



## Organometallic osmium and iridium complexes as phosphorescent dye in barometric sensitive coatings

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### ABSTRACT

Pressure sensitive paints (PSP) that measure changes in barometric pressure through oxygen quenching are an important analytical tool in wind tunnel and other research. PSPs are often used during the development phase of new aircraft, cars, and trucks where the performance of the proposed vehicle is researched. Previously, many PSPs have been based upon charged phosphorescent metal complex salts that may have poor solubility in the oxygen permeable host material. Charge neutral phosphorescent dyes should have better solubility, and to demonstrate this, neutral osmium and iridium complexes are presented in this report. X-ray structures are measured and DFT calculations are used to explain many of their properties. The complexes are dissolved into poly(1,1,1,3,3,3-hexafluoroisopropylmethacrylate-co-1H,1H-dihydroperfluorobutyl-methacrylate) (FIB), an oxygen permeable host polymer. The complexes exhibit good solubility and compatibility with the FIB polymer. The photo-degradation, temperature sensitivity, and Stern–Volmer curves of PSPs based on these complexes are presented. The complexes show great promise for use in PSPs.

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### 1. Introduction

Coatings that measure concentrations of oxygen or barometric pressure often use phosphorescent metal complexes as the active sensor [1]. The complexes are salts if the ligands used to form the complex are neutral and counter ions balance the charge of the metal. The complexes are charge-neutral if the ligands are charged and balance the charge on the metal. We offered a series of pressure sensitive paints (PSP) based upon divalent osmium complex salts dissolved in a fluoroacrylic polymer in our previous report [2]. One of the challenges to the use of phosphorescent salts such as those based upon ruthenium, osmium, or other heavy metals is that the solubility of the phosphorescent salt in the polymer host matrix is low. Aggregates of the phosphorescent salt may phase separate within the polymer host, which will greatly affect the pressure sensitivity and the Stern–Volmer calibration curves. The aggregates often luminescence brightly and do not efficiently record pressure changes [3].

There are various methods to prevent aggregation of the phosphorescent dye. Complexes functionalized with moieties such as styrene or acrylic are reported to be polymerized with other monomers resulting in phosphorescent polymers [1q,r]. With

this method the phosphorescent dye is attached to the polymer backbone and cannot phase separate. An alternative to covalent attachment to a polymer host is to select counter ions to increase compatibility and solubility in the hosts, thereby tuning the phosphorescent salts to a variety of host materials. As an example, PSPs based on ruthenium phosphorescent salts have used tetraphenylborate as a counter ion to increase solubility in polymer hosts [4]. Tetraphenylborate is more oligophilic than hexafluorophosphate and leads to increased solubility. Another method to increase compatibility with polymer hosts is to synthesize complexes with ligands that balance the positive valence on the metal. The use of these ligands results in complexes with an overall neutral charge. These complexes, especially the octahedral ones, often have high solubility and compatibility with polymeric materials, and have little tendency to form aggregates. We report the synthesis of osmium and iridium charge neutral metal complexes for use in FIB (Fig. 1) based PSP's. Stern–Volmer curves, temperature dependence and photo-degradation of the resulting PSP's are measured. DFT calculations are used to explain observations in photo-physical properties and the pressure sensitivity of the complexes in the FIB polymer.

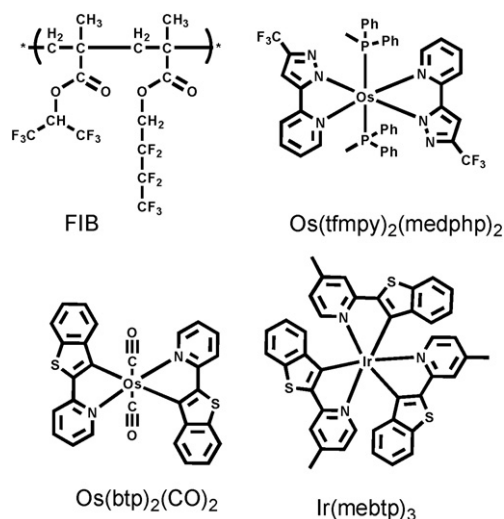
### 2. Results and discussion

#### 2.1. Synthesis and characterization

2-Benzo[b]thiophene-2-yl-4-methyl-pyridine (mebtp) and 2-benzo[b]thiophene-2-yl-pyridine (btp) were synthesized from

