0.014</td>
<td>4.79</td>
<td>0.999</td>
</tr>
<tr>
<td>PtDOCI-Sµsp</td>
<td>0.066</td>
<td>0.026</td>
<td>2.53</td>
<td>0.999</td>
</tr>
</tbody>
</table>

$^a$ intercept = $A$ in equation (2-2), $^b$ slope = $B$ in equation (2-2), $^c$ $K_{SV} = B/A$

**[Ru(dpp)$_3$]Cl$_2$/SPDMS**

An SPDMS polymer sample containing [Ru(dpp)$_3$]Cl$_2$ was analyzed using the fluorescence microscope to determine the distribution of the luminophore in the polymer binder.

A thin layer of [Ru(dpp)$_3$]Cl$_2$/SPDMS was air-bushed onto a clean borosilicate microscope slide and kept at 50 % relative humidity in the dark for three months. The polymer film was then lifted from the glass plate with a razor blade, embedded in an epoxy formvar resin and microtomed into 250 nm thick slices. The slices were placed on
clean borosilicate microscope slides and cover-slips were cemented over the polymer slices. Sectioned slices were imaged with the microscope using the 40X objective set at 60X magnification by the microscope’s 1.5X magnification knob. An IR filter and a 425 nm 40 nm, bandpass filter were placed in front of the excitation source, and emission light was filtered through a 630 nm 60 nm, bandpass filter.

Fluorescence microscope images of the [Ru(dpp)₃]Cl₂/SPDMS film are displayed in Figure 2-39. Each image size is 146 µm x 115 µm (1300 x 1030 pixels; calibration 0.112 µm-pixel⁻¹). The film slices imaged in Figure 2-39 are ribbon strips of polymer embedded in the non-fluorescing epoxy resin. Moderate photoluminescence of the [Ru(dpp)₃]Cl₂ luminophore defines the outline of the polymer strips. Areas of intense photoluminescence define a spherical texture in the polymer strips, which was first imaged as droplets in the TEM images (Figure 2-29). Since the polymer slices were sealed under glass, the [Ru(dpp)₃]Cl₂ is imaged in its unquenched state. It is possible the [Ru(dpp)₃]Cl₂ complex exists as highly luminescent nm size microcrystals indiscernible by EDS studies. Further analysis of [Ru(dpp)₃]Cl₂ and other Ru(II) α-diimine complexes’ microscopic spatial SV response to oxygen concentration are outlined in Chapter Three.
Figure 2-39: Fluorescence microscopy images of 250 μm thick [Ru(dpp)$_2$]Cl$_2$/SPDMS strips embedded in formvar resin obtained with a CCD camera through a 60X objective. White scale bars are 24.5 μm long.

Image Testing

Static-calibration chamber

Calibration tests were conducted on the PtDOClµsp/VPDMS and PtDOCl-Sµsp/VPDMS coatings to access their pressure measurement accuracy when exposed to a spatial temperature gradient. Aluminum coupons (4 in. x 2 in. x 1/8 in.) were coated with primer and four layers of each coating were air-brushed onto the individual coupons. The plates were individually placed in a pressure and temperature controlled environment chamber. A relatively linear temperature gradient (> 20 K) was imposed over the length of the coupons using a heated plate at the top of the coupon and a water-cooled bath at the bottom of the coupon. The overall pressure was varied between 2 to 14.7 psi, and a temperature gradient existed on the plate (300 – 320 K) for a series of images. Images were acquired at two emission wavelengths: 550 nm and 650 nm. The optical bandwidth was 40 nm FWHM. The sample was excited using two two-72-element blue LED lamps (peak emission ca. 460 nm).

Analysis of the luminescence response to pressure and temperature for the PtDOClµsp/VPDMS coating is depicted in the plots of Figure 2-40.
Figure 2-40: Stern-Volmer plot and ratioed emission plots versus pressure and temperature for PtDOClipsp/VPDMS coating analyzed and imaged in a static calibration cell. A) SV plot, emission integrated over an approximate area of 630 - 670 nm, excitation at 460 nm, B) Ratioed emission plot versus pressure, emission integrated over an approximate area of 530 - 570 nm, excitation at 460 nm, C) Ratioed emission plot versus temperature, emission integrated over an approximate area of 630 - 670 nm, excitation at 460 nm, and D) Ratioed emission plot versus temperature, emission integrated over an approximate area of 530 - 570 nm, excitation at 460 nm.

Clearly the PtTFPP pressure probe’s response to variation in $P_{\text{air}}$ is strong, but it is also temperature dependent as seen in images A and C. The DOClipsp temperature-sensitive probe exhibits very little response to variation is $P_{\text{air}}$; although, this response could be spectral leakage of the PtTFPP emission ($\sim$ 600 nm) thru the filter. A considerable temperature response is seen in both images B and D. It is the temperature dependence and pressure independence of the temperature probe that corrects for the temperature dependence of the PtTFPP probe.
When the coatings are exposed to a temperature gradient (300 – 320 K) at constant pressure, the ratioed intensity images of the PtDOClµsp/VPDMS coating for a series of pressures exhibit a temperature-dependence. This temperature-dependence will cause the 650 nm (pressure) emission to be attenuated in regions of high T. If converted to pressure via $I_{\text{REF}}/I$ ratio and displayed with a false color map to represent pressure, the upper (height) portion of the plate will show a false (high) pressure measurement and the lower portion will show a false low-pressure measurement. The uncorrected luminescence ratioed intensity images at seven pressures between 2 – 14.8 psi for the PtDOClµsp/VPDMS coating are illustrated in Figure 2-41, and the accompanying pressure data are listed in Table 2-26.

![Figure 2-41: Luminescence ratioed intensity images at seven pressures from 2 – 14.8 psi for PtDOClµsp/VPDMS coating on an aluminum plate assuming a constant temperature distribution over the plate. Emission collected at 650 nm peak and excitation at 460 nm. Intensity scale bars appear to the right of each image for 0 – 18.0 psi.](image-url)
Table 2-26: Corresponding pressure values and statistical distributions for the uncorrected ratioed intensity images of the PtDOClµsp/VPDMS coating on an aluminum plate at seven pressures between 2 – 14.8 psi.

<table>
<thead>
<tr>
<th>P(psi)(^a)</th>
<th>P(_{\text{avg}}) (^b)</th>
<th>(\sigma_{\text{avg}})</th>
<th>(%) (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>2.06</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>4.05</td>
<td>4.20</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>6.03</td>
<td>6.18</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>8.07</td>
<td>8.17</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>10.07</td>
<td>10.14</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>12.04</td>
<td>12.11</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td>14.79</td>
<td>15.09</td>
<td>7.8</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) pressure manually set for calibration chamber, \(^b\) measured pressure average for each image, \(^c\) \(\sigma_{\text{avg}}\% = \sigma_{\text{avg}}/P_{\text{avg}}\)

When the temperature dependence of the pressure component is corrected, the true pressure values for each intensity image are determined. To convert the intensity ratio images to pressures, first a temperature is assumed and a pressure is calculated using the 650 calibration curve in Figure 2-40 (quadratic: \(I_{\text{ratio}} = 650 = A + BP + CT + DP^2 + ET^2 + FPT\)). The coefficients (A-F) are determined using a least-squares regression fit from the calibrated data points shown in Figure 2-40. Once the pressure is calculated, it is used to update the temperature using the 550 calibration curve in Figure 2-40 (also a quadratic fit with six coefficients). This is iterated until convergence (fairly quickly ~ 2-3 iterations) for each pixel intensity ratio value. The color homogeneity seen in the accompanying pressure data (Figure 2-42) indicates that the temperature-dependence has been corrected for by using the 550 data. The corrected luminescence intensity images of Figure 2-41 are illustrated in Figure 2-42, and the accompanying pressure data are listed in Table 2-27.
Figure 2-42: Corrected luminescence ratioed intensity images at seven pressures from 2 – 14.8 psi for PtDOClµsp/VPDMS coating on an aluminum plate. Emission collected at 650 nm peak and excitation at 460 nm. Intensity scale bars appear to the right of each image for 0 – 18.0 psi.

Table 2-27: Corresponding pressure values and statistical distributions for the corrected ratioed intensity images of PtDOClµsp/VPDMS coating on an aluminum plate at seven pressures between 2 – 14.8 psi.

<table>
<thead>
<tr>
<th>P(psi)</th>
<th>P_avg</th>
<th>σ_avg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>1.95</td>
<td>4.61</td>
<td></td>
</tr>
<tr>
<td>4.05</td>
<td>4.06</td>
<td>2.22</td>
<td></td>
</tr>
<tr>
<td>6.03</td>
<td>6.04</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>8.07</td>
<td>8.03</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>10.07</td>
<td>10.02</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>12.04</td>
<td>11.92</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>14.79</td>
<td>14.88</td>
<td>0.90</td>
<td></td>
</tr>
</tbody>
</table>

a pressure manually set for calibration chamber, 
b measured pressure average for each image, 
c $\sigma_{avg} % = \sigma_{avg}/P_{avg}$

Analysis of the luminescence response to pressure and temperature for the PtDOCl-Sµsp/VPDMS coating is depicted in the calibration curves of Figure 2-43.
Figure 2-43: Stern-Volmer plot and ratioed emission plots versus pressure and temperature for PtDOCI-Ssusp/VPDMS coating analyzed and imaged in a static calibration cell. A) SV plot, emission integrated over an approximate area of 630 - 670 nm, excitation at 460 nm, B) Ratioed emission plot versus pressure, emission integrated over an approximate area of 530 - 570 nm, excitation at 460 nm, C) Ratioed emission plot versus temperature, emission integrated over an approximate area of 630 - 670 nm, excitation at 460 nm, and D) Ratioed emission plot versus temperature, emission integrated over an approximate area of 530 - 570 nm, excitation at 460 nm.

The results are similar to that of the PtDOCIpμsp/VPDMS coating except for the ratioed emission plots versus pressure and temperature for emission integrated over an approximate area of 530 to 570 nm (images B and D, respectively). The DOCI-Sμsp temperature probe exhibits less pressure and temperature sensitivity as compared to the DOClpμsp temperature probe.

The uncorrected ratioed intensity images at 650 nm and corresponding pressure data for the PtDOCI-Ssusp/VPDMS coating are similar to those of the
PtDOClµsp/VPDMS coating. Placing a (> 20 K) temperature gradient across the aluminum plate induces temperature sensitivity in the pressure probe’s luminescence intensity. Only the corrected ratioed intensity images for the PtDOCl-Sµsp/VPDMS coating are illustrated in Figure 2-44 along with the accompanying pressure data listed in Table 2-28.

Figure 2-44: Corrected luminescence ratioed intensity images at seven pressures from 2 – 14.8 psi for PtDOCl-Sµsp/VPDMS coating on an aluminum plate. Emission collected at 650 nm peak and excitation at 460 nm. Intensity scale bars appear to the right of each image for 0 – 18.0 psi.

Table 2-28: Corresponding pressure values and statistical distributions for the corrected ratioed intensity images of PtDOCl-Sµsp/VPDMS coating on an aluminum plate at seven pressures between 2 – 14.8 psi.

<table>
<thead>
<tr>
<th>P(psi)</th>
<th>P_avg</th>
<th>σ_avg</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.02</td>
<td>1.95</td>
<td>7.18</td>
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</tr>
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<td>4.03</td>
<td>4.08</td>
<td>2.45</td>
<td></td>
</tr>
<tr>
<td>6.06</td>
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<td>8.08</td>
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</tr>
<tr>
<td>14.76</td>
<td>14.83</td>
<td>1.48</td>
<td></td>
</tr>
</tbody>
</table>

a pressure manually set for calibration chamber, b measured pressure average for each image, c \( \sigma_{avg} \% = \sigma_{avg}/P_{avg} \)
Shifting of the images during analysis and resolution of the microspheres is seen in the last image of the series. The pressure data is more scattered than that for the PtDOClµsp/VPDMS coating. The PtDOClµsp/VPDMS coating statistically and visually appears to be the better of the two coatings for calibration cell imaging.

The statistical distribution of the raw intensity values which lead to the pressure and temperature values are imaged in Figure 2-45 at 550 and 650 nm for the two coatings. The coupons in each image are 4 in. x 2 in. in size. The raw intensity coefficient of variance for each image is listed at the bottom of each image. As can be seen in the four images, the intensity distributions for the PtDOClµsp/VPDMS coating are smaller, indicating less possible disturbance of the imaging process from luminophore distribution.

Several questions can be raised concerning the images in Figure 2-45. Do the microspheres interfere with the wind-tunnel airflow and image registration? Could the coatings be sprayed thicker or the microspheres filtered to eliminate the bumpy coating texture and gritty effect in the luminouseance images due to microsphere build-up? The PtDOClµsp/VPDMS and PtDOCl-Sµsp/VPDMS coatings are approximately 20 µm and 10 µm thick, respectively. Prior microscopic imaging of the coatings' microsphere content was illustrated in Figure 2-30. Clearly, the microscope images display
Figure 2-45: Calibration cell intensity images of the PtDOCIµsp/VPDMS and PtDOCI-Sµsp/VPDMS coatings on an aluminum plate imaged at 650 nm and 550 nm. Excitation at 460 nm. A) PtDOCIµsp/VPDMS at 650 nm, B) PtDOCIµsp/VPDMS at 550 nm, C) PtDOCI-Sµsp/VPDMS at 650 nm, D) PtDOCI-Sµsp/VPDMS at 550 nm.

Several questions can be raised concerning the images in Figure 2-45. Do the microspheres interfere with the wind-tunnel airflow and image registration? Could the coatings be sprayed thicker or the microspheres filtered to eliminate the bumpy coating texture and gritty effect in the luminescence images due to microsphere build-up? The PtDOCIµsp/VPDMS and PtDOCI-Sµsp/VPDMS coatings are approximately 20 µm and 10 µm thick, respectively. Prior microscopic imaging of the coatings' microsphere content was illustrated in Figure 2-30. Clearly, the microscope images display
microspheres of sizes between 1-15 μm in length; however, the pixel size of the camera used for the calibration cell is approximately 200 μm². Therefore, the clusters of spheres imaged during the calibration cell experiment are much larger than the microspheres imaged with the microscope. Whether the visually resolved aggregation in Figure 2-45 is inherent to the formulation or a product of the application needs to be determined.

Discussion

The development of dual-luminophore coatings is not new. There have been several attempts to use inorganic phosphors, rhodamine B, and silicon octaethylporphine as temperature sensing luminophores. One of the biggest problems with such formulations is that they suffer from negative chemical and physical interactions between the two luminophores. Therefore, encapsulating the temperature dependent luminophore makes perfect sense for avoiding these problems.

PtTFPP

Other research groups have employed the use of PtTFPP porphyrin for the pressure sensing probe. The halogenated metalloporphyrin is more photostable, less temperature dependent, and more susceptible to oxygen quenching than other pressure sensing probes investigated (Ru(II) α-diimine complexes or Pt(II) octaethylporphyrin).

The increased photostability of PtTFPP is due to the addition of fluorinated phenyl rings at the meso-positions of the porphyrin ring. The electron withdrawing effect of the fluorines raises the PtTFPP oxidation potential making it more difficult to oxidize thereby stabilizing it with respect to attack by singlet oxygen.
The temperature dependence of the photoluminescence for PtTFPP is less than other pressure probes (Ru(II) α-diimine complexes), because PtTFPP does not possess low-energy charge transfer (CT) states or (d-d) excited states that can be thermally populated like the Ru(II) α-diimine complexes do. The photoluminescence emission of PtTFPP is due to spin-orbit coupling resulting in emission which is less temperature dependent.73,81

The increased oxygen sensitivity of PtTFPP is facilitated by its long phosphorescence lifetime due in part to π-π* transitions centered on the porphyrin ring—in particular, the \(^3T_1(\pi,\pi^*)\) state.16 Back bonding between the \(d_{xz}\) and \(d_{yz}\) orbitals of the Pt with the empty \(e_g(\pi^*)\) orbitals of the porphyrin macrocycle produces a strong spin-orbit coupling. This leads to singlet-triplet mixing which increases the radiative decay rate from \(^3T_1(\pi,\pi^*) \rightarrow ^1S_0\). Spin-orbit coupling significantly decreases the triplet lifetime and increases the phosphorescence yield. The long lifetime of the phosphorescent state facilitates efficient oxygen quenching of the luminescence.71 Therefore, a decrease in \(P_{air}\) above the sample results in quenched photoluminescence emission. In addition to its enhanced ability to be quenched by oxygen, PtTFPP is also easily excited in the visible region, and it possesses a large Stokes shift.16,50

**DOClµsp and DOCI-Sµsp**

The use of carbocyanine dyes has been predominately reported in photography as photosensitizers to silver halide colloids, and in laser technology as active dye laser materials.82 Recently, photochemical and photophysical studies have focused on investigating these cyanine dyes adsorbed onto microcrystalline cellulose,83 cyclodextrins,84 and functionalized polymer particles.85 Therefore, it is conceivable to
utilize polystyrene microspherical particles for encapsulation of cyanine dyes. In general, dye adsorption onto polystyrene particles is not uncommon and has been employed in the study of energy transfer between particles, and solid surface photoreactions.

The DOCI dye was chosen as the temperature-dependent pressure-independent probe because its fluorescence lifetime is ca. 0.3 ns in ethanol at 25°C and too quick for adequate luminescence quenching by oxygen. The fluorescence emission of the DOCI dye arises upon excitation of the π-π* visible absorption band (λ_max = 484 nm, ε = 22,000 cm⁻¹M⁻¹ in ethanol) and is dominated by a fast isomerization process from the first excited singlet state. The isomerization begins with a twisting of the molecule around one of the carbon-carbon polymethine chain bonds to form an excited state twisted molecule. The twisted excited state species decays to the ground state either to a ground state photoisomer or to a thermodynamically stable ground state species. The isomerization is an activated process and influenced by temperature and medium effects. Therefore the twisting process competes with fluorescence and internal conversion from the first excited state. As the molecules environment rises in temperature, the fluorescence emission of the DOCI dye decreases.

The microspheres utilized in the PtDOCIµsp/VPDMS and PtDOCI-Sµsp/VPDMS coatings were prepared in two different manners. The differing manners gave rise to unique physical effects. First, the microspheres of the PtDOCIµsp/VPDMS coating were prepared using a precipitation polymerization. As seen in the SEM images (Figures 2-19 – 2-22 and 2-27 and 2-28), the spheres are tightly packed and highly cross-linked. The spheres' surface charge is neutral; therefore, dye adsorption is not an electrostatic process. The dye molecules are loosely held to the spheres, essentially trapped in the small pores and bonded by van der Waals and hydrophobic
interactions. The main benefit of the entrapment is separation of the DOCI molecules from the PtTFPP luminophore in the polymer binder. The two luminophores could not and did not negatively interact spectroscopically with one another.

The microspheres of the PtDOCI-Sµsp/VPDMS coating were prepared by employing a modified suspension polymerization followed by a sulfonation. The spheres are smaller and more porous compared to the DOCIpµsp. Sulfonation imparted a negative charge to the microspheres which can tightly hold the dye molecules in place with strong ionic forces.

For the most part, both sets of microspheres exhibit the same ratioed emission response \( (I_{\text{REF}}/I) \) to continuous illumination and temporal analysis. The only major difference between the two types of spheres is seen in their temperature dependence and thermal-stability. The DOCI-Sµsp are less temperature dependent and respond more consistently to temperature changes from hot to cold and cold to hot than the DOCIpµsp. This physical characteristic could be due to the way in which the dye molecules are bound to the spheres. The ionically bound dye (DOCI-Sµsp) is more tightly bound and rigidly held. It is less likely to rotate and experience fluorescence temperature-dependent effects than the DOCIpµsp.

**PtDOCIpµsp/VPDMS and PtDOCI-Sµsp/VPDMS Coatings**

The PtTFPP, DOCIpµsp and DOCI-Sµsp ratioed photoluminescence emission for the two coatings is temporal-, thermal-, and photostable. The DOCI-Sµsp fluorescence emission is less temperature dependent and more thermally stable than the DOCIpµsp fluorescence emission. The smaller DOCI-Sµsp particles (0.5 – 2.5 µm) are more evenly distributed throughout the polymer binder and would be thought to impart a positive effect to the coatings physical characteristics; however, CCD imaging of the two
coatings reveals that the PtDOCI-Sssp/VPDMS coating suffers from large variations in raw intensity values across the coating. There are numerous intense fluorescent agglomerations throughout the images. These areas are due to clustering of the microspheres. The PtDOCIµsp/VPDMS coating exhibits less areas of intense fluorescence and is therefore the better choice of the two coatings. Unfortunately, the presence of microspherical aggregates of either formulation negatively affects the imaging results by generating visually gritty images (microspheres > 1 mm in size). These are difficult to correct for using standard image registration techniques. Further development of the coatings needs to be implemented to improve these complications.

Experimental

Preparation of DOCI Highly Cross-linked Polymer Microspheres (DOCIµsp)

Precipitation polymerization (µsp)

The particles were prepared via a precipitation polymerization following a procedure adapted from Stöver. In a 100 mL round-bottom flask fashioned with a reflux condenser and nitrogen inlet were combined 55 mL distilled acetonitrile, 2.6 g divinylbenzene, 55 % divinylbenzene isomers (DVB55) (5 vol % relative to total volume) from Aldrich, and 46 mg AIBN, 98 % (2 wt. % relative to DVB55) from Aldrich. The temperature of the polymerization was steadily ramped to 70° C over a 50 min. period and maintained at 70° C with continual stirring for 24 h. The initially homogenous mixture became milky white after 2 h. At the end of the polymerization, a white polymer precipitate settled to the bottom of the round-bottom. Any unreacted monomer and initiator were suction filtered away from the precipitate with 15 X 20 mL aliquots of 95 % ethanol. The polymer particles were dried in vacuo at 50° C overnight.
**DOCI incorporation (DOCIppsp)**

The microspheres (53 mg) were combined with 10 mg of 3,3'-diethyloxacarbocyanine iodide (DOCI), 98% from Aldrich, dissolved in 1 mL methanol. The suspension was sonicated for 1 h. and allowed to stand in the dark for 7 days. The particles were filtered and successively washed with alternating 5 mL aliquots of methanol and dichloromethane, until the excess dye was removed. Dye removal was determined by monitoring the dye concentration in the solvent washes via UV/Vis absorption. The particles were dried *in vacuo* at 30° C overnight. A fine orange powder was obtained. Dye loading was 7.27 % DOCI. Elemental analysis found: C, 90.65 %; N, 0.45 %; H, 8.62 %.

\[
\text{N, 0.45 \% in 1.58 mg sample = 7 \times 10^{-6} \text{ g N}}
\]
\[
\frac{(7 \times 10^{-6} \text{ g N})}{(14 \text{ g/mol})} = 5 \times 10^{-7} \text{ mol N} = 2.5 \times 10^{-7} \text{ mol DOCI in sample}
\]
\[
2.5 \times 10^{-7} \text{ mol DOCI} \times 460.32 \text{ g/mol} = 1.15 \times 10^{-4} \text{ g DOCI}
\]
\[
\frac{(1.15 \times 10^{-4} \text{ g})}{(1.58 \times 10^{-3} \text{ g})} = 7.27 \% \text{ DOCI}
\]

**Preparation of DOCI Sulfonated Polymer Microspheres (DOCI-Ssμsp)**

**Suspension polymerization (μsp)**

The particles were prepared via a conventional suspension polymerization adapted from Stöver.76 A 250 mL three-neck flask was fitted with a stainless steel stirring rod with two tilted blades, a reflux condenser with a nitrogen inlet, and a thermometer. In 100 mL DI H₂O (DI H₂O:porogen = 2.5:1 v/v) was dispersed 14.7 mg sodium laurylsulfate (0.3 mol % relative to monomer) as stabilizer, 5 g divinylbenzene 55 \% divinylbenzene isomers (DVB55) (45 vol % relative to total volume) from Aldrich, porogen (1-dodecanol:toluene = 1:1; porogen:monomer = 1:1.4 v/v), and 79 mg AIBN (3.5 wt % relative to monomer). The polymerization initiation was conducted at 26° C under a nitrogen atmosphere at 250 rpm followed by a gradual increase in temperature to 70° C over 7 h. and a final 21 h. at 70° C. The particles were allowed to cool to room
temperature. The particles were transferred to a beaker and suspended in DI H₂O. A stir bar was added, whereupon the particle aggregates were broken down. The suspension was allowed to stand for several hours to free small oligomeric material into the supernate, which was then decanted. This process was repeated again with DI H₂O and twice with acetone. Residual impurities were removed with tetrahydrofuran in a Soxhlet reactor overnight. The polymer particles were collected and dispersed in DI H₂O. A stir bar was again added to break-up polymer aggregates; afterwards, the particles were resuspended in the DI H₂O for several hours to further remove impurities, and the solution was decanted. This process was repeated again and then twice with acetone. A Soxhlet extraction with tetrahydrofuran was performed again to remove residual impurities. The resin particles were dried in vacuo overnight at 48° C. Approximately 2 g of material was obtained. A fine, white powder was achieved when the particles were ground in a mortar with pestle.

