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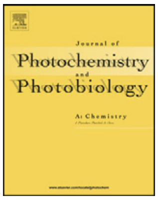

Luminophore charge effects in water-based oxygen sensor films

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ABSTRACT

The neutral luminophore [Ir(ppy)$_2$(fppy)], where fppy = 4-(2-pyridyl)benzaldehyde and ppy = 2-phenylpyridine were prepared and bound to the water soluble amine-functionalized polymer Silamine D208-EDA by either reductive amination or coupling reactions. Pressure sensitive paint (psp) formulations were made by blending microcrystalline cellulose (MC) with these polymer-luminophores and the psp photophysical properties, oxygen sensitivities and luminescent microscopies were compared to psps made from the charged luminophore [Ir(fppy)$_2$(*t*-Bu-iCN)$_2$]CF$_3$SO$_3$, where *t*-Bu-iCN = *tert*-butyl isocyanide, attached by reductive amination to Silamine D208-EDA. The excited-state lifetime for the neutral luminophore in psp blends was almost independent of MC concentration whereas those of the charge luminophore increased with MC concentration. The nearly 30% increase in oxygen sensitivity of psps made with the charged compared to neutral polymer luminophores is ascribed to the association of charged luminophores with polar groups on the surface of MC.

1. Introduction

Research in optical oxygen sensors has found application in a variety of fields including in vivo imaging [1,2], aerodynamics [3], environmental analysis [4], analytical chemistry [5], food industry [6], and biochemistry [7]. We are interested in the application of optical oxygen sensors to barometric measurements to determine the aerodynamics of surfaces in wind tunnel experiments. In a typical experiment, the surface to be examined is covered with a layer of pressure sensitive paint (psp) containing a luminescent molecule whose excited state is quenched by oxygen. Diffusion-limited collisional oxygen quenching of excited states can be described by the Stern–Volmer relationship, in terms of either luminescence lifetime or intensity,

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k_q\tau_0[\mathrm{O_2}] = 1 + K_{\mathrm{SV}}(p_{\mathrm{O_2}}) \quad (1)$$

where I_0 and I are the luminescence intensities, and τ_0 and τ are the lifetimes in the absence and presence of oxygen, respectively, k_q is the bimolecular quenching constant, and K_{SV} is the Stern–Volmer constant. k_q is described by a modified Smoluchowski equation [8,9]:

$$k_q = 4\pi N_p(D_{\mathrm{A}} + D_{\mathrm{B}}) \times 10^3 \quad (2)$$

where N is Avogadro's number, p is a factor representing the probability of a collision resulting in quenching and relates to the radius of interaction between the donor (luminophore) and the acceptor (oxygen), and D_{A} and D_{B} are the diffusion coefficients of the donor and acceptor, respectively. Normally, k_q is considered constant under defined experimental conditions.

The Stern–Volmer relationship (Eq. (1)) can be utilized to correlate luminescence intensity with oxygen pressure in oxygen quenching sensors. However, calibrations at zero oxygen pressure, especially in wind tunnel tests, are not practical. Provided that Henry's law is applicable to oxygen concentration in pressure sensitive materials ($p = kc$, where p is the partial pressure of oxygen, c is molar concentration of oxygen, and k is the Henry's law constant), it is expected that the oxygen concentration will be linearly dependent on global air pressure.

In order to make the Stern–Volmer relation more practical, it is possible to substitute oxygen concentration with air pressure and do reference measurements at 1 atm pressure. This yields the equation [10].

$$\frac{I_{\mathrm{ref}}}{I} = \frac{\tau_{\mathrm{ref}}}{\tau} = C + Q_s\frac{P}{P_{\mathrm{ref}}} \quad (3)$$

where P_{ref} is the reference pressure (generally 1 atm) at which the luminescent compound's intensity is I_{ref} and C is normally $1 - Q_s$ if temperature is constant. Oxygen quenching sensitivity (Q_s) is obtained from the slope of a linear fit to the modified Stern–Volmer plot (Eq. (3)).

In a previous study, the complex [Ir(fppy)$_2$(*t*-Bu-iCN)$_2$]CF$_3$SO$_3$, **1** (fppy = 4-(2-pyridyl)benzaldehyde, and *t*-Bu-iCN = *tert*-butyl

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isocyanide) was used to prepare the first psp formulation that was entirely water based [11]. Water-based psps do not possess the workplace harzard concerns of organic-based psps and are easily recycled. The iridium complex was covalently attached to the water soluble amine-functionalized polymer Silamine D208-EDA by reductive amination yielding **2** and to compensate for the poor mechanical properties of the water-soluble polymer, microcrystalline cellulose (MC) was included in the psp formulations. Oxygen-sensor films prepared from aqueous blends of **2** and MC showed sensitivities which were dependent on the Silamine:MC ratio and obeyed Stern–Volmer kinetics. The optimum psp formulation (Silamine:MC ratio = 1:1) had an oxygen sensitivity of $Q_S = 0.50$ over an atmospheric pressure range of 0.007–45 psi [11]. Luminescence microscopy of different films showed that the charged iridium luminophore associates with the surface of MC and the excited state lifetime of these films increased with increasing MC fraction. It was suggested that an electrostatic interaction of the charged luminophore with MC restricted the movement of the luminophore and reduced the non-radiative rate of decay [11].

