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Barometric Sensitive Coatings Based upon Osmium Complexes Dissolved in a Fluoroacrylic Polymer

Brenden Carlson,*,† John P. Bullock,‡ Timothy M. Hance,† and Gregory D. Phelan†,§

Department of Chemistry, University of Washington, P.O.Box 351700, Seattle, Washington 98195, Chemistry Department, Bennington College, Bennington, Vermont 05201, and Department of Chemistry and Biochemistry, Seattle Pacific University, Seattle, Washington 98119

Pressure sensitive paints (PSP) that measure the changes in air pressure have proved to be useful in the design of aircraft and other vehicles. In this study we incorporate highly luminescent divalent osmium complexes into PSP. The divalent osmium complexes were heptafluorobutyrate salts of $[Os(N-N)_2(L-L)]^{2+}$ or $[Os(L-L)_2(N-N)]^{2+}$, where N−N is a derivative of 1,10-phenanthroline, and L−L is a diphosphine or diarsine ligand. The complexes were dissolved into poly(1,1,1,3,3,3-hexafluoroisopropylmethacrylate-co-1H,1H-dihydroperflurobutylmethacrylate) (FIB) at a concentration of 0.002 g of complex to 1.000 g of polymer. The luminescence of the coatings was tested for pressure sensitivity, temperature dependence, and photodegradation. The paints featured strong pressure response, and the temperature dependence of the luminescence was measured as low as -0.11% $°C^{-1}$. Several of the complexes exhibited little photodegradation upon prolonged exposure to 400 nm light. These attributes make the complexes very desirable luminescent dyes for PSP.

Pressure sensitive paints (PSPs) are luminescent coatings used to map barometric pressure gradients across a surface. PSP typically consists of a polymer host material with a luminescent dye dissolved in it. The emission from the dye is quenched by oxygen. Measurement of the emission intensity from the PSP across a surface provides pressure information. PSP provides an easier alternative to conventional pressure taps to measure the pressure gradients and determine aerodynamic efficiency of a moving vehicle. Because PSP responds directly to oxygen partial pressure and not total pressure, it has been adapted for use as oxygen probes in fields such as medicine,[1] beer manufacturing,[2] among others.

Despite the successful use of PSP, presently reliable quantitative measurements are not easily obtained. This is due to a number of complications arising from the operative mechanism behind PSP pressure response. Specifically, the luminescence of PSPs is quenched by energy transfer between ground-state triplet oxygen and the luminescent dye while it is in the excited triplet state, and any other process which leads to a change in luminescence or lifetime gives error in the pressure measurement. Unfortunately, the luminescence quantum yield is often temperature dependent and decreases with increasing temperature.[3] There is a continuing search for new dyes with emission that is less sensitive to changes in temperature. Such a luminophore would lead to more accurate pressure sensors. Moreover, some luminescent dyes undergo photodegradation that results in reduced emission intensity which, if not compensated for, will lead to error in the resulting pressure measurements. In this report we focus on maximizing PSP properties which include reducing the temperature dependence of emission and photodegradation while maintaining strong response to pressure changes.

Several types of luminescent transition metal coordination compounds have been used in PSP, including porphyrin complexes of palladium(II) or platinum(II)[4] and other complexes utilizing iridium(III) or ruthenium(II).[5] Heavy metals are typically used as the luminophores since the large spin−orbit coupling constants afford a break down in the spin selection rules and allow for rapid intersystem crossing to the triplet state. Osmium, despite its similarities with ruthenium, its Group 8 congener, has been rarely used in PSP. The greater crystal field splitting expected for osmium, owing to its position in the third row of the transition metals, can potentially impart reduced temperature dependence and improved resistance to photodegradation because of increased

* To whom correspondence should be addressed. E-mail: wcarlson@u.washington.edu.
† University of Washington.
‡ Bennington College.
§ Seattle Pacific University.
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Complex	X	R1	R2	Y	Z
1	P	CH₃	CH₃	CH₂-CH₂	CH₃
2	P	CH₃	CH₃	CH₂-CH₂	C₆H₁₁
3	As	CH₃	CH₃	C₆H₄	CH₃
6	P	H	C₆H₅	CH₂-CH₂	CH₃
7	P	H	MeOC₆H₄	C−C	C₆H₅
8	As	H	McOC₆H₄	C=C	C₆H₅
9	P	CH₃	CH₃	C=C	C₆H₅
10	As	CH₃	CH₃	C=C	C₆H₅
4		H	C₆H₅		
5		CH₃	CH₃		