**Sulfonation of polymer microspheres (S₅μsp)**

The polymer particles were sulfonated following a procedure adapted from Winnik and Stöver.⁹³ The particles (800 mg) were dispersed in 40 mL of dichloromethane and sonicated for 10 min. to eliminate trapped air. The flask was cooled to 0° C and an addition funnel was added. A solution of 0.5 mL of chlorosulfonic acid (Aldrich) dissolved in 40 mL of dichloromethane was added drop-wise to the dispersed particles over a 3 h. period. Upon addition of the first drop, the mixture turned pink in color. After the addition, the flask was gradually warmed to room temperature with continuous stirring. The suspension was stirred for an additional 24 h. period at room temperature. The particles were transferred to a beaker and suspended in 100 mL dichloromethane. A stir bar was added to break apart large particle agglomerations. The
suspension was allowed to stand for several hours, and the dichloromethane solution was decanted. The process was repeated twice. Dark brown resin particles were obtained and allowed to dry in the hood at room temperature.

**Preparation of charged, sulfonated polymer microspheres (Ssµsp')**

The sulfonated polymer particles were dispersed in 150 mL of DI \( \text{H}_2\text{O} \). A 50 mL solution of NaOH (150 mM) was added to the dispersed particles. The color of the solution changed from brown to beige upon addition of the NaOH solution. The dispersion was stirred at room temperature for 100 min. The particles were then filtered and washed with 100 mL of DI \( \text{H}_2\text{O} \) three times; the pH of the suspension was 7.0. The particles were then washed with 100 mL of acetone and dried *in vacuo* at 53° C for 40 h. Beige particles were obtained. Elemental analysis of the particles was: S, 8.37 %; Na, 6.58 %; C, 53.92 %; H, 5.56 %. Sulfonation of microspheres was 49 %.

![Diagram of sulfonated polymer microspheres](image)

\[
m:n = 1:1
\]
\[
\frac{32 \text{ g/mol} \times 0.5}{(234.25 \text{ g/mol} \times 0.5) + (132 \text{ g/mol} \times 0.5)} \times 100 = \frac{16 \text{ g/mol}}{183.13 \text{ g/mol}} \times 100 = 8.74 \% \text{ S}
\]
\[
8.37 \% \sim 8.74 \%
\]
\[
\frac{32 \text{ g/mol} \times X}{(234.25 \text{ g/mol} \times X) + (132 \text{ g/mol} \times Y)} \times 100 = 8.37 \% \text{ S}
\]
\[
\frac{32 \text{ g/mol } X}{234.25 \text{ g/mol } X + 132 \text{ g/mol } - 132 \text{ g/mol } X} \times 100 = 8.37 \% \text{ S}
\]

\[
X = 0.47 = 47 \% \text{ sulfonation}
\]

**DOCI incorporation (DOCI-S_{sulf})**

The charged, sulfonated microspheres (30 mg) were dispersed in a solution of 2.76 mg of 3,3’-diethyloxacarbocyanine iodide (DOCI), 98% from Aldrich, dissolved in 4 mL methanol and 2 mL DI H₂O. The mixture was sonicated for 20 min. and stirred at room temperature for 18 h. The mixture was again centrifuged for 30 min., and the solvent layer was decanted. The resulting solid was washed with 6 mL methanol and centrifuged for an additional 30 min. This process was repeated three times. The particles were then washed with 6 mL of acetone and centrifuged for 40 min. The dye-loaded particles were filtered and dried *in vacuo* at 45° C for 24 h. Dye loading was 3.83 % of DOCI. Elemental analysis found: C, 53.53%; N, 0.28%; H, 5.41%.

\[
\frac{28 \text{ g/mol } X}{130 \text{ g/mol } (0.53) + 234.25 \text{ g/mol } (0.47 - X) + 545.68 \text{ g/mol } X} \times 100 = 0.28 \% \text{ N}
\]

\[
545.68 \text{ g/mol} = \text{DOCI incorporated repeat unit}
\]

\[
X = 0.018
\]

\[
0.018/0.47 \times 100 = 3.83 \% \text{ DOCI}
\]

**Oligomers**

- **SPDMS**: silanol terminated polydimethylsiloxanes (PDMS) 0.2 % OH (average MW 18,000) and methyltriacetoxy silane 95 % were purchased from Gelest (Tullytown, PA).
- **VPDMS**: methylhydrosiloxanes-dimethylsiloxane copolymer 15-18 mole % MeHSiO (average MW 1900 – 2000), vinyl terminated polydimethylsiloxanes (PDMS) 0.37 - 0.43 wt. % vinyl (average MW 17,200), and platinum-divinyltetramethyldisiloxane 3 - 3.5 % Pt catalyst were purchased from Gelest (Tullytown, PA).
Luminophores

[Ru(dpp)_3]Cl_2: *Tris-(4,7-diphenyl-1,10-phenanthroline)ruthenium (II) dichloride* (Rudpp) was synthesized by a literature procedure and purified by repeated recrystallizations from water.47,94

PtTFPP: Pt(II) *meso*-tetrakis(pentafluorophenyl)porphine was purchased from Porphyrin Products Inc. (Logan, UT).

DOCI: 3,3′*diethyloxacarbocyanine iodide, 98%* was purchased from Aldrich Chemical Company.

Preparation of Coatings

RuDOCIpμsp

Silanol PDMS (500 mg, 0.056 mmol of Si-OH endgroups), methyltriacetoxy silane (26 mg, 0.12 mmol) and DOCIpμsp (3.2 mg) were mixed for approximately 20 min. or until well dispersed. [Ru(dpp)_3]Cl_2 (1 mg) was dissolved in 4 mL dichloromethane and added to the oligomer/microsphere mixture. The mixture was stirred for 5 min. and one drop of glacial acetic acid was added to catalyze the reaction. The coating was applied using a commercially available air-brush at 15 psi onto clean and primer-coated borosilicate glass slides. The coatings were allowed to cure to the touch at room temperature for 12 – 24 h. A [Ru(dpp)_3]Cl_2 coating void of pμsp was prepared in the same manner.

PtDOCIpμsp and PtDOCI-Ssμsp

Vinyl PDMS (500 mg, 0.058 mmol of Si-vinyl endgroups) and DOCIpμsp(3 mg) or DOCI-Ssμsp (1 mg) were mixed for approximately 20 min. or until well dispersed. PtTFPP (1.2 mg) was dissolved in 0.5 mL of a 2 X 10^{-2} M stock solution of methylhydrosiloxane copolymer in chloroform, and the luminophore/copolymer solution
was added to the PDMS mixture with stirring. Prior to application of the coating, 1.5 mL of a stock solution of 30 mg of the Pt catalyst in 25 mL chloroform was added to the luminophore/copolymer/PDMS mixture. The coating was applied using a commercially available air-brush at 15 psi onto clean and primer-coated borosilicate glass slides. The coatings were allowed to cure to the touch at room temperature for 1 h.

**Primer**

Silanol PDMS (1000 mg, 0.11 mmol of Si-OH endgroups) and 800 or 822 TiO$_2$ powder (Kerr-McGee) (60 mg) were mixed for 2 d. or until well blended. The milky white mixture was then filtered through a plug of cotton to remove any TiO$_2$ aggregates. Methyltriaceotoxysilane (110 mg, 0.5 mmol) and 4 mL dichloromethane were added and the resulting mixture was stirred. Prior to application of the primer, 2 drops of glacial acetic acid were added to catalyze the reaction. The coating was applied using a commercially available air-brush at 15 psi onto clean borosilicate glass slides. The coatings were allowed to cure to the touch at room temperature for 12 h. or within 1 h. at 60° C.

**Instrumentation**

**Fluorescence microscope**

The fluorescence microscope system consisted of an inverted microscope platform (Olympus, model IX 70) fitted with a 100 W Hg source (USH-102DH) and a CCD camera (Princeton, RTE 1300 x 1030) mounted to the side port. Fluorescence microscopy was conducted with a blue-violet modular filter cube (Chroma Technology, excitation 425 nm, 40 nm bandpass; 475 nm dichroic splitter). The emission filter was interchangeable among an emission 630 nm 60 nm bandpass filter, an emission 525 nm 50 nm bandpass filter, or a 475 nm long pass filter (Chroma Technology). Fluorescence
images were collected through 10X and 40X objective lenses (Olympus U Plan Fl, 0.30 NA and SLC Plan Fl, 0.55 NA, respectively). Neutral density filters and an IR blocking filter were used to adjust excitation intensity and prevent extraneous excitation light from reaching the CCD.

The coating formulations were applied as thin films to the surface of a 1/16 in. thick borosilicate glass disk with a commercially available air-brush operated at 15 psi. Profilometry determined that the films were typically 10 – 20 μm thick. The disk was mounted in a stainless steel air-tight chamber with an o-ring seal (the sensor film was on the inside surface of the glass disk) as displayed in Figure 2-46. A vacuum pump was used to control the air pressure inside the chamber (0.4 psi – 14.7 psi) and pressure was monitored using a Druck (model DPI 260) pressure gauge. The sensor film was imaged through the 1/16 in. glass disk that supported the film. This was possible because of the long-focal length objectives used with the Olympus microscope.

Figure 2-46: Inverted Fluorescence Microscope set-up for imaging of luminescent oxygen sensing thin films.
In order to allow direct comparison of the CCD fluorescence image data obtained from the thin film samples under the same S/N conditions, care was taken to insure that the absolute fluorescence intensity from the samples was adjusted to be the same at $P_{\text{air}} \approx 0$ atm (the "high" light condition for the sensor films). This light-level adjustment was made by using neutral density filters to attenuate the excitation light reaching the sample. For all images on all specimens the CCD exposure time was 300 ms.

**Fluorimeter**

Conventional corrected steady state emission spectroscopy of the coating formulations was carried out using a SPEX F-112 fluorimeter. Fluorescence data obtained on coatings represents the average over an area of approximately $15 \text{ mm}^2$ (spot size defined by the excitation light). A special chamber similar to Figure 2-46 was designed for the fluorimeter apparatus. The chamber (8.5 cm x 7.5 cm x 7.5 cm) was equipped with vacuum tubing attached to a gas manifold fashioned with a pressure gauge for monitoring the chamber air pressure and a vacuum pump for regulating the chamber air pressure. Cooling tubes attached to a water circulation bath were fed into the chamber along the back wall adjacent to the sample. The sample temperature was monitored via an interior thermo-couple installed along the back of the wall adjacent to the sample. The sample (1 mm x 1 mm x 10 mm) was mounted in the chamber 13 mm away from the 4 mm thick glass window. The photoluminescence of the sample was monitored front-face to the chamber window.

**UV/Vis**

Steady state absorption spectra were recorded on a Varian Cary 100 dual-beam spectrophotometer.
Scanning electron microscope

The microspheres were imaged using a Hitachi S-4000 FE scanning electron microscope (SEM). The microsphere specimens were prepared by redispersing the microspheres in methanol, and a drop was placed on a piece of circular glass slip-cover which was mounted on an aluminum stud with carbon tape. After solvent evaporation, the particles were sputter-coated with 15 nm of gold. The DOClµsp and DOCl-Sµsp dispersed in VPDMS specimens were prepared by coating a glass circular slip-cover with two layers (approximately 5 - 10 µm thick) of the microsphere/polymer coating, and mounting the cover slip on an aluminum stud with carbon tape. After film cure, the coatings were sputter-coated with 15 nm of gold. The fractured images were achieved by snapping in half the gold coated microsphere/polymer coated glass slip-covers; propping the glass pieces on end; and attaching the pieces to the aluminum stud with carbon glue and tiny balls of aluminum foil as support.

Transmission electron microscope

The microspheres were imaged using a Hitachi H-7000 transmission electron microscope (TEM). The TEM specimens were prepared by embedding cured [Ru(dpp)₃]Cl₂ dispersed in SPDMS in formvar (0.25% polyvinyl formula in ethylene dichloride); microtoming slices to a thickness of < 100 nm; attaching the slices to a 400 mesh copper grid, and coating with 1-5 nm carbon.

Energy dispersive X-ray spectroscopy

The Rudpp/SPDMS samples were imaged using an EDAX 5800 energy dispersive x-ray system (EDS) attached to a Phillips EM420 TEM. The EDS specimens were prepared as above for TEM.
Calibration chamber

Calibration tests were conducted on PtDOCIPµsp/VPDMS and PtDOCISµsp/VPDMS coatings to access their pressure measurement accuracy when exposed to a spatial temperature gradient. Aluminum coupons (4 in. x 2 in. x 1/8 in.) were coated with primer, and the coatings were air-brushed onto the coupons (4 layers). The plates were individually placed into a pressure and temperature controlled environment chamber. A temperature gradient (> 20 K) was imposed on the coupons using a heated plate and a water-cooled bath. The overall pressure was varied between 2 to 14.7 psi.

Images were acquired at two emission wavelengths: 550 nm and 650 nm. The optical bandwidth was 40 nm FWHM. The sample was excited using two two-72-element blue LED lamps (peak emission @ 460 nm).
CHAPTER 3
MICROSCOPIC ANALYSIS OF LUMINESCENT OXYGEN SENSOR THIN FILMS

Introduction

As outlined in Chapter One, there is considerable recent interest in the development and application of solid-state thin film photoluminescence-based sensors for detection and quantification of gas- and solution-borne analytes. These thin film sensors consist of a photoluminescent dye molecule dispersed or dissolved in a gas permeable polymer binder. The binder encapsulates the luminophore and allows it to be distributed across an object and held in place for detection of gas molecules. Particular interest has focused on the development of luminescent sensors for the measurement of the oxygen partial pressure ($pO_2$) in the gas and/or condensed phases.

Luminescence quenching that occurs in an oxygen permeable luminescent coating can be modeled by the Stern-Volmer (SV) equation (3-1),

$$\frac{I(P_{air} = 0)}{I(P_{air})} = 1 + K'_{SV} [O_2]_{poly} \tag{3-1}$$

where $I$ is the emission intensity, $K'_{SV}$ is the Stern-Volmer quenching constant, and $[O_2]_{poly}$ is the concentration of oxygen in the polymer binder. Assuming Henry’s Law holds, $[O_2]_{poly}$ is proportional to air pressure ($P_{air}$), and the SV equation reduces to equation (3-2) which is an appropriate form for a solid state thin film sensor that is in equilibrium with air.

$$\frac{I(P_{air} = 0)}{I(P_{air})} = 1 + K_{SV} P_{air} \tag{3-2}$$
In many applications it is impractical to use $P_{\text{air}} = 0$ as a reference condition, and consequently the SV equation is recast as equation (3-3), where the reference condition is taken as $P_{\text{air}} = 1$ atm. A and B are non-zero coefficients, and the ratio $(B/A) = K_{SV}$.

$$\frac{I(P_{\text{air}} = 1 \text{ atm})}{I(P_{\text{air}})} = A + BP_{\text{air}}$$

(3-3)

Some thin film oxygen sensors feature linear SV calibrations in accord with equations (3-2) or (3-3); however, many films exhibit non-linear calibrations that are curved downward. Although a number of studies have attempted to identify the basis for this non-ideal SV response, the fundamental process(es) responsible are still not well understood. Several mathematical models have been developed to fit the non-linear SV correlations. These mathematical models are based on the physical hypothesis that the film morphology is inhomogeneous, possibly due to nano- or meso-scale irregularities in the polymer environment surrounding the luminescent sensor molecules. The models that have received the most attention include the two-site quenching model, the Gaussian or log-Gaussian distribution in luminophore emission decay time ($\tau$), and the dual-sorption model. All models were extensively explained in Chapter One.

Advances in the area of fluorescence microscopy, specifically the development of near-field scanning optical microscopy and single-molecule fluorescence spectroscopy, have led to new studies that are focused on examining the morphology and heterogeneity of luminescent dye molecule/polymer composites with nm and \(\mu\)m spatial resolution. Recently reported fluorescence microscopy studies have used environmentally sensitive fluorescent probe molecules to explore the heterogeneity of thin polymer films.
These studies reveal that significant insight can be obtained concerning the spatial distribution of molecular environments provided by the polymer matrix on the nano- and meso-scale.99-104

Presented in this chapter is a novel application of fluorescence microscopy for exploration of the spatial distribution of the luminescence response to oxygen concentration in luminescent oxygen sensor thin films. Specifically, fluorescence microscopy and CCD image analysis techniques are employed to create spatially-resolved "image maps" of the SV constant ($K_{SV}$) for luminescent oxygen sensor thin films. These image maps provide quantitative information concerning the SV response of the sensors with greater than 5 μm spatial resolution. Several series of luminescent oxygen sensor thin films are examined using this technique.

The first series of oxygen sensing thin films evaluated are PtTFPP/SPDMS thin films (PtTFPP = Pt(II) tetra(pentafluorophenyl)porphyrin dispersed in a polymer binder SPDMS = silanol polydimethylsiloxanes 18,000 MW methyltriacetoxysilane cross-linker) incorporating increased concentrations (mM) of PtTFPP sensor. The second series of thin films evaluated are PtTFPP/SPDMS thin films incorporating increased mole ratios of cross-linker (methyltriacetoxysilane). The third series of thin films evaluated are six Ru(II) α-diimine complexes, varying in counter ion or ligand structure, dispersed in SPDMS. The fourth and final series evaluated is a combination of thin films. [Ru(dpp)$_3$]Cl$_2$ is dispersed in two similar polymers: SPDMS and a commercially synthesized polydimethylsiloxane (PDMS 1900 – 2000 MW) binder (DMS-D33). Both films incorporate increased weight percents of a hydrophilic fumed silica gel. These four
series were chosen to illustrate the relationships between sensor distribution, polymer cross-linking, or filler additives and the films' SV response.

Results

Fluorescence Microscopy of Increased Concentrations of PtTFPP in SPDMS

Six sensor films were prepared with increased concentrations (mM) of PtTFPP dispersed in SPDMS polymer binder. A general scheme for the polymer binder formulation is shown in Figure 3-1.

Figure 3-1: Scheme for preparation of PtTFPP/SPDMS luminescent thin films.

The concentrations of PtTFPP are calculated as mole of PtTFPP-L$^{-1}$ of polymer (density of polymer = 1 g/mL). For each thin film in the series, the samples are first analyzed on the macroscopic level utilizing the fluorimeter. Macroscopic Stern-Volmer (SV) plots for increased concentrations (mM) of PtTFPP dispersed in SPDMS binder are displayed in Figure 3-2.
Figure 3-2: Macroscopic SV plots for increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass. $A_{REF}$: area between 630 - 670 nm at 14.7 psi.

For the most part, increased concentrations of PtTFPP do not negatively affect the SV response of the sensor films. Luminescence intensity consistently decreases for all sensor films by more than a factor of ten when $P_{air}$ increases from 0 – 14.7 psi. The macroscopic SV response linear regression data are listed in Table 3-1. As was seen in Chapter Two for PtTFPP sensor films, small variations in the intercept ($A$) at maximum slope ($B$) values for equation (3-3) result in large deviations in the calculated $K_{SV}$ values. In Table 3-1, the slope values are near maximum ($1/14.7\text{psi} = 0.068 \text{psi}$), so relatively small variations in the intercept value cause the $K_{SV}$ values to also vary. By looking at the raw intensity values at near vacuum conditions for the sensor films in Table 3-2, it is seen that the intensity values do vary and by the same magnitude as the corresponding $K_{SV}$ values. The $K_{SV}$ values in Table 3-1 are indicative of the sensor films’ raw intensity characteristics (the extent of oxygen quenching) and are based on real clean data.
Table 3-1: Macroscopic SV response data for increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>Slope (psi¹)</th>
<th>Intercept</th>
<th>Ksv (psi¹)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.066</td>
<td>0.076</td>
<td>0.868</td>
<td>0.991</td>
</tr>
<tr>
<td>3</td>
<td>0.067</td>
<td>0.044</td>
<td>1.52</td>
<td>0.995</td>
</tr>
<tr>
<td>5</td>
<td>0.066</td>
<td>0.083</td>
<td>0.795</td>
<td>0.985</td>
</tr>
<tr>
<td>10</td>
<td>0.066</td>
<td>0.056</td>
<td>1.18</td>
<td>0.988</td>
</tr>
<tr>
<td>17</td>
<td>0.065</td>
<td>0.066</td>
<td>0.985</td>
<td>0.990</td>
</tr>
</tbody>
</table>

- PtTFPP concentration in 500 mg of SPDMS polymer binder, \( b \) intercept = A in equation (3-3), \( c \) slope = B in equation (3-3), \( d \) \( K_{sv} = (B/A) \) in equation (3-3)

Table 3-2: PtTFPP emission intensity area (\( \lambda = 630 – 670 \) nm) values for increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>2 mM⁹</th>
<th>3 mM⁹</th>
<th>5 mM⁹</th>
<th>10 mM⁹</th>
<th>17 mM⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1650438</td>
<td>4372167</td>
<td>1986260</td>
<td>4980864</td>
<td>12763170</td>
</tr>
<tr>
<td>2</td>
<td>260795</td>
<td>679724</td>
<td>276934</td>
<td>619479</td>
<td>1253054</td>
</tr>
<tr>
<td>4</td>
<td>151282</td>
<td>361038</td>
<td>156497</td>
<td>270506</td>
<td>815546</td>
</tr>
<tr>
<td>6</td>
<td>109394</td>
<td>251175</td>
<td>109809</td>
<td>223869</td>
<td>516944</td>
</tr>
<tr>
<td>8</td>
<td>85503</td>
<td>183637</td>
<td>88630</td>
<td>162543</td>
<td>444968</td>
</tr>
<tr>
<td>10</td>
<td>71324</td>
<td>156463</td>
<td>75627</td>
<td>142058</td>
<td>368623</td>
</tr>
<tr>
<td>14.7</td>
<td>54268</td>
<td>114959</td>
<td>57728</td>
<td>102420</td>
<td>267282</td>
</tr>
</tbody>
</table>

- PtTFPP concentration in 500 mg of SPDMS polymer binder

While the SV response plots are unaffected by increased sensor concentration, microscopic analysis of the sensor films reveals formation of PtTFPP fluorescent microcrystals (bright spots) and non-fluorescent aggregates (dark spots) with increased sensor concentration. The onset of substantial visual image heterogeneity occurs for the sensor film at 10 mM PtTFPP. Qualitative fluorescence microscope images of the sensor films obtained at 0.5 psi (maximum fluorescence) with a 10X objective are imaged in Figure 3-3. Each image size is 871 µm x 690 µm or 1300 x 1030 pixels. The calibration for each pixel at 10X magnification is 0.67 µm-pixel⁻¹.
Figure 3-3: Qualitative microscopic fluorescence images (10X, 0.5 psi) for increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass. White scale bars are 153 μm long. A) 2 mM, B) 3 mM, C) 5 mM, D) 10 mM, E) 17 mM PtTFPP in 500 mg SPDMS polymer binder.