In this study, neutral $[Ir(ppy)_2(fppy)]$, **3** where fppy = 4-(2-pyridyl)benzaldehyde, and ppy = 2-phenylpyridine, was covalently attached to amine-functionalized polymer Silamine D208-EDA by either reductive amination or coupling reactions to yield the neutral luminophore polymers **4** and **5** respectively. The influence of various Silamine:MC concentration ratios on the photophysical properties and oxygen quenching sensitivities of these luminophore polymers were determined and compared to those of the charged luminophore polymer **2** in order to increase our understanding of charge effects in these psp formulations.

2. Experimental

2.1. Materials

Iridium (III) chloride hydrate (Pressure Chemical), 4-(2-pyridyl)benzaldehyde (fppy) (≥97%, Aldrich), 2-phenylpyridine (ppy) (98%, Aldrich), silver trifluoromethanesulfonate (AgOTf) (99 + %, Aldrich), *tert*-butyl isocyanide (CN-*t*-Bu) (≥97%, Aldrich), cellulose (colloidal microcrystalline, Aldrich), and pyridine–borane (Aldrich) were used as received without further purification. Silamine D208 EDA (MW 2475, amine value 30, Siltech Corp.) was heated to 80 °C under vacuum for 30 min before use in reductive attachment reaction. Dichloromethane (Technical, ACP Chemicals) was dried over calcium hydride (90–95%, Aldrich) and distilled and stored under argon before use. Methanol (HPLC Grade, J.T. Baker), diethyl ether (Anhydrous ACS, Fisher Scientific), and hexanes (Spectro grade, Caledon) were used as received. Acetone (ACS Reagent grade, Anachemia) was distilled before use. For the reductive amination reaction, dichloromethane (Spectro grade, Caledon, 24 mL) was dried over activated 4 Å molecular sieves (0.53 g) overnight. For absorption and emission spectroscopies, dichloromethane (Spectro grade, Caledon) was used as received. $[Ir(ppy)_2(fppy)]$, **3** was prepared according to Evans et al. [12].

2.2. Spectroscopic measurements

Absorption spectra were acquired on a Varian Cary 5 UV-vis-NIR spectrophotometer at ambient temperatures using 1000 cm path length quartz cells (Wilmad). Scans were performed at 500 nm/min versus solvent background, with a spectral bandwidth of 200 nm, a signal averaging time of 0.033 s, and a data interval of 1000 nm.

Steady-state emission spectra were acquired on a Shimadzu RF-1501 spectrofluorophotometer at ambient temperatures using quartz fluorimeter cells (Wilmad) of 1000 cm path length.

To obtain time-resolved fluorescence decays, the samples were excited with the third harmonic of a Continuum Surelite 2 Nd:YAG laser generating pulses at 355 nm of 6 ns duration and 15 mJ energy. The signals from the monochromator/photomultiplier system were initially captured by a Tetronix TDS 2012 oscilloscope and transferred to a Macintosh PC clone computer with software LFP V3.0 developed in the LabVIEW environment from Luzchem. A total of 10 shots were averaged to obtain the decay traces. All solution lifetime experiments were done in static 1.0 cm × 1.0 cm fused silica cuvettes, following purging with inert gas for 30 min. Each thin-film lifetime measurement was acquired on a plain microscope slide (Globe Scientific Inc.), sprayed with the paint using a conventional airbrush and mounted in a pressure chamber described elsewhere [13,14].

For the quantum yield determinations, the samples were optically matched to solutions of Coumarin 1 (Laser grade, Fisher) in ethanol ($\varphi = 0.73$) [15] at room temperature using a Shimadzu RF-1501 spectrofluorophotometer. Quartz fluorimeter cells (Wilmad) of 1000 cm path length were used in quantum yield measurements.