Figure 1. Structure of the osmium complexes being utilized for PSP. All complexes are divalent in charge and had heptafluorobutyrate counterions when incorporated into PSP.

energy separation of the emitting state from higher energy states that decay non-radiatively. PSP performance is also strongly influenced by the properties of the host material, and a wide variety of polymer matrixes have been used including poly(dimethylsiloxane) RTV's,[6] trimethylsilyl propyne,[7] and fluoroacrylic polymers.[4a] Another approach has been to chemically link the dye to the polymer itself.[5n]

In this work we prepared several PSP formulations utilizing osmium complexes, shown in Figure 1, made with the ligands shown in Figure 2, as the luminophores and a fluoroacrylic polymer, FIB (Figure 3), as the oxygen-permeable host material. FIB was chosen as the polymer matrix on the basis of previous work in which it was successfully employed in PSP coatings.[4a] These PSPs were tested for pressure sensitivity, temperature dependence, and photodegradation.

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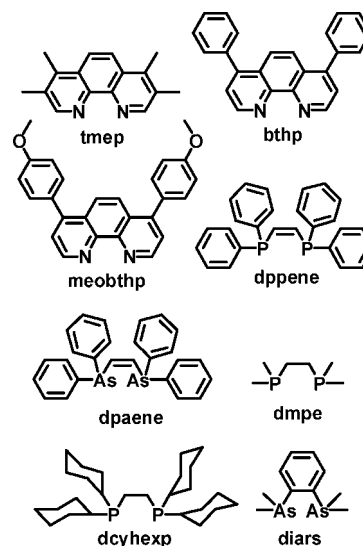
Figure 2. Ligands used to form the osmium complexes in this study. tmpe = 3,4,7,8-tetramethyl-1,10-phenanthroline, bthp = 4,7-diphenyl-1,10-phenanthroline, meobthp = 4,7-bis(*p*-methoxyphenyl)-1,10-phenanthroline, dppene = *cis*-1,2-vinylenebis(diphenylphosphine), dpaene = *cis*-1,2-vinylenebis(diphenylarsine), dmpe = 1,2-bis(dimethylphosphino)ethane, dcyhexp = 1,2-bis(dicyclohexylphosphino)-ethane, diars = 1,2-bis(dimethylarseno)benzene.
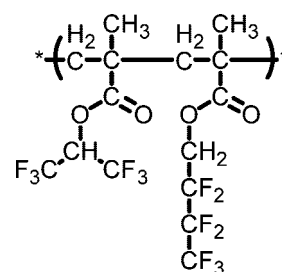

Figure 3. Structure drawing of poly(1,1,1,3,3,3-hexafluoroisopropyl methacrylate-co-1H, 1H-dihydroperfluorobutyl methacrylate) commonly known as the FIB polymer.

RESULTS AND DISCUSSION

The synthesis, x-structures, density-functional theory (DFT) calculations, photophysical, and other properties of the complexes as the hexafluorophosphate salt are published in our previous reports.[8] A metathesis to heptafluorobutyrate counterions was done to increase compatibility with the FIB host material. The
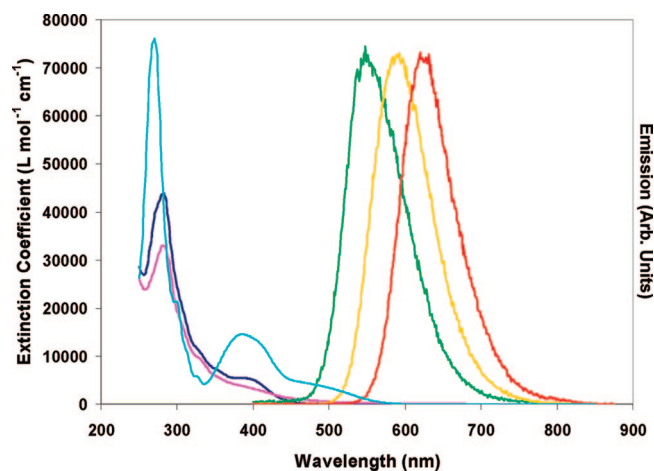
Figure 4. Absorbance of complexes (light blue) **3**, (dark blue) **4**, (magenta) **5**, and emission of complexes (red) **3**, (yellow) **4**, and (green) **5** in deoxygenated acetonitrile.

