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Concurrent Sensing of Benzene and Oxygen by a Crystalline Salt of Tris(5,6-dimethyl-1,10-phenanthroline)ruthenium(II)

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The complex $[Ru(5,6\text{-}Me_2Phen)_3]tfpb_2$ has been examined as a solid-state benzene and oxygen sensor. The crystalline solid undergoes a reversible vapochromic shift of the emission λ_{max} to higher energy in the presence of benzene. Additionally, in the presence of oxygen the solid exhibits linear Stern-Volmer quenching behavior. When simultaneously exposed to benzene vapor and oxygen the crystals uptake benzene which inhibits the diffusion of oxygen in the lattice; very little quenching is observed. However, when benzene is removed from the carrier gas, partial loss of benzene occurs and oxygen diffusion is restored resulting in quenching of the emission. The practicality of this crystalline solid as a benzene sensor was investigated by examination of a lower concentration of benzene vapor (0.76%).

Transition-metal complexes that exhibit low-lying excited states [i.e., metal-to-ligand charge-transfer (MLCT) excitations] can make them particularly well-suited for the detection of small molecules with environmental or industrial relevance.[1−3] Optical sensors built around metal complexes of this type have become increasingly popular.[1c,2] The detection of gases with crystalline platinum salts that can uptake volatile organic compounds (VOCs)[4] has been an area of interest to us for several years. The reversible change in the unit cell composition results in a perturbation of the Pt−Pt distance, which controls the color of the complexes ("vapochromism").[5] Many of these compounds also show a dramatic reversible shift in the position and/or intensity of the luminescence ("vapoluminescence") that may be excited by light-emitting diodes and detected with inexpensive photodiode array spectrometers.

More recently, we have reported an alternative to the currently used polymer-supported sensors for luminescence quenching-based oxygen detection that relies on crystalline salts of $Ru(phen)_3^{2+}$. These salts have void space channels that allow oxygen to diffuse freely through the crystal to quench the luminescence.[6] These channels are produced by the poor packing of bulky anions with the propellor-shaped cations.[6]

We hypothesized that these two crystalline sensing systems might be combined into a single system that could sense VOCs and oxygen through their respective mechanisms by choosing a solvatochromic chromophore (MLCT) with a long lifetime that could undergo oxygen quenching but also exhibit a vapoluminescent shift upon solvent molecule uptake into the crystal lattice. The melding of these two sensor mechanisms into a functioning example has been realized. We report here the preliminary investigation of $[Ru(5,6\text{-}Me_2Phen)_3](tfpb)_2$ (5,6-Me_2Phen = 5,6-dimethyl-1,10-phenanthroline; $tfpb^-$ = tetrakis(bis-3,5-trifluoromethylphenylborate), a crystalline complex that senses benzene and oxygen, simultaneously, by different mechanisms (see Figure 1).

$Ru(5,6\text{-}Me_2Phen)_3(Cl)_2$ was synthesized by a standard method[7] and converted to the $tfpb^-$ salt, which was characterized by ^1H NMR and an X-ray crystal structure (vida infra). The emission behavior of a solvent-free crystalline sample of $[Ru(5,6\text{-}Me_2Phen)_3](tfpb)_2$ in the presence of

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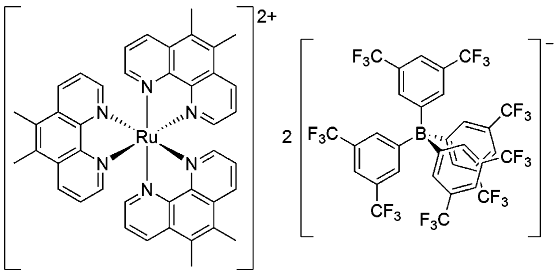

Figure 1. Structure of [Ru(5,6-Me_2Phen$)_3$](tfpb$)_2$.

