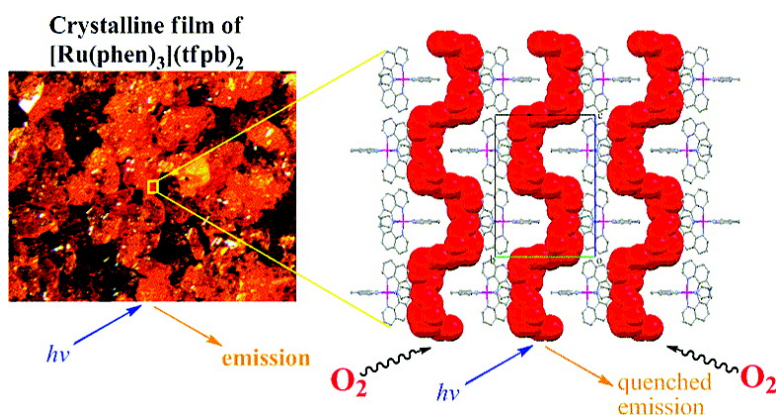


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## Porous Crystalline Ruthenium Complexes Are Oxygen Sensors

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Transition-metal complexes have long been used as oxygen sensors in solution, polymer films, or sol gels.<sup>1</sup> Sensors based on the Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy = 2,2'-bipyridine) lumophore that undergoes efficient quenching via energy transfer to produce singlet oxygen have been commercialized<sup>2</sup> for dissolved oxygen (DO) measurements in aqueous solutions. The Ru(bpy)<sub>3</sub><sup>2+</sup> ion can also be used as a solid-state sensor by adsorption to the large internal surface areas of zeolitic materials<sup>3</sup> to give composites that allow nearly "solution-like" diffusional oxygen quenching. DO measurements with these systems are complicated by matrix effects: multiple sites that are quenched to differing extents<sup>4</sup> and by decomposition reactions initiated by the high-energy singlet oxygen produced in the quenching events.<sup>5</sup>

Our recent work with vapochromic complexes<sup>6</sup> suggested that DO measurements could be improved if oxygen molecules could diffuse in and out of a nanoporous crystalline lumophore with a significant fraction of void space. The crystallographically imposed site symmetry contrasts the multiple sites present in amorphous matrices, a distinct advantage for studies of the quenching processes. Single-crystal studies could even be envisioned. The careful design of crystalline matrices (i.e., incorporation of inert fluorine phases<sup>7</sup>) could also mitigate decomposition modes and increase the solubility and perhaps the diffusivity of oxygen molecules in crystals of this type.

To test these ideas, we screened<sup>8</sup> several simple salts of Ru(bpy)<sub>3</sub><sup>2+</sup> and Ru(phen)<sub>3</sub><sup>2+</sup> and three substituted tetraphenyl-borate salts<sup>8</sup> for solid-state emission quenching by air. Freshly grown crystals were pressed into the surface of a "perfect scatter" Fluorolon target<sup>8</sup> and the absolute emission quantum yield<sup>8</sup> ( $\lambda_{\text{ex}} = 400 \text{ nm}$ ) was measured under nitrogen and in air. As expected, all of the compounds emit in the solid state, but surprisingly, even the simple salts (ClO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and BF<sub>4</sub><sup>-</sup>) showed some emission quenching in air relative to nitrogen; two of the substituted tetraphenylborate salts showed much better behavior.

These salts show (Figure 1) a monotonic increase in the fraction quenched,  $\Delta\phi/\phi_0$  (defined as:  $1 - (\phi_{\text{air}}/\phi_{\text{nitrogen}})$ ) with the fraction of void space calculated from X-ray structural data.<sup>8</sup> This result suggests that void space is important for oxygen quenching in these systems, particularly in the case of [Ru(phen)<sub>3</sub>](tfpb)<sub>2</sub> (phen = 1,10-phenanthroline; tfpb<sup>-</sup> = tetrakis(bis-3,5-trifluoromethylphenyl)borate) where the channels (Figure 2) could allow oxygen molecules to freely move in the crystals.