complexes feature a series of absorption peaks centered at ∼300 nm, ∼400 nm, and ∼500 nm, which gives an option to use a variety of excitation sources (Figure 4). The 300 nm peak is due to the ligand centered $\pi-\pi^*$ (LC) absorption, the 400 nm peak to the metal to ligand charge transfer (^{1}MLCT), and the 500 nm peak to the spin forbidden ^{3}MLCT absorption. Another state, the metal centered $d\pi$-$d\sigma^*$ (MC) is possible but is often not observed in the absorption spectra since it is Laporte forbidden and weak ($\varepsilon \sim 100$ L mol^{-1} cm^{-1}). Emission from the complexes generally occurs from the MLCT, but can be a hybrid of LC and MLCT,[8c,9] and is observed between 550 to 660 nm, depending upon the complex. The excited-state lifetimes range from 1.5 to 10 μs.

Samples of PSP were prepared by dissolving the osmium complexes into the FIB matrix at a concentration of 0.002 g of dye per 1.000 g of polymer, and tested for pressure sensitivity, temperature dependence, and photodegradation. The results are summarized in Table 1 and illustrated in Figures 5–7.

The emission temperature dependence of the osmium-based PSPs show promise (Figure 5). These ranged from 0.11% °C^{-1} for complex **4** to 1.00% °C^{-1} for complex **5**, with the majority of complexes having temperature dependencies below 0.5% °C^{-1}. The low temperature dependence can be explained by crystal field theory. The third row position of osmium and the coordination of strong field ligands lead to increased energy separation (Δ_o) of filled and empty d-orbitals; transitions from the filled to the vacant d orbitals result in the MC state. As a result, the antibonding metal centered state (MC) is higher in energy for osmium than ruthenium. Direct MC absorption is usually not observed, but population of the MC state can occur thermally. Once occupied the MC state decays via non-radiative means; thus, increasing temperature can lead to decreasing

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Table 1. PSP Properties of the Complexes As the Heptafluorobutyrate Salt Dissolved in the FIB Polymer

complex	I_{vac}/I_{atm}	$k_q{}^a$	temperature dependence[b]	degradation[c]	τ(ns)
1	2.63	1.845	0.23	0.1	2400
2	2.15	2.114	0.25	2.3	1700
3	3.04	3.265	0.22	0.8	1700
4	3.41	0.761	0.11	0.5	8900
5	4.83	1.101	1.00	13.7	10100
6	1.59	1.388	0.24	5.7	1600
7	1.72	1.023	0.43	5.0	1970
8	1.57	1.007	0.17	1.3	1550
9	2.75	1.426	0.86	0.8	3400
10	2.62	1.618	0.25	0.0	2800

^{a} s^{-1} torr^{-1} × 10^8. ^{b} Percent intensity loss per degree C. ^{c} Percent intensity loss after 90 min of illumination.

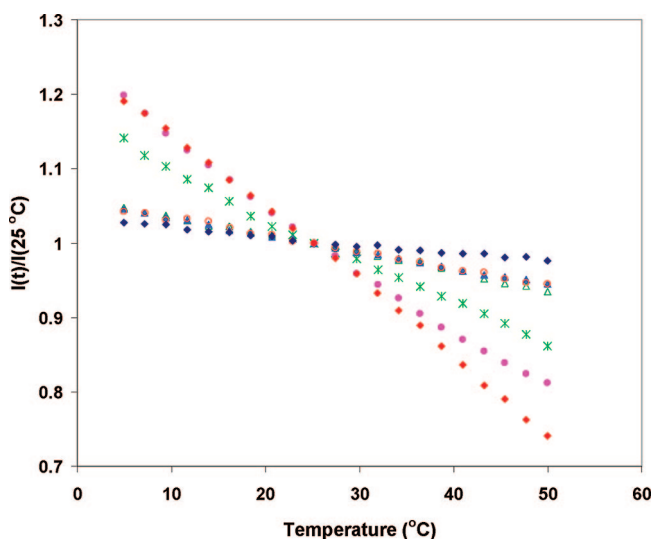**Figure 5.** Temperature dependence of luminescence intensity referenced to 25 °C and taken under vacuum for complex **1** (red open circle), complex **2** (green open triangle), complex **3** (blue solid triangle), complex **4** (black solid diamond), complex **5** (red solid diamond), complex **7** (asterisk), and complex **9** (red solid circle). All complexes are dissolved in the FIB polymer. Temperature dependence of complexes **6**, **8**, and **10** are available in the Supporting Information.