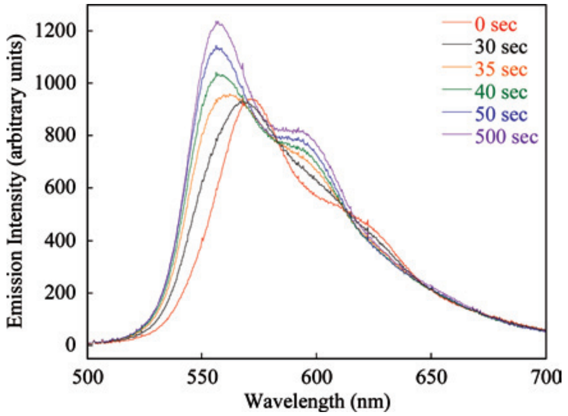

Figure 2. Emission spectral change that results from [Ru(5,6-Me_2Phen$)_3$](tfpb$)_2$ in the presence of nitrogen saturated with benzene.

different oxygen concentrations in nitrogen was investigated. Significant quenching of the solid-state emission was observed, and the resulting Stern−Volmer plot (Supporting Information) is linear with a slope of 0.83.[8] The slope is less than that found for the recently studied [Ru(phen$)_3$](tfpb$)_2$ system, but [Ru(5,6-Me_2Phen$)_3$](tfpb$)_2$ is still a significant oxygen sensor relative to many of the solid ruthenium polypyridine complexes that we examined.[6]

A sample was then studied to measure the spectroscopic changes in the emission spectrum in the presence of benzene. The microcrystalline solid was finely ground to maximize the surface area and then placed in a small depression in the center of a 100 °C thermistor. After an initial heating cycle to 100 °C, followed by cooling to room temperature, the sample was exposed to nitrogen gas saturated with benzene vapor. The resulting spectral changes are shown in Figure 2. A fast spectral change that is dominated by a shift in λ_{max} from 572 to 558 nm is apparent. This change is fast (less than 50 s to reach 90% of the total change). The reverse process that results from purging of the benzene-loaded sample with pure nitrogen is slower (1 h to reach 90% of the total change). The sample can be repeatedly cycled with no loss of emission intensity. Heating the benzene-loaded sample with the thermistor results in a much more rapid reversal (90 s, including cooling time) to the solvent-free state; again, the sample may be cycled repeatedly. Of initial interest here is the cause of the large reversible shift in the emission λ_{max}. We suggest that this spectral change is a vapoluminescence effect that occurs as a result of the interaction of benzene with the luminescent cation.

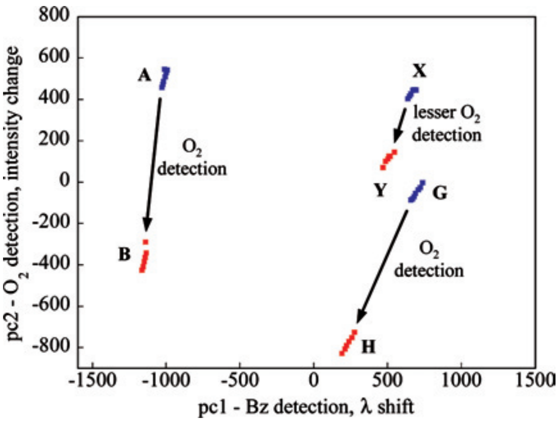

Figure 3. PCA score plot. Blue squares indicate data collected under nitrogen, and red squares indicate data collected under air.