The effect of the inhomogeneous distribution of PtTFPP in the SPDMS binder on the spatial distribution of the microscopic SV response is probed by taking a series of quantitative 10X intensity image maps of the sensor’s luminescence response to variation in $P_{air}$. For each sensor film, seven image maps were obtained for pressures ranging from 0.4 – 14.7 psi. Figure 3-4 illustrates the corrected luminescence intensity distribution ($\Gamma(x,y; P_{air} = 0.4 \text{ psi})$) of one representative image map for one region from each coating at 0.4 psi. For each 436 μm x 345 μm intensity image obtained, a “dark image” is subtracted to correct for extraneous sources of light and noise. The dark image is obtained when the excitation light is blocked. The color of the intensity images are not scaled relative to each other, so each image possesses a different maximum intensity value listed in Table 3-3. The maximum intensity values in Table 3-3 are used to
calibrate the intensity color bars to the right of the intensity images. The maximum intensity values are yellow and scale to dark blue for zero emission intensity in the images of Figure 3-4.

Table 3-3: Maximum fluorescence intensity values for 10X microscopic regions of increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass at 0.4 psi.

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>Maximum Intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>11812</td>
</tr>
<tr>
<td>3</td>
<td>27431</td>
</tr>
<tr>
<td>5</td>
<td>27983</td>
</tr>
<tr>
<td>10</td>
<td>23919</td>
</tr>
<tr>
<td>17</td>
<td>22440</td>
</tr>
</tbody>
</table>

* PtTFPP concentration in 500 mg of SPDMS polymer binder, * a.u. = arbitrary units

Figure 3-4: Quantitative microscopic fluorescence intensity images (10X, 0.4 psi) for increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass. White scale bars are 92 µm long. Intensity color scale bars are shown to the right of all images. A) 2 mM, B) 3 mM, C) 5 mM, D) 10 mM, E) 17 mM PtTFPP in 500 mg SPDMS polymer binder.

As was expected, the quantitative fluorescence images are consistent with the initial qualitative fluorescence images displayed in Figure 3-3. The onset of sensor
crystallization is actually illustrated in images B and C of Figure 3-4 which both exhibit a few fluorescent microcrystallites. Pronounced development of microcrystallization and aggregation is seen in images D and E.

The percent standard deviations for the intensity values of each 0.4 psi image in Figure 3-4 and the remaining six intensity image maps obtained for each sensor film are listed in Table 3-3. The list quantifies the effect microcrystallization and aggregation has on the intensity distribution for each sensor film.

Table 3-4: Percent standard deviation (σ1, %) in intensities at seven pressures for microscopic regions of increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass using the 10X objective.

<table>
<thead>
<tr>
<th>Concentration (mM)ᵃ</th>
<th>0.4 psi</th>
<th>2 psi</th>
<th>4 psi</th>
<th>6 psi</th>
<th>8 psi</th>
<th>10 psi</th>
<th>14.7 psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.48</td>
<td>3.65</td>
<td>3.59</td>
<td>3.80</td>
<td>3.93</td>
<td>4.08</td>
<td>4.08</td>
</tr>
<tr>
<td>3</td>
<td>3.19</td>
<td>3.29</td>
<td>3.30</td>
<td>3.33</td>
<td>3.27</td>
<td>3.22</td>
<td>3.36</td>
</tr>
<tr>
<td>5</td>
<td>3.04</td>
<td>3.55</td>
<td>4.22</td>
<td>3.50</td>
<td>3.28</td>
<td>3.23</td>
<td>3.20</td>
</tr>
<tr>
<td>10</td>
<td>3.79</td>
<td>2.73</td>
<td>3.55</td>
<td>4.00</td>
<td>4.63</td>
<td>4.80</td>
<td>4.92</td>
</tr>
<tr>
<td>17</td>
<td>4.35</td>
<td>2.87</td>
<td>3.98</td>
<td>5.76</td>
<td>5.42</td>
<td>6.43</td>
<td>4.86</td>
</tr>
</tbody>
</table>

ᵃ PtTFPP concentration in 500 mg of SPDMS polymer binder, ᵇ σ₁ % = σ/Iavg × 100 %

The percentages listed in Table 3-4 are not large and do not deviate significantly from one pressure to the next. Therefore, even for the films with higher concentrations of PtTFPP, microcrystallization and aggregation do not impact the intensity value distributions significantly.

In actuality, the percentages comprise at least 2.5 % error due to variance in the excitation field. Imaging of a polished silicon wafer with a 10X objective results in a
rather homogeneous illumination field for a 650 x 515 pixel area centered on the 1300 x 1030 pixel CCD chip. The intensities deviate by ca. 2.5 % due to random noise.

The dark areas (low intensity) in images D and E of Figure 3-4 are small relative to the intensity field and do not contribute significantly to the sensor films’ overall intensity response to variation in $P_{air}$. To further prove the insignificance the bright and dark spots have on the intensity distributions, distribution curves of the intensity values for each pressure of the least (2 mM) and most (17 mM) visually heterogeneous sensor films are displayed in Figure 3-5.

![Figure 3-5: Intensity distribution curves for intensities obtained with a 10X objective at seven pressures for A) 2 mM PtTFPP dispersed in SPDMS binder on glass and B) 17 mM PtTFPP dispersed in SPDMS binder on glass.](image)

Image A displays seven intensity distribution curves that decrease and broaden as the peaks approach 0 psi. The peaks overlap slightly between 6 to 10 psi and exhibit a jagged peak shape at each pressure. The distribution curves in image B overlap greatly between 6 and 14.7 psi and are less broad than the curves in image A. The broadening and overlap of the curves can be due to several reasons: uneven excitation field, unquenchable sensor crystallites, or other luminescent species photo-bleached early in the
analysis at lower pressures. For image A, each pressure curve possesses a distinct
distribution of intensity values with little nearest neighbor overlap. Bi-modal or eclipsing
distribution curves indicate numerous species of differing luminescence quenching and
possible cause for non-linear SV response. For image B, the intensity heterogeneity
caused by the PtTFPP aggregates and microcrystallites is evidenced by higher intensity
values as well as nearest neighbor overlap. Overall, the two images do not vary greatly,
which explains why the macroscopic SV responses are not that different even though, at
the microscopic level, the sensor films become more heterogeneous with increased
concentrations of PtTFPP.

The series of five quantitative intensity image maps afforded five corresponding
$K_{SV}(x,y)$ image maps in Figure 3-6 and accompanying statistical data in Tables 3-6a and
3-6b. Each image map displayed possesses a different maximum $K_{SV}$ value. The
maximum $K_{SV}$ value for each image map is listed in Table 3-5. The maximum $K_{SV}$
values in Table 3-5 are used to calibrate the $K_{SV}$ color scale bars to the right of the
intensity images. The maximum $K_{SV}$ values are yellow and scale to dark blue for no SV
response in the images of Figure 3-6.

<table>
<thead>
<tr>
<th>Concentration (mM)$^a$</th>
<th>Maximum $K_{SV}$ (psi)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.780</td>
</tr>
<tr>
<td>3</td>
<td>0.770</td>
</tr>
<tr>
<td>5</td>
<td>3.05</td>
</tr>
<tr>
<td>10</td>
<td>4.22</td>
</tr>
<tr>
<td>17</td>
<td>4.86</td>
</tr>
</tbody>
</table>

$^a$ PtTFPP concentration in 500 mg of SPDMS polymer binder, $^b$ $K_{SV} = (B/A)$ in
equation (3-3)
Figure 3-6: Quantitative microscopic $K_{SV}(x,y)$ image maps for increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass. White scale bars are 92 μm long. $K_{SV}$ color scale bars are shown to the right of all images. A) 2 mM, B) 3 mM, C) 5 mM, D) 10 mM, E) 17 mM PtTFPP in 500 mg SPDMS polymer binder.

The $K_{SV}$ image maps in Figure 3-6 correlate nicely with the intensity images in Figure 3-4. In particular, the more heterogeneous images, D and E, exhibit high and low regions of SV response for corresponding regions of yellow and blue in Figure 3-4.

Some of the low quenching regions (dark blue spots) in images D and E of Figure 3-6 are situated around the high quenching regions (red spots). These dark areas are most likely due to image shifting during analysis, while the remaining dark areas correlate with the non-fluorescent PtTFPP aggregates. By comparing the percent standard deviation data in Table 3-3 and the $K_{SV}$ data in Tables 3-6a and 3-6b, it is seen that the deviations in intensity and $K_{SV}$ values increase in magnitude with increased concentrations of PtTFPP. However, as was established earlier, the microscopic visual heterogeneity exhibited by the sensor films, especially at higher concentrations of PtTFPP, is negligible as illustrated by the excellent macroscopic SV correlation plots in Figure 3-2.
Table 3-6a: Microscopic SV analysis of five 10X regions for increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>2 mM</th>
<th>3 mM</th>
<th>5 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>$K_{sv}^{avg}$ (psi$^{-1}$)</td>
<td>$\sigma_{K_{sv}}^{b}$</td>
<td>$K_{sv}^{avg}$ (psi$^{-1}$)</td>
</tr>
<tr>
<td>1</td>
<td>0.576</td>
<td>3.47</td>
<td>0.463</td>
</tr>
<tr>
<td>2</td>
<td>0.579</td>
<td>3.28</td>
<td>0.531</td>
</tr>
<tr>
<td>3</td>
<td>0.567</td>
<td>3.17</td>
<td>0.465</td>
</tr>
<tr>
<td>4</td>
<td>0.594</td>
<td>2.86</td>
<td>0.491</td>
</tr>
<tr>
<td>5</td>
<td>0.607</td>
<td>3.46</td>
<td>0.493</td>
</tr>
</tbody>
</table>

a PtTFPP concentration in 500 mg of SPDMS polymer binder,

$\sigma_{K_{sv}}^{\%} = \frac{\sigma_{K_{sv}}}{K_{sv}^{avg}} \times 100 \%$

Table 3-6b: Microscopic SV analysis of five 10X regions for increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>10 mM</th>
<th>17 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>$K_{sv}^{avg}$ (psi$^{-1}$)</td>
<td>$\sigma_{K_{sv}}^{b}$</td>
</tr>
<tr>
<td>1</td>
<td>0.654</td>
<td>7.49</td>
</tr>
<tr>
<td>2</td>
<td>0.819</td>
<td>9.04</td>
</tr>
<tr>
<td>3</td>
<td>0.946</td>
<td>12.3</td>
</tr>
<tr>
<td>4</td>
<td>0.806</td>
<td>8.06</td>
</tr>
<tr>
<td>5</td>
<td>0.863</td>
<td>7.18</td>
</tr>
</tbody>
</table>

The luminescence distribution and SV response of increased concentrations of PtTFPP in SPDMS was also microscopically analyzed utilizing a 40X objective. Five regions (650 x 515 pixels = 110 µm x 88 µm) were interrogated for each film. At each region, seven intensity images for pressures between 0.4 – 14.7 psi were obtained. $K_{sv}(x,y)$ image maps similar to Figure 3-6 were generated for each region with accompanying statistical data listed in Tables 3-7a and 3-7b. It is interesting to note that the data presented in Tables 3-6a and 3-6b are not consistent with the data in Tables 3-7a and 3-7b. This is due to the differing magnification between the two cases. The 40X images are 1/36 the size of the 10X images. Small areas of dark and bright spots
illustrated in a 10X image are enlarged and more substantial in a 40X image. Their contribution to the SV statistical data for that region then has a greater impact upon the $K_{SV}^{avg}$ values and percent standard deviations.

Table 3-7a: Microscopic SV analysis of five 40X regions for increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>2 mM</th>
<th>3 mM</th>
<th>5 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>$K_{SV}^{avg}$ (psi$^{-1}$)</td>
<td>$\sigma_{K_{SV}}$ %</td>
<td>$K_{SV}^{avg}$ (psi$^{-1}$)</td>
</tr>
<tr>
<td>1</td>
<td>0.854</td>
<td>6.67</td>
<td>0.982</td>
</tr>
<tr>
<td>2</td>
<td>1.54</td>
<td>3.70</td>
<td>0.882</td>
</tr>
<tr>
<td>3</td>
<td>1.37</td>
<td>3.21</td>
<td>1.23</td>
</tr>
<tr>
<td>4</td>
<td>1.47</td>
<td>4.15</td>
<td>0.945</td>
</tr>
<tr>
<td>5</td>
<td>1.62</td>
<td>4.88</td>
<td>1.52</td>
</tr>
</tbody>
</table>

$^a$ PtTFPP concentration in 500 mg of SPDMS polymer binder, $^b\sigma_{K_{SV}}$ % = $\frac{\sigma_{K_{SV}}}{K_{SV}^{avg}} \times 100\%$

Table 3-7b: Microscopic SV analysis of five 40X regions for increased concentrations (mM) of PtTFPP dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>10 mM</th>
<th>17 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>$K_{SV}^{avg}$ (psi$^{-1}$)</td>
<td>$\sigma_{K_{SV}}$ %</td>
</tr>
<tr>
<td>1</td>
<td>1.30</td>
<td>29.2</td>
</tr>
<tr>
<td>2</td>
<td>1.46</td>
<td>32.6</td>
</tr>
<tr>
<td>3</td>
<td>1.39</td>
<td>32.8</td>
</tr>
<tr>
<td>4</td>
<td>1.16</td>
<td>26.9</td>
</tr>
<tr>
<td>5</td>
<td>0.906</td>
<td>20.3</td>
</tr>
</tbody>
</table>

Clearly increased concentrations of PtTFPP to the SPDMS sensor films do not impart a negative affect to the macroscopic SV response (Figure 3-2). Microscopic analysis did reveal that the sensor distribution is heterogeneous at higher concentrations (fluorescent microcrystallites and non-fluorescent aggregates). The microcrystallites and background emission exhibit excellent SV responses; accordingly, the lack of SV
response from the non-fluorescent aggregates is small and of no overall consequence to the performance of the sensor films.

**Fluorescence Microscopy of Increased Mole Ratios of Cross-linker in PtTFPP/SPDMS**

PtTFPP/SPDMS sensor films with a fixed concentration of PtTFPP and increased mole ratio of methyltriacetoxysilane cross-linker relative to silanol polydimethylsiloxane oligomer end-groups (i.e. $1:4 = 1$ mole of oligomer with two Si-OH end-groups for every 4 moles of methyltriacetoxysilane) are evaluated. Macroscopic Stern-Volmer (SV) plots for the sensor films are displayed in Figure 3-7.

![Figure 3-7: Macroscopic SV plots for PtTFPP/SPDMS on glass at five different mole ratios of cross-linker. $A_{REF}$: area between 630 - 670 nm at 14.7 psi.](image)

The sensor films' response to variation in $P_{air}$ was similar to the previous series of PtTFPP sensor films. The SV response is strong and consistent regardless of mole ratio of cross-linker. Corresponding macroscopic SV response data for the sensor films are displayed in Table 3-8. The $K_{SV}$ values correspond to the deviations in emission area ($\lambda = 630 - 670$ nm) for PtTFPP at near vacuum conditions for each sensor film in Table 3-9.
Table 3-8: Macroscopic SV response data for PtTFPP/SPDMS on glass at five different mole ratios of cross-linker.

<table>
<thead>
<tr>
<th>Mole Ratio</th>
<th>Slope (psi(^{-1}))</th>
<th>Intercept</th>
<th>K(_SV) (psi(^{-1}))</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4</td>
<td>0.066</td>
<td>0.076</td>
<td>0.868</td>
<td>0.991</td>
</tr>
<tr>
<td>1:5</td>
<td>0.067</td>
<td>0.035</td>
<td>1.91</td>
<td>0.995</td>
</tr>
<tr>
<td>1:7</td>
<td>0.068</td>
<td>0.066</td>
<td>1.02</td>
<td>0.984</td>
</tr>
<tr>
<td>1:9</td>
<td>0.064</td>
<td>0.090</td>
<td>0.711</td>
<td>0.982</td>
</tr>
<tr>
<td>1:19</td>
<td>0.064</td>
<td>0.072</td>
<td>0.889</td>
<td>0.986</td>
</tr>
</tbody>
</table>

a oligomer:cross-linker, b intercept = A in equation (3-3), c slope = B in equation (3-3), d \(K_{SV} = (B/A)\) in equation (3-3)

Table 3-9: PtTFPP emission intensity area (\(\lambda = 630 - 670\) nm) values for increased mole ratios of cross-linker in PtTFPP/SPDMS on glass.

<table>
<thead>
<tr>
<th>Pressure (psi)</th>
<th>1:4(^a)</th>
<th>1:5(^a)</th>
<th>1:7(^a)</th>
<th>1:9(^a)</th>
<th>1:19(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1650438</td>
<td>12473164</td>
<td>2229603</td>
<td>1964753</td>
<td>2664233</td>
</tr>
<tr>
<td>2</td>
<td>260795</td>
<td>1225965</td>
<td>231994</td>
<td>148413</td>
<td>206711</td>
</tr>
<tr>
<td>4</td>
<td>151282</td>
<td>632750</td>
<td>119140</td>
<td>87189</td>
<td>122548</td>
</tr>
<tr>
<td>6</td>
<td>109394</td>
<td>433654</td>
<td>83082</td>
<td>68127</td>
<td>94833</td>
</tr>
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<td>8</td>
<td>85503</td>
<td>322693</td>
<td>64966</td>
<td>54246</td>
<td>73265</td>
</tr>
<tr>
<td>10</td>
<td>71324</td>
<td>279773</td>
<td>53875</td>
<td>47294</td>
<td>66277</td>
</tr>
<tr>
<td>14.7</td>
<td>54268</td>
<td>197662</td>
<td>42620</td>
<td>34567</td>
<td>45187</td>
</tr>
</tbody>
</table>

a oligomer:cross-linker

Microscopic fluorescence image analysis reveals that the sensor films' morphology changes with increased cross-linker mole ratio. Qualitative fluorescence microscope analysis of \(\mu m^2\) image regions for each sensor film unveils the details of the morphological changes. Figure 3-8 illustrates the fluorescence microscopic images (871 \(\mu m \times 690 \mu m\)) obtained with a 10X objective at 0.5 psi. Visual heterogeneity due to polymer dewetting (black spots) increases with mole ratio of cross-linker.
Figure 3-8: Qualitative microscopic fluorescence images (10X, 0.5 psi) for PtTFPP/SPDMS at five different mole ratios of cross-linker on glass. White scale bars are 153 μm long. A) 1:4, B) 1:5, C) 1:7, D) 1:9, E) 1:19 mole ratio of oligomer:cross-linker.

Increased mole ratios of cross-linker cause the sensor films to be increasingly polar and separate from the glass on which they were applied. In image D, small spots appear where the polymer is thinning, and in image E, the polymer exhibits areas of complete dewetting. While the polymer dewetting does not impact the macroscopic SV response, its impact on the spatial distribution of the microscopic SV response is quite dramatic.

Quantitative fluorescence microscopic image maps of the sensor films’ SV response to variation in $P_{atm}$ using the 10X objective were obtained to probe the effects of increased mole ratios of cross-linker on the microscopic intensity spatial distribution. Seven images at pressures ranging from 0.4 – 14.7 psi were obtained for each film. Figure 3-9 illustrates one representative region from each sensor film at 0.4 psi. The
image intensities were not scaled the same, and the maximum intensities for each image are listed in Table 3-10. The maximum intensity values are yellow and scale to dark blue for zero emission intensity in the images of Figure 3-9.

Table 3-10: Maximum fluorescence intensity values for 10X microscopic regions of PrTFPP/SPDMS on glass at five different mole ratios of cross-linker at 0.4 psi.

<table>
<thead>
<tr>
<th>Mole Ratio(^a)</th>
<th>Maximum Intensity (a.u.)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4</td>
<td>11812</td>
</tr>
<tr>
<td>1:5</td>
<td>6230</td>
</tr>
<tr>
<td>1:7</td>
<td>10070</td>
</tr>
<tr>
<td>1:9</td>
<td>17772</td>
</tr>
<tr>
<td>1:19</td>
<td>8073</td>
</tr>
</tbody>
</table>

\(^a\) oligomer:cross-linker, \(^b\) a.u. = arbitrary units

Figure 3-9: Quantitative microscopic fluorescence intensity images (10X, 0.4 psi) for PrTFPP/SPDMS on glass at five different mole ratios of cross-linker. White scale bars are 92 µm long. Intensity color scale bars are shown to the right of all images. A) 1:4, B) 1:5, C) 1:7, D) 1:9, E) 1:19 mole ratio oligomer:cross-linker.

The quantitative fluorescence images resemble the qualitative fluorescence images displayed in Figure 3-8. In Figure 3-9, image C displays the onset of polymer
dewetting (dark yellow/green circles). As the mole ratio of cross-linker increases, the dewetting spots increase in size. Image E exhibits the most substantial polymer dewetting and image heterogeneity (dark blue and red spots). In order to quantify the intensity changes for each image map, the intensity percent standard deviations were calculated as well as those for the remaining six intensity pressure images analyzed for each sensor film. The percent standard deviations are listed in Table 3-11.

<table>
<thead>
<tr>
<th>Mole Ratio</th>
<th>0.4 psi</th>
<th>2 psi</th>
<th>4 psi</th>
<th>6 psi</th>
<th>8 psi</th>
<th>10 psi</th>
<th>14.7 psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4</td>
<td>3.48</td>
<td>3.65</td>
<td>3.59</td>
<td>3.80</td>
<td>3.93</td>
<td>4.08</td>
<td>4.08</td>
</tr>
<tr>
<td>1:5</td>
<td>4.33</td>
<td>4.04</td>
<td>3.78</td>
<td>3.39</td>
<td>3.04</td>
<td>2.56</td>
<td>2.28</td>
</tr>
<tr>
<td>1:7</td>
<td>2.13</td>
<td>2.25</td>
<td>2.38</td>
<td>2.60</td>
<td>2.87</td>
<td>2.93</td>
<td>3.25</td>
</tr>
<tr>
<td>1:9</td>
<td>3.41</td>
<td>3.10</td>
<td>2.60</td>
<td>2.52</td>
<td>3.33</td>
<td>2.65</td>
<td>2.86</td>
</tr>
<tr>
<td>1:19</td>
<td>17.5</td>
<td>16.0</td>
<td>14.2</td>
<td>13.0</td>
<td>11.6</td>
<td>10.9</td>
<td>-</td>
</tr>
</tbody>
</table>

\( \sigma_1 \% = \sigma/I_{avg} \times 100 \% \),  
\( b \) oligomer:cross-linker

Not surprising, only the 1:19 mole ratio sensor film exhibits increased deviations in the intensity values. This is naturally due to the large dark areas created by polymer dewetting. The remaining sensor films experience small deviations ca. 2.5 % of which belong to excitation field fluctuations.

To visually understand the intensity distributions, intensity distribution curves for the intensity values at each pressure of the 1:4 and 1:19 mole ratio PtTFPP/SPDMS sensor films are shown in Figure 3-10.
Figure 3-10: Intensity distribution curves for intensities obtained with a 10X objective at seven pressures for A) 1:4 mole ratio of oligomer:cross-linker in PtTFPP/SPDMS on glass and B) 1:19 mole ratio of oligomer:cross-linker in PtTFPP/SPDMS on glass.

The distribution curves in image B overlap greatly between 6 to 14.7 psi, and the intensity values are not as large as those for image A. The peaks in image A, overlap slightly at the bases between 6 and 10 psi and exhibit a jagged peak shape for each pressure. For image B, the curve overlap and broadening is due to areas in the pressure intensity images where the polymer is dewetting, and considerable low intensity values are registering. The trends in Figure 3-10 correlate with the increased percent standard deviation data in Table 3-12. Regardless of the curve overlap in images A and B, the curves are still representative of distinct intensities and a clear indication as to why even polymer dewetting has no effect on the macroscopic SV plot (Figure 3-7).

