Macromol. Symp. ***196***, *235–248 (2003)*

Iridium(III) Complexes as Polymer Bound Oxygen Sensors

Maria C. DeRosa, Peter J. Mosher, Christopher E. B. Evans, Robert J. Crutchley**

Chemistry Department, Carleton University, ON, K1S 5B6, Canada and the National Research Council of Canada, Ottawa, ON, Canada
E-mail: robert_crutchley@carleton.ca

Summary: New luminescent oxygen sensors have been prepared by covalent attachment of iridium complex luminophores to a silicone polymer. The oxygen sensor properties of these novel materials were compared to related sensors in which the luminophore is dispersed within the polymer matrix. Covalently bound luminophore materials showed increased sensitivity to oxygen over dispersions in pure silicone polymer as well as in blends with polystyrene, which was added to improve the mechanical properties of the material.

Keywords: luminescence; metal-polymer complexes; oxygen sensors; photochemistry; silicones

Introduction

It has been known for many years that the luminescent excited state of many molecules is quenched by oxygen, forming highly reactive singlet oxygen.[1] This is of great concern to polymer chemists as singlet oxygen formation is thought to be the main cause of polymer photodegradation. On the other hand, researchers in the field of sensor technology have taken advantage of this behavior to create oxygen sensors for *in vivo*, groundwater and barometric measurements.[2,3] The latter is of particular interest to aerospace and automotive industries as an understanding of aerodynamics is crucial to stability and fuel efficiency concerns. Traditional methods for measuring surface pressure require pressure taps or transducers. These are time consuming and expensive to employ and impractical for moving parts (i.e. propeller blades). A far more efficient method is to employ pressure sensitive paints (PSP) in which a luminescent molecule (a luminophore) is dispersed in the polymer matrix/solvent that composes the bulk of the PSP. The luminescence derived from a model painted with a PSP will ideally be in direct proportion to the air pressure over the model's surface and this is illustrated schematically in Figure 1.

CCC 1022-1360/00/$ 17,50+.50/0

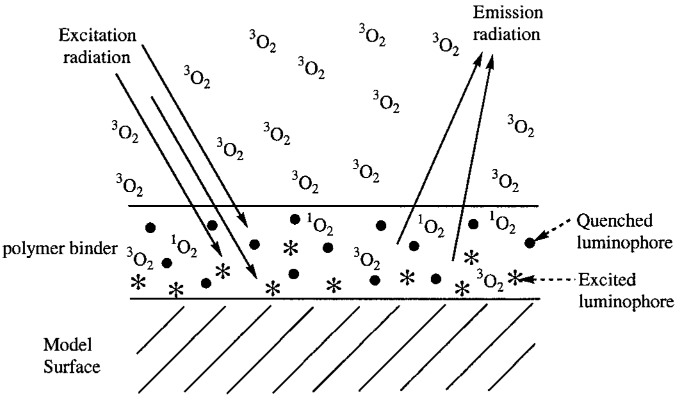

Figure 1. Schematics of a pressure sensitive paint coating a model surface. Filled circles are ground state luminophores while asterisks are excited state luminophores.

Bimolecular collisions between excited luminophores and ground state (triplet) oxygen quench the luminophore non-radiatively, producing singlet oxygen and ground state luminophore. The relationship between the luminophore's emission intensity, I, or excited state lifetime, τ, and oxygen concentration is given by the Stern-Volmer equation (1),

$$\frac{I^0}{I} = \frac{\tau^0}{\tau} = 1 + K_{SV}[O_2] \qquad (1)$$

in which I^0 and τ^0 are, respectively, the luminophore's intensity and lifetime in the absence of oxygen, and K_{SV} is the Stern-Volmer constant. Equation 1 assumes a single luminophore environment, and deviations from the expected linear behavior occur when this is not the case, or when quenching occurs by mechanisms other than bimolecular collisions.