To determine the applicability and cross-sensitivities of [Ru(5,6-Me_2Phen$)_3$](tfpb$)_2$ for the simultaneous sensing of benzene and oxygen, a series of emission spectra were taken while cycling between the carrier gases (either air or nitrogen), benzene vapor plus the carrier gas, and again the carrier gas after exposure of the crystals to benzene (see the Supporting Information for more detail). A total of 13 cycles (6 with air and 7 with nitrogen) for a total of 39 spectra were taken over a period of 2 h. These data were analyzed via a principle component analysis (PCA; for more details, see the Supporting Information). Almost all of the variance (98%) was modeled with two principle components. A score plot (score 2 vs score 1) is shown in Figure 3. The data show a high degree of reversibility, and the six different data clusters that correspond to each of the six different conditions generated by the experimental design are apparent. The small systematic drift of data points within each cluster may be due to a slight loss in reversibility due to the rapid heating employed. The loading plots of score 1 and score 2 show that score 1 is associated with benzene sensing (a spectral shift) and score 2 (an intensity change) with oxygen sensing. Switching the nonsolvated form from a nitrogen atmosphere to air (cluster A to B) causes a large shift along the score 2 axis, consistent with the simple Stern−Volmer oxygen-sensing behavior reported above. A similar exposure change between nitrogen and air but with the carrier gas saturated with benzene (cluster X to Y) results in a much smaller excursion along the score 2 axis, with both conditions significantly shifted along the score 1 axis. Finally, the prior loading of benzene into the sample with nitrogen followed by the removal of benzene from the purge at room temperature results in a change from cluster X to G; a subsequent change in the purge gas between nitrogen and air without benzene in the purge (cluster G to H) retains a similar large excursion along score 1, but now the large change along the score 2 axis is mostly restored.

A model that is consistent with this sensing behavior can be formulated by examining the X-ray crystal structure of [Ru(5,6-Me_2Phen$)_3$](tfpb$)_2$. Solvated crystals that contain half-occupied CH_2Cl_2 and 1.5 benzene molecules per Ru unit were grown by slow evaporation of a CH_2Cl_2/benzene solution. The structure consists of discrete cations and anions

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[8] Oxygen concentration is expressed as the mole fraction in nitrogen at an atmospheric pressure of 0.97 atm.

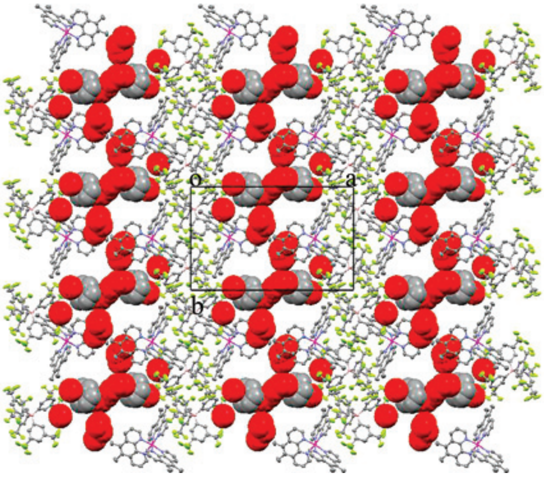

Figure 4. View down the *c* axis of the **Ru·1bz** phase showing the channels running through the structure. The red spheres represent void space, while the gray spheres represent benzene molecules. Hydrogen atoms are omitted for clarity.

separated by the benzene molecules, which lie in a channel, and the methylene chloride molecules, which occupy isolated void chambers in the structure. One of the benzene molecules is ordered, while the other is approximately centered in the channel and is highly disordered over a special position. This disordered benzene molecule was removed from the structure with PLATON SQUEEZE to improve the structural refinement.[9] We suggest that the disordered benzene molecule is not tightly held and easily leaves the crystal lattice under a carrier gas flow absent of benzene vapor; the second, ordered benzene is held much more tightly by the lattice and is lost much more slowly. Additional details of the crystal structure refinement can be viewed in the Supporting Information. These structural data are consistent with three different benzene solvation states for the crystalline solid (after the methylene chloride is removed and never replaced) that are produced in the sensing experiments: one state that contains no benzene (**Ru·0bz**, where Ru is [Ru(5,6-Me_2Phen)$_3$]-(tfpb)$_2$) is formed under pure carrier gas prior to benzene exposure; a fully solvated form with 1.5 benzene molecules per Ru (**Ru·1.5bz**) formed when the carrier gas is saturated with benzene vapor; and an intermediate form that contains only the tightly held benzene molecule (**Ru·1bz**), which is formed under pure carrier gas after benzene exposure (see Figure 4).