The series of intensity images in Figure 3-9 afforded five corresponding microscopic quantitative $K_{SV}(x,y)$ image maps illustrated in Figure 3-11. The colors of the image maps are not scaled the same. The maximum $K_{SV}$ value for each image is listed in Table 3-12. The maximum $K_{SV}$ values are represented by yellow and scale to dark blue for no SV response in the images of Figure 3-11.
Table 3-12: Maximum $K_{SV}$ values for 10X microscopic regions for PtTFPP/SPDMS on glass at five different mole ratios of cross-linker.

<table>
<thead>
<tr>
<th>Mole Ratio$^a$</th>
<th>Maximum $K_{SV}$ (psi$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:4</td>
<td>0.780</td>
</tr>
<tr>
<td>1:5</td>
<td>1.33</td>
</tr>
<tr>
<td>1:7</td>
<td>1.07</td>
</tr>
<tr>
<td>1:9</td>
<td>0.870</td>
</tr>
<tr>
<td>1:19</td>
<td>0.860</td>
</tr>
</tbody>
</table>

$^a$ oligomer:cross-linker, $^b$ $K_{SV} = (B/A)$ in equation (3-3)

Figure 3-11: Quantitative microscopic $K_{SV}(x,y)$ image maps for PtTFPP/SPDMS on glass at five different mole ratios of cross-linker. White scale bars are 92 $\mu$m long. $K_{SV}$ color scale bars are shown to the right of all images. A) 1:4, B) 1:5, C) 1:7, D) 1:9, E) 1:19 mole ratio oligomer:cross-linker.

The $K_{SV}$ image maps correlate with the image trends depicted in Figure 3-9. Regions of polymer binder dewetting experience low intensity values (blue spots) and low $K_{SV}$ values (blue spots). Images D and E illustrate the areas of low intensity arising from polymer dewetting void SV response. In image E, the red ovals near the blue spots are erroneous $K_{SV}$ data due to image shifting during analysis.
The average $K_{SV}(x,y)$ values were determined for each image, and the percent standard deviations are listed in Tables 3-13a and 3-13b. These numbers quantitatively demonstrate the effect of polymer dewetting on SV response and distribution for a given region. The $K_{SV}^{avg}$ values are larger than the macroscopic $K_{SV}$ values in Table 3-9. As was explained for the previous series of PtTFPP films, any areas of homogeneity or heterogeneity in the sensor film are enlarged for microscopic image maps. Therefore it is possible to obtain high $K_{SV}$ values depending on the image field (homogeneous versus polymer dewetting). A good example of this is seen for the 1:19 mole ratio PtTFPP/SPDMS film. The $K_{SV}^{avg}$ values fluctuate due to imaging of areas with concentrated polymer dewetting and low $K_{SV}^{avg}$ values and areas with little to moderate polymer dewetting and high $K_{SV}^{avg}$ values.

Table 3-13a: Microscopic SV analysis of five 10X regions for PtTFPP/SPDMS on glass at five different mole ratios of cross-linker.

<table>
<thead>
<tr>
<th>Mole Ratio</th>
<th>1:4</th>
<th>1:5</th>
<th>1:7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>$K_{SV}^{avg}$ (psi $^{-1}$)</td>
<td>$\sigma_{K_{SV}}$</td>
<td>$%_b$</td>
</tr>
<tr>
<td>1</td>
<td>0.576</td>
<td>3.47</td>
<td>0.699</td>
</tr>
<tr>
<td>2</td>
<td>0.579</td>
<td>3.28</td>
<td>0.652</td>
</tr>
<tr>
<td>3</td>
<td>0.567</td>
<td>3.17</td>
<td>0.659</td>
</tr>
<tr>
<td>4</td>
<td>0.594</td>
<td>2.86</td>
<td>0.717</td>
</tr>
<tr>
<td>5</td>
<td>0.607</td>
<td>3.46</td>
<td>0.676</td>
</tr>
</tbody>
</table>

$^a$ oligomer:cross-linker, $^b$ $\sigma_{K_{SV}} \% = \frac{\sigma_{K_{SV}}}{K_{SV}^{avg}} \times 100\%$
Table 3-13b: Microscopic SV analysis of five 10X regions for PtTFPP/SPDMS on glass at five different mole ratios of cross-linker.

<table>
<thead>
<tr>
<th>Mole Ratio</th>
<th>1:9</th>
<th>1:19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>(K^{\text{avg}}_{\text{SV}}) (psi(^{-1}))</td>
<td>(\sigma_{K_{\text{SV}}}) %</td>
</tr>
<tr>
<td>1</td>
<td>0.630</td>
<td>8.26</td>
</tr>
<tr>
<td>2</td>
<td>0.672</td>
<td>4.46</td>
</tr>
<tr>
<td>3</td>
<td>0.644</td>
<td>4.50</td>
</tr>
<tr>
<td>4</td>
<td>0.694</td>
<td>3.75</td>
</tr>
<tr>
<td>5</td>
<td>0.702</td>
<td>12.3</td>
</tr>
</tbody>
</table>

The effects of increased mole ratio of cross-linker in PtTFPP/SPDMS sensor films were also analyzed microscopically utilizing a 40X objective. Five regions of each sensor film were analyzed. Each region produced seven pressure image maps and a \(K_{\text{SV}}(x,y)\) image map with accompanying statistical data. \(K_{\text{SV}}(x,y)\) data for five regions are listed in Tables 3-14a and 3-14b. As is expected, the \(K^{\text{avg}}_{\text{SV}}\) values in Table 3-14a and 3-14b are higher than the values in Tables 3-13a and 3-31b. Again, this is most likely due to greater magnification of the image areas creating more spatially homogeneous images.

Table 3-14a: Microscopic SV analysis of five 40X regions for PtTFPP/SPDMS on glass at five different mole ratios of cross-linker.

<table>
<thead>
<tr>
<th>Mole Ratio(^a)</th>
<th>1:4</th>
<th>1:5</th>
<th>1:7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>(K^{\text{avg}}_{\text{SV}}) (psi(^{-1}))</td>
<td>(\sigma_{K_{\text{SV}}}) % (^b)</td>
<td>(K^{\text{avg}}_{\text{SV}}) (psi(^{-1}))</td>
</tr>
<tr>
<td>1</td>
<td>0.854</td>
<td>6.67</td>
<td>1.24</td>
</tr>
<tr>
<td>2</td>
<td>1.54</td>
<td>3.70</td>
<td>1.27</td>
</tr>
<tr>
<td>3</td>
<td>1.37</td>
<td>3.21</td>
<td>1.22</td>
</tr>
<tr>
<td>4</td>
<td>1.47</td>
<td>4.15</td>
<td>1.24</td>
</tr>
<tr>
<td>5</td>
<td>1.62</td>
<td>4.88</td>
<td>1.14</td>
</tr>
</tbody>
</table>

\(^a\) oligomer:cross-linker, \(^b\) \(\sigma_{K_{\text{SV}}}\) % = \(\sigma_{K_{\text{SV}}} / K^{\text{avg}}_{\text{SV}} \times 100\%\)
Table 3-14b: Microscopic SV analysis of five 40X regions for PtTFPP/SPDMS on glass at five different mole ratios of cross-linker.

<table>
<thead>
<tr>
<th>Mole Ratio</th>
<th>( K_{sv}^{avg} (\text{psi}^{-1}) )</th>
<th>( \sigma_{sv} )</th>
<th>( K_{sv}^{avg} (\text{psi}^{-1}) )</th>
<th>( \sigma_{sv} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.986</td>
<td>9.94</td>
<td>1.30</td>
<td>31.6</td>
</tr>
<tr>
<td>2</td>
<td>1.18</td>
<td>7.80</td>
<td>1.10</td>
<td>38.5</td>
</tr>
<tr>
<td>3</td>
<td>1.28</td>
<td>9.06</td>
<td>1.27</td>
<td>18.5</td>
</tr>
<tr>
<td>4</td>
<td>1.26</td>
<td>7.78</td>
<td>1.31</td>
<td>22.3</td>
</tr>
<tr>
<td>5</td>
<td>0.915</td>
<td>2.62</td>
<td>1.45</td>
<td>27.6</td>
</tr>
</tbody>
</table>

The increased mole ratios of cross-linker in the PtTFPP/SPDMS sensor films pose no effect to the macroscopic SV response and analysis in Figure 3-7 and Table 3-8.

Dewetting of the polymer binder detected at the microscopic level affects the microscopic SV response. The SV responses are strong but plagued with large percent deviations. Even with polymer dewetting and definite pixel-to-pixel \( K_{sv}(x,y) \) heterogeneity, the SV response from the background field is still substantial enough to compensate for the cross-linker’s negative emission effects as seen by the intensity distribution curves in Figure 3-10.

**Fluorescence Microscopy of Ru(II) \( \alpha \)-diimine Complexes in SPDMS**

A series of Ru(II) \( \alpha \)-diimine complexes with different diimine ligands and/or counter ions were separately dispersed in SPDMS polymer binder. Figure 3-12 illustrates the Ru(II) metal complexes employed. The macroscopic Stern-Volmer (SV) plots for the series of Ru(II) \( \alpha \)-diimine complexes are displayed in Figure 3-13.
**Metal Complexes**

![Metal Complexes Diagram]

**Counter Ions**

\[
\begin{align*}
\text{Ru(II)} & \quad \text{a-diimine complexes.} \\
& \\
& \\
& \\
& \\
& \\
& \\
\end{align*}
\]

- \[\text{Ru(dpp)}_{2}^2\]

4,7-diphenyl-1,10-phenanthroline

- \[\text{Ru(dpp)}_{2}^2\]

3,8-di-n-butyl-4,7-di(tolylacetylenyl)-1,10-phenanthroline

**Figure 3-12:** Ru(II) α-diimine complexes.

**Figure 3-13:** Macroscopic SV plots of Ru(II) α-diimine complexes dispersed in SPDMS binder on glass. \(A_{\text{REF}}\): area between 600 - 640 nm at 14.7 psi.
There are varying degrees of SV response to oxygen concentration within the series. The [Ru(dpp)\textsubscript{3}](B(Ph\textsubscript{F}\textsubscript{5})\textsubscript{4})\textsubscript{2} sensor film exhibits the largest quenching response with a $K_{SV}$ value of 0.128 psi\textsuperscript{-1} ($r^2 = 0.972$). The luminescence intensity decreases by approximately than a factor of three when $P_{air}$ increases from 0 – 14.7 psi. Conversely, the [Ru(dpp)\textsubscript{3}](BPh\textsubscript{4})\textsubscript{2} sensor film, which is visually heterogeneous, does not respond to variation in $P_{air}$. Its SV plot in Figure 3-13 is simply a scattered noise plot. The macroscopic SV response data for the other Ru(II) \textalpha-diimine complexes plotted in Figure 3-13 are listed in Table 3-15. The emission area ($\lambda = 600 – 640$ nm) for the Ru(II) \textalpha-diimine complexes at 0.1 psi (most intense luminescence) are listed in Table 3-16. The molar concentration of Ru(II) \textalpha-diimine complex in each sensor film is listed in Table 3-17.

Table 3-15: Macroscopic SV response data for Ru(II) \textalpha-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Luminophore</th>
<th>Slope (psi\textsuperscript{-1})\textsuperscript{a}</th>
<th>Intercept\textsuperscript{b}</th>
<th>$K_{SV}$ (psi\textsuperscript{-1})\textsuperscript{c}</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(dpp)\textsubscript{3}]Cl\textsubscript{2}</td>
<td>0.013</td>
<td>0.820</td>
<td>0.016</td>
<td>0.968</td>
</tr>
<tr>
<td><a href="PF%5Ctextsubscript%7B6%7D">Ru(dpp)\textsubscript{3}</a>\textsubscript{2}</td>
<td>0.029</td>
<td>0.604</td>
<td>0.048</td>
<td>0.974</td>
</tr>
<tr>
<td><a href="BPh%5Ctextsubscript%7B4%7D">Ru(dpp)\textsubscript{3}</a>\textsubscript{2}</td>
<td>0.003</td>
<td>1.000</td>
<td>0.003</td>
<td>0.108</td>
</tr>
<tr>
<td><a href="B(Ph(CF%5Ctextsubscript%7B3%7D)%5Ctextsubscript%7B2%7D)%5Ctextsubscript%7B4%7D">Ru(dpp)\textsubscript{3}</a>\textsubscript{2}</td>
<td>0.031</td>
<td>0.595</td>
<td>0.052</td>
<td>0.943</td>
</tr>
<tr>
<td><a href="PF%5Ctextsubscript%7B6%7D">Ru(dbdtap)\textsubscript{3}</a>\textsubscript{2}</td>
<td>0.039</td>
<td>0.460</td>
<td>0.085</td>
<td>0.987</td>
</tr>
<tr>
<td><a href="B(PhF%5Ctextsubscript%7B5%7D)%5Ctextsubscript%7B4%7D">Ru(dpp)\textsubscript{3}</a>\textsubscript{2}</td>
<td>0.047</td>
<td>0.367</td>
<td>0.128</td>
<td>0.972</td>
</tr>
</tbody>
</table>

\textsuperscript{a} intercept = A in equation (3-3), \textsuperscript{b} slope = B in equation (3-3), \textsuperscript{c} $K_{SV} = (B/A)$ in equation (3-3)
Table 3-16: Ru(II) α-diimine complex emission intensity area (λ = 600 – 640 nm) values at 0.1 psi for Ru(II) α-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Luminophore</th>
<th>Emission Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(dpp)₃]Cl₂</td>
<td>800968</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Ru(dpp)₃</a>₂</td>
<td>157832</td>
</tr>
<tr>
<td><a href="BPh%E2%82%84">Ru(dpp)₃</a>₂</td>
<td>24978</td>
</tr>
<tr>
<td><a href="B(Ph(CF%E2%82%83)%E2%82%82)%E2%82%84">Ru(dpp)₃</a>₂</td>
<td>89029</td>
</tr>
<tr>
<td><a href="B(PhF%E2%82%85)%E2%82%84">Ru(dpp)₃</a>₂</td>
<td>764384</td>
</tr>
<tr>
<td><a href="B(PhF%E2%82%85)%E2%82%84">Ru(dpp)₃</a>₂</td>
<td>187422</td>
</tr>
</tbody>
</table>

Table 3-17: Ru(II) α-diimine complex molar concentration (mM) for Ru(II) α-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Luminophore</th>
<th>mM⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(dpp)₃]Cl₂</td>
<td>1.71</td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Ru(dpp)₃</a>₂</td>
<td>1.44</td>
</tr>
<tr>
<td><a href="BPh%E2%82%84">Ru(dpp)₃</a>₂</td>
<td>1.15</td>
</tr>
<tr>
<td><a href="B(Ph(CF%E2%82%83)%E2%82%82)%E2%82%84">Ru(dpp)₃</a>₂</td>
<td>0.71</td>
</tr>
<tr>
<td><a href="B(PhF%E2%82%85)%E2%82%84">Ru(dpp)₃</a>₂</td>
<td>1.07</td>
</tr>
<tr>
<td><a href="B(PhF%E2%82%85)%E2%82%84">Ru(dpp)₃</a>₂</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Ru(II) α-diimine complex concentration in 500 mg of SPDMS polymer binder

The varied quenching responses of the Ru(II) α-diimine complexes are intriguing. If the responses are a consequence of sensor distribution creating unique and distinct quenching microenvironments, then the origins of the responses are better understood by imaging the films’ microscopic fluorescence emission distribution. Qualitative fluorescence microscopy images (871 µm x 690 µm) of the Ru(II) α-diimine complexes dispersed in SPDMS binder obtained at 0.5 psi with a 10X objective are displayed in Figure 3-14. All images illustrate a varied yet striking “star-field appearance”—there are very bright fluorescent spots with sizes ranging from 1 - 10 µm. The bright spots are superimposed on background fields of varying fluorescence intensity. Quite clearly the Ru(II) α-diimine complexes are not evenly dispersed within the SPDMS binder. Indeed,
it is possible that the luminophores are present in some regions as microcrystals or in a strongly aggregated state. How these microenvironments responded to oxygen concentration provides further evidence for the varied SV responses plotted in Figure 3-13.

![Figure 3-14: Qualitative microscopic fluorescence images (10X, 0.5 psi) for Ru(II) α-diimine complexes dispersed in SPDMS binder on glass. White scale bars are 153 μm long. A) [Ru(dpp)₃]Cl₂, B) [Ru(dpp)₃](PF₆)₂, C) [Ru(dpp)₃](BPh₄)₂, D) [Ru(dpp)₃](B(Ph(CF₃)₂)₄)₂, E) [Ru(dbdtap)₃](PF₆)₂, F) [Ru(dpp)₃](B(PhF₅)₄)₂.](image)

Images C, D, and F exhibit the most homogeneous distributions in intensity with very few discrete bright spots as compared to images A, B, and E. Although, looking at Table 3-15, the sensor films which exhibit the best SV response are [Ru(dpp)₃](B(Ph(CF₃)₂)₄)₂ and [Ru(dpp)₃](B(PhF₅)₄)₂, and the worst response is from [Ru(dpp)₃](BPh₄)₂.

When the bright field images of the Ru(II) α-diimine complexes are compared, it can be seen that the bright spots in the fluorescence image A of Figure 3-15 compare well
with the dark spots in image D. The bright field image is obtained with a 10X objective and transmission illumination from a Tungsten 100 W bulb filtered through a BG-7 blue filter shown on the surface of the sensor film. The images in Figure 3-15 are 871 µm x 690 µm in size. If the fluorescent microcrystallites in image A are Ru(II) α-diimine complexes, then they should absorb the blue light in the bright-field mode and appear as dark spots. This is precisely the case. Comparing the series of fluorescence and bright-field images, the [Ru(dpp)₃]Cl₂ sensor film is clearly the most populated with fluorescent microcrystallites. The [Ru(dpp)₃](B(Ph(CF₃)₂)₄)₂ sensor film shows less microcrystallite formation, and the [Ru(dpp)₃](B(PhF₅)₄)₂ is the best sensor film yet. Clearly, simple imaging of the sensor films’ fluorescence morphology starts to give an indication as to why the sensor films respond the way they do on the macroscopic level.

Figure 3-15: Qualitative microscopic fluorescence (A-C) and bright-field (D-F) images (10X, 14.7 psi) for Ru(II) α-diimine complexes dispersed in SPDMS binder on glass. White scale bars are 153 µm long. A and D) [Ru(dpp)₃]Cl₂, B and E) [Ru(dpp)₃](B(Ph(CF₃)₂)₄)₂, and C and F) [Ru(dpp)₃](B(PhF₅)₄)₂.
Overall, the [Ru(dpp)₃]Cl₂ sensor film is the most heterogeneous image (fluorescence and bright-field) with many star-like areas. Not surprising, it produced the most intense emission on the macroscopic level but also the near lowest SV response. Counter to this is the [Ru(dpp)₃](BPh₄)₂ sensor film which is visually heterogeneous. It produced a nearly homogeneous weakly emissive intensity response in Figure 3-14 and a corresponding low macroscopic $K_{SV}$ value in Table 3-15. The remaining Ru(II) $\alpha$-diimine complexes’ intensity and SV responses are complicated yet interesting. Several factors are involved in understanding their characteristic responses. Depending on their concentration (mM) and solubility in the SPDMS binder, high or low emission intensity and high or low $K_{SV}$ values were obtained. For example, the [Ru(dpp)₃](B(PhF₅)₄)₂ sensor film was the least concentrated film. It produced a homogeneous fluorescence image in Figures 3-14 and 3-15 indicating its excellent solubility in the polymer binder with high macroscopic emission intensity and $K_{SV}$ values in Tables 3-16 and 3-15, respectively. The other Ru(II) $\alpha$-diimine complexes produced emission intensity and SV responses in accord with their concentrations and degree of solubility in the SPDMS polymer binder. Therefore, further analysis of such effects needs to be probed at the microscopic level.

The effects of concentration and inhomogeneous distribution of Ru(II) $\alpha$-diimine complexes in SPDMS binder on the spatial intensity distribution and subsequent SV response is investigated by taking a series of quantitative image maps of the sensors’ responses to variation in $P_{air}$ using the 10X objective. For all of the sensor films, the same CCD integration times and filter combinations were used. Five 436 $\mu$m x 345 $\mu$m regions of each Ru(II) $\alpha$-diimine sensor film were interrogated at seven pressures from
0.4 - 14.7 psi. One representative intensity image at 0.4 psi for each Ru(II) α-diimine sensor film is illustrated in Figure 3-16. The colors for each image were not scaled the same, and the maximum intensity value for each image is listed in Table 3-18. The maximum intensity values are yellow and scale to dark blue for zero emission in the images of Figure 3-16.

Table 3-18: Maximum fluorescence intensity values for 10X microscopic regions of Ru(II) α-diimine complexes dispersed in SPDMS binder on glass at 0.4 psi.

| Luminophore                          | Maximum Intensity (a.u.)
|--------------------------------------|--------------------------
| [Ru(dpp)₃]Cl₂                        | 13400                    
| [Ru(dpp)₃](PF₆)₂                     | 3955                     
| [Ru(dpp)₃](BPH₄)₂                    | 245                      
| [Ru(dpp)₃](B(Ph(CF₃)₂)₄)₂           | 2751                     
| [Ru(dbdtap)₃](PF₆)₂                  | 10645                    

Table 3-18: Maximum fluorescence intensity values for 10X microscopic regions of Ru(II) α-diimine complexes dispersed in SPDMS binder on glass at 0.4 psi.

\[ a \text{ u.} = \text{arbitrary units} \]

Figure 3-16: Quantitative microscopic fluorescence intensity images (10X, 0.4 psi) for Ru(II) α-diimine complexes dispersed in SPDMS binder on glass. White scale bars are 92 μm long. Intensity color scale bars are shown to the right of all images. A) [Ru(dpp)₃]Cl₂, B) [Ru(dpp)₃](PF₆)₂, C) [Ru(dpp)₃](BPH₄)₂, D) [Ru(dpp)₃](B(Ph(CF₃)₂)₄)₂, E) [Ru(dbdtap)₃](PF₆)₂, F) [Ru(dpp)₃](B(PhF₅)₄).
The quantitative intensity images are fairly consistent with the qualitative fluorescence images displayed in Figure 3-14. Clearly, there are varying distributions for the Ru(II) α-diimine complexes in the polymer binder. Images A, D, and E in Figure 3-16 illustrate a star-speckled image field while images B, C, and F possess less structured luminescence.

Quantification of the intensity distributions is achieved by calculating the percent standard deviations in intensity (σ_1 %) for the intensity pressure images of Figure 3-16 and the remaining six intensity pressure images analyzed for each Ru(II) α-diimine sensor film. The percent standard deviations are listed in Table 3-19.