In luminescence barometry applications, changes in ambient pressure alter the concentration of dissolved oxygen within the sensor film. Measurements at zero oxygen concentration are often impractical, and it is therefore convenient to use an alternate point of reference, such as $P = 1$ atmosphere. In this case the relationship between luminescence intensity and air pressure becomes

$$\frac{I_{ref}}{I} = A + Q_S \frac{P}{P_{ref}} \qquad (2)$$

in which P_{ref} is the reference pressure at which the luminophore's intensity is I_{ref}. The slope of the Stern-Volmer plot, Q_S, is nominally constrained to values between 0 and 1 and is a measure of the sensitivity of the PSP to changes in oxygen pressure.[4]

Pressure sensitive paints must meet a number of criteria before they are of practical value. These are:

1. Luminophore excitation wavelengths should be at long wavelengths
2. Emission properties should be largely temperature independent
3. The luminophores Stokes shift should be large
4. Good stability
5. Short response time
6. Appropriate sensitivity to oxygen concentration

Excitation at short wavelengths is likely to increase photodegredation of the polymer and the cost and safety concerns associated with the light source are also disadvantageous. Temperature independence of luminophore emission is a very desirable property because without it small changes in intensity of emission due to oxygen quenching could be equivalent to that created by changes in temperature. Deconvoluting this temperature effect from that produced by varying oxygen pressure is not straightforward and can lead to only qualitative results. In practice, all luminophores show some temperature dependence to their emission. The goal is to find a luminophore with a low temperature dependence so that the correction is reasonable and leads to quantitative results. If the overlap between the absorption and emission band envelopes is significant, the luminophore in the PSP will absorb emission radiation. A large Stokes shift, a measure of the separation energy between absorption and emission energies, will minimize this effect. The PSP must be stable during the entire course of the experiment in order to demonstrate reproducibility of the measurements. It is especially important that the luminophore be resistant to reaction with the singlet oxygen that is produced during the experiment. The establishment of equilibrium conditions within the PSP for a given pressure of oxygen over its surface determines the response time (time required afterwhich measurement is constant). This is directly related to the permeability of the PSP to oxygen or more specifically the diffusion of oxygen molecules within the PSP layer. The required response time and oxygen sensitivity depend upon the application. For example, the short air bursts in blow-down wind tunnels require PSP response times of ≤ 1 second and, for the changes in oxygen pressures created, Q_s values of 0.4 to 0.7 are the norm.[3] For ground water measurements, where changes in concentration of oxygen are small, greater sensitivity is required but response times can be much longer.

Low gas-permeability polymers such as polystyrene (PS) and poly(methylmethacrylate) (PMMA) have good mechanical stability but PSPs based on these polymers would have very long response times. Fluorination is known to increase gas permeability, and PSPs using polymers such as poly(hexafluoroisopropyl-*co*-heptafluoro-*n*-butyl methacrylate) and poly(2,2,2-trifluoroethyl-*co*-isobutyl methacrylate)[5] have significantly shorter response times. Silicones (polysiloxanes, *e.g.* polydimethylsiloxane, PDMS) were investigated from very early on due to their extremely large gas permeabilities. Unlike high glass transition temperature (T_g) organic polymers such as PS (90 °C) or PMMA (110 °C), many silicones have extremely low T_g (*e.g.* PDMS, -127 °C) and thus form films with rather poor mechanical properties unless cured (*i.e.* crosslinked) or mixed with hardening additives.

Commonly used luminophores include polycyclic aromatic hydrocarbons,[6] metalloporphyrins,[7] or polypyridyl transition metal complexes.[8] Sensors based *e.g.* on pyrene, PtOEP (OEP = octaethylporphyrin), and $[Ru(dpp)_3]Cl_2$ (dpp = 4,7-diphenylphenanthroline) have all been studied. The sensors studied to date have predominantly been ones in which the luminophore is dispersed within the host matrix as a solid solution. This can lead to the following behaviors that can lead to undesirable properties:

1. Aggregation
2. Leaching
3. Solvation by blend polymers

Luminophore aggregation can lead to self-quenching and loss of emission. Further emission losses can occur by luminophore leaching or sublimation from the PSP layer.[9] If additives or polymer blends are desired to improve PSP properties, the luminophore may partition between the various components, leading to complex or unexpected behavior.[4,10] These problems could be eliminated or at least moderated by covalently attaching the luminophore to the polymer matrix.[11]

Recent studies by Manners and Winnik et al[12] have demonstrated the efficacy of this approach. These authors covalently attached ruthenium phenanthroline complexes to polythionylphosphazenes and found improved Stern-Volmer behavior and significantly increased sensitivity compared to analogous two-component materials where luminophores are dispersed in a polythionylphosphazene matrix.