The quenching process(es) in [Ru(phen)<sub>3</sub>](tfpb)<sub>2</sub> was examined further. A gas mixing apparatus<sup>8</sup> constructed with mass-flow control valves was used to produce specific concentrations of oxygen in nitrogen at atmospheric pressure. Emission intensity data for microcrystalline [Ru(phen)<sub>3</sub>](tfpb)<sub>2</sub> were collected and are displayed as a Stern–Volmer (SV) plot ( $I_0/I$  vs mole fraction of oxygen, ○

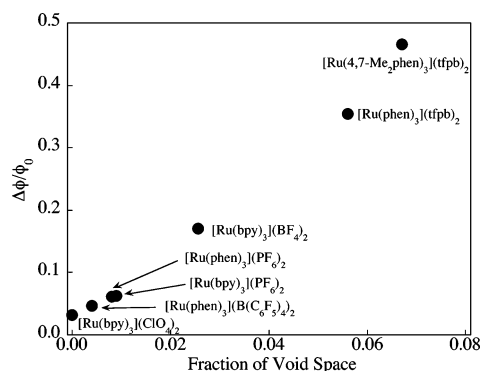


Figure 1. Graph of  $\Delta\phi/\phi_0$  vs void space for some Ru(pp)<sub>3</sub><sup>2+</sup> salts.

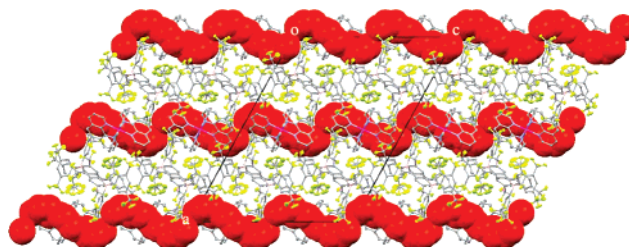


Figure 2. View down the *b*-axis showing alternating layers of cations and anions. The void space channels (red spheres, 136 Å<sup>3</sup> per Ru) run through the cationic layers. Hydrogen atoms are omitted for clarity.

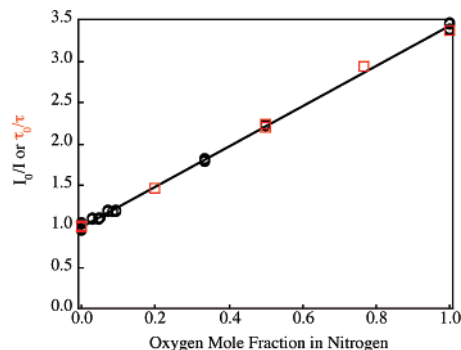
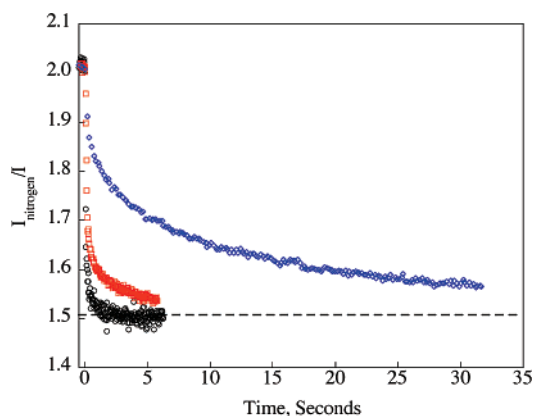


Figure 3. Stern–Volmer plot of  $I_0/I$  (○) and  $\tau_0/\tau$  (□) vs oxygen mole fraction for [Ru(phen)<sub>3</sub>](tfpb)<sub>2</sub>.

points) (Figure 3) with strictly linear ( $R^2 = 0.9996$ ) behavior and a slope of 2.43. A second SV determination nearly a year later with the same sample but with a slightly different apparatus gave a slope of 2.41, identical within experimental error. Microscopic examination<sup>8</sup> of the sample before and after the SV studies showed no apparent decomposition or change in crystallinity; long-term stability tests under continuous illumination in the presence or absence of oxygen over a 24 h period showed no change in emission

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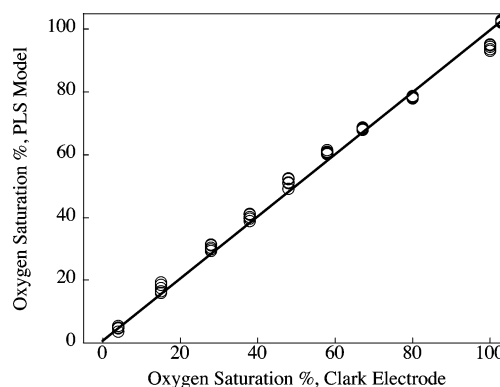


**Figure 4.** Plot of  $I_{\text{nitrogen}}/I$  vs time for air pressure jump from 2 to 1 atm. The  $\diamond$ ,  $\square$ , and  $\circ$  points are 518, 470, and 400 nm excitation, respectively; dashed line is the  $I_{\text{nitrogen}}/I$  infinity value for all data.

intensity. A second sample was used for many oxygen-sensing experiments for more than a year with no apparent change in responsivity.