Table 3-19: Percent standard deviation (σ_1 %) in intensities at seven pressures for microscopic regions of Ru(II) α-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Luminophore</th>
<th>0.4 psi</th>
<th>2 psi</th>
<th>4 psi</th>
<th>6 psi</th>
<th>8 psi</th>
<th>10 psi</th>
<th>14.7 psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(dpp)_3]Cl_2</td>
<td>14.4</td>
<td>10.8</td>
<td>7.73</td>
<td>6.49</td>
<td>6.32</td>
<td>6.01</td>
<td>5.14</td>
</tr>
<tr>
<td><a href="PF_6">Ru(dpp)_3</a>_2</td>
<td>6.60</td>
<td>6.73</td>
<td>7.01</td>
<td>7.38</td>
<td>6.86</td>
<td>6.51</td>
<td>6.45</td>
</tr>
<tr>
<td><a href="BPh_4">Ru(dpp)_3</a>_2</td>
<td>10.8</td>
<td>14.0</td>
<td>18.2</td>
<td>20.3</td>
<td>22.8</td>
<td>25.5</td>
<td>19.6</td>
</tr>
<tr>
<td><a href="B(Ph(CF_3)_2)_4">Ru(dpp)_3</a>_2</td>
<td>14.6</td>
<td>10.5</td>
<td>8.89</td>
<td>7.65</td>
<td>6.27</td>
<td>5.24</td>
<td>3.99</td>
</tr>
<tr>
<td><a href="PF_6">Ru(dbdtap)_3</a>_2</td>
<td>14.5</td>
<td>17.1</td>
<td>13.9</td>
<td>12.2</td>
<td>11.4</td>
<td>10.6</td>
<td>10.9</td>
</tr>
<tr>
<td><a href="B(PhF_5)_4">Ru(dpp)_3</a>_2</td>
<td>8.60</td>
<td>7.77</td>
<td>7.82</td>
<td>9.30</td>
<td>8.77</td>
<td>6.96</td>
<td>-</td>
</tr>
</tbody>
</table>

σ_1 % = σ/I_avg x 100 %

In correlation to the images in Figure 3-16, the star-speckled films [Ru(dpp)_3]Cl_2, [Ru(dpp)_3](B(Ph(CF_3)_2)_4)_2, and [Ru(dbdtap)_3](PF_6)_2 also exhibit the largest intensity percent standard deviations. The [Ru(dpp)_3](BPh_4)_2 film which is visually heterogeneous demonstrates significant deviation as well.
Rather than look at the numbers, it is easier to visualize these distributions and their true significance by plotting the intensity distributions at each pressure for each sensor film. The curves are plotted in Figure 3-17. The most striking attribute of the curves is that they overlap - exhibiting no intensity distribution. The Ru(II) \( \alpha \)-diimine sensor films' intensity distribution curves exhibit varying degrees of overlap due to luminescent regions in the films that are not homogeneously quenched with changes in \( P_{\text{air}} \). Upon further inspection, some distribution curves exhibit a bi-modal distribution pattern which is indicative of discrete microenvironments with varied emission response.

For images A, D, and E, which exhibit the greatest percent deviation, the distribution curves are eclipsing one another. The \([\text{Ru(dpp)}_3]\text{Cl}_2\) film even displays a distinct bimodal distribution at higher pressures. Clearly there are discrete luminescent species for this sensor film, and this is the cause for its low macroscopic \( K_{SV} \) values in Table 3-15. Not surprising, the \([\text{Ru(dpp)}_3](\text{B(PhF}_5)_4)_2\) film which exhibits the best macroscopic \( K_{SV} \) value and low intensity percent standard deviations also experiences the best distribution curves with the least amount of nearest neighbor overlap over the widest intensity value range for the series of sensor films (image F).
Figure 3-17: Intensity distribution curves for intensities obtained with a 10X objective at seven pressures for Ru(II) \(\alpha\)-diimine complexes dispersed in SPDMS binder on glass. A) \([\text{Ru}(dpp)_3]\text{Cl}_2\), B) \([\text{Ru}(dpp)_3](\text{PF}_6)_2\), C) \([\text{Ru}(dpp)_3]\text{(BPh}_{4})_2\), D) \([\text{Ru}(dpp)_3]\text{(B(Ph(CF}_{3})_{2})_2)\), E) \([\text{Ru}(dbdtap)_3](\text{PF}_6)_2\), F) \([\text{Ru}(dpp)_3]\text{(B(PhF}_5)_{2})_2\).

The series of intensity images in Figure 3-16 afforded six corresponding microscopic quantitative \(K_{SV}(x,y)\) image maps displayed in Figure 3-18. The image maps are not scaled the same, and the maximum \(K_{SV}\) value for each sensor film is listed.
in Table 3-20. The maximum $K_{SV}$ values are yellow and scale to dark blue for no SV response in the images of Figure 3-18.

Table 3-20: Maximum $K_{SV}$ values for 10X microscopic regions of Ru(II) α-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Luminophore</th>
<th>Maximum $K_{SV}$ (psi)(^{-1})(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(dpp)(_3)]Cl(_2)</td>
<td>0.082</td>
</tr>
<tr>
<td><a href="PF(_6)">Ru(dpp)(_3)</a>(_2)</td>
<td>0.045</td>
</tr>
<tr>
<td><a href="BPh(_4)">Ru(dpp)(_3)</a>(_2)</td>
<td>0.360</td>
</tr>
<tr>
<td><a href="B(Ph(CF(_3))(_2))(_4)">Ru(dpp)(_3)</a>(_2)</td>
<td>0.110</td>
</tr>
<tr>
<td><a href="PF(_6)">Ru(dbdtap)(_3)</a>(_2)</td>
<td>0.135</td>
</tr>
<tr>
<td><a href="B(PhF(_5))(_4)">Ru(dpp)(_3)</a>(_2)</td>
<td>0.310</td>
</tr>
</tbody>
</table>

\(^a\) $K_{SV} = (B/A)$ in equation (3-3)

Figure 3-18: Quantitative microscopic $K_{SV}(x,y)$ image maps of Ru(II) α-diimine complexes dispersed in SPDMS binder on glass. White scale bars are 92 μm long. $K_{SV}$ color scale bars are shown to the right of all images. A) [Ru(dpp)\(_3\)]Cl\(_2\), B) [Ru(dpp)\(_3\)](PF\(_6\))\(_2\), C) [Ru(dpp)\(_3\)](BPh\(_4\))\(_2\), D) [Ru(dpp)\(_3\)](B(Ph(CF\(_3\))\(_2\))\(_4\))\(_2\), E) [Ru(dbdtap)\(_3\)](PF\(_6\))\(_2\), F) [Ru(dpp)\(_3\)](B(PhF\(_5\))\(_4\))\(_2\).

The high and low $K_{SV}$ values in Figure 3-18 correspond to the regions of high and low intensity in the images of Figure 3-16. One exception to this are the broad intensity
bands in image B of Figure 3-16 which are much narrower in Figure 3-18. At higher pressures, only portions of the high intensity bands in image B of Figure 3-16 are quenched. Therefore, the bright $K_{SV}$ value bands (yellow and green areas) in image B of Figure 3-18 appear narrower divided by regions of low SV response (red and blue areas).

The percent standard deviations in $K_{SV}(x,y)$ for each image are listed in Tables 3-21a, 3-21b, and 3-21c. The microscopic SV data correlate fairly well with the macroscopic SV data in Table 3-15. The macroscopic data comprise higher $K_{SV}$ values often doubling the microscopic $K_{SV}^{avg}(x,y)$ values. It is important to remember that the $K_{SV}$ data in Tables 3-21a, 3-21b, and 3-21c are average values.

Table 3-21a: Microscopic SV analysis of five 10X regions for Ru(II) α-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Region</th>
<th>$K_{SV}^{avg}$ (psi$^{-1}$)</th>
<th>$\sigma_{K_{SV}}$ %</th>
<th>$K_{SV}^{avg}$ (psi$^{-1}$)</th>
<th>$\sigma_{K_{SV}}$ %</th>
<th>$K_{SV}^{avg}$ (psi$^{-1}$)</th>
<th>$\sigma_{K_{SV}}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.007</td>
<td>71.4</td>
<td>0.024</td>
<td>12.5</td>
<td>0.037</td>
<td>29.7</td>
</tr>
<tr>
<td>2</td>
<td>0.008</td>
<td>62.5</td>
<td>0.025</td>
<td>8.00</td>
<td>0.072</td>
<td>22.2</td>
</tr>
<tr>
<td>3</td>
<td>0.007</td>
<td>71.4</td>
<td>0.023</td>
<td>13.0</td>
<td>0.081</td>
<td>30.9</td>
</tr>
<tr>
<td>4</td>
<td>0.008</td>
<td>87.5</td>
<td>0.023</td>
<td>17.4</td>
<td>0.051</td>
<td>27.5</td>
</tr>
<tr>
<td>5</td>
<td>0.008</td>
<td>75.0</td>
<td>0.024</td>
<td>8.33</td>
<td>0.073</td>
<td>27.4</td>
</tr>
</tbody>
</table>

$^{a} \sigma_{K_{SV}} \% = \frac{\sigma_{K_{SV}^{avg}}}{K_{SV}^{avg}} \times 100 \%$

Table 3-21b: Microscopic SV analysis of five 10X regions for Ru(II) α-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Region</th>
<th>$K_{SV}^{avg}$ (psi$^{-1}$)</th>
<th>$\sigma_{K_{SV}}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.036</td>
<td>22.2</td>
</tr>
<tr>
<td>2</td>
<td>0.034</td>
<td>23.5</td>
</tr>
<tr>
<td>3</td>
<td>0.033</td>
<td>30.3</td>
</tr>
<tr>
<td>4</td>
<td>0.034</td>
<td>29.1</td>
</tr>
<tr>
<td>5</td>
<td>0.033</td>
<td>27.3</td>
</tr>
</tbody>
</table>
Table 3-21c: Microscopic SV analysis of five 10 X regions for Ru(II) α-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Region</th>
<th>$K_{SV}^{av}$ (psi⁻¹)</th>
<th>$\sigma_{K_{SV}}$%</th>
<th>$K_{SV}^{av}$ (psi⁻¹)</th>
<th>$\sigma_{K_{SV}}$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.022</td>
<td>45.4</td>
<td>0.170</td>
<td>17.6</td>
</tr>
<tr>
<td>2</td>
<td>0.037</td>
<td>32.4</td>
<td>0.152</td>
<td>17.1</td>
</tr>
<tr>
<td>3</td>
<td>0.036</td>
<td>44.4</td>
<td>0.169</td>
<td>11.8</td>
</tr>
<tr>
<td>4</td>
<td>0.026</td>
<td>42.3</td>
<td>0.153</td>
<td>13.7</td>
</tr>
<tr>
<td>5</td>
<td>0.048</td>
<td>35.4</td>
<td>0.167</td>
<td>11.4</td>
</tr>
</tbody>
</table>

Since the $K_{SV}(x,y)$ values listed in Tables 3-21a, 3-21b and 3-21c are average values, it is beneficial to quantify the values by looking at $K_{SV}^{av}(x,y)$ values for discrete regions within the $K_{SV}(x,y)$ image maps for each Ru(II) α-diimine film in Figure 3-19. Tables 3-22a and 3-22b are lists of the discrete $K_{SV}^{av}(x,y)$ values obtained for the boxes outlined in the images. The white boxes are an approximation of the area of $K_{SV}(x,y)$ values analyzed. As can be seen, the $K_{SV}^{av}(x,y)$ values do vary greatly for discrete regions within a single image. Therefore, the $K_{SV}^{av}(x,y)$ values listed in Tables 3-21a, 3-21b, and 3-21c are plausible representations of the sensor films’ $K_{SV}^{av}(x,y)$ values and respective standard deviations.
Figure 3-19: Analysis of discrete regions (white boxes) in quantitative microscopic $\kappa_{SV}(x,y)$ image maps of Ru(II) $\alpha$-diimine complexes dispersed in SPDMS binder on glass. White scale bars are 92 $\mu$m long. $\kappa_{SV}$ color scale bars are shown to the right of all images. A) $[\text{Ru(dpp)}_3]\text{Cl}_2$, B) $[\text{Ru(dpp)}_3](\text{PF}_6)_2$, C) $[\text{Ru(dpp)}_3](\text{BPh}_4)_2$, D) $[\text{Ru(dpp)}_3](\text{B(Ph(CF}_3)_2)_4)_2$, E) $[\text{Ru(dbdtap)}_3](\text{PF}_6)_2$, F) $[\text{Ru(dpp)}_3](\text{B(PhF}_5)_4)_2$.

Table 3-22a: Discrete $\kappa_{SV}^{avg}(x,y)$ values for three regions outlined in 10X microscopic $\kappa_{SV}(x,y)$ image maps of Ru(II) $\alpha$-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Region</th>
<th>$\kappa_{SV}^{avg}(\text{Cl}_2)$ (psi$^{-1}$)</th>
<th>$\kappa_{SV}^{avg}(\text{PF}_6)_2$ (psi$^{-1}$)</th>
<th>$\kappa_{SV}^{avg}(\text{BPh}_4)_2$ (psi$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.006</td>
<td>0.021</td>
<td>0.082</td>
</tr>
<tr>
<td>b</td>
<td>0.010</td>
<td>0.025</td>
<td>0.073</td>
</tr>
<tr>
<td>c</td>
<td>0.008</td>
<td>0.026</td>
<td>0.065</td>
</tr>
</tbody>
</table>
Table 3-22b: Discrete $K_{SV}^{avg}(x,y)$ values for three regions outlined in 10X microscopic $K_{SV}(x,y)$ image maps of Ru(II) $\alpha$-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Region</th>
<th>$K_{SV}^{avg}$ (psi$^{-1}$)</th>
<th>$K_{SV}^{avg}$ (psi$^{-1}$)</th>
<th>$K_{SV}^{avg}$ (psi$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.031</td>
<td>0.026</td>
<td>0.146</td>
</tr>
<tr>
<td>b</td>
<td>0.038</td>
<td>0.025</td>
<td>0.163</td>
</tr>
<tr>
<td>c</td>
<td>0.033</td>
<td>0.025</td>
<td>0.146</td>
</tr>
</tbody>
</table>

An easier way to look at the numbers in Tables 3-22a and 3-22b, is to plot the SV plots for the given regions of each sensor film. Figure 3-20 displays the SV plots of the discrete microscopic regions of each sensor film. The macroscopic SV plot for each sensor film is also plotted for comparison.
Figure 3-20: Macroscopic and microscopic SV plots of Ru(II) α-diimine complexes dispersed in SPDMS binder on glass. $A_{\text{REF}}$: area between 600 – 640 nm at 14.7 psi.

The Ru(II) α-diimine sensors were also analyzed microscopically utilizing a 40X objective. Five $K_{SV}(x,y)$ image maps were produced for each sensor film with accompanying statistical data listed in Tables 3-23a, 3-23b and 3-23c. It is interesting to note that the data in Tables 3-21a, 3-21b, and 3-21c are not consistent with the data in Tables 3-23a, 3-23b and 3-23c. As explained earlier, small areas of heterogeneity
exhibited by a 10X image are magnified for a 40X image. As an example, the small bright stars experienced by the [Ru(dpp)3]Cl2 film in image A of Figure 3-18 are greatly magnified in a 40X image. By doing so the bright spots dominate the image and yield a higher $K_{sv}^{avg}$ value with smaller percent standard deviations. This trend is seen throughout Tables 3-23a, 3-23b, and 3-23c.

Table 3-23a: Microscopic SV analysis of five 40X regions for Ru(II) $\alpha$-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Region</th>
<th>$K_{sv}^{avg}$ (psi$^{-1}$)</th>
<th>$\sigma_{K_{sv}}$ %$^{a}$</th>
<th>$K_{sv}^{avg}$ (psi$^{-1}$)</th>
<th>$\sigma_{K_{sv}}$ %$^{a}$</th>
<th>$K_{sv}^{avg}$ (psi$^{-1}$)</th>
<th>$\sigma_{K_{sv}}$ %$^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.013</td>
<td>53.8</td>
<td>0.058</td>
<td>10.3</td>
<td>0.024</td>
<td>25.0</td>
</tr>
<tr>
<td>2</td>
<td>0.014</td>
<td>35.7</td>
<td>0.012</td>
<td>50.0</td>
<td>0.030</td>
<td>30.0</td>
</tr>
<tr>
<td>3</td>
<td>0.023</td>
<td>26.1</td>
<td>0.013</td>
<td>46.2</td>
<td>0.020</td>
<td>30.0</td>
</tr>
<tr>
<td>4</td>
<td>0.010</td>
<td>60.0</td>
<td>0.016</td>
<td>37.5</td>
<td>0.018</td>
<td>55.6</td>
</tr>
<tr>
<td>5</td>
<td>0.012</td>
<td>33.3</td>
<td>0.014</td>
<td>57.1</td>
<td>0.022</td>
<td>31.8</td>
</tr>
</tbody>
</table>

$a \quad \sigma_{K_{sv}} % = \frac{\sigma_{K_{sv}}}{K_{sv}^{avg}} \times 100 \%$

Table 3-23b: Microscopic SV analysis of five 40X regions for Ru(II) $\alpha$-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Region</th>
<th>$K_{sv}^{avg}$ (psi$^{-1}$)</th>
<th>$\sigma_{K_{sv}}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.252</td>
<td>11.1</td>
</tr>
<tr>
<td>2</td>
<td>0.240</td>
<td>10.8</td>
</tr>
<tr>
<td>3</td>
<td>0.220</td>
<td>14.5</td>
</tr>
<tr>
<td>4</td>
<td>0.236</td>
<td>6.36</td>
</tr>
<tr>
<td>5</td>
<td>0.237</td>
<td>11.4</td>
</tr>
</tbody>
</table>
Table 3-23c: Microscopic SV analysis of five 40X regions for Ru(II) α-diimine complexes dispersed in SPDMS binder on glass.

<table>
<thead>
<tr>
<th>Region</th>
<th>$K_{SV}^{avg}$ (psi$^{-1}$)</th>
<th>$\sigma_{K_{SV}}$ %</th>
<th>$K_{SV}^{avg}$ (psi$^{-1}$)</th>
<th>$\sigma_{K_{SV}}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.050</td>
<td>18.0</td>
<td>0.508</td>
<td>10.4</td>
</tr>
<tr>
<td>2</td>
<td>0.084</td>
<td>11.9</td>
<td>0.418</td>
<td>7.42</td>
</tr>
<tr>
<td>3</td>
<td>0.066</td>
<td>12.1</td>
<td>0.415</td>
<td>13.3</td>
</tr>
<tr>
<td>4</td>
<td>0.076</td>
<td>11.8</td>
<td>0.452</td>
<td>13.1</td>
</tr>
<tr>
<td>5</td>
<td>0.069</td>
<td>13.0</td>
<td>0.491</td>
<td>7.94</td>
</tr>
</tbody>
</table>

A brief analysis of the data presented reveals that qualitative fluorescence microscopic images may not tell the whole story as to why a sensor film behaves poorly on the macroscopic level. Further analysis into the microscopic fluorescence response to variation in $P_{air}$ reveals the sensors intensity distributions. Plotting these intensities as distribution curves visually explains whether the intensities homogeneously decrease with pressure changes from 0.4 – 14.7 psi or the curves overlap and/or eclipse from bi-modal distributions. Microscopic analysis of the $K_{SV}$ values generated from the intensity images verifies the degree of heterogeneous spatial SV response. Clearly, analysis of the spatial intensity and $K_{SV}$ values lends evidence to how the sensors are dispersed in the polymer binders and how this dispersion causes the sensor films to behave poorly at the macroscopic level.

**Fluorescence Microscopy of [Ru(dpp)$_3$]Cl$_2$ in SPDMS and PDMS with Fumed SiO$_2$**

It has been known for some time now that adding a filler such as fumed silica gel to the polymer binder enhances the SV response to variation in $P_{air}$. A series of sensor films is evaluated with [Ru(dpp)$_3$]Cl$_2$ dispersed either in silanol polydimethylsiloxanes (SPDMS 18,000 MW with methyltriacetoxylysilane cross-linker) or a commercially synthesized polydimethylsiloxane (PDMS (DMS-D33)1900 – 2000 MW).
polymer binder incorporating varying weight percents (relative to total weight of polymer binder, 500 mg) of a hydrophilic fumed silica gel. The films are first analyzed on the macroscopic level utilizing the fluorimeter. The macroscopic Stern-Volmer (SV) plots are displayed in Figure 3-21. SPDMS and PDMS sensor films incorporating [Ru(dpp)_3]Cl_2 without fumed silica gel are also presented for comparison.

The addition of silica particles creates micro-domains in the polymer binder where the [Ru(dpp)_3]Cl_2 complex adsorsbs and experiences increased luminescence oxygen sensitivity. Consequently, the addition of fumed silica gel has a positive effect on the SV response of the sensor films. For this series of sensor films, the greatest SV response is exhibited by the film incorporating 1 wt. % of fumed silica gel in PDMS binder. However, the luminescence intensity only decreases by less than a factor of five when P_{air} increases from 0 – 14.7 psi. Although the most dramatic response is seen for addition of 10 wt. % fumed silica gel to SPDMS binder. Comparing the two non-silica
filled films, the SV response for [Ru(dpp)₃]Cl₂ in PDMS binder is larger with a KSV value of 0.141 psi⁻¹ (r² = 0.928) than its response in SPDMS binder with a KSV value of 0.016 psi⁻¹ (r² = 0.968). It is possible that the PDMS polymer may possess more polar sites or micro-domains on which the [Ru(dpp)₃]Cl₂ can adsorb. Therefore, addition of fumed silica gel to PDMS binder is not as beneficial to the SV response as seen in Figure 3-21. The remaining macroscopic SV response data for [Ru(dpp)₃]Cl₂ dispersed in SPDMS or PDMS binder with increased weight percents of fumed silica gel are displayed in Table 3-24.

Table 3-24: Macroscopic SV response data for [Ru(dpp)₃]Cl₂ dispersed in SPDMS or PDMS binder on glass with increased weight percents of fumed silica gel.

<table>
<thead>
<tr>
<th>Binder</th>
<th>wt. %</th>
<th>Slope (psi⁻¹)</th>
<th>Intercept</th>
<th>KSv (psi⁻¹)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPDMS</td>
<td>0 %</td>
<td>0.013</td>
<td>0.820</td>
<td>0.016</td>
<td>0.968</td>
</tr>
<tr>
<td>SPDMS</td>
<td>1 %</td>
<td>0.009</td>
<td>0.892</td>
<td>0.010</td>
<td>0.738</td>
</tr>
<tr>
<td>SPDMS</td>
<td>10 %</td>
<td>0.032</td>
<td>0.551</td>
<td>0.058</td>
<td>0.990</td>
</tr>
<tr>
<td>PDMS</td>
<td>0 %</td>
<td>0.049</td>
<td>0.348</td>
<td>0.141</td>
<td>0.928</td>
</tr>
<tr>
<td>PDMS</td>
<td>1 %</td>
<td>0.058</td>
<td>0.201</td>
<td>0.289</td>
<td>0.987</td>
</tr>
<tr>
<td>PDMS</td>
<td>10 %</td>
<td>0.050</td>
<td>0.289</td>
<td>0.173</td>
<td>0.993</td>
</tr>
</tbody>
</table>

a intercept = A in equation (3-3), b slope = B in equation (3-3), c KSV = (B/A) in equation (3-3)

For the SPDMS polymer, addition of 1 wt. % of fumed silica gel essentially has no effect upon the SV response, since the intercept values between the 1 wt. % and 0 wt. % are not all that different. The difference in the SV plots is most likely due to noise. However at 10 wt. % of fumed silica gel, the SV response drastically improves. The silica particles are creating micro-domains of increased SV response within the polymer binder. Increased weight percents of silica gel improve the SV response but not substantially before the films become extremely porous and powdery. The PDMS
polymer exhibits the same trends upon addition of silica gel. Addition of 1 wt. % of fumed silica gel improves the SV response slightly, but further additions do not improve the response and may actually hinder it. Since neither addition dramatically changed the SV response of the sensor film, further increased weight percents were not analyzed. Smaller weight percents of silica gel were not added either due to the inability to accurately weigh the fumed silica gel.

Clearly addition of fumed silica gel influences the SV response, and to further analyze the above observations, qualitative fluorescence microscope images of sensor films of [Ru(dpp)$_3$]Cl$_2$ dispersed in SPDMS and PDMS binder incorporating various weight percents of fumed silica gel were obtained at 0.5 psi with a 10X objective. The images are illustrated in Figure 3-22.