The behavior of the emission data illustrated in the score plot can be understood within the structural context if the oxygen diffusion though the crystalline solid is significant for the form with no benzene (A = **Ru·0bz**) or with only the tightly held benzene molecule (G = **Ru·1bz**) present. In these two cases, a significant channel is still present in the solid for oxygen molecules to diffuse through to enable emission quenching. If the last benzene is loaded into the crystal to form the **Ru·1.5bz** phase (cluster X), the channel is significantly blocked and the oxygen diffusion is greatly diminished. Again, all three of these forms can be interconverted and tested for oxygen sensing by exposure of the crystalline solid to a proper sequence of carrier gas/benzene/heating.

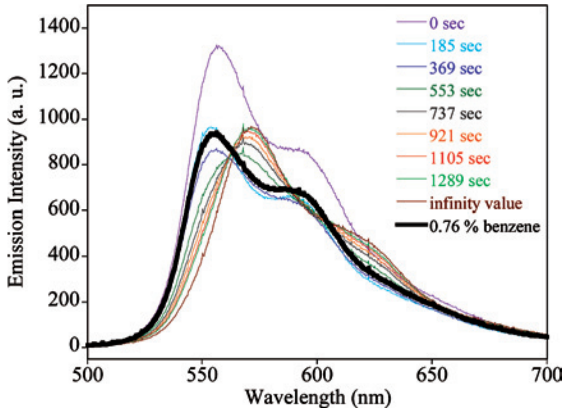

Figure 5. Plot showing loss of benzene from **Ru·1.5bz** to **Ru·1bz** (spectra at 0 and 185 s) and from **Ru·1bz** to **Ru·0bz** (spectra at 185 s to infinity) under air flow. The spectrum for detection of 0.76% benzene (thick black line) is very near the **Ru·1.0bz** form (185 s).

Of final interest is an estimation of the sensitivity of Ru(5,6-Me_2Phen)$_3$](tfpb)$_2$ to lower levels of benzene. Assuming the vapor pressure of benzene at 20 °C is ~75 Torr with an atmospheric pressure at 760 Torr, the concentration of benzene in a saturated nitrogen stream is about 9.9%, a very high value. A lower concentration was made by saturating a known gas flow with benzene by bubbling the gas through liquid benzene and then diluting this stream with a much larger known flow of carrier gas. By this method, the sensitivity of the vapochromic shift of Ru(5,6-Me_2Phen)$_3$](tfpb)$_2$ was investigated at a lower concentration of 0.76% (7600 ppm).[10] Relative to the 9.9% data, a slower response was observed. Including the data for the full response of the 0.76% point in a PCA study of the time response of the sample to the 9.9% benzene concentration suggests that approximately the same level of change is observed for 0.76% as for **Ru·1bz** (Figure 5). Thus, we infer that a greatly improved version of Ru(5,6-Me_2Phen)$_3$](tfpb)$_2$ might allow optical measurement of low concentrations of benzene in air.[10] Further studies to fully explore the benzene sensing properties of Ru(5,6-Me_2Phen)$_3$](tfpb)$_2$ are underway.

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Supporting Information Available: Synthesis and characterization, experimental details for emission experiments, Stern−Volmer plot, crystal structure refinement and disorder modeling details, and X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) This compares with a flammable limit of 120 000 ppm, an immediately dangerous to life or health (IDLH) level of >1000 ppm, and an occupational exposure limit (OEL) of 0.5 ppm. *Benzene*; CHEMINFO, Canadian Centre for Occupational Health and Safety, http://ccinfoweb2.ccohs.ca (accessed 8/29/08).