In this study, we present our results for PSPs composed of luminophores covalently attached to silicones. Silicones have very high gas permeabilities relative to most organic polymers.[13] The main drawback of silicones is that, without curing, they form films with poor mechanical properties. To provide mechanical stability, silicones can be blended with high T_g polymers and/or rigidifying additives such as silica or alumina. The multitude of microenvironments created in these heterogenous materials can create unexpected behaviors in PSP applications. For example, it has been noted that luminophores such as $[Ru(dpp)_3]Cl_2$ have a strong tendency to aggregate within these blended matrices,[14] or to adsorb to the surface of silica.[10] Covalent attachment of the luminophore to silicones should alleviate aggregation and lead to improved PSP properties.

As our luminophore we have selected cyclometallated complexes of iridium(III). The complex $[Ir(ppy)_3]$ (ppy = 2-phenylpyridine, $\tau^0 = 2\ \mu s$, $\phi = 0.4$)[15] has previously been examined as a luminescent oxygen sensor,[15,16] and provides the advantage over analogous ruthenium complexes such as $[Ru(bpy)_3]Cl_2$ (bpy = 2,2'-bipyridine, $\tau^0 = 0.6\ \mu s$, $\phi = 0.042$)[17] or $[Ru(phen)_3]Cl_2$ (phen = 1,10-phenanthroline, $\tau^0 = 0.74\ \mu s$, $\phi = 0.08$)[14] of a longer lifetime and much higher quantum yield. In addition, the non-ionic iridium complexes should be soluable in a greater range of organic solvents compared to charged luminophores, increasing its synthetic utility, and avoiding any deleterious electrostatic interactions.

Synthesis

Cyclometallated complexes of Ir(III) are well known and the synthetic route to the family of luminophores used in this study are shown in Figure 2 and 3.

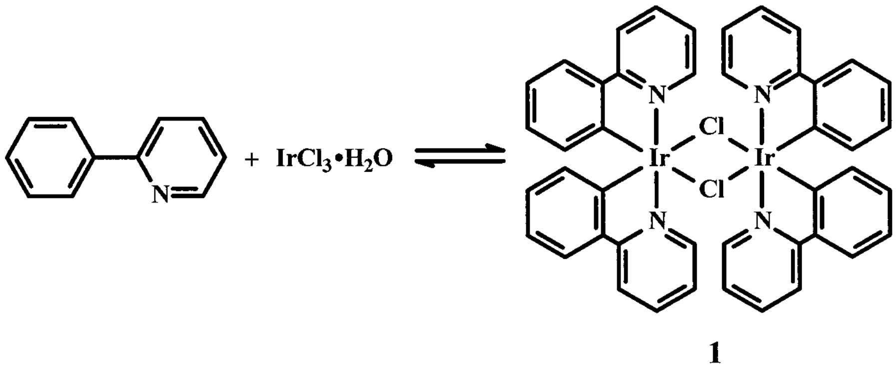

Figure 2. Preparation of **1.**

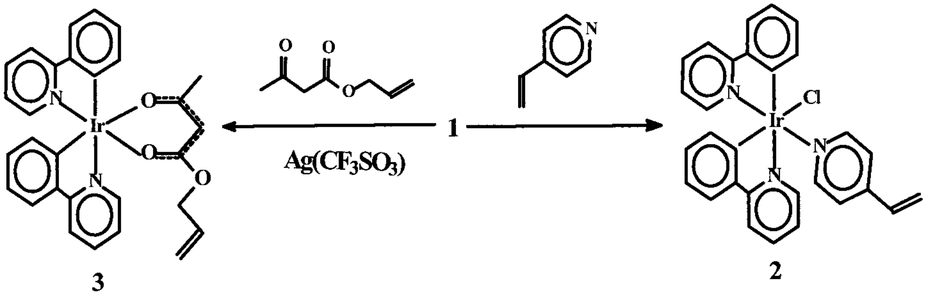

Figure 3. Preparation of the Iridium(III) luminophores.