![Figure 3-22: Qualitative microscopic fluorescence images (10X, 0.5 psi) for [Ru(dpp)$_3$]Cl$_2$ dispersed in SPDMS or PDMS binder on glass with increased weight percents of fumed silica gel. White scale bars are 153 μm long. A) 0 wt. % in SPDMS, B) 1 wt. % in SPDMS, C) 10 wt. % in SPDMS, D) 0 wt. % in PDMS, E) 1 wt. % in PDMS, F) 10 wt. % in PDMS.](image-url)
The addition of fumed silica gel to the polymer binders is striking. Fumed silica gel in SPDMS and PDMS dramatically changes the image field. The star pattern in images A and D gives way to intense aggregates of [Ru(dpp)$_3$]Cl$_2$ adsorbed fumed silica gel in images B and E which are heavily populated in images C and F. Subsequent additions of fumed silica gel yield concentrated regions of good SV luminescence response. If only image A and D are compared, clearly image D is less punctuated with fluorescent bright spots and possesses more of a consistent luminescent background than image A. The luminescence consistency is one of the reasons why the PDMS sensor film’s SV response is far better than that of the SPDMS sensor film (Figure 3-21).

Further analysis of the effect fumed silica gel quantity has on the spatial distribution of the microscopic SV response is probed by taking a series of quantitative intensity image maps of the sensor’s response to variation in $P_{\text{air}}$ using the 10X objective. Thus, five 436 µm x 345 µm regions of each sensor film were interrogated, and the luminescence intensity distribution of one representative region from each film ($I^c(x,y; P_{\text{air}} = 0.4 \ \text{psi})$) is illustrated in Figure 3-23. The colors for the images are not scaled the same, and the maximum intensity for each image is listed in Table 3-25. The maximum intensity values are yellow and scale to dark blue for zero emission in the images of Figure 3-23.
Table 3-25: Maximum fluorescence intensity values for 10X microscopic regions of [Ru(dpp)_3]Cl_2 dispersed in SPDMS or PDMS binder on glass with increased weight percents of fumed silica gel.

<table>
<thead>
<tr>
<th>Binder</th>
<th>wt. %</th>
<th>Maximum Intensity (a.u.)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPDMS</td>
<td>0 %</td>
<td>13400</td>
</tr>
<tr>
<td>SPDMS</td>
<td>1 %</td>
<td>11295</td>
</tr>
<tr>
<td>SPDMS</td>
<td>10 %</td>
<td>32358</td>
</tr>
<tr>
<td>PDMS</td>
<td>0 %</td>
<td>4302</td>
</tr>
<tr>
<td>PDMS</td>
<td>1 %</td>
<td>25218</td>
</tr>
<tr>
<td>PDMS</td>
<td>10 %</td>
<td>8494</td>
</tr>
</tbody>
</table>

^a a.u. = arbitrary units

Figure 3-23: Quantitative microscopic fluorescence intensity images (10X, 0.4 psi) for [Ru(dpp)_3]Cl_2 dispersed in SPDMS or PDMS binder with increased weight percents of fumed silica gel on glass. White scale bars are 92 μm long. Intensity color scale bars are shown to the right of all images. A) 0 wt. % in SPDMS, B) 1 wt. % in SPDMS, C) 10 wt. % in SPDMS, D) 0 wt. % in PDMS, E) 1 wt. % in PDMS, F) 10 wt. % in PDMS.

The quantitative images are very similar to the qualitative images. In the quantitative images, a greater sense of the overall intensity values is achieved. For the SPDMS sensor films, images A to C, the distribution of [Ru(dpp)_3]Cl_2 luminescence becomes more clustered with greater deviations of the intensity values. For the PDMS 1 wt. % film, briefly comparing the data in Table 3-24 with image E in Figure 3-23, it is
seen that the dynamic SV response is due to the adsorption of [Ru(dpp)$_3$]Cl$_2$ to the fumed silica gel particles.

The percent standard deviation for the intensities ($\sigma_1$, %) of the images in Figure 3-23, and the remaining six intensity pressure images analyzed for each [Ru(dpp)$_3$]Cl$_2$ sensor film are listed in Table 3-26.

Table 3-26: Percent standard deviation ($\sigma_1$, %) in intensities at seven pressures for microscopic regions of [Ru(dpp)$_3$]Cl$_2$ dispersed in SPDMS or PDMS binder on glass with increased weight percents of fumed silica gel.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>wt. %</th>
<th>0.4 psi</th>
<th>2 psi</th>
<th>4 psi</th>
<th>6 psi</th>
<th>8 psi</th>
<th>10 psi</th>
<th>14.7 psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPDMS</td>
<td>0 %</td>
<td>14.4</td>
<td>10.8</td>
<td>7.73</td>
<td>6.49</td>
<td>6.32</td>
<td>6.01</td>
<td>5.14</td>
</tr>
<tr>
<td>SPDMS</td>
<td>1 %</td>
<td>17.6</td>
<td>16.1</td>
<td>14.8</td>
<td>14.0</td>
<td>14.7</td>
<td>13.4</td>
<td>-</td>
</tr>
<tr>
<td>SPDMS</td>
<td>10 %</td>
<td>43.2</td>
<td>39.6</td>
<td>36.3</td>
<td>38.1</td>
<td>35.6</td>
<td>35.5</td>
<td>38.5</td>
</tr>
<tr>
<td>PDMS</td>
<td>0 %</td>
<td>7.16</td>
<td>7.61</td>
<td>6.88</td>
<td>6.38</td>
<td>5.65</td>
<td>4.85</td>
<td>3.56</td>
</tr>
<tr>
<td>PDMS</td>
<td>1 %</td>
<td>24.2</td>
<td>34.1</td>
<td>39.7</td>
<td>40.6</td>
<td>40.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PDMS</td>
<td>10 %</td>
<td>77.1</td>
<td>69.6</td>
<td>71.5</td>
<td>66.4</td>
<td>52.7</td>
<td>42.7</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a\sigma_1 \% = \sigma/I_{avg} \times 100\%$

The large percent deviations, especially for the 10 wt. % of fumed silica gel in PDMS, indicate that the [Ru(dpp)$_3$]Cl$_2$ is adsorbed onto the silica particles in varying concentrations thus creating intensity distributions and partitioning of the luminescent particles from the weakly emissive background field.

As is expected, the corresponding intensity distributions at each pressure for each sensor film also exhibit varying degrees of overlap due to the heterogeneous adsorption of the [Ru(dpp)$_3$]Cl$_2$ onto the silica particles and its distribution between the silica gel and
the polymer binder. The distribution curves for 1 wt. % and 10 wt. % of fumed silica gel in PDMS and SPDMS binder, respectively, are displayed in Figure 3-24.

Figure 3-24: Intensity distribution curves for intensities obtained with a 10X objective at six pressures for [Ru(dpp)3]Cl2 dispersed in PDMS or SPDMS binder on glass with increased weight percent of fumed silica gel. A) 1 wt. % in PDMS, B) 10 wt. % in SPDMS.

Image A and B display curves which overlap, decrease in size, and exhibit considerable fine structure. The overlap proves that there are regions in each pressure image which are not quenched with increased $P_{air}$. Short, broad, structured peaks indicate that there are many luminescent species (different intensity values) at lower $P_{air}$ values that are not quenched at higher $P_{air}$ values. Comparing image A and B, it is seen why the SV response is better for the 1 wt. % film curves. While the sensor films’ intensity distribution curves overlap, they are still more spatially distributed than the 10 wt. % curves.

The series of six intensity images in Figure 3-23 afforded six corresponding microscopic quantitative $K_{SV}(x,y)$ image maps illustrated in Figure 3-25. The images are not scaled the same, and the maximum $K_{SV}$ value for each sensor film is listed in Table 3-
The maximum $K_{SV}$ values are yellow and scale to dark blue for no SV response in the images of Figure 3-25.

Table 3-27: Maximum $K_{SV}$ values for 10X microscopic regions of $[\text{Ru(dpp)}_3]\text{Cl}_2$ dispersed in SPDMS or PDMS binder on glass with increased weight percents of fumed silica gel.

<table>
<thead>
<tr>
<th>Binder</th>
<th>wt. %</th>
<th>Maximum $K_{SV}$ (psi$^{-1}$)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPDMS</td>
<td>0 %</td>
<td>0.082</td>
</tr>
<tr>
<td>SPDMS</td>
<td>1 %</td>
<td>0.065</td>
</tr>
<tr>
<td>SPDMS</td>
<td>10%</td>
<td>0.340</td>
</tr>
<tr>
<td>PDMS</td>
<td>0 %</td>
<td>0.220</td>
</tr>
<tr>
<td>PDMS</td>
<td>1 %</td>
<td>0.900</td>
</tr>
<tr>
<td>PDMS</td>
<td>10%</td>
<td>0.900</td>
</tr>
</tbody>
</table>

$a$ $K_{SV} = (B/A)$ in equation (3-3)

Figure 3-25: Quantitative microscopic $K_{SV}(x,y)$ image maps for $[\text{Ru(dpp)}_3]\text{Cl}_2$ dispersed in SPDMS or PDMS binder with increased weight percents of fumed silica gel on glass. White scale bars are 92 $\mu$m long. $K_{SV}$ color scale bars are shown to the right of all images. A) 0 wt. % in SPDMS, B) 1 wt. % in SPDMS, C) 10 wt. % in SPDMS, D) 0 wt. % in PDMS, E) 1 wt. % in PDMS, F) 10 wt. % in PDMS.
The quantitative $K_{SV}(x,y)$ image maps in Figure 3-25 correspond well with high and low intensity values for the quantitative intensity images in Figure 3-23. The areas where $[\text{Ru(dpp)}_3]\text{Cl}_2$ is adsorbed onto the fumed silica gel exhibit the most dynamic SV responses in images C and E. Image E and F were scaled to show the dramatic change in $K_{SV}$ across the image. The actual $K_{SV}$ maximum values are $2.01\text{ psi}^{-1}$ and $2.59\text{ psi}^{-1}$ for images E and F, respectively. This was done because the tips of the silica particles produced the greatest SV response which over shadowed the color scaling of the background signal.

The percent standard deviations in $K_{SV}(x,y)$ for each image are listed in Tables 3-28a and 3-28b.

Table 3-28a: Microscopic SV analysis of five 10X regions for $[\text{Ru(dpp)}_3]\text{Cl}_2$ dispersed in SPDMS binder on glass with increased weight percents of fumed silica gel.

<table>
<thead>
<tr>
<th>Wt. %</th>
<th>0 %</th>
<th>1 %</th>
<th>10 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>$K_{SV}^{av}$ (psi$^{-1}$)</td>
<td>$\sigma_{K_{SV}}^{a}$</td>
<td>$K_{SV}^{av}$ (psi$^{-1}$)</td>
</tr>
<tr>
<td>1</td>
<td>0.007</td>
<td>71.4</td>
<td>0.013</td>
</tr>
<tr>
<td>2</td>
<td>0.008</td>
<td>62.5</td>
<td>0.014</td>
</tr>
<tr>
<td>3</td>
<td>0.007</td>
<td>71.4</td>
<td>0.014</td>
</tr>
<tr>
<td>4</td>
<td>0.008</td>
<td>87.5</td>
<td>0.011</td>
</tr>
<tr>
<td>5</td>
<td>0.008</td>
<td>75.0</td>
<td>0.012</td>
</tr>
</tbody>
</table>
Table 3-28b: Microscopic SV analysis of five 10X regions for [Ru(dpp)₃]Cl₂ dispersed in PDMS binder on glass with increased weight percents of fumed silica gel.

<table>
<thead>
<tr>
<th>Region</th>
<th>K_{SV}^{avg} (psi⁻¹)</th>
<th>σ_{K_{SV}} %</th>
<th>K_{SV}^{avg} (psi⁻¹)</th>
<th>σ_{K_{SV}} %</th>
<th>K_{SV}^{avg} (psi⁻¹)</th>
<th>σ_{K_{SV}} %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.112</td>
<td>13.7</td>
<td>0.396</td>
<td>38.6</td>
<td>0.132</td>
<td>94.7</td>
</tr>
<tr>
<td>2</td>
<td>0.111</td>
<td>9.91</td>
<td>0.390</td>
<td>38.5</td>
<td>0.124</td>
<td>97.6</td>
</tr>
<tr>
<td>3</td>
<td>0.117</td>
<td>12.0</td>
<td>0.465</td>
<td>37.0</td>
<td>0.193</td>
<td>54.9</td>
</tr>
<tr>
<td>4</td>
<td>0.115</td>
<td>13.9</td>
<td>0.517</td>
<td>57.8</td>
<td>0.198</td>
<td>92.4</td>
</tr>
<tr>
<td>5</td>
<td>0.117</td>
<td>15.4</td>
<td>0.386</td>
<td>50.0</td>
<td>0.189</td>
<td>98.9</td>
</tr>
</tbody>
</table>

The microscopic and macroscopic data (Table 3-24) vary greatly from one another. Similar to the previous series of Ru(II) α-diimine complexes, the microscopic data is merely an average of the K_{SV}(x,y) data. To illustrate this, 1 wt. % and 10 wt. % of fumed silica gel in PDMS and SPDMS binder, respectively, were analyzed at discrete regions for their respective K_{SV}(x,y) image maps. Table 3-29 is a list of the discrete K_{SV}^{avg}(x,y) values obtained for the boxes outlined in the images of Figure 3-26. The white boxes are an approximation of the area of K_{SV}(x,y) values analyzed. The values correlate with the average values in Tables 3-28a and 3-28b and seem reasonable in comparison to the macroscopic data.

Figure 3-26: Analysis of discrete regions (white boxes) in quantitative microscopic K_{SV}(x,y) image maps of [Ru(dpp)₃]Cl₂ dispersed in PDMS or SPDMS binder on glass with increased weight percents of fumed silica gel. White scale bars are 92 μm long. K_{SV} color scale bars are shown to the right of all images. A) 1 wt. % in PDMS, B) 10 wt. % in SPDMS.
Table 3-29: Discrete $K_{SV}^{avg}(x,y)$ values for three regions outlined in 10X microscopic $K_{SV}(x,y)$ image maps of [Ru(dpp)$_3$]Cl$_2$ dispersed in PDMS or SPDMS binder on glass with increased weight percents of fumed silica gel.

<table>
<thead>
<tr>
<th>Region</th>
<th>$K_{SV}^{avg}$(psi$^{-1}$) PDMS</th>
<th>$K_{SV}^{avg}$(psi$^{-1}$) SPDMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.30</td>
<td>0.11</td>
</tr>
<tr>
<td>b</td>
<td>0.28</td>
<td>0.12</td>
</tr>
<tr>
<td>c</td>
<td>0.57</td>
<td>0.12</td>
</tr>
</tbody>
</table>

One way to visually understand these numbers is to plot the discrete regions as SV plots. Figure 3-27 displays the SV plots of the discrete microscopic regions for [Ru(dpp)$_3$]Cl$_2$ with 1 wt. % SiO$_2$ in PDMS and 10 wt. % SiO$_2$ in SPDMS. The macroscopic SV plots for the two sensor films are also plotted as a comparison.

![SV plots](image)

Figure 3-27: Macroscopic and microscopic SV plots of [Ru(dpp)$_3$]Cl$_2$ dispersed in PDMS or SPDMS binder on glass with weight percents of fumed silica gel. $A_{REF}$: area between 600 – 640 nm at 14.7 psi. A) 1 wt. % in PDMS and B) 10 wt. % in SPDMS.

The [Ru(dpp)$_3$]Cl$_2$ sensor films were also analyzed microscopically utilizing a 40X objective. Five regions of each sensor film were interrogated producing five $K_{SV}(x,y)$ image maps for each sensor film with accompanying statistical data listed in Tables 3-30a and 3-30b. Similar to the data for the previous series of Ru(II) $\alpha$-diimine...
complexes, the data in Tables 3-30a and 3-30b possesses higher $K_{SV}^{avg}(x,y)$ values with smaller deviations. The 40X images are highly magnified regions of the heterogeneous films often times yielding more homogeneous images, higher $K_{SV}^{avg}$ values and smaller percent standard deviations.

Table 3-30a: Microscopic SV analysis of five 40X regions for [Ru(dpp)$_3$]Cl$_2$ dispersed in SPDMS binder on glass with increased weight percents of fumed silica gel.

<table>
<thead>
<tr>
<th>Wt. %</th>
<th>0 %</th>
<th>1 %</th>
<th>10 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>$K_{SV}^{avg}$ (psi$^{-1}$)</td>
<td>$\sigma_{K_{SV}}$ %</td>
<td>$K_{SV}^{avg}$ (psi$^{-1}$)</td>
</tr>
<tr>
<td>1</td>
<td>0.013</td>
<td>53.8</td>
<td>0.044</td>
</tr>
<tr>
<td>2</td>
<td>0.014</td>
<td>35.7</td>
<td>0.021</td>
</tr>
<tr>
<td>3</td>
<td>0.023</td>
<td>26.1</td>
<td>0.023</td>
</tr>
<tr>
<td>4</td>
<td>0.010</td>
<td>60.0</td>
<td>0.019</td>
</tr>
<tr>
<td>5</td>
<td>0.012</td>
<td>33.3</td>
<td>0.026</td>
</tr>
</tbody>
</table>

$\sigma_{K_{SV}}$ % = $\frac{\sigma_{K_{SV}}}{K_{SV}^{avg}}$ x 100%

Table 3-30b: Microscopic SV analysis of five 40X regions of [Ru(dpp)$_3$]Cl$_2$ dispersed in PDMS binder on glass with increased weight percents of fumed silica gel.

<table>
<thead>
<tr>
<th>Wt. %</th>
<th>0 %</th>
<th>1 %</th>
<th>10 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region</td>
<td>$K_{SV}^{avg}$ (psi$^{-1}$)</td>
<td>$\sigma_{K_{SV}}$ %</td>
<td>$K_{SV}^{avg}$ (psi$^{-1}$)</td>
</tr>
<tr>
<td>1</td>
<td>0.221</td>
<td>6.33</td>
<td>0.448</td>
</tr>
<tr>
<td>2</td>
<td>0.195</td>
<td>8.21</td>
<td>0.399</td>
</tr>
<tr>
<td>3</td>
<td>0.265</td>
<td>5.28</td>
<td>0.281</td>
</tr>
<tr>
<td>4</td>
<td>0.251</td>
<td>5.18</td>
<td>0.346</td>
</tr>
<tr>
<td>5</td>
<td>0.229</td>
<td>6.55</td>
<td>0.393</td>
</tr>
</tbody>
</table>

Overall analysis of the data presented reveals that, in general, the SV response at the macroscopic level for [Ru(dpp)$_3$]Cl$_2$ sensor films improves with increased weight percents of fumed silica gel (Figure 3-21). At the microscopic level, the 10 wt. % of fumed silica gel in SPDMS and 1 wt. % of fumed silica gel in PDMS produced the
highest intensity values in Table 3-25, strong $K_{SV}$ responses in Table 3-27, and the least deviations in $\sigma_{K_{SV}} \%$ for fumed silica gel films in Tables 3-28a, 3-28b, 3-30a, and 3-30b.

**Discussion**

**Analysis of PtTFPP Films**

Macroscopic SV analyses of each PtTFPP sensor film series are unaffected by changes in the sensor concentration or the mole ratio of polymer cross-linker (Figures 3-2 and 3-7). Upon microscopic inspection of the sensor films, sensor distribution and polymer morphology become visually heterogeneous as the sensor concentration (Figure 3-4) and mole ratio of cross-linker (Figure 3-9) are increased. The visual heterogeneity only has a slight effect on the intensity percent standard deviations ($\sigma_1 \%$). Visual representations of the intensity distributions for the “worse” sensor films are seen in the distribution curves displayed in Figures 3-5 and 3-10. Clearly, the effects from increased sensor concentration and mole ratio of cross-linker do not substantially impact the intensity distributions, since the curves represent discrete distributions.

The influence of these two conditions upon the microscopic SV response is minimal as well (Figures 3-6 and 3-11). The $K_{SV}^{avg}$ values (Tables 3-6a and 3-6b) are higher than the macroscopic $K_{SV}$ values for the PtTFPP films with increased concentration of sensor. The formation of PtTFPP microcrystals and aggregates is therefore inconsequential. Not too surprising is the fact that the $K_{SV}^{avg}$ values (Tables 3-13a and 3-13b) are lower for the PtTFPP films with increased mole ratio of cross-linker and the percent standard deviations are higher. The areas of polymer dewetting are larger and more influential upon the $K_{SV}$ distribution.
Overall for each PtTFPP sensor film, it is clear from the $K_{SV}$ image maps that the sensor response is uniform up to 5 mM PtTFPP and 1:7 mole ratio oligomer:cross-linker, even on length scales of < 5 μm. This uniformity is also seen on longer length scales as demonstrated by the overall consistency of the $K_{SV}^{\text{avg}}$ values. The uniformity within each microscopic region is confirmed by the fact that the percent standard deviations ($\sigma_{K_{SV}}$ %) in $K_{SV}^{\text{avg}}$ are low. Indeed the $\sigma_{K_{SV}}$ % values observed for the PtTFPP sensor films are likely representative of scatter due to random noise in the imaging experiments (shot, excitation, etc.)

The PtTFPP films appear to behave as ideal oxygen sensor films on length scales from mm to μm. This ideal behavior clearly arises because the hydrophobic PtTFPP sensor is well dispersed within the generally hydrophobic SPDMS polymer binder, at least with respect to oxygen permeability, on length scales approaching 1 μm. Even increased concentrations of luminophore and mole ratios of cross-linker do not disturb the macroscopic SV response to variation in $P_{\text{air}}$. This is due to the minimal effects sensor microcrystallization and aggregation or polymer dewetting has on the overall macroscopic SV response of the sensor films.

**Analysis of Ru (II) α-diimine Films**

Macroscopic SV analyses of the Ru(II) α-diimine complexes in SPDMS polymer binder yield varying $K_{SV}$ values (Figure 3-13 and Table 3-15). Previous studies of luminescent oxygen sensing thin films that contain $[\text{Ru(dpp)}_3]^{2+}$ salts suggest that the sensor response may be reduced when the metal complex exists in the film as microcrystallites or aggregates. There has been no direct evidence for this theory.
except the assumption that the Ru(II) α-diimine complexes, by virtue of their polar nature, dissolve and disperse differently in the relatively non-polar SPDMS polymer binder. Determination of the microscopic SV response distribution of the Ru(II) α-diimine complexes in SPDMS polymer binder reveals a number of significant features.

On a qualitative level, the K SV images in Figure 3-18 and the statistical data listed in Tables 3-21a, 3-21b and 3-21c clearly demonstrates that the inhomogeneous distribution of the Ru(II) α-diimine complexes in the SPDMS polymer binder causes the sensor films to exhibit a spatially heterogeneous SV response. Indeed, over the five different regions of each sensor film analyzed with the 10X objective, the SV response varies significantly, reaching a maximum K SV avg at 0.170 psi⁻¹ for the [Ru(dpp)₃](B(PhF₅)₄)₂ film and a minimum K SV avg at 0.007 psi⁻¹ for the [Ru(dpp)₃]Cl₂ film. However, even more interesting is the fact that the SV response varies strongly within an individual microscopic region—inspection of the images of Figure 3-19 illustrates that K SV avg data in Tables 3-22a and 3-22b varies strongly on length scales of < 5 μm.

A subtle and interesting effect is seen when one compares intensity and K SV images. Specifically, there is a spatial correlation between K SV and luminescence intensity: microscopic regions that feature bright emission (yellow regions in Figure 3-16) also tend to exhibit comparatively larger K SV values (yellow and red regions in Figure 3-18). This feature indicates that in regions where the luminescence is more intense, the sensor is more susceptible to oxygen quenching.

A possible physical model for the spatial correlation between the luminescence intensity and K SV values for the Ru(II) α-diimine complexes in the SPDMS polymer binder is based on the effect of aggregation on the luminescence intensity and lifetime of
the Ru(II) α-diimine complexes. It is known that when Ru-polypyridine complexes exist in an aggregated or microcrystalline state their luminescence lifetime and intensity (quantum yield) is significantly reduced. The reduction in lifetime and intensity is believed to arise from self-quenching due to the close proximity of the aggregated chromophores. Consequently, in regions of the polymer where the Ru(II) α-diimine complex is aggregated, the expected luminescence intensity and decay time of the sensor are lower. Due to low luminescence lifetime, the aggregated sensor will be less susceptible to quenching by oxygen (i.e., \( K_{SV} \) is lower). This effect may explain the observation that \( K_{SV} \) is less in regions of the Ru(II) α-diimine films where the luminescence intensity is lower. As for the bright spots imaged for the sensor films, the metal complexes exist either as amorphous solids or microcrystallites. When solid \([\text{Ru(dpp)}_3]\text{Cl}_2\) without a polymer binder was analyzed with the microscope set-up, variation in \( P_{af} \) led to linear SV response from the \([\text{Ru(dpp)}_3]\text{Cl}_2\) particles similar to the Ru(II) α-diimine sensor films' microscopic SV response.