emission quantum yields. The higher energy of the osmium MC state decreases its thermal population relative to that of ruthenium, resulting in reduced temperature dependence of the emission. The relation between the MC state, emitting states, and temperature dependence can be observed by comparing complexes **4** and **5**. The two complexes differ with respect to the substituents on the phenanthroline ligand but exhibit temperature dependences that are separated by an order of magnitude. Thermal population of the MC state becomes increasingly possible if the MLCT state is high in energy. The MLCT absorption of **5** is 0.223 eV higher in energy than for **4**,[8c] and as a result the energy separation between the MLCT and MC states is narrowed with respect to **4**. Thus at any given temperature, the population of the MC state is less for **4** with respect to **5**. Greater thermal energy is required to populate the MC state for **4**, and lesser thermal energy is required to populate the MC state for **5**. The observation is that the emission quantum yield temperature dependence of
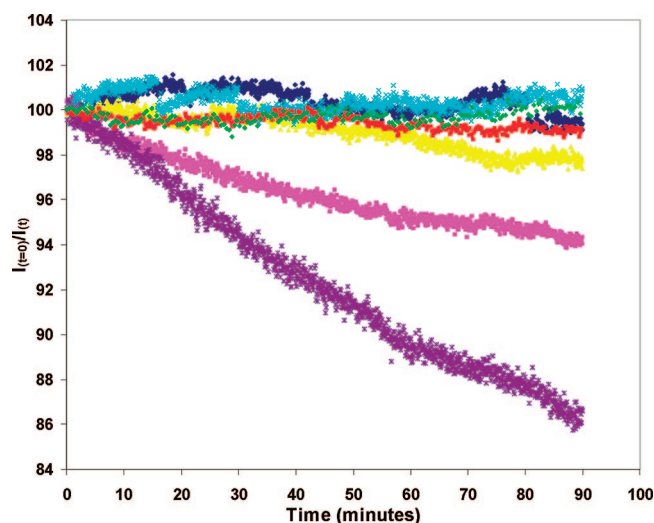
Figure 6. Photodegradation of seven complexes used in this study: complex **1** (light blue ×), complex **2** (yellow solid triangle), complex **3** (red solid square), complex **4** (dark blue solid diamond) and complex **5** (purple asterisk), complex **6** (magenta solid square), and complex **10** (green solid diamond). All complexes are dissolved in the FIB polymer. Photodegradation of complexes **7**, **8**, and **9** are available in the Supporting Information.
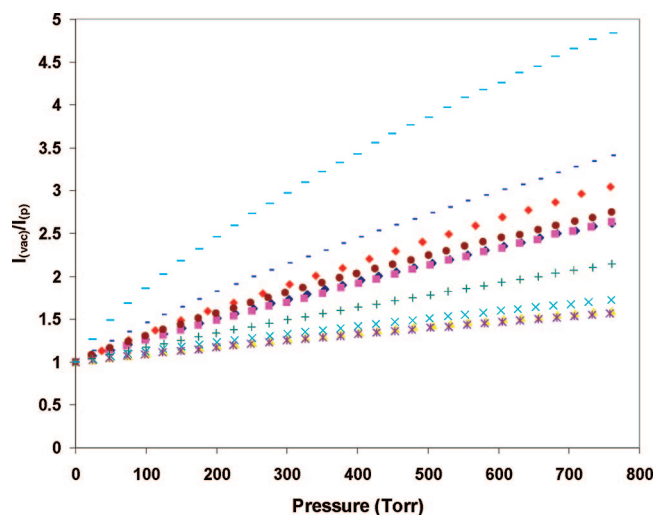

Figure 7. Stern−Volmer plot measured at 25 °C for complex **1** (magenta solid square), complex **2** (light blue +), complex **3** (red solid diamond), complex **4** (dark blue −) and complex **5** (light blue −), complex **6** (yellow solid triangle), complex **7** (light blue ×), complex **8** (magenta asterisk), complex **9** (brown solid circle), and complex **10** (dark blue solid diamond). All complexes are dissolved in the FIB polymer.