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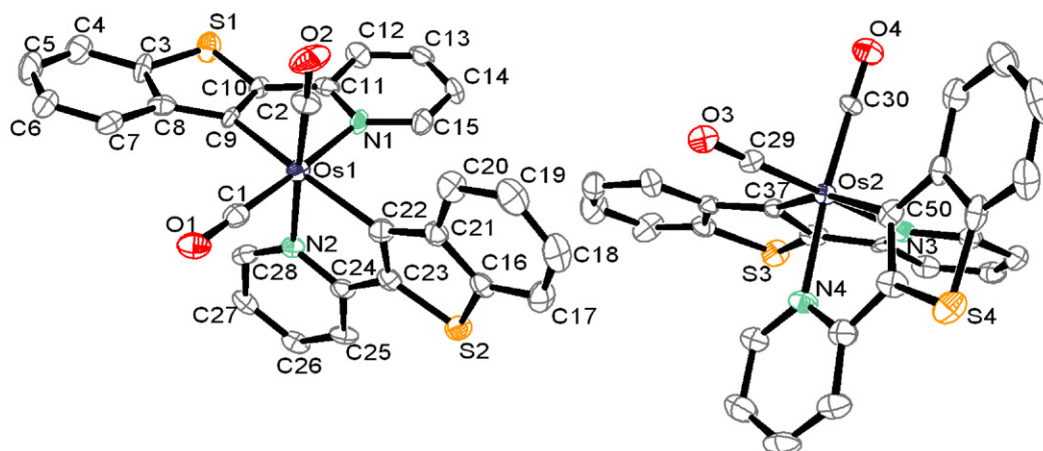
E-mail address: [wcarlson@u.washington.edu](mailto:wcarlson@u.washington.edu) (B. Carlson).



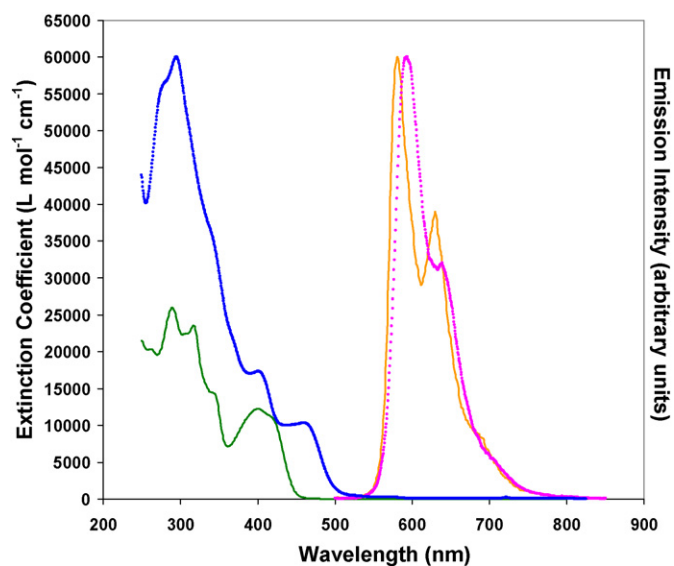
**Fig. 1.** Structure drawing of the FIB polymer and structure drawings of the phosphorescent dyes used in PSP for this study.

the Suzuki cross-coupling of the 2-bromo-pyridine derivative and benzo[*b*]thiophene-2-boronic acid. The complex  $\text{Os}(\text{tfmpy})_2(\text{medphp})_2$  has been previously characterized [5] while  $\text{Os}(\text{btp})_2(\text{CO})_2$  and  $\text{Ir}(\text{me btp})_3$  were synthesized using an adaptation of previously published techniques [6]. The structures of the complexes are shown in Fig. 1.