It is important to consider why the Ru(II) α-diimine complexes exist as aggregates or microcrystals in the SPDMs polymer binder. First, all of the components used to fabricate the films are freely soluble in the dichloromethane solution that is used during the aerosol deposition. However, because SPDMs is relatively non-polar, it is likely that the ionic metal complex salts are not very soluble in the pure polymer matrix. The metal complexes seek solubilization areas in the polymer which are fairly polar. The SPDMs formulation used for this work employs four moles of cross-linker for every mole of Si-OH end group on the silanol polydimethylsiloxane oligomer. Therefore, there exists unterminated Si-acetoxy components which can produce micro-domains to
solubilize the Ru(II) α-diimine metal complexes. The less polar polymer environment will also induce strong complexation between the ionic species of the metal complexes resulting in reduced lifetimes and decreased oxygen quenching. Thus the Ru(II) α-diimine complexes and SPDMS must phase separate (or crystallize) either during the aerosol deposition step (i.e., as the more polar dichloromethane carrier solvent vaporizes) or during the period of time when the polymer cures. Each of the Ru(II) α-diimine metal complexes chosen possess either a different ligand or counter ion. Depending on the size, structure, and solubility of the given complex, the film’s SV response will vary. These facts, coupled with the relatively high concentration of the sensor used in the films (0.2 % by weight Ru(II) α-diimine complex in SPDMS, which corresponds to roughly 1-2 mM in the cured coatings) are some of the likely reasons for phase separation or microcrystallization within the polymer binder.

There are several interesting addendums to the remarks in the last paragraph. One, preliminary studies using energy dispersive spectroscopy on a [Ru(dpp)₃]Cl₂/SPDMS film detected no signals due to ruthenium. This suggests that the sensor is not present in the films as µm sized crystals, but rather is inhomogeneously distributed through the polymer in nm-scale aggregates. Two, decrease of the [Ru(dpp)₃]Cl₂ sensor concentration to 0.02 wt. % did not improve the macroscopic SV response. Microscopic fluorescence imaging reveals that even decreased concentrations of the sensor display micro-domains of luminescence. Three, increased cross-linker concentrations might induce more micro-regions of polarity into the polymer morphology allowing for better solubilization of the sensor. This was not the case for [Ru(dpp)₃]Cl₂ dispersed in SPDMS polymer with 1:5 or 1:7 mole ratios of oligomer:cross-linker. The
films’ macroscopic SV response was worse with unquenchable micro-domains in the films. Four, addition of hydrophilic fumed silica gel improves the macroscopic SV response of the [Ru(dpp)$_3$]Cl$_2$ sensor films in SPDMs or PDMS polymer binder. The silica particles create polar sites for sensor solubilization and increased luminescence oxygen quenching.25,29,56

**Experimental**

**Oligomers**

SPDMS: silanol terminated polydimethylsiloxanes (PDMS) 0.2 % OH (average MW 18,000) and methyltriacetoxyasilane 95% were purchased from Gelest (Tullytown, PA). DMS-D33: diacetoxyethylterminated polydimethylsiloxane (PDMS) was purchased from Gelest (Tullytown, PA).

**Luminophores**

[Ru(dpp)$_3$]Cl$_2$: *tris-(4,7-diphenyl-1,10-phenanthroline)ruthenium (II)* dichloride was synthesized by a literature procedure and purified by repeated recrystallizations from water.47,94

[Ru(dpp)$_3$](PF$_6$)$_2$: *tris-(4,7-diphenyl-1,10-phenanthroline)ruthenium (II)* di-hexafluorophosphine was prepared by metathesis of the dichloride salt.

[Ru(dpp)$_3$](BPh$_4$)$_2$: *tris-(4,7-diphenyl-1,10-phenanthroline)ruthenium (II)* di(tetrakisphenylborate) was prepared by metathesis of the dichloride salt.40,110

[Ru(dpp)$_3$](B(PhF$_5$)$_4$)$_2$: *tris-(4,7-diphenyl-1,10-phenanthroline)ruthenium (II)* di(tetrakis(pentafluorophenyl)borate) was synthesized by combining 26 mg of [Ru(dpp)$_3$]Cl$_2$ dissolved in 2 mL of dichloromethane with 70 mg of sodium tetra(pentafluorophenyl)borate dissolved in 5 mL of 100 % ethanol. The resulting
mixture was stirred for 2 h. at room temperature and allowed to sit overnight at room temperature. The product, fine crystals, was suction-filtered and washed with 100% ethanol three times. After the crystals were dried, 45 mg of the product was collected.

[Ru(dpp)₃][B(Ph(CF₃)₂)₄]₂: tris-(4,7-diphenyl-1,10-phenanthroline)ruthenium (II) di(tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) was synthesized by gently refluxing RuCl₃·xH₂O (28 mg, 0.11 mmol) dissolved in 20 mL of 1:1 EtOH/H₂O (v:v) with continuous bubbling of argon. The color of the solution changed gradually from a dark brown to a deep blue color via a dark green color within approximately 4 h. To the hot blue solution was added 4,7-diphenyl-1,10-phenanthroline (107 mg, 0.33 mmol) dissolved in EtOH (10 mL). The mixture was refluxed for 48 h., during which time the solution color changed from blue to deep red. The solution was evaporated to dryness.

SodiumTFPB CH₂Cl₂ solution was added to the solid resulting materials. The mixture was extracted several times with DI H₂O, and the organic solvent was removed with evaporation to yield a red-orange solid, 151 mg (80%). ¹H NMR (300 MHz, δ/ppm, CD₃COCD₃) 7.61 (m, 30H), 7.75 (m, 24H), 7.78 (d, 6H), 8.68 (d, 2H).

Preparation of sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (SodiumTFPB): SodiumTFPB was synthesized using the procedure described by Bahr and coworkers.¹¹¹ Mg turnings (100 mg, 4.2 mmol) and 15 mL of ether were placed into a 250 mL 3-necked flask fitted with a condenser/N₂ inlet and a 50 mL addition funnel. 3,5-Bis(trifluoromethyl)-1-bromobenzene (1.0472 g, 3.57 mmol) and 15 mL of ether were placed in the addition funnel and added drop-wise to the 3-neck flask. The solution was gently heated till reflux. The mixture was stirred for 4 h. yielding a dark brown solution. NaBF₄ (100 mg, 0.89 mmol) dried at 110°C for 1 h. in vacuo was
quickly added to the solution, and the mixture was stirred for another 12 h. A light tan suspension resulted. The suspension was slowly poured into 50 mL of DI H₂O water saturated with NaCl. The resulting brown organic layer was separated and an additional 50 mL portion of ether was added to the aqueous/organic mixture and extracted. The two organic portions were combined, and the ether was removed by evaporation yielding a thick, dark brown oil. The crude product was purified by chromatography on silica gel using acetonitrile as eluant and yielding 600 mg (65%) of product. \(^1\)H NMR (300 MHz, \(\delta/\text{ppm, CD}_3\text{COCD}_3\)) 7.65 (s, 4H), 7.79 (s, 8H). \(^13\)C NMR (75 MHz, CD₃COCD₃) \(\delta\) 118.4, 125.5 (q, \(J_{\text{CF}} = 269\) Hz, CF3), 129.9 (m), 135.5, 162.9 (q, \(J_{\text{BC}} = 49\) Hz).

[Ru(dbdtap)_3](PF₆)₂: The synthetic route used for preparation of the precursor to the substituted 1,10-phenanthroline: (3,8-di(n-butyl)-4,7-dibromo-1,10-phenanthroline) is based on a literature report by Schmittel et al.\(^{112}\)

\(\text{Tris-(3,8-di-n-butyl-4,7-di(tolylacetylenyl)-1,10-phenanthroline)ruthenium (II) di(hexafluorophosphine)}\) was synthesized by adding 13 mg of RuCl₃xH₂O to a 50 mL round bottom flask, which contained a mixture of DI H₂O (3 mL) and 95% ethanol (5 mL). The resulting brown solution was degassed with argon for 40 min. The degassed solution was then heated to reflux under nitrogen with stirring. The color of the solution changed from deep brown to light brown to light green to deep green and finally to deep blue within 4 h. At which time, 129 mg of 3,8-di-n-butyl-4,7-di(tolylacetylenyl)-1,10-phenanthroline dissolved in 8 mL of 95% ethanol and a NH₄PF₆ solution were added to the hot solution. The resulting mixture was refluxed under nitrogen for 48 h. A deep reddish solution was collected after filtration through celite. The solvents were removed by rotary evaporation, and the resulting residue was washed three times with 15 mL
aliquots of ether. The product (70 mg) was isolated after a cold recrystallization from a mixture of 95% ethanol (2 mL) and DI H2O (0.4 mL).

Synthesis of ethyl hexanoate: In a 250 mL round bottom flask, hexanoic acid (58 g) was mixed with 20 g of ethanol and 0.6 g of H2SO4 (96%). The resulting mixture was heated at reflux for 40 h. A normal pressure distillation was conducted, and the product was collected as the fraction distilled from 166° C to 169° C (31 g of pure product). The fraction distilled from 170° C to 179° C (about 40 mL) was mixed with 100 mL of ether and transferred to a separatory funnel, washed with 100 mL of 2 M NaHCO3 three times and 100 mL of DI H2O twice. The organic layer was separated and dried over MgSO4 (anhydrous). Once the solvent was removed, 30 g of product was isolated. 1H NMR (300 MHz, δ/ppm, CDCl3) 0.91 (t, 3H), 1.0-1.1 (m, 7H), 1.60 (tt, 2H), 2.25 (t, 2H), 4.16 (q, 2H).

Synthesis of ethyl 2-formyl-hexanoate: A solution of 5.06 mL (0.05 mol) of diisopropylamine was added to 50 mL of dry THF and treated with 21.3 mL of 2.5 M n-butyllithium in hexanes at room temperature under nitrogen. The resulting pale yellow solution was cooled to -78° C with a dry ice/isopropyl bath, at which time, a solution of 7.2 g (0.05 mol) of ethyl hexanoate in 15 mL of dry THF was slowly added for 0.5 h. keeping the temperature of the reaction at -78° C. Ethyl formate, 11.1 g (0.15 mol), was added by syringe to the solution. After stirring for 5 min., the dry ice/isopropanol bath was removed. The temperature of the reaction was warmed to room temperature, 25° C, and kept stirring for an additional 2 h. under nitrogen. At this point, the reaction mixture changed consistency from a clear pale yellow solution to a milky suspension. To the suspension, 350 mL of ether was added. Acetic acid (ca. 15 mL) was added until the
suspension turned to a clear yellow color. The clear yellow solution was then washed twice with DI H₂O, neutralized with a NaHCO₃ solution (2 M) and washed twice with DI H₂O. The ether layer was collected and dried over MgSO₄ (anhydrous). Once the solvent was removed, 7 g of the product was isolated (pure enough for the next step of the reaction). ¹H NMR (300 MHz, δ/ppm, CDCl₃) 0.87 (t, 3H), 1.0-1.1 (m, 7H), 1.8-2.1 (m, 2H), 3.10 (t, 0.5H), 4.25 (m, 2H), 6.95 (d, 0.5H), 9.68 (s, 0.5H), 11.40 (d, 0.5H).

Synthesis of 3,8-di(n-butyl)-1,10-phenanthroline-4,7-dione: Ethyl 2-formyl-hexanoate, 7 g (0.041 mol), was dissolved in 200 mL of dichloromethane. To the solution, 1.9 g (0.018 mol) of 1,2-phenylenediamine was added. The resulting solution was heated at reflux in a Dean-Stark apparatus for 2 h. The solvent was removed to afford 7.8 g of an oily brown residue. The residue was used without further purification, and 4 g of it was added to diphenyl ether (100 mL). The solution was heated to 230° C using a sand bath under a continuous nitrogen stream. The solution was charged with a vigorous stream of nitrogen, and the temperature of the sand bath was raised to 245° C. After 25 min., the sand bath was removed. The temperature of the solution cooled to 50° C, and a white precipitate formed. The suspension was then added to 200 mL of hexanes to induce more precipitation. The precipitate was suction-filtered and washed with ether. The washed precipitate was added to 50 mL of acetone and heated at reflux for 30 min. The suspension was cooled to room temperature, and the resulting precipitate was filtered and dried in vacuo at room temperature to afford 2 g of product. ¹H NMR (300 MHz, δ/ppm, DMSO) 0.94 (t, 6H), 1.3-1.6 (m, 6H), 7.96 (s, 4H).

Synthesis of 3,8-di(n-butyl)-4,7-dibromo-1,10-phenanthroline: 1.2 g of 3,8-di(n-butyl)-1,10-phenanthroline-4,7-dione was added to 25 g of melted phosphoryl tribromide
(POBr₃) under nitrogen. The resulting mixture was heated overnight at 70°C with stirring. The hot solution was slowly added drop-wise to well-stirred ice water (100 g of ice and 200 mL of water). After 15 min., a solid precipitate formed, and 60 mL of chloroform was added. A KOH solution (concentrated, 10 g in 10 mL water) was added drop-wise to bring the solution pH to 11. The organic layer was separated, and the water layer was extracted three times with 100 mL of chloroform. The combined chloroform layers were washed with 150 mL of a 1 M KOH solution, three times with 150 mL of DI H₂O and dried over MgSO₄ (anhydrous). After removing the solvent, 1.4 g of the product was isolated. ¹H NMR (300 MHz, δ/ppm, CDCl₃) 1.02 (t, 3H), 1.45 (m, 4H), 1.72 (m, 4H), 3.06 (t, 4H), 8.33 (s, 2H), 8.91 (s, 2H).

Synthesis of 3,8-di(n-butyl)-4,7-di(tolyl-acetylenyl)-1,10-phenanthroline: 3,8-di(n-butyl)-4,7-dibromo-1,10-phenanthroline, 300 mg, was mixed with 260 mg of tolylacetylene dissolved in 6 mL of THF, 5 mL of diisopropylamine, 6 mol % Pd(PPh₃)₂Cl₂ and 3 mol % CuI. The mixture was degassed under argon for 20 min. The resulting mixture was heated at 65°C under argon for 24 h. The solvents were removed, and the residue was passed through a short silica gel column. To remove the excess tolylacetylene, the starting eluant was hexanes. The eluant was gradually replaced with pure chloroform. The product washed out as a brown band. After removing the solvent, the residue was recrystallized in a mixture of acetone and ethanol. A light yellow crystalline solid, 160 mg, was collected (prolonging the reaction time may increase the yield). ¹H NMR (300 MHz, δ/ppm, CDCl₃) 0.96 (t, 6H), 1.43 (m, 4H), 1.80 (m, 4H), 2.41 (s, 6H), 3.10 (t, 4H), 7.25 (d, 4H), 4.58 (d, 4H), 8.42 (s, 2H), 9.03 (s, 2H).
PtTFPP: Pt(II) *meso*-tetrakis(pentafluorophenyl)porphine (PtTFPP) was purchased from Porphyrin Products Inc. (Logan, UT).

**Preparation of Coatings**

Ru(II) α-diimine complexes/SPDMS: Silanol PDMS (500 mg, 0.056 mmol of Si-OH endgroups) and methyltriacetoxysilane (48.9 mg, 0.22 mmol) were dissolved in 4 mL dichloromethane and stirred for 0.5 h. Then 1 mg of the luminescent dye was added to the polymer solution and the mixture was stirred for 5 min. (All of the components are freely soluble in this solution.) Finally, two drops of glacial acetic acid were added to catalyze the condensation polymerization. The solution was sprayed onto a clean borosilicate microscope slide and a 2 in. diameter x 1/16 in. thick borosilicate glass disk using a commercially available air-brush operated at 15 psi. The coatings were cured at ambient temperature and 33 % relative humidity for 12 – 24 h. Profilometry demonstrated that the cured films were typically 5 μm thick.

Various concentrations of PtTFPP in SPDMS binder: The films were prepared in the same manner as the above Ru(II) α-diimine complex films. The concentration of PtTFPP was increased: 2 mM, 3 mM, 5 mM, 10 mM, and 17 mM.

Various mole ratios of cross-linker in PtTFPP/SPDMS films: The films were prepared in the same manner as the above Ru(II) α-diimine complex films. The mole ratio of the cross-linker, methyltriacetoxysilane, was increased: 1:4, 1:5, 1:7, 1:9, and 1:19 mole ratio of oligomer:cross-linker.

[Ru(dpp)₃]Cl₂/SiO₂/SPDMS: The films were prepared in the same manner as the above Ru(II) α-diimine complex films. Increased weight percents of a hydrophilic fumed silica gel were added to the SPDMS polymer binder with stirring for 20 min.: 1 wt. %
and 10 wt. % relative to total weight of polymer binder (500 mg). Cab-O-Sil amorphous Fumed Silica Grade M-5 was purchased from CABOT Corporation (Tuscola, IL).

[Ru(dpp)$_3$]Cl$_2$/SiO$_2$/PDMS: The films were prepared in the same manner as the above [Ru(dpp)$_3$]Cl$_2$/SiO$_2$/SPDMS films; however, 500 mg of commercially synthesized PDMS, DMS-D33, was used as the polymer binder. No cross-linking oligomers were needed. One drop of glacial acetic acid was added to catalyze the condensation polymerization. Increased weight percents of hydrophobic fumed silica gel were added: 1 wt. % and 10 wt. %.

[Ru(dpp)$_3$]Cl$_2$/PDMS: The films were prepared in the same manner as the above [Ru(dpp)$_3$]Cl$_2$/SPDMS films; however, 500 mg of commercially synthesized PDMS, DMS-D33, was used as the polymer binder. No cross-linking oligomers were needed. One drop of glacial acetic acid was added to catalyze the condensation polymerization. The polymer solution and 1 mg of luminophore needed only 5 min. to stir.

**Instrumentation**

The set-up for the inverted fluorescence microscope, fluorimeter and UV/Vis apparatus are extensively explained in the Experimental section of Chapter 2.

**Fluorescence Microscope Image Analysis**

In every case, the raw fluorescence intensity image matrix, $I[x,y;P_{air}]$, was an average of seven individual 300 ms CCD exposures where $x$ and $y$ were the orthogonal pixel locations of the CCD and $P_{air}$ was the air pressure. For a given spatial field of view $I[x,y;P_{air}]$ is obtained at seven $P_{air}$ values. Subsequent image analysis is performed using a PV-Wave (Visual Numerics, Inc.) macro that was written in-house. The macro carries out the following mathematical operations on the $I[x,y;P_{air}]$ data.

1. Each raw image was background corrected according to equation (3-4)
\[ I^c[x,y;P_{air}] = I[x,y;P_{air}] - I_{dark}[x,y;P_{air}] \]  

(3-4)

where \( I_{dark} \) is the "dark-count" intensity matrix collected with the excitation light blocked.

2. A smoothing-routine (3 x 3 pixels) is applied to the intensity images to correct for subtle shifts in the image registration.

3. The SV coefficients (A and B, (3-3)) were computed on a pixel-by-pixel basis by carrying out a linear least-squares regression of the image data at seven \( P_{air} \) values according to equation (3-5)

\[ \frac{I^c[x,y;P_{air} = \text{1 atm}]}{I^c[x,y;P_{air}]} = A[x,y] + B[x,y]P_{air} \]  

(3-5)

The pixel-by-pixel least-squares computation also affords a matrix of regression coefficients (\( r[x,y] \)). The regression coefficients are simply used as an indication of SV linearity. Values less than one indicate a non-linear response.

4. A matrix of SV constants was then computed from the \( A \) and \( B \) matrices according to equation (3-6)

\[ K_{sv}[x,y] = \frac{B[x,y]}{A[x,y]} \]  

(3-6)

5. Standard deviations in \( r[x,y] \) and \( K_{sv}[x,y] \) (\( \sigma_r \) and \( \sigma_{K_{sv}} \), respectively) are computed for each spatial field of view. Each of these operations was carried out for images obtained on 5 separate microscopic regions of a sensor film.

6. An average SV constant (\( \overline{K_{sv}}^{av} \)) was computed for each microscope spatial field of view according to equation (3-7)
\[
K_{sv}^{av} = \frac{\sum \sum K_{sv}[i, j]}{i \times j}
\] (3-7)

where \(i \times j\) represent the size of the CCD image (typically 650 x 515 pixels).

(7) Finally, the macro allowed the user to create false-colored images that delineated the pixel-by-pixel values of \(K_{sv}\) (and other parameters), where the individual values of \(K_{sv}\) are indicated by a color map.

The PV-Wave macro appears in the appendix with accompanying subroutines.
CHAPTER 4
CONCLUSIONS

In the preceding two chapters, two independent yet intimately related projects were defined. Several dual-luminophore, optical oxygen sensing coatings were developed and characterized utilizing numerous physical and spectroscopic methods. Interest in spectroscopic techniques, particularly fluorescence microscopy, led to the development of a novel microscopy technique. Examining the results for the dual-luminophore coatings in Chapter Two as well as the mono-luminophore coatings in Chapter Three leads to several conclusions:

1) Several dual-luminophore coatings were developed which conjointly incorporate a pressure-sensitive luminophore and a pressure-independent but temperature dependent luminophore. The PtDOClµsp/VPDMS and PtDOCl-Sµsp/VPDMS coatings comprise Pt(II) tetra(pentafluorophenyl)porphyrin (PtTFPP) as the pressure-sensitive luminophore and 3,3'-diethyloxacarbocyanine iodide (DOCI) loaded microspheres (DOClµsp and DOCl-Sµsp) as the pressure-insensitive but temperature-sensitive luminophore dispersed in vinyl polydimethylsiloxanes (VPDMS 17,200 MW) polymer binder. When coated onto bare or primed (TiO₂/silanol polydimethylsiloxanes MW 18,000, methyltriacetoxysilane cross-linker) borosilicate microscope slides, the formulations are shown to exhibit spectrally resolved photoluminescence emissions with no evidence of dubious chemical interactions between the two luminophores.
a) Both coatings are thermally stable over a 40 K range (273 – 313 K) and exhibit no indication of hysteresis with respect to repeated thermal cycling over the 273 – 313 K range. Therefore, these coatings can be utilized at wind-tunnel conditions where the temperature ranges have been documented to vary from 283° C to 323° C.16

b) The coatings’ SV response is temporally stable over a minimum four-month period. Therefore, a model may be coated and stored without immediate evaluation. This aspect facilitates model preparation without the immediacy of scheduling wind-tunnel runs.

c) The coatings’ PtTFPP photoluminescence emission intensity is photostable over a minimum four-hour illumination period. The DOCIµsp and DOCI-Sµsp did exhibit some photodegradation but no more than a 0.77 %·min⁻¹ degradation for the DOCIµsp in the PtDCIµsp/VPDMS coating. Therefore, coated wind-tunnel models can be exposed to extended periods of excitation illumination with consistent photoluminescence emission response during run-times.

d) Scanning electron microscopy imaged the interior and exterior morphology of the polystyrene microspheres before and after dye adsorption. Fluorescence microscopy illustrated the average length and relative distribution of the microspheres in the two coatings as well as the distribution of PtTFPP molecules relative to DOCIµsp and DOCI-Sµsp.

e) Application of the coatings in an imaging calibration cell reveals that the temperature dependence of the pressure probe’s emission intensity can be
corrected, and a true analysis of the pressure probe’s response to variation in $P_{\text{air}}$ is obtained. Analysis of the raw intensity images of the two coatings at 550 nm and 650 nm reveals that the intensity data of the PtDOCl-Ssp/VPDMS coating is more heterogeneous. The preparation techniques or the coating components need to be further developed in such a way as to eliminate the heterogeneous distribution of intensity values.