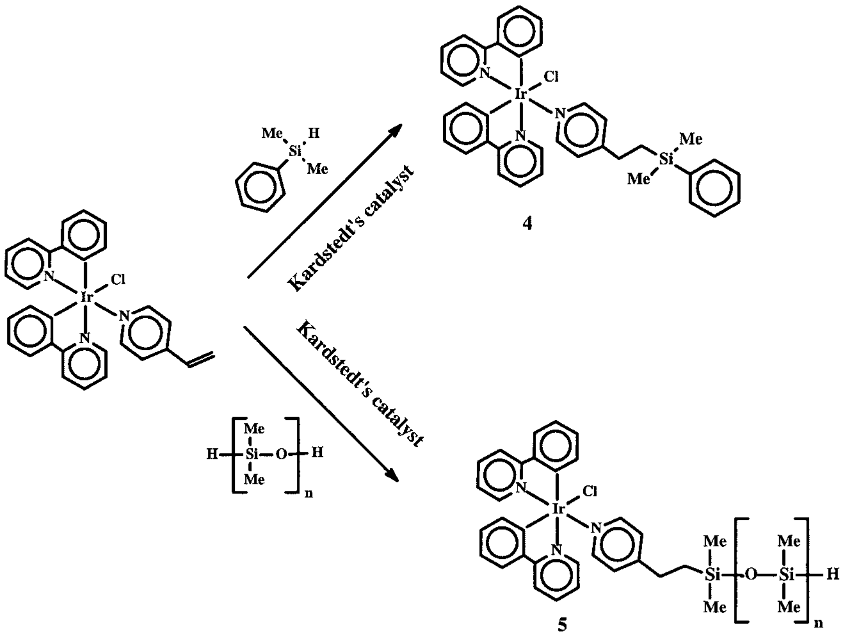

Figure 4. Hydrosilation reaction for the attachment of luminophores to silicones.

Transition metal catalyzed hydrosilation is a facile route to the covalent attachment of luminophores to a silicone backbone as there are a number of commercially available hydride-containing and hydride-terminated silcones. Of these silcones, the hydride-terminated polydimethylsiloxanes PDMS were the easiest to work with because cross-linking reactions, which had a tendency to generate insoluable polymers, were avoided. Figure 4 illustrates the general reaction scheme for luminophore attachment by hydrosilation. In addition to **4**, hydrosilation reactions of complexes **2** and **3**, with hydride-terminated silicones yielded the novel PSP materials **5** and **6,** respectively.

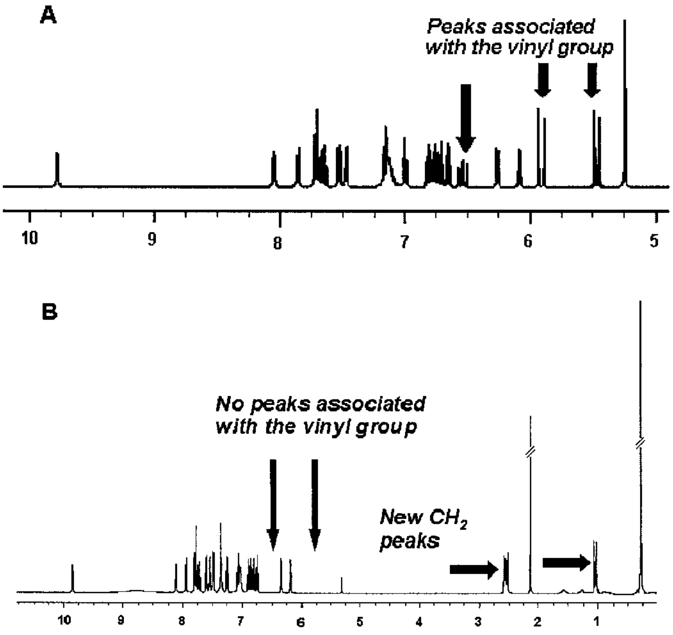

Figure 5. ^1H NMR spectra of complexes **2** and **4** in deuterated methylene chloride.