2.3. Synthesis of **4** by reductive attachment of **3** to Silamine D208-EDA

To Silamine D208-EDA (1.5 g, 0.6 mmol, M.W. 2400, pre-dried by heating at 80 °C under vacuum for 30 min) was added dichloromethane (24 mL). The solution was degassed with argon for 10 min and then 0.53 g of activated 4 Å molecular sieves and **3** (0.08 g, 0.12 mmol, F.W. 682.80 g mol^{-1}) were added followed by pyridine–borane (0.01 mL, 0.099 mmol). After the solution was stirred at room temperature under argon for 16 h, methanol (10 mL) was added and the resultant solution was treated with 6 N HCl (10 mL) for 15 min, and then pH was adjusted to 12 using concentrated aqueous NaOH solution. NaCl was precipitated by addition of diethyl ether (100 mL) and filtered off. The filtrate was solvent stripped and the residue dissolved in a small volume of acetone which was filtered sequentially through 1.0 μm and 0.45 μm Gelman Acrodiscs. The filtered solution was added dropwise to rapidly stirred hexanes, yielding a clear, yellow polymer fluid. The IR spectrum of **4** showed no evidence of a $\nu(C{=}O)$ band.

2.4. Synthesis of **5** by attachment of **3** to Silamine D208-EDA

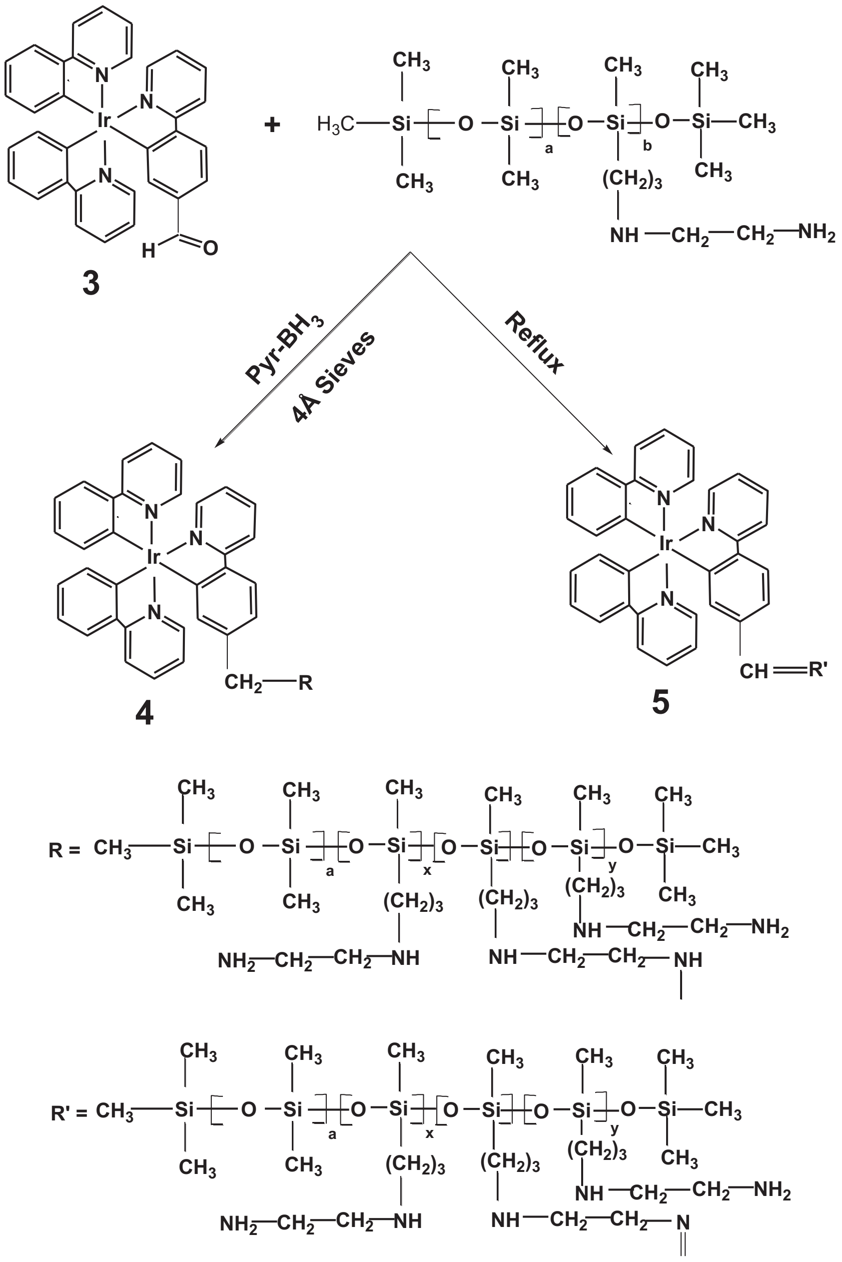
A solution of **3** (34 mg, 0.05 mmol, F.W. 682.80 g mol^{-1}) in dichloromethane (5 mL) was added to a solution of Silamine D208-EDA (0.25 g, 0.10 mmol, M.W. 2400) in dichloromethane (10 mL). The resultant solution was stirred at reflux under argon for 2 days. It was solvent stripped to dryness and the product was dissolved in acetone (5 mL) and filtered through 1.0 μm and 0.45 μm Gelman AcrodiscsTM. The filtered solution was added dropwise to rapidly stirred hexanes, yielding a clear, yellow polymer fluid. The IR spectrum of **5** showed no evidence of a $\nu(C{=}O)$ band.