Three *cis* and two *trans* geometrical isomers are possible for  $\text{Os}(\text{btp})_2(\text{CO})_2$ . Crystals of the complex suitable for X-ray analysis were grown from methylene chloride and hexane. The X-ray structure of  $\text{Os}(\text{btp})_2(\text{CO})_2$  is illustrated in Fig. 2. The X-ray analysis resulted in two symmetrically unique compound molecules of the same connectivity with minor differences between them. Refinement data and selected bond angles and lengths of both structures are listed in the supplementary materials (Table 1). X-ray analysis confirms  $\text{Os}(\text{btp})_2(\text{CO})_2$  as octahedral and as the *cis* isomer. The CO ligands are *trans* to the pyridine moiety of btp and the two carbanions are *trans* to each other for both symmetry unique molecules. The arrangement is unusual for osmium complexes of this type as the strong  $\pi$  acceptor often bonds *trans* to the strong electron donor. The Os–CO bond lengths are shorter than the Os–C<sub>btp</sub> bonds. The Os–CO bond lengths indicate strong interaction between the Os d and the CO  $\pi$  which is consistent with IR CO stretch frequencies of 1994 and 1924  $\text{cm}^{-1}$ .



**Fig. 2.** X-ray structure of  $\text{Os}(\text{btp})_2(\text{CO})_2$  with 50% probability ellipsoids. Solvent and hydrogen atoms removed for clarity.



**Fig. 3.** Absorbance of  $\text{Ir}(\text{me btp})_3$  (blue dotted line) and  $\text{Os}(\text{btp})_2(\text{CO})_2$  (green solid line). Emission in deoxygenated methylene chloride of  $\text{Ir}(\text{me btp})_3$  (magenta dotted line) and  $\text{Os}(\text{btp})_2(\text{CO})_2$  (orange solid line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

$\text{Os}(\text{btp})_2(\text{CO})_2$  exhibited absorptions at 289 nm ( $\epsilon = 26,000 \text{ L mol}^{-1} \text{cm}^{-1}$ ), and 398 nm ( $\epsilon = 12,000 \text{ L mol}^{-1} \text{cm}^{-1}$ ) and emission at 581 and 630 nm (Fig. 3) with an emission lifetime of 53.2  $\mu\text{s}$ .  $\text{Ir}(\text{me btp})_3$  (*fac*-isomer) exhibited absorption at 296 nm ( $\epsilon = 60,000 \text{ L mol}^{-1} \text{cm}^{-1}$ ) and emission at 595 and 640 nm (Fig. 3) with an emission lifetime of 9.2  $\mu\text{s}$ . Both  $\text{Ir}(\text{me btp})_3$  and  $\text{Os}(\text{btp})_2(\text{CO})_2$  had similar emission profiles with a harmonic shoulder at lower energy, although the harmonic is much more pronounced for the osmium complex. The emission and long-lived lifetime indicates that luminescence occurs largely from the ligand centered (LC) state of  $\text{Ir}(\text{me btp})_3$  and  $\text{Os}(\text{btp})_2(\text{CO})_2$ .

Electrochemical properties of  $\text{Ir}(\text{me btp})_3$  and  $\text{Os}(\text{btp})_2(\text{CO})_2$  were measured in dry, deoxygenated acetonitrile, using a  $50 \text{ mV s}^{-1}$  scan rate, and calibrated to ferrocene.  $\text{Ir}(\text{me btp})_3$  exhibits a near reversible one electron oxidative process with oxidation onset at 633 mV (peak value,  $E_p = 780 \text{ mV}$ ,  $|E_{pc} - E_{pa}| = 63 \text{ mV}$ ) and an irreversible reduction peak ( $E_p$ ) at  $-2009 \text{ mV}$ , with reduction onset at  $-1932 \text{ mV}$ .  $\text{Os}(\text{btp})_2(\text{CO})_2$  exhibits a irreversible one electron oxidation process with oxidation onset at 721 mV ( $E_p = 840 \text{ mV}$ , irreversible) and a near reversible one electron reduction process

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