PSP is reduced for **4** relative to **5** because of the increased energy of the emitting state of **5**. The temperature dependence epitomizes the tuning of excited states required in the design of complexes for PSP.

The use of osmium reduces the rate of photodegradation of the PSP (Figure 6). The population of the MC increases the potential of decomposition of the complex because of the antibonding nature of the state. Photodegradation of the dye leads to errors in pressure measurement in a similar manner as temperature, that is, via loss in luminescence intensity that can be read as increased pressure. While correction for photodegradation is

sometimes possible by recalibration, the intensity of the PSP signal decreases and leads to greater uncertainties of pressure measurements. The osmium complexes degraded at low rates (Figure 6). The relation of the energy between the emitting MLCT and/or LC states and the nonemitting MC state and photodegradation can be observed. Complex **5** had a degradation rate greater than the other complexes. The emission energy is greatly blue-shifted from that of the other complexes, which reflects a reduced energy separation between the LC/MLCT states and the antibonding MC state. The reduced energy separation between the states allows for greater population of the MC state and, when combined with longer N−Os bonds[8c] because of the *trans* effect of the arsine ligands, leads to greater photodegradation rates.

Stern−Volmer data is presented in Figure 7 and Table 1. Theoretically, the inverse of the emission intensity varies linearly with quencher concentration if the excited-state follows an exponential decay and assuming each luminophore has equivalent access to the quenching species. The Stern−Volmer plots of many of the complexes feature nearly linear fits ($r^2 = 0.999$). The deviations from linearity can be caused by differences in local oxygen solubility, quenching constant (which is affected by diffusion coefficient), and environment around the sensor.[10] Relative rates ($k_{q_{rel}}$) of quenching are estimated from the relationship:

$$\frac{I_{vac}}{I_p} = 1 + k_{q_{rel}} \times \tau_o \times p \tag{1}$$

I_{vac} is the intensity of emission under vacuum, I_p is the emission intensity at pressure p, τ_o is the emission lifetime, and p is the pressure. The values of the quenching constant are dependent upon the presence of either phenyl substituted phenanthrolines (bthp or meobthp) or tmep. The complexes with tmep had longer emission lifetimes[8] and larger quenching constants than the complexes of similar structure using bthp. Thus, the complexes synthesized with tmep had much greater pressure sensitivity. The quenching rate was not a function of the size of the complex from the molecular volumes calculated from the X-ray structures.[11] Increased size of the complex, and hence larger collision cross-section, did not correlate to increased pressure sensitivity in this study. The electrochemical potentials of the complexes show a distinction between the two sets of phenanthroline ligands used. The complexes with tmep had reduction potentials that were more negative than complexes with bthp.[8] The more negative reduction potential of complexes with the tmep ligand allows for an increase in the quenching constant by increasing the efficiency of energy transfer of the complex to oxygen through electron transfer processes.[12]

Additional insight into the performance of these complexes as PSP luminophores was provided by DFT calculations performed

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on complexes **3** and **4**.[8c] Complexes **4−5** had increased emission lifetime and quantum yields when compared to the other complexes. The increased emission lifetime of complexes **4** and **5** produced PSPs that had increased pressure sensitivity even though complexes **4** and **5** had smaller quenching constants. However, the tmpe complex, **5**, had greater pressure sensitivity than the bthp complex, **4,**, because of the enhanced ability of the tmpe ligand to transfer energy to ground-state oxygen. Complex **4** had greater quenching than other tmpe complexes in the study (**1−3**, **9**, **10**) because of its substantially longer emission lifetime. The increased emission lifetime allowed time for oxygen to diffuse to and collide with the complex while in the excited-state leading to greater pressure sensitivity. Comparison between complex **3** ($\tau = 1.7~\mu s$) with complex **4** ($\tau = 8.9~\mu s$) shows the effect of increased energy transfer to oxygen because the tmpe ligand as complex **3** has nearly the same pressure sensitivity as complex **4** despite the much faster emission lifetime. Complexes **4−5** were of a different structure in that they had a single phenanthroline ligand bonded to osmium, whereas the other complexes had two phenanthroline ligands bonded to osmium. The change in structure results in I_{vac}/I_p that increases for complexes **4** and **5** mainly because of longer emission lifetime, which DFT calculations showed were a result of the mixing of the LC state into the MLCT manifold.[8c]