Characterization

^1H NMR of **2** and the model complex **4** (see Figure 5) provide evidence that the hydrosilation reaction between the luminophore and silicones is indeed possible. In Figure 5a, the ^1H NMR spectrum of **2** shows clearly the presence of vinyl proton chemical shifts. Hydrosilation to form **4** results in the lost of these chemical shifts (Figure 5b) and the appearance of methylene chemical shifts. Unfortunately, the low concentration of the luminophore in **5** and **6**, meant that NMR could not be used to probe the attached luminophore directly. Luminophore attachment was, however, evident by the different behavior of **5** and **6** relative to a dispersion of **2** and **3** in PDMS. For example, while PDMS and **5** are both soluble in hexanes, **2** is not. A sample of **5** can thus be wholly dissolved in hexanes, whereas with a dispersion of **2** in PDMS (prepared by solvent stripping a dichloromethane solution of the two components to dryness) only the polymer dissolves, leaving behind a suspension of **2**. Figure 6 shows the absorption and emission spectra of **5** in acetonitrile solution. The concentration of the luminophore in **5** and **6** were estimated from the π-π* absorption band (a combination of phenyl and pyridine π-π* transitions) that is seen in the ultraviolet region by using the quantitative electronic absorption spectra of **2** and **3** and assuming equivalency of spectral properties and no absorption from PDMS. In this way, the concentrations of luminophore complex in **5** and **6** were estimated to be 3.6 and 3.5 mM, respectively. For **5**, 100% attachment of the luminophore would have resulted in a luminophore concentration of 18.9 mM. The hydrosilation reaction yield is therefore approximately 20%.

Method of Analyses

Each sample was treated as follows: a solution of the sample was applied to an aluminum plate previously covered with a layer of Tristar Starpoxy fluid resistant white epoxy primer (DHMS C4.01 Ty3) using a conventional airbrush. The painted plate was then mounted in an in-house designed pressure chamber. Pressure was controlled via a Scanivalve Corp model PCC100 Pressure Calibrator/Controller in manual mode, and the temperature of the mounting plate was controlled via a thermoelectric cooler coupled to a model LFI-3551 Temperature Controller using a model TCS650 thermistor in the 10 μA range, both

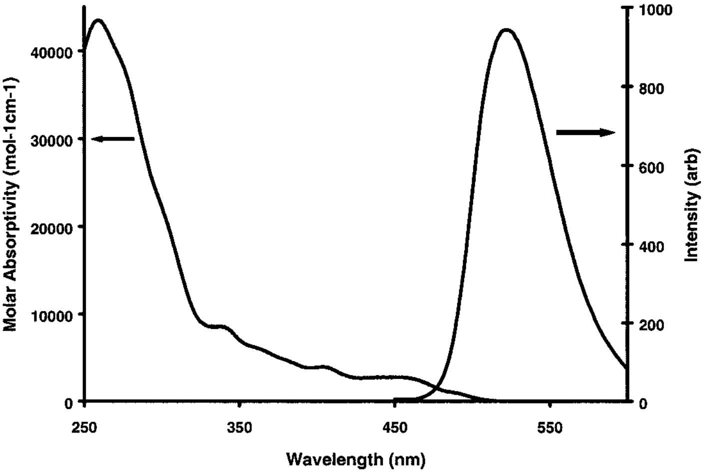

Figure 6. Absorption and emission spectra of **6** in acetonitrile solution. The molar absorptivity has been estimated (see text) and the emission spectrum is uncorrected.