2.5. PSP formulations

The different Silamine:MC PSP formulations were made by dissolving 0.02 mmol of the polymer attached dye in 7.3 mL H_2O followed by filtering through a 1.0 μm Gelman Acrodisc and then mixing with appropriate solution of Silamine D208-EDA in H_2O and microcrystalline cellulose in H_2O. Each formulation contained 0.02 mmol dye per total 1 g weight of matrix (Silamine D208-EDA plus microcrystalline cellulose).

2.6. Determination of oxygen quenching sensitivity (Q_S)

Each psp formulation was applied to a primed aluminum plate with a Tristar Starpoxy fluid resistant white epoxy primer (DHMS



Scheme 1. Reactions of **3** with Silamine D208-EDA to make **4** and **5**.

Table 1
Solution absorption[a], emission[b], and photophysical data for **1–5**.

	1[c]	**2**[c]	**3**[d]	**4**[e]	**5**[e]
λ_{max} π–π	258 (2.51×10^4)[f]	239, 263, 317[f]	290 (3.60×10^4)	285	282
λ_{max} MLCT	367 (6.92×10^3)[f]	359[f]	379 (7.40×10^3) 454 (2.60×10^3)	360, 444	350, 463
λ_{max} emission (nm)	496[e]	461[e]	510, 540[g]	528, 597[g]	523, 575[g]
Φ	0.35[e]	0.23[e]	0.05	0.03	0.03
τ (μs)	17.3[e]	20.6[e]	0.9	1.4	3.0

[a] In nm, ε (M^{-1} cm^{-1})
[b] In nm.
[c] Ref. [11].
[d] Ref. [12], toluene.
[e] This work, CH_2Cl_2.
[f] CH_3CN.
[g] Low energy shoulder.

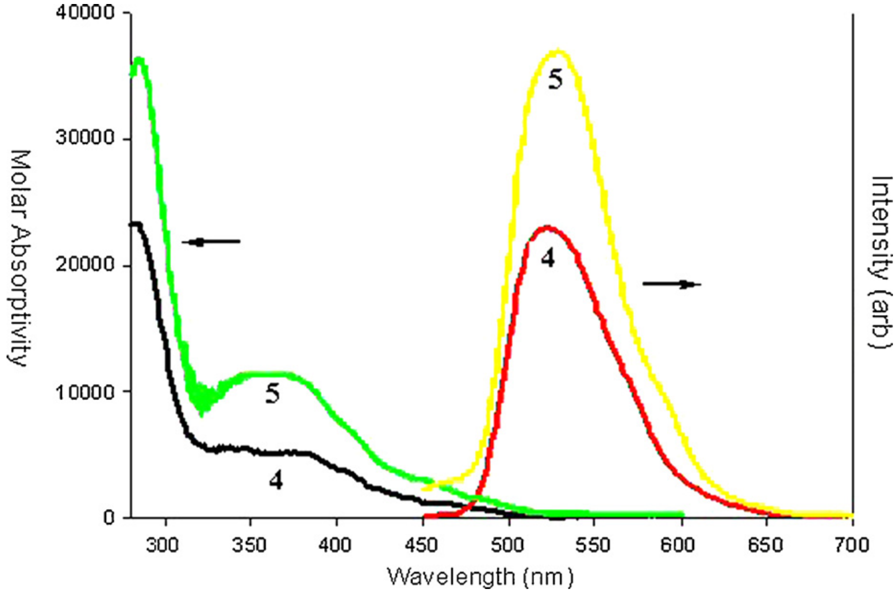


Fig. 1. Electronic absorption and emission spectra of **4** and **5** in CH_2Cl_2.