Ruthenium dyes with phenyl substituted phenanthrolines have commonly been used in PSPs.[13] The phenyl substitution results in longer emission lifetimes and increased sensitivity to changes in pressure. Our work shows that it is not advantageous to use phenyl substitution on the phenanthroline for the creation of PSPs with osmium charge transfer complexes. Every complex tested with the tmep ligand had greater pressure sensitivity than its phenyl counterpart. This is due to two factors: one is that the tmpe complexes have longer emission lifetimes, and second the tmpe complexes feature reduction potentials that are more negative than the bthp complexes, increasing the efficiency of energy transfer to oxygen. Presumably the same would hold true for tmpe complexes of ruthenium; however, the tmpe complex of ruthenium has much lower emission quantum yields and much shorter emission lifetime than the bthp complex of ruthenium.[14] In the creation of pressure sensitive paints with osmium complexes, it is the 3,4,7,8-tetramethyl-1,10-phenanthroline ligand and not 4,7-diphenyl-1,10-phenanthroline that creates PSPs with high sensitivity to pressure with low temperature dependence and low rates of photodegradation.

CONCLUSION

A series of ten osmium complexes were utilized in PSPs. It was found that the complexes based upon 3,4,7,8-tetramethyl-1,10-

phenanthroline had increased pressure sensitivity when compared to complexes with phenyl substituted phenanthroline ligands because of a longer emission lifetime and larger quenching constant. DFT calculations showed that changing the structure of the osmium complex resulted in increased LC contribution to the excited state, which results in an increase in emission lifetime and pressure sensitivity. The PSPs based upon the osmium dyes had very low rates of photodegradation and very low temperature dependence. The PSPs were sensitive to pressure changes and measurements of I_{vac}/I_{atm} up to a factor of 4.8 have been reached.