from Wavelength Electronics. Excitation was provided by a Hamamatsu Lightningcure LC5 200W model L8333 Hg/Xe source via a 10 m × 8 mm Oriel UV-Vis Liquid Light Guide (transmission window 300-650 nm). The source was equipped with 011FG09 and 300FS40 filters from Melles-Griot, transmitting approximately in the range 280-320 nm. Emission was measured by a 512×512 Photometrics CH350 12-bit CCD camera equipped with a 500 ± 40 nm bandpass filter (500FS80-50, Melles Griot). Measurements were taken at 10 °C, scanning from low to high pressure. At each pressure, multiple measurements were taken to ensure the oxygen concentration in the film had come to equilibrium. The time required for this to occur provided a qualitative measure of response time. At the end of each calibration a second reading at 15 psi was taken to ensure no significant photodegradation had occurred on the timescale of the experiment. Backgrounds were measured on a section of primed plate. Spectra were also collected for various calibrations using an Acton Research Corporation SpectruMM CCD Detection System. A fiber optic lightguide (LG-455-020) equipped with a Kodak #3 gelatin filter passed the emission through a SpectraPro-150 Imaging Dual Grating Monochromator/Spectrograph onto a 16-bit Hamamatsu 1024×256 CCD.

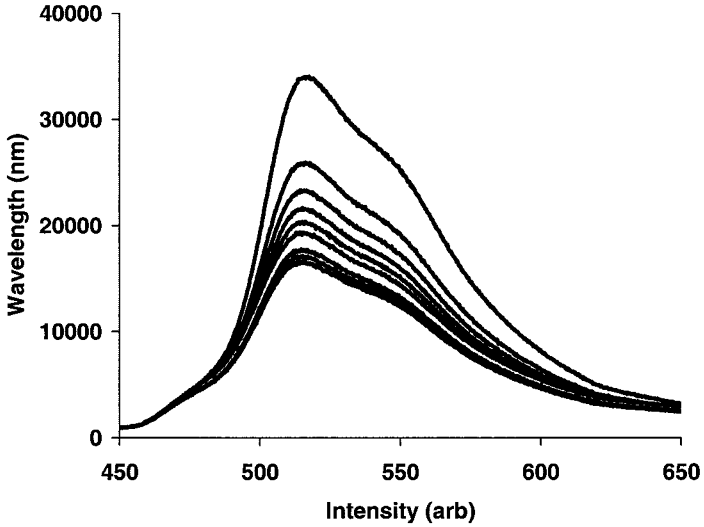

Figure 7. Emission spectra of a thin film of 1:9 **6**/PS showing the loss of intensity with increasing total air pressure. Spectra were taken at 5 psi increments over the range 0.05 to 45 psi and have been corrected for background.

Oxygen Sensitivity

Figure 7 shows the effect of changing air pressure (0 to 45 psi) on the emission spectrum of a thin film of a 1:9 blend of **6** with PS. Similar behavior was seen for **5**. It is clear that the sensitivity of the emission spectrum to oxygen is greatest at low pressures. This is more quantitatively represented by the Stern-Volmer plots (Eqn. 2) in Figure 8.

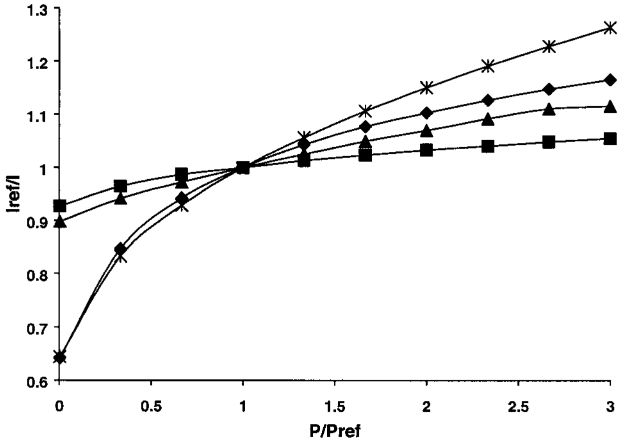

Figure 8. Stern-Volmer Calibration Curves for films of **5** (◆), **2** dispersed in PDMS (■), **2** dispersed in PS (▲) and **5** blended with PS 1:9 (✳)