C4.01 Ty3) using a conventional airbrush and compressed argon as the propellant. It was then mounted in a pressure chamber described elsewhere [13,14]. The average film thickness was estimated to be 2 ± 1 μm by a Positector 6000 model thickness gauge. Excitation in the UV was provided by a Hamamatsu Lightningcure LC5 200W (model L8333 Hg–Xe) source by a 10 mm × 8 mm Oriel UV–vis liquid light guide. Several optical filters in parallel were placed inside the lamp, before the light guide, to block wavelengths greater than 400 nm (Rapp Optoelectronic UV-1 and Hamamatsu A7028-05 filter). Background correction was performed with the light source turned off to remove the dark noise from the detector. Dark levels do not exceed 10% of the signal coming from the paint and are fairly uniform across the spectrum. Thin-film emission spectra were collected using an Acton Research Corporation SpectruMM CCD detection system. A fiber optic light guide (LG-455-020), equipped with a Kodak Wratten Gelatin 3 filter absorbing ultraviolet radiations passed the emission through a SpectraPro-150 imaging dual grating monochromator/spectrograph onto a 16-bit Hamamatsu 1024 × 256 CCD. Following the dark current subtraction, the spectra were normalized by the maximum intensity at atmospheric pressure to produce the spectra variations with pressure. Data for the Stern–Volmer plots were obtained by integrating the spectra over wavelengths between 460 and 560 nm. These measurements were taken at 24 °C, between 0.007 and 45 psi. A Scanivalve Corp. pressure calibrator/controller and a thermoelectric cooler coupled to a temperature controller were used to control pressure and temperature, respectively. Measurements at the reference pressure of 14.7 psi were taken two times during the calibration in order to estimate the photostability of the paints. The excitation light source stability was monitored with a temperature controlled Oriel 7123 photodiode.

The decrease in emission intensity with increasing air pressure relative to the emission intensity at 1 atm pressure was treated according to Stern–Volmer kinetics and modified Stern–Volmer plots were acquired. Oxygen quenching sensitivity (Q_s) data were calculated from linear fits to the Stern–Volmer plots. Multiple quenching processes arising from heterogeneous luminophore environments result in curvature in the Stern–Volmer plots of thin films. In these cases criteria for acceptable range of P/P_{ref} was considered as $r^2 > 0.95$. Measurements were repeated at least three times and the error in reported Q_s data was estimated at ±0.01.

2.7. Luminescence microscopy

All microscopy was performed at Agriculture Canada. PSP films were sprayed on plain microscope slides (Globe Scientific Inc.). The luminescence images were observed in air using a confocal microscope Carl Zeiss LSM510 Meta (405 nm, 42.6% laser intensity) with an ECPlan-Neofluar 40×/1.30 Oil Dic M27 objective exciting at 405 nm and collecting image data at 505 nm. The observed images were analyzed with LSM510 V.4.0 SP2.

3. Results and discussion

Scheme 1 shows the synthetic route to the oxygen-sensing polymers **4** and **5**. The luminophore-functionalized Silamine, **4**, a yellow polymer, was produced by reductive amination reaction between the neutral complex **3** and the water-soluble amine-functionalized Silamine D208-EDA. For **5**, synthesis was achieved by simple condensation which created an imine link between the Ir complex and Silamine. The attachment yields for **4** and **5** were nearly quantitative if it is assumed that the extinction coefficients of $Ir(ppy)_3$ [16] and **3** are the same as those of **4** and **5**, respectively.

Fig. 1 shows the absorption and emission spectra of both **4** and **5** and Table 1 gives the electronic absorption and photophysical data for **1**–**5**. The absorption and emission spectra of **4** and **5** are very similar except for the significantly greater absorptivity of **5**. This effect is also seen for **3** which suggests that the increased conjugation due to imine or aldehyde groups is responsible. In Table 1, the photophysical properties of **3** are not greatly perturbed by attachment to Silamine; emission energy shows a slight shift to the red while the quantum yield of emission slightly decreases and lifetime increases for both **4** and **5**. The luminophore polymers **4** and **5** are entirely water soluble in contrast to **3** which is important for green industrial applications.

The pressure-dependent emission spectra of **3**–**5** in Silamine:MC psp formulations were collected and a representative example (**4** in 2.3:1 Silamine:MC) is shown in Fig. 2.

Examples of Stern–Volmer plots of the pressure-sensitive emission data of various psp formulations of **3**–**5** are shown in Fig. 3 and, from the least-square fits of these plots, the quenching sensitivity Q_s of psp formulations have been placed in Table 2. In