2) A fluorescence microscopy technique has been developed that allows for the investigation of the luminescence properties of film-based oxygen sensors with spatial resolution of $< 5 \mu m$. The new technique has been applied to explore the properties of four series of mono-luminophore pressure-sensitive coatings that differ widely in their luminescence response to variation in $P_{\text{air}}$.

   a) A sensor series based on increased concentrations (mM) of PtTFPP in a silanol polydimethylsiloxanes (SPDMS 18,000 MW) polymer binder exhibits increased aggregation and microcrystallization of the PtTFPP luminophore at the microscopic level with no hindrance in macroscopic SV response to variation in $P_{\text{air}}$. The formation of aggregates and microcrystallites has no apparent effect, since the luminophore, sufficiently solubilized in other regions of the polymer, provides adequate background luminescence intensity to compensate for the formation of a heterogeneous luminescence field.

   b) A series of PtTFPP/SPDMS coatings incorporating increased mole ratios of cross-linker (methyltriacetoxy silane) exhibit dewetting of the polymer binder with no affect to the macroscopic SV response with variation in
While increased mole ratios of cross-linker induced polymer dewetting, the luminescence intensity of the intact polymer is sufficient enough to compensate for areas void luminescence.

c) A sensor series based on Ru(II) α-dimine complexes dispersed in an SPDMS polymer binder exhibit widely differing SV responses to variation in $P_{air}$. The degree of luminophore solubility is evident in the microscopic spatial intensity distribution of the luminophores, degree of luminescent intensity, and spatial SV response to variation in $P_{air}$. Less soluble luminophores ([Ru(dpp)$_3$]Cl$_2$ and [Ru(dpp)$_3$](BPh$_4$)$_2$) produce more luminophore aggregation and microcrystallization and depressed or non-linear SV responses.

d) A series of [Ru(dpp)$_3$]Cl$_2$ dispersed in SPDMS and PDMS polymer binders with increased weight percents of hydrophilic fumed silica gel exhibit enhanced SV response. This is due to adsorption of the luminophore onto the silica gel. The silica gel particles possess increased surface areas for better facilitation of [Ru(dpp)$_3$]Cl$_2$ luminescence quenching. While microscopic SV analysis illustrates a very heterogeneous spatial distribution of intensity and $K_{SV}$ values, the macroscopic analysis is positively affected by the addition of fumed silica gel and produces linear plots of increased SV sensitivity.
Macro to read PSP images (.spe format) and analyze pixel-by-pixel Stern-Volmer plots.

; Created: 07-08-99, JPH
pro pixelsv, fileout

; User input
region = 'r7'  ; Region designation
suppix = 3    ; Size of window (nxn) for smoothing, 0 = no smoothing
plotint = 0   ; Plot color intensity images if = 1
savebmp = 0   ; Save color intensity images as bitmaps if = 1 and plotint = 1
subksv = 1    ; Interrogate Ksv over subregion if = 1

p = [ 14.658, 10.15, 8.11, 6.09, 4.27, 2.19, 0.43] ; Array of values

; Region designation
Suppix = 3 ; Size of window (nxn) for smoothing, 0 = no smoothing
Plotint = 0 ; Plot color intensity images if = 1
Savebmp = 0 ; Save color intensity images as bitmaps if = 1 and plotint = 1
Subksv = 1 ; Interrogate Ksv over subregion if = 1

Files to read: follows specified format for file name. region + pressure number + spe extension.
Files = 
filesbmp =
fdark ='dark'+region+'.spe'

Pct = 1
KSV_cntr_min = 0.00
KSV_cntr_max = 0.14

define column and row region: 0 < c1 < c2 < ncol (1500), 0 < r1 < r2 < nrol (1500)

r1 = 357 ;257
r2 = 672 ;772
c1 = 425 ;325
c2 = 875 ;975

; Define contour settings
ctrs = 41
ctr_high = 225. ; High contour color value
ctr_low = 10. ; Low contour color value
ctr_space = (ctr_high-ctr_low)/ctrs  
clev = fltarr(ctrs); Contour values  
clab = intarr(ctrs); Contour labels on/off  
cin = intarr(ctrs+1); Contour color index  
loadct, 0

; Declare arrays  
nfiles = n_elements(files)  
fileref = files(0)  
filedk = ''  
intavg = fltarr(nfiles)  
intstd = fltarr(nfiles)  
nc = c2-c1+1  
nr = r2-r1+1  
intdata = fltarr(nc, nr, nfiles)  
intdark = fltarr(nc, nr)  
intnorm = fltarr(nc, nr, nfiles)  
ratio = fltarr(nc, nr, nfiles)  
svm = fltarr(nc, nr)  
svb = fltarr(nc, nr)  
corr = fltarr(nc, nr)

; Read files and set data manipulation files  
loadct, 5  
for loop = 0, nfiles-1 do begin  
    speread, dir, files(loop), data, ncol, nrow  
    intdata(*,*,loop) = data(c1:c2,r1:r2)  
    if loop eq 0 then begin  
        speread, dir, fdark, data, ncol, nrow  
        intdark = data(c1:c2,r1:r2)  
    endif  
    intdata(*,*,loop) = intdata(*,*,loop)-intdark(*,*)  
    count = 0  
    for ii = 0, nc-1 do begin  
        for jj = 0, nr-1 do begin  
            if intdata(ii,jj,loop) le 0. then begin  
                intdata(ii,jj,loop) = 0.1  
                count = count+1  
            endif  
        endfor  
    endfor  
    if count gt 0 then print, 'Pct pixels <= 0: ', files(loop), count/float(nc*nr)*100.
    print, 'Max and min intensity: ', files(loop), max(intdata(*,*,loop)), min(intdata(*,*,loop))  
    intavg(loop) = avg(intdata(*,*,loop))  
    intstd(loop) = stdev(intdata(*,*,loop))  
    ratio(*,*,loop) = intdata(*,*,0)/intdata(*,*,loop)
endfor
print, 'Avg & Stdev Dark Intensity', avg(intdark), stdev(intdark)
print, 'Avg Intensity'
print, transpose(intavg)
print, 'Stdev Intensity'
print, transpose(intstd)
print,

; Calculate average SV plot
; Quad fit: Window 10
; Linear fit: Window 11
temp = poly_fit(p,intavg(0)/intavg,2,svfitquad,abc,sigquad)
svq_avg = temp(2)
svm_avg = temp(1)
svb_avg = temp(0)
print, 'Quadratic fit coefficients (ROI): ', svq_avg, svm_avg, svb_avg
print, 'Std Dev of Fit: ', sigquad
print,
window, 10, xsize = 400, ysize = 400, title = 'Global Quad Fit'
plot, p, intavg(0)/intavg, psym = 6, yrange=[0,max(intavg(0)/intavg)]
oplot, p, svfitquad, psym = 0
temp = poly_fit(p,intavg(0)/intavg,1,svfitlin,abc,siglin)
svm_avg = temp(1)
svb_avg = temp(0)
corrlin = correlate(p,intavg(0)/intavg)
print, 'Linear fit coefficients & KSV (ROI): ', svm_avg, svb_avg, svm_avg/svb_avg
print, 'Std Dev of Fit: ', siglin
print, 'Correlation of Data: ', corrlin
print,
window, 11, xsize = 400, ysize = 400, title = 'Global Linear Fit'
plot, p, intavg(0)/intavg, psym = 6, yrange=[0,1.2]
oplot, p, svfitlin, psym = 0

; Perform spatial convolution (moving window averaging)
if suppix gt 1 then begin
for loop = 0, nfiles-1 do begin
print, 'Smoothing file...', files(loop)
intdata(*,*,loop) = smooth(intdata(*,*,loop), suppix)
endfor
endif
print,

; Set countour limits for image plots
maxint = max(intdata)
minint = min(intdata)
cmin = 0.
\[ c_{\text{max}} = \text{maxint} \times 1.05 \]
\[ c_{\text{diff}} = c_{\text{max}} - c_{\text{min}} \]

for \( i = 0, \text{ctrs} - 1 \) do begin
\[ c_{\text{lev}}(i) = c_{\text{min}} + (c_{\text{max}} - c_{\text{min}}) \times \left( \frac{\text{float}(i)}{\text{float}(\text{ctrs} - 1)} \right) \]
\[ c_{\text{in}}(i) = c_{\text{tr_low}} + (c_{\text{tr_high}} - c_{\text{tr_low}}) \times \frac{\text{float}(i)}{\text{ctrs}} \]
\[ c_{\text{lab}}(i) = 1 \]
endfor

\[ c_{\text{in}}(\text{ctrs}) = c_{\text{tr_high}} \]
\[ c_{\text{tr_diff}} = c_{\text{tr_high}} - c_{\text{tr_low}} \]
\[ \text{lgth} = r_2 - r_1 \]
if \( c_2 - c_1 \) gt \( r_2 - r_1 \) then \( \text{lgth} = c_2 - c_1 \)

; Plot images of raw intensities: Windows 1 through nfiles
if plotint eq 1 then begin
  for loop = 0, nfiles - 1 do begin
    \[ \text{temp_int} = (c_{\text{tr_diff}} \times (\text{intdata}(*, *, \text{loop}) - c_{\text{min}})) / (c_{\text{max}} - c_{\text{min}}) + c_{\text{tr_low}} \]
    \[ \text{window, loop, xsize} = \text{lgth} + 90, \text{ysize} = \text{lgth} + 10, \text{title} = \text{files(\text{loop})} \]
    \[ \text{tv, reverse(\text{temp_int}, 2)} \]
    \[ \text{cntrleg2, lgth, ctrs, clev, cin} \]
    if savebmp eq 1 then begin
      \[ \text{print, 'Saving bitmap: ', filesbmp(\text{loop})} \]
      \[ \text{status} = \text{WWRITE_DIB(\text{loop}, Filename=dir+filesbmp(\text{loop}))} \]
    endif
  endfor
endif
print, ''

; Plot Intensity Histograms
\( bs = 10 \)
window, 20, xsize = 500, ysize = 500, title = 'Intensity Histogram'
for i = 0, nfiles - 1 do begin
  \[ \text{intnorm(*, *, i)} = \text{intdata(*, *, i)} \]
  \[ \text{inthist} = \text{histogram(intnorm(*, *, i)), binsize = bs} \]
  \[ \text{nelem} = \text{n_elements(inthist)} \]
  \[ \text{xintdata} = \text{fltarr(nelem)} \]
  \[ \text{minintnorm} = \text{min(intnorm(*, *, i))} \]
  for j = 0, nelem - 1 do xintdata(j) = j*bs + minintnorm
  if i eq 0 then plot, xintdata, inthist, xrange = [min(intdata), max(intdata)]
  if i gt 0 then oplot, xintdata, inthist, color = i*25
  status = DC_WRITE_FREE(dir+'hist'+string(i)-i+fileout, xintdata, inthist, /column)
endfor

; Calculate pixel SV over ROI
print, 'Calculating pixel-by-pixel Ksv statistics over ROI...'
\[ \text{count} = 0 \]
for i = 0, \text{nc} - 1 do begin
for j = 0, nr-1 do begin
    temp = poly_fit(p,intdata(i,j,0)/intdata(i,j,*),l,svfit)
    svm(i,j) = temp(1)
    svb(i,j) = temp(0)
    corr(i,j) = correlate(p,intdata(i,j,0)/intdata(i,j,*))
endfor
eendfor
KSV = svm/svb
svm_avg_pix = avg(svm)
svb_avg_pix = avg(svb)
KSV_avg_pix = avg(KSV)
svm_std_pix = stdev(svm)
svb_std_pix = stdev(svb)
KSV_std_pix = stdev(KSV)
corr_avg = avg(corr)
KSV_max = max(KSV)
KSV_min = min(KSV)
print, 'Average & Std of Stern-Volmer KSV w/ avg corr-coef (Pixels): ', KSV_avg_pix,
KSV_std_pix, corr_avg
print, '
print, 'Max and Min of KSV: ', KSV_max, KSV_min
print, '

; Plot of correlation coefficient

cmin = 0.0

cmax = 1.0

cdiff = cmax-cmin
for i = 0, ctrs-1 do begin
    clef(i) = cmin + (cmax-cmin)*(float(i)/float(ctrs-1))
    cin(i) = ctr_low + (ctr_high-ctr_low)*float(i)/ctrs
    clab(i) = 1
endfor

\text{cin(ctrs) = ctr_high}

ctr_diff = ctr_high-ctr_low
lgth = r2-r1
if c2-c1 gt r2-r1 then lgth = c2-c1

\text{temp_corr = ((ctr_diff)*(corr-cmin))/(cmax-cmin)+ctr_low}

window, 21, xsize = lgth+90, ysize = lgth+10, title = 'Correlation Plot'
tv, reverse(temp_corr,2)
cntrleg2, lgth, ctrs, clef, cin

; Plot Ksv Histogram

bs = KSV_std_pix/3.
KSVhist = histogram(KSV, binsize = bs)
nelem = n_elements(KSVhist)
xdata = fltarr(nelem)
for i = 0, nelem-1 do xdata(i) = i*bs+KSV_min
window, 22, xsize = 300, ysize = 300, title = 'Ksv Histogram'
plot, xdata, KSVhist
print, 'Bin size for histogram plot: ', bs

: Plot of KSV

cmin = KSV_cntr_min ; KSV_cntr_min ; KSV_avg_pix*(1.-pct)
cmax = KSV_cntr_max ; KSV_cntr_max ; KSV_avg_pix*(1.+pct)
cdiff = cmax-cmin
for i = 0, ctrs-1 do begin
clev(i) = cmin + (cmax-cmin)*(float(i)/float(ctrs-1))
cin(i) = ctr_low + (ctr_high-ctr_low)*float(i)/ctrs
clab(i) = 1
endfor
cin(ctrs) = ctr_high
ctr_diff = ctr_high-ctr_low
lgth = r2-r1
if c2-c1 gt r2-r1 then lgth = c2-c1
temp_KSV = ((ctr_diff)*(KSV-cmin)/(cmax-cmin)+ctr_low)
result = size(temp_KSV)
for i = 0, result(1)-1 do begin
for j = 0, result(2)-1 do begin
if temp_KSV(i,j) lt ctr_low then temp_KSV(i,j) = 0.
if temp_KSV(i,j) gt ctr_high then temp_KSV(i,j) = 255.
endfor
endfor

window, 23, xsize = lgth+90, ysize = lgth+10, title = 'Ksv plot'
tv, reverse(temp_KSV,2)
cntrleg2, lgth, ctrs, clev, cin

: Subregion interrogation
if subksv eq 1 then begin
flag = 1
tempint = fltarr(nfiles)
while flag eq 1 do begin
window, 24, xsize = nc+10, ysize = nr+70, xpos = 10 , ypos = 30
data = KSV
ksvroi, data, 'KSV Plot', cmin, cmax, rmin, rmax, flag
if flag eq 1 then begin ; Calculate Ksv over subregion
for i = 0, nfiles-1 do begin
tempint(i) =
avg(intdata(cmin:cmax,rmin:rmax,0))/avg(intdata(cmin:cmax,rmin:rmax,i))
endfor
temp = poly_fit(p,tempint,1,svfitlin,abc,siglin)
print, 'Linear fit coefficients & KSV (ROI): ', temp(1), temp(0), temp(1)/temp(0)
print, 'Std Dev of Fit: ', siglin
print, ''
window, 25, xsize = 400, ysize = 400, title = 'Subregion Linear Fit'
plot, p, tempint, psym = 6, yrange=[0,1.2]
opl, p, svfitlin, psym = 0
xyouts, 50, 380, temp(1)/temp(0), Size = 1., font = 5., /device
xyouts, 50, 360, siglin, Size = 1., font = 5., /device
print, 'Enter 1 to SAVE data or 0 to continue:'
read, opt
filename = 'temp.csv'
if opt eq 1 then begin
  print, 'Enter file name with extension:'
  read, filename
  status = DC_WRITE_FREE(dir+filename, p, tempint, svfitlin, temp(0), temp(1), c1, cmin, cmax, r1, rmin, rmax, /column)
endif
endif
wdelete, 25
endwhile
endif
wdelete, 24

; Write data to file(s)
status = DC_WRITE_FREE(dir+fileout, KSV, /column)
status = DC_WRITE_FREE(dir+'coor'+fileout, corr, /column)
status = DC_WRITE_FREE(dir+'sv'+fileout, p, intavg, intstd, sigquad, siglin, svm_avg, svb_avg, KSV_avg_pix, KSV_std_pix, KSVHist, min(KSV), /column)
QUIT:
return
end

Ksvroi
pro ksvroi, data, out_str, xmin, xmax, ymin, ymax, flag
false = 0
ture = 1

;window, 0, xsize = 520, ysize = 540
data = reverse(data,2)
erase
tvscl, data, /device
elements = size(data)
nc = elements(1)
nr = elements(2)
first = true
repeat begin
  if first then begin
  ; xyouts, 2, nr+30, out_str, Size = 1., font = 5., /device
xyouts, 2, nr+10, "Select ROI...", Size = 1., font = 5., /device

cursor, x1, y1, 3, /device

plots, [x1-4, x1+4], [y1, y1], color = 250, /device
plots, [x1, x1], [y1+4, y1-4], color = 250, /device
cursor, x2, y2, 4, /device
plots, [x1, x2], [y1, y1], color = 250, /device
plots, [x1, x2], [y2, y2], color = 250, /device
plots, [x2, x2], [y1, y2], color = 250, /device
plots, [x2, x2], [y1, y2], color = 250, /device

x1 = 10
x2 = 20
y1 = 10
y2 = 20
first = false
endif
erase
tvsc1, data, /device
plots, [x1, x2], [y1, y1], color = 250, /device
plots, [x1, x2], [y2, y2], color = 250, /device
plots, [x1, x2], [y1, y2], color = 250, /device
plots, [x2, x2], [y1, y2], color = 250, /device
xyouts, 2, nr+50, "ENTER", Size = 1.5, font = 5., /device
xyouts, 2, nr+30, "QUIT", Size = 1.5, font = 5., /device
xyouts, 2, nr+10, "Re-select ROI or Click Enter or Click Quit", Size = 1., font = 5., /device
cursor, tempx1, tempy1, 3, /device
if (tempx1 le 150) and (tempy1 ge nr+50) then begin
  flag = 1
  goto, quit
endif
if (tempx1 le 150) and (tempy1 ge nr+30) then begin
  flag = 0
  goto, quit
endif
x1 = tempx1
y1 = tempy1
erase
tvsc1, data, /device
plots, [x1-4, x1+4], [y1, y1], color = 250, /device
plots, [x1, x1], [y1+4, y1-4], color = 250, /device
cursor, x2, y2, 4, /device
endrep until false
QUIT:
xmin = x1
xmax = x2
if x2 lt x1 then begin
\[ \text{xmin} = x_2 \]
\[ \text{xmax} = x_1 \]
endif
\[ \text{ymin} = y_1 \]
\[ \text{ymax} = y_2 \]
if \( y_2 \) \text{lt} \( y_1 \) then begin
  \[ \text{ymin} = y_2 \]
  \[ \text{ymax} = y_1 \]
endif
return
end

\textbf{Centrleg2}

\texttt{pro centrleg2, len, ctrs, clev, cin}
\[ \text{jstep} = \frac{\text{len}}{\text{ctrs}} \]
\[ j = 0 \]
for \( i = 0, \text{ctrs} - 1 \) do begin
  polyfill, [len+85, len+85, len+89, len+89], [j, j+jstep, j+jstep, j], /device, color = cin(i)
  \[ j = j + \text{jstep} \]
endfor
\texttt{xyouts, len+5, 10, string(clev(0), format = "(f8.2)")}, /device, color = 250, charsise = 1
\texttt{xyouts, len+5, j+jstep, string(clev(ctrs-1), format = "(f8.2)")}, /device, color = 250, 
charsize = 1
return
end

\textbf{Speread}

; This procedure reads WINVIEW .spe image files. It determines the
; size of the 2-D image. An array of floating point
; values representing the b/w intensity is the output: data(ncol,nrow).
; Notes:
; 12/13/99: Currently reads the data (after the image header) as long words (LONARR).
; The header is read as words (INTARR). The header length is hard coded at
2050 words.
pro speread, dir, file, data, ncol, nrow
\texttt{spehead} = \texttt{intarr(2050)}
\texttt{print, 'Reading file: ', dir+file}
\texttt{openr, 1, dir+file}
\texttt{readu, 1, spehead}
nrow = spehead(21)
ncol = spehead(328)
;print, ncol, nrow
;print, spehead
if (ncol \text{lt} 1) or (ncol \text{gt} 1024) then begin
  print, 'Number of columns = ', ncol, ' Out of Range!'
close, 1
goto, quit
endif
if (nrow lt 1) or (nrow gt 1024) then begin
    print, 'Number of rows = ', nrow, ' Out of Range!'
    close, 1
    goto, quit
endif
print, 'Columns: ', ncol, ' Rows: ', nrow
data = lonarr(ncol, nrow)
readu, 1, data
close, 1
;WINDOW, 1, xsize = ncol+10, ysize = nrow+10
;TVSCL, data, /device
QUIT:
return
end

Macro written by Dr. J. Paul Hubner, Adjunct Professor, Aerospace Engineering, Mechanics and Engineering Science, University of Florida
LIST OF REFERENCES


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Assuming Henry's Law holds, $K_{SV}$ is related to $K'SV$ by the equation,

$$K_{SV} = (0.21) \sigma K'SV$$

where $\sigma$ is the solubility coefficient of $O_2$ in the polymer film and 0.21 is the mole fraction of $O_2$ in the air.


BIOGRAPHICAL SKETCH

Joanne M. Bedlek-Anslow was born on July 12, 1973, in Chicago, IL to Anne and John Bedlek. She has a younger sister, Jeanne, a First Lieutenant in the United States Air Force. The two grew-up as best friends and one another's biggest champion. As a young woman, Joanne was active in Girl Scouting, swimming, volunteering and church stewardship. She obtained her Scouting Gold Award, numerous swimming medals and ribbons, and commendations for her community service. Accordingly, she did well throughout grammar and high schools excelling in arts, languages, and science and graduated with honors from J. B. Conant High School.

She began her degree in biology/pre-medicine at Loyola University of Chicago in the fall of 1991. In her sophomore year, she became a chemistry major after attending an organic chemistry course taught by Dr. Mary K. Boyd, Joanne's mentor and friend. During her time at Loyola, Joanne was involved in the university ministry, orchestra, and student affiliate American Chemical Society.

After completing her chemistry major and German minor, Joanne chose a year of Italian immersion at the Loyola University Rome Center, Rome, Italy. Her passionate vocations as a child were centered in the arts and foreign languages. She took advantage of the opportunity abroad to stop, listen, look and breathe in the expansive culture of Italy and Europe. Joanne considers this time away instrumental in developing her awareness of self and presence as a young woman with an extraordinary life still to live.
Joanne, still savoring her newfound self, returned to the states to graduate from Loyola *cum laude*. Shortly thereafter she relocated to Gainesville, FL, to pursue her other more practical passion, chemistry.

During her time at the University of Florida, Joanne learned that she could recreate herself once more. She developed the analytical critical thinking aspects of her persona in pursuing her Ph.D. Long hours spent in the library and laboratory left very little time for other pleasures; however, she balanced her studies with an active involvement in her church, art, and various outdoor recreations. In the midst of all this, she married her college sweetheart, Paul. The two share similar dreams and aspirations forming a relationship full of love and support.

Upon graduation, Joanne, Paul and their two kitties will relocate to Columbia, SC, where she will begin her career as a Senior Chemist with DuPont Nylon.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kirk Schanze, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William Dolbier
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Lisa McElwee-White
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

James Boncella
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Bruce Carroll
Associate Professor of Aerospace Engineering

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 2000

Dean, Graduate School