The marked downward curvature of the Stern-Volmer plots of **5** and its blend with PS has been seen for transition metal complexes in PDMS by other researchers, and has been ascribed to the luminophore being solvated in different microenvironments within the polymer matrix, having different accessibilities to oxygen.[14,18,19] Thus at low pressures only the most accessible luminophore molecules interact with oxygen, leading to high sensitivity, whereas at higher pressures the easily accessible luminophore molecules are largely quenched, and the quenching sensitivity is increasingly dominated by the luminophore molecules in the less accessible domains. Often the luminescence emission decay profile in these cases can be modelled with two exponentials (luminophore lifetimes), and the downward curvature of the Stern-Volmer plots is then attributed to the 'two-site model'. This is, of course, a great oversimplification, and it is generally accepted that a range of different solvation microenvironments is likely to occur in any given sample.[18]

As shown by Figure 8, the oxygen sensitivity of a thin film of **5** is greater than the sensitivity of films of dispersions of **2** in PDMS or PS. Importantly, the blending of PS with **5** to increase the mechanical properties of the film has resulted in a further increase in oxygen sensitivity compared to the film made up of **5** alone. This unexpected albeit gratifying result is suggested to arise from an increase in lifetime of the luminophore because of a reduction in its freedom of movement.

The oxygen sensitivity of various films is given in Table 1 and, where curvature in the Stern-Volmer plots exists, Q_s values are given for an approximately linear range of data. The data clearly illustrate the advantage of polymer bound luminophores over dispersions of luminophores in a given polymer matrix. However, the overall Q_s values of **5** and **6** at pressures greater than 10 psi are too low to be suitable for wind tunnel experiments (Q_s values ranging from 0.4 to 0.7 are preferred).[3] It will be necessary to research other polymer bound luminophores to yield PSPs with greater sensitivity.

Sensor response times were not measured quantitatively. Nevertheless, the 'dispersed-in-PS' luminophores exhibited markedly longer response times to changes in total pressure (on the order of tens of seconds) relative to the 'dispersed-in-PDMS' luminophores (which responded as quickly as the pressure could be changed). The response times of PS blends of **5** and **6** remained very short, however, being at most a few seconds. Maintaining a short response time in the presence of rigidifying additives is a distinct advantage brought about by attachment of the luminophore.

Table 1. Q_s Values from CCD luminescence quenching data over the pressure range 0.05 to 45 psi

	Matrix	
	PDMS	PS
2	0.11,[b] 0.04,[c] 0.02[d]	0.13,[b] 0.08,[c] 0.05[d]
3	0.18,[b] 0.07,[c] 0.05[d]	0.20[bcd]
5[a]	0.62,[b] 0.06,[c] 0.02[d]	0.57,[b] 0.19,[c] 0.12[d]
6[a]	1.00,[b] 0.17,[c] 0.07[d]	0.63,[b] 0.24,[c] 0.17[d]

a) For **5** and **6** the matrices are **5** and **6** alone and **5** and **6** blended with PS at a ratio of 1:9.
b) 0.05 to 5 psi
c) 10 to 45 psi
d) 25 to 45 psi

Conclusion

Luminescent oxygen sensors **5** and **6** based on cyclometallated iridium complexes have been synthesized via hydrosilation of luminophores **2** and **3** onto hydride-terminated PDMS. These novel PSP materials compared favorably with related luminophore-dispersed sensors both in sensitivity and versatility. Not only is the oxygen sensitivity of these luminophore-bound films greater than dispersions of the luminophore in PDMS, but the physical properties of the sensor films can be improved by blending without compromising sensor behavior (higher sensitivity and short response times).

The strategy of polymer bound luminophores offers exciting opportunities in PSP research that we expect to address shortly in future publications.