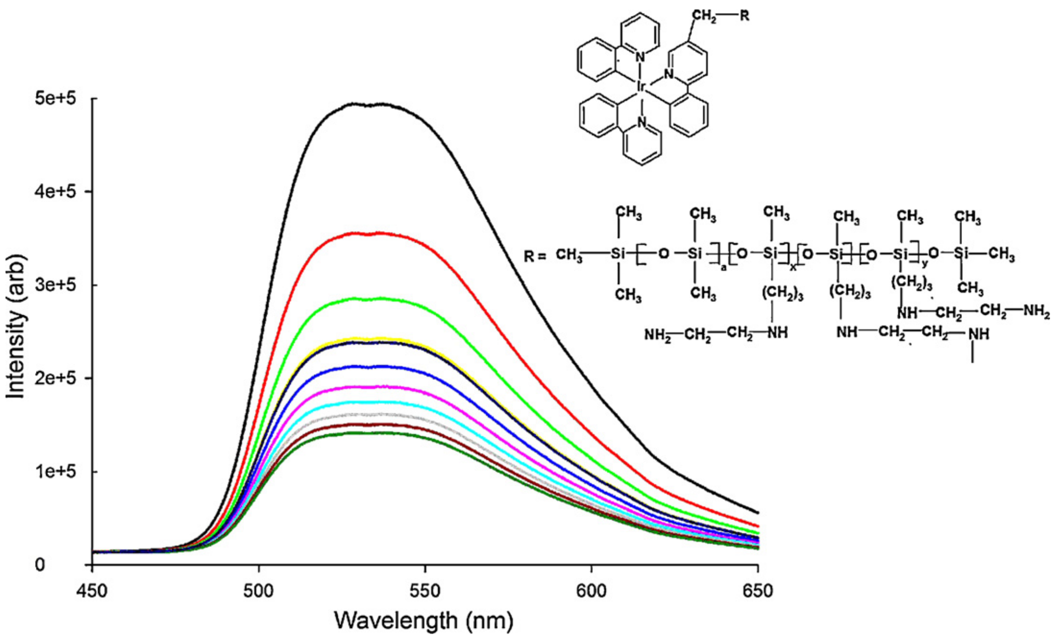


Fig. 2. Effect of pressure on thin film luminescence of **4** in 2.3:1 Silamine:MC. The decrease of intensity with increasing the air pressure is displayed. Spectra were acquired at 1.3 mbar, 0.34 bar, 0.68 bar, 1 bar, 1.36 bar, 1.70 bar, 2.04 bar, 2.38 bar, 2.72 bar, and 3.06 bar. Background correction has been performed.

some cases, Fig. 3 curvature in the Stern–Volmer plots required the determination of more than one Q_S for a given pressure range. Comparison of the data in Table 2 shows only a slight increase in Q_S upon luminophore attachment which may be due to the slight increase of excited state lifetimes of **4** and **5** and the effect this has on Q_S (Eqs. (1) and (3)). The optimum psp formulation was found for **4** in 2.3:1 Silamine:MC with $Q_S = 0.39$. This is lower than that determined previously for **2** in 1:1 Silamine:MC which had $Q_S = 0.50$.

The luminescence microscopy of films of **4** are shown in Fig. 4 and indicate that at low concentration of MC (Fig. 4A), the luminescence from film of **4** is largely dispersed with little evidence of association of the luminophore around particles of MC. This is dramatically different from the behavior of the charged luminophore-polymer 2 [11]. Increasing MC concentration (Fig. 4B and C) results in only a slight increase in luminescence around MC particles. In addition, lifetime measurements of the films of **4** (Table 3) in vacuum or ambient pressure were significantly different from **2**. For example, for **2** in Silamine:MC blends of 9:1, 1:1 and 1:5, lifetime varied from 5.9, 17.6 to 25.8 μs under vacuum, respectively while similar blends with **4** showed no significant change in lifetime (Table 3). The general decrease in oxygen sensitivity seen in Table 2 for **3**–**5** can therefore be ascribed to a decrease in oxygen diffusivity (Eq. (2)) with increasing concentration of MC. For **2** an optimum ratio of 1:1 Silamine:MC arises because of the opposing effects of increase luminophore lifetime and decrease oxygen diffusivity on Q_S (Eqs. (2) and (3)) with increasing MC concentration. The optimum PSP formulation in Table 3 is **4** in 2.3:1 Silamine:MC which gave an oxygen sensitivity of 0.39, with good linear behavior in a pressure range of 0.007–45 psi.

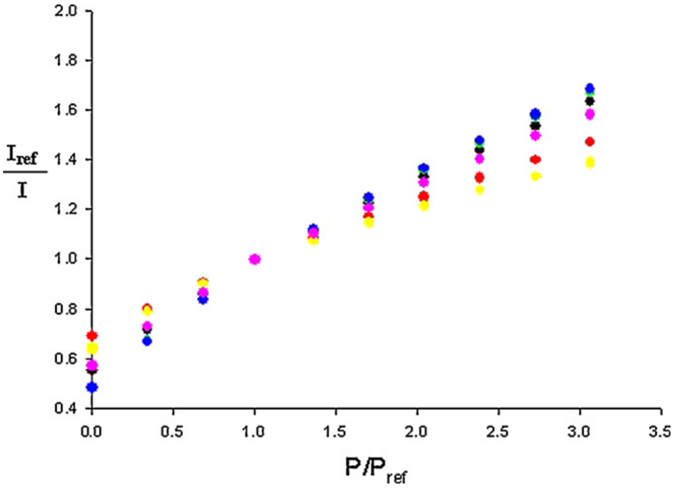


Fig. 3. Stern–Volmer plots of **3** in 2.3:1 Silamine:MC, ●; **3** in 1:1 Silamine:MC, 🔴 ; **4** in 2.3:1 Silamine:MC, 🔵 ; **4** in 1:1 Silamine:MC, 🟣 ; **5** in 2.3:1 Silamine:MC, 🟢 ; **5** in 1:1 Silamine:MC, 🟡 . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The temperature dependence of emission intensity of **4** and **5** in 2.3:1 Silamine:MC films were examined in the temperature range of 10–40 °C under 1 bar atmospheric pressure. The emission intensities were normalized to that at 10 °C and the results plotted in Fig. 5.