EXPERIMENTAL SECTION

The metathesis of the complexes from hexafluorophosphate to heptafluorobutyrate (HFB) was accomplished by taking 50 mg of the complex and dissolving it into 3 mL of methylene chloride. A volume of 17 mL of a saturated solution of sodium heptafluorobutyrate in water was added to the methylene chloride solution. The two were blended together until a fine emulsion formed between the two. The two were continued to be stirred for 24 h and then stopped, and the two phases were allowed to separate. The complex in the methylene chloride layer was removed, dried, and the solvent was removed by rotary vacuum. The complex as the heptafluorobutyrate salt was crystallized from a mixture of toluene and acetonitrile. **Complex 1:** [(3,4,7,8-tetramethyl-1,10-phenanthroline)$_2$ 1,2-(dimethylphosphino)ethane osmium]$^{2+}$(HFB)$_2$. Elemental analysis calculated for $C_{46}H_{48}F_{14}N_4O_4OsP_2$: C, 44.59; H, 3.90; N, 4.52, found: C, 44.37; H, 3.81; N, 4.62. **Complex 2:** [(3,4,7,8-tetramethyl-1,10-phenanthroline)$_2$ cis-1,2-bis(dicyclohexylphosphino)ethane osmium]$^{2+}$(HFB)$_2$. Elemental analysis calculated for $C_{66}H_{80}F_{14}N_4O_4OsP_2$: C, 52.44; H, 5.33; N, 3.71, found: C, 52.31; H, 5.51; N, 3.90. **Complex 3:** [(3,4,7,8-tetramethyl-1,10-phenanthroline)$_2$ 1,2-(dimethylarseno)benzene osmium]$^{2+}$(HFB)$_2$. Elemental analysis calculated for $C_{50}H_{48}As_2F_{14}N_4O_4Os$: C, 43.68; H, 3.52; N, 4.07, found C, 43.89; H, 3.66; N, 4.03. **Complex 4:** [(1,2-(dimethylarseno)benzene)$_2$ 4,7-diphenyl-1,10-phenanthroline osmium]$^{2+}$(HFB)$_2$. Elemental analysis calculated for $C_{52}H_{48}As_4F_{14}N_2O_4Os$: C, 41.07; H, 3.18; N, 1.84, found C, 40.91; H, 3.25; N, 1.96. **Complex 5:** [(1,2-(dimethylarseno)benzene)$_2$ 3,4,7,8-tetramethyl-1,10-phenanthroline osmium]$^{2+}$(HFB)$_2$. Elemental analysis calculated for $C_{44}H_{48}As_4F_{14}N_2O_4Os$ C, 37.09; H, 3.40; N, 1.97, found C, 37.21; H, 3.29; N, 1.91. **Complex 6:** [(4,7-diphenyl-1,10-phenanthroline)$_2$ 1,2-bis(dimethylphosphino)ethane osmium]$^{2+}$(HFB)$_2$. Elemental analysis calculated for $C_{62}H_{48}F_{14}N_4O_4OsP_2$: C, 52.03; H, 3.38; N, 3.91, found C, 52.32; H, 3.55; N, 4.03. **Complex 7:** [(4,7-bis(4-methoxyphenyl)-1,10-phenanthroline)$_2$ 1,2-cis-vinylenebis(diphenylphosphine) osmium]$^{2+}$(HFB)$_2$. Elemental analysis calculated for $C_{86}H_{62}F_{14}N_4O_8OsP_2$: C, 57.46; H, 3.48; N, 3.12, found C, 57.30; H, 3.62; N, 3.07. **Complex 8:** [(4,7-bis(4-methoxyphenyl)-1,10-phenanthroline)$_2$ 1,2-cis-vinylenebis(diphenylarsine) osmium]$^{2+}$(HFB)$_2$ Elemental analysis calculated for $C_{86}H_{62}As_2F_{14}N_4O_8Os$: C, 54.78; H, 3.31; N, 2.97, found C, 54.89; H, 3.27; N, 3.01. **Complex 9:** [(3,4,7,8-tetramethyl-1,10-phenanthroline)$_2$ 1,2-cis-vinylenebis(diphenylphosphine) osmium]$^{2+}$(HFB)$_2$. Elemental analysis calculated for $C_{66}H_{54}F_{14}N_4O_4OsP_2$: C, 53.37; H, 3.66; N, 3.77, found C, 53.54; H, 3.60; N, 3.86. **Complex 10:** [(3,4,7,8-tetramethyl-1,10-phenanthroline)$_2$ 1,2-cis-vinylenebis(diphenylarsine) osmium]$^{2+}$(HFB)$_2$. Elemental analysis calculated for $C_{66}H_{54}As_2F_{14}N_4O_4Os$: C, 50.39; H, 3.46; N, 3.56, found C, 50.50; H, 3.42; N, 3.48.

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Preparation of PSP. Osmium complex (0.002 g) was added to a 25 mL vial, and 2.000 g of acetone was used to dissolve the complex. To this vial 1.000 g of FIB and 18.000 g of α,α,α-trifluorotoluene were added. Both the polymer and the complexes were readily soluble in the solvent. The solutions were then applied to pre-cleaned gold-plated silicon plates that were 1 in. × 1 in. × 1/32 in. in size. After air dying, the films were placed in a vacuum oven overnight at 50 °C. The films were examined under a fluorescence microscope to verify that the films were free of precipitated or aggregates of the complex.

The paints contain organo-arsenic and organo-phosphorus chelates of osmium(II), a fluoropolymer, and are applied as a spray. Proper respiratory protection is needed when applying the paints.

Testing of PSP. The films were tested in a "survey apparatus" of custom design.[15] This apparatus simultaneously monitors, and controls pressure, temperature, and luminescence intensity. The thickness of the tested films was 15 μm as measured by a Tencor P-15 profilometer. Excitation source was a quartz halogen lamp passed though a 400 nm band-pass filter (fwhm = 20 nm) at a power density of 350 μw cm^{-2} for the Stern−Volmer and temperature runs and 925 μw cm^{-2} for the photodegradation experiments. Photon flux was measured using a power density meter by Newport. Emission was monitored using a photomultiplier tube with a filter appropriate for the emission of the complex.

SUPPORTING INFORMATION AVAILABLE

Further details are given in Figure 1 and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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