[1] M. C. DeRosa, R. J. Crutchley, *Coord. Chem. Rev.* **2002**, *233-234*, 351.

[2] D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537.

[3] J. H. Bell, E. T. Schairer, L. A. Hand, R. D. Mehta, *Annu. Rev. Fluid Mech.* **2001**, *33*, 155.

[4] R. Ruffolo, C. E. B. Evans, X.-H Liu, Y. Ni, Z. Pang, P. Park, A. R. McWilliams, X. Gu, X. Lu, A. Yekta, M. A. Winnik, I. Manners, *Anal. Chem.*, **2000**, *72*, 1894.

[5] E. Puklin, B. Carlson, S. Gouin, C. Costin, E. Green, S. Ponomarev, H. Tanji, M. Gouterman, *J. Appl. Polym. Sci.*, **2000**, *77*, 2795; C. S. Subramanian, R. T. Amer, D. M. Oblesby, C. G. Burkett Jr., *AIAA J.*, **2002**, *40*, 582.

[6] K. A. Kneas, W. Xu, J. N. Demas, B. A. DeGraff, *Applied Spectr.*, **1997**, *51*, 1346; M. E. Cox, B. Dunn, *Applied Optics*, **1985**, *24*, 2114.

[7] P. Douglas, K. Eaton, *Sens. Actuators B*, **2002**, *82*, 200; V. V. Vasil'ev, S. M. Borisov, S. M. *Sens. Actuators B*, **2002**, *82*, 272; G. DiMarco, M. Lanza, *Sens. Actuators B*, **2000**, *63*, 42.

[8] A. Mills A. *Sens. Actuators B*, **1998**, *51*, 60; A. Mills, M. D. Thomas, *Analyst*, **1998**, *123*, 1135; W. Xu, K. A. Kneas, J. N. Demas, B. A. DeGraff, *Anal. Chem.*, **1996**, *68*, 2605.

[9] H. Wang, G. Xu, S. Dong, *Analyst*, **2001**, *126*, 1095; J. P. Hubner, B. F. Carroll, K. S. Schanze, H. F. Ji, *Exp. Fluids*, **2000**, *28*, 21; I. Klimant, O. S. Wolfbeis, *Anal. Chem.*, **1995**, *67*, 3160.

[10] X. Lu, I. Manners, M. A. Winnik, *Macromolecules*, **2001**, *34*, 1917.

[11] M. Yafuso, P. F. Korkowski, R. A. Mader, C. Yan, J. T. Carlock, *US Patent 5,296,381*, **1994**; R. R. Holloway, T. T. Kiang, *US Patent 5,070,158*, **1991**; L. Hsu, H. Heitzmann, *US Patent 4,712,865*, **1987**.

[12] Z. Wang, A. R. McWilliams, C. E. B. Evans, X. Lu, S. Chung, M. A. Winnik, I. Manners, *Adv. Func. Mat.* **2002**, *12*, 415.

[13] *The Polymer Handbook*, 3rd Ed., J. Brandrup, E. H. Immergut, Eds., Wiley, New York, **1989**; *Polymer Data Handbook*, J. E. Mark, Ed., Oxford University Press, New York, **1999**

[14] I. Klimant, O. S. Wolfbeis, *Anal. Chem.*, **1995**, *67*, 3160.

[15] E. Vander Donckt, B. Camerman, F. Hendrick, R. Herne, R. Vandeloise, *Bull. Soc. Chim. Belg.*, **1994**, *103*, 207.

[16] Y. Amao, Y. Ishikawa, I. Okura, *Anal. Chim. Acta*, **2001**, *445*, 177.

[17] A. Mills, A. Lepre, *Anal. Chem.*, **1997**, *69*, 4653.

[18] J. N. Carraway, J. N. Demas, B. A. DeGraff, J. R. Bacon, *Anal. Chem.*, **1991**, *63*, 337.

[19] J. N. Demas, B. A. DeGraff, *J. Chem. Educ.*, **1997**, *74*, 690.