Table 2
PSP films oxygen sensitivity data for **3**–**5**.

Luminophore	Matrix	Q_S (r^2)
3	2.3:1 Silamine:MC	0.35 (0.993)[a]
	1:1 Silamine:MC	0.25 (0.994)[a]
	1:9 Silamine:MC	0.15 (0.950)[b], 0.05 (0.980)[c]
4	2.3:1 Silamine:MC	0.39 (0.988)[a]
	1:1 Silamine:MC	0.24 (0.973)[a]
	1:9 Silamine:MC	0.66[d], 0.12 (0.966)[e]
5	2.3:1 Silamine:MC	0.38 (0.989)[a]
	1:1 Silamine:MC	0.32 (0.991)[a]
	1:9 Silamine:MC	0.23 (0.980)[a]

[a] 0.007–45 psi.
[b] 5–14.7 psi.
[c] 20–45 psi.
[d] 0.007–5 psi.
[e] 10–45 psi.

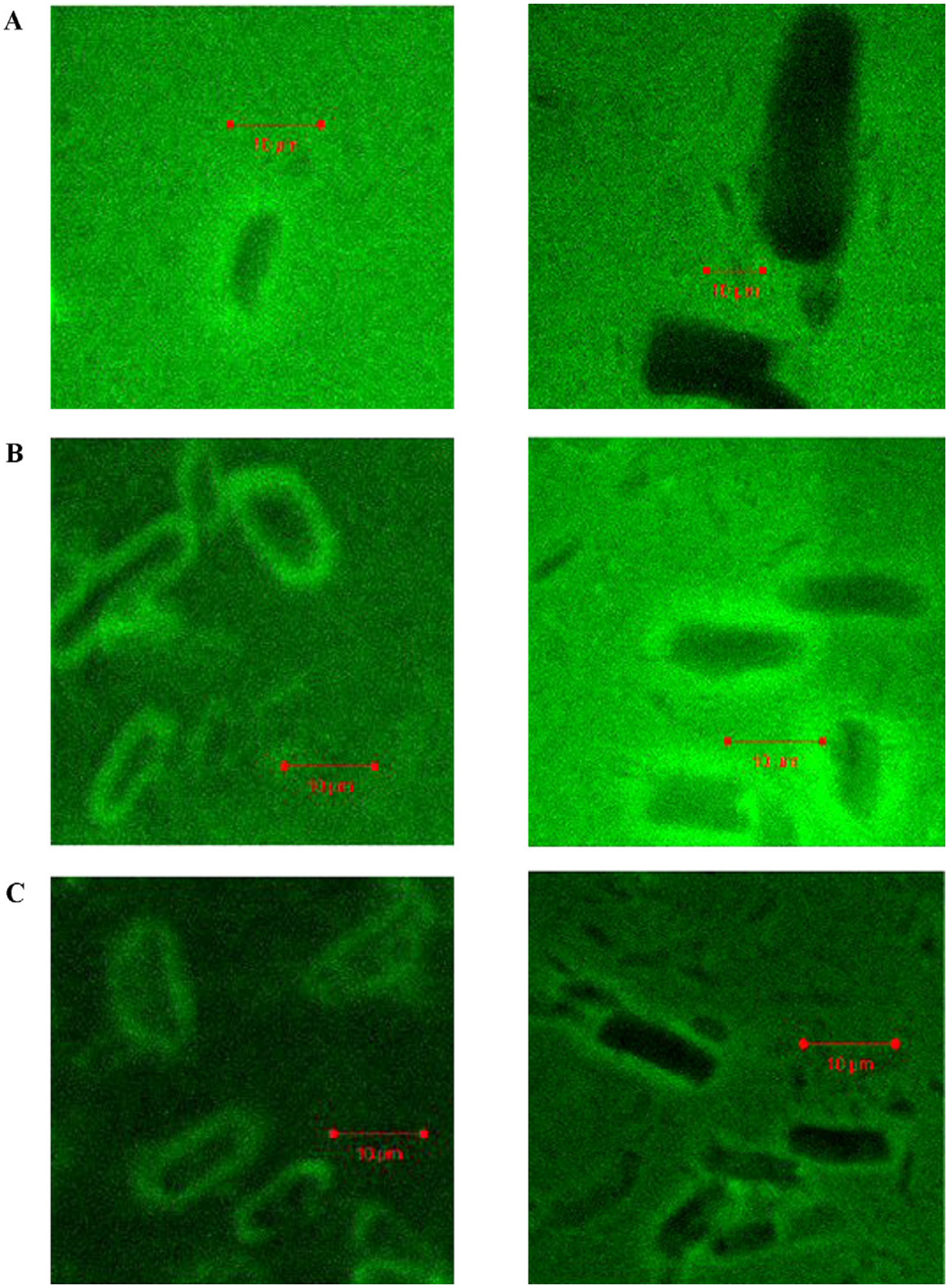


Fig. 4. Luminescence microscopy of films of **4** performed under ambient conditions: A, 9:1 Silamine:MC; B, 1:1 Silamine:MC; D, 1:5 Silamine:MC. The scale in red is 10 μm. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

In Fig. 5, the data for the temperature dependence of emission gave good linear least-squares fits passing through or at least closely approaching the normalization value at 10 °C. The temperature sensitivities (percent intensity loss per degree) of the films were determined to be −0.8% °C^{-1} for **4** at 1 bar atmospheric pressure and −1.3% °C^{-1} for **5**. Although the temperature sensitivity of **4** in 2.3:1 Silamine:MC film is improved compared to **2** and **3** [11], it still must be compensated for by using

Table 3
Luminescence lifetime data[a] in μs of 4 in Silamine:MC films.

Silamine:MC film	Vacuum			Ambient pressure		
	τ_1	τ_2	r^2	τ_1	τ_2	r^2
2.3:1	0.04 (0.4)	0.7 (0.6)	0.992	0.01 (0.5)	0.7 (0.5)	0.996
1:1	0.07 (0.4)	1.1 (0.6)	0.990	0.03 (0.8)	0.5 (0.2)	0.979
1:5	0.04 (0.4)	0.9 (0.6)	0.994	0.04 (0.6)	0.8 (0.4)	0.993

[a] Pre-exponential in parentheses.