Our conjecture that oxygen molecules diffuse in and out of  $[\text{Ru}(\text{phen})_3](\text{tfpb})_2$  crystals is supported by lifetime and pressure jump experiments. SV quenching determined by emission intensity can (among other things) be a result of static quenching, diffusional quenching, or both. Solid-state emission lifetime measurements<sup>8</sup> of  $[\text{Ru}(\text{phen})_3](\text{tfpb})_2$  show that the emission can be fit at all oxygen concentrations for at least 6 half-lives to a single-exponential decay ( $\tau = 640$  nsec under pure nitrogen) that is significantly faster ( $\tau = 190$  nsec) under pure oxygen. The observation of a single-exponential decay suggests that identical emitting sites in one crystalline phase produce the emission and the oxygen concentration is uniform at least throughout the penetration depth of the light. The SV plot for these lifetime data (Figure 3,  $\square$ ) is linear and shows the same  $K_{\text{sv}}$  as the intensity data. The agreement in  $K_{\text{sv}}$  for the two techniques shows that the quenching is dynamic in nature. Previous studies<sup>9</sup> of solid-state emission from several  $\text{Ru}(\text{bpy})_3^{2+}$  salts that vary the Ru–Ru distance suggest that excitonic hopping of the excited-state to trapped oxygen molecules is too slow ( $D \approx 10^{-14}$   $\text{cm}^2/\text{s}$ ) to account for the quenching in solid  $[\text{Ru}(\text{phen})_3](\text{tfpb})_2$ ; internal oxygen molecule diffusion was confirmed by pressure jump experiments.<sup>8</sup>

A crystalline sample of  $[\text{Ru}(\text{phen})_3](\text{tfpb})_2$  was pressurized with air to about 2 atm in a pressure cell that allowed “front face” emission spectra to be acquired as a function of time. At time zero the pressure was allowed to escape ( $t_{1/2} = 5$  ms) back to 1 atm and the emission spectra as a function of time were acquired. Plots of  $I_{\text{nitrogen}}/I$  vs time are shown in Figure 4. The time for  $1/2$  response,  $t_{1/2}$  for 400 nm excitation is  $<20$  ms and the characteristic shape of the  $I_{\text{nitrogen}}/I$  vs  $t$  curve expected for a diffusional process is readily apparent (fast change at early times with a characteristic long tail at later times). The apparent diffusion time was increased (at 470 nm,  $t_{1/2} = 120$  ms; at 518 nm,  $t_{1/2} = 2200$  ms) by changing the excitation to longer wavelengths where the extinction coefficient is significantly smaller and the penetration depth of the light is greater. These measurements are consistent<sup>8</sup> with an oxygen diffusion coefficient on the order of  $10^{-7}$ – $10^{-8}$   $\text{cm}^2/\text{s}$  in the solid. Further data analysis is planned to fit these curves to the characteristic functions previously used by Demas et al.<sup>10</sup> in their study of oxygen diffusion in polymer films.



**Figure 5.** Plot of the oxygen saturation level from a PLS model vs that measured by a Clark electrode. Each concentration was measured five times.

Dissolved oxygen (DO) sensing in aqueous media is an important application for oxygen sensing materials.<sup>11</sup> A fiber optically coupled ball probe<sup>8</sup> with a thin film of crystalline  $[\text{Ru}(\text{phen})_3](\text{tfpb})_2$  deposited on the end was immersed in water saturated with different oxygen/nitrogen mixtures. The percent oxygen saturation from a partial least-squares (PLS) model calibrated against a Clark DO electrode is shown in Figure 5. The close agreement is evident.

In summary, we have shown that crystals of emissive ruthenium complexes with significant void space are oxygen sensors.  $[\text{Ru}(\text{phen})_3](\text{tfpb})_2$  with the partially fluorinated  $\text{tfpb}^-$  counterion shows simple behavior as a gas phase and aqueous solution oxygen molecule detector. The linear SV plots for both emission intensity and emission lifetime measurements and the pressure jump studies are readily explained by assuming that oxygen molecules enter the crystal lattice of  $[\text{Ru}(\text{phen})_3](\text{tfpb})_2$  and are able to diffuse internally with an effective diffusion coefficient on the order of  $10^{-7}$ – $10^{-8}$   $\text{cm}^2/\text{s}$ .

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**Supporting Information Available:** Synthesis and characterization information; experimental details for emission, lifetime, and pressure jump experiments; additional references; X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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