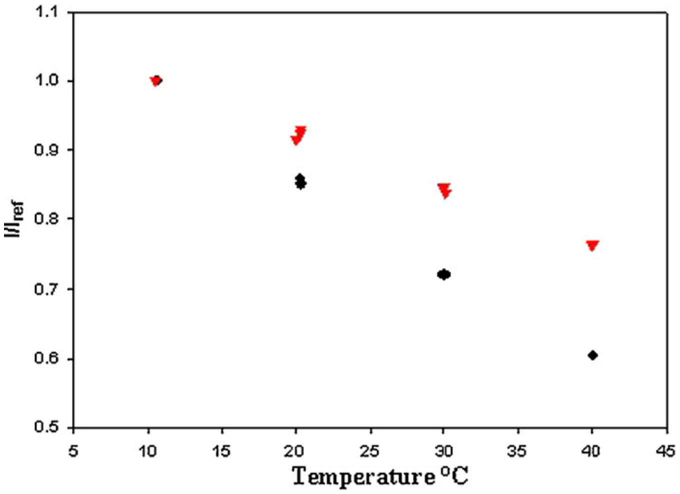


Fig. 5. Temperature versus emission intensity ratio (I_{ref} is the intensity at 10 °C) of **5** in 2.3:1 Silamine:MC: 1 bar, ●; **4** in 2.3:1 Silamine:MC: 1 bar, ▼.

a temperature sensitive calibrant to obtain correct barometric data.

4. Conclusions

Neutral polymer luminophores **4** and **5** have been synthesized by the covalent attachment of [Ir(ppy)$_2$(fppy)] to the amine-functionalized polymer Silamine D208-EDA. In addition to reductive amination [11], condensation of the amine polymer with an aldehyde group of the iridium luminophore was found to be an efficient method of attachment. Oxygen quenching sensitivities Q_S of psp films, composed of varying Silamine:MC blends and luminophores **3**–**5**, decreased with increasing MC concentration. It was suggested that the decreasing oxygen diffusivity with increasing MC concentration reduces Q_S as the excited state lifetimes of **4** and **5** do not change significantly. The Q_S of psps made with the charged polymer luminophore **2** are significantly greater than those of **4** and **5**. For **2** in a 1:1 Silamine:MC blend, optimum $Q_S = 0.5$ [11], while for **4** and **5** in a 2.3:1 Silamine:MC blend, optimum $Q_S = 0.39$ and 0.38 respectively. As shown by luminescence microscopy and photophysical studies, association of charged **2** with MC increased its excited state lifetime and resulted in an approximately 30% increase in oxygen sensitivity compared to neutral luminophores. This effect will be explored to optimize psp performance in future studies.

Acknowledgements

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