
Luminescent Gold Compounds in Optical Oxygen Sensors

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The use of luminescent gold(I) phosphine complexes as oxygen sensors is reported. Room temperature phosphorescent-based sensors have advantages over those based on fluorescence, and they have significant potential for development in clinical applications.

The ubiquitous Clark cell may soon be usurped as *the* device for making dissolved or gaseous measurements of oxygen partial pressure, P_{O_2} , in blood, water or air. For too long now the problems of electrical interference, bulkiness, drifting signals and expense have been tolerated in the Clark cell - it may no longer be the best technology available for its cost - its challenger, albeit in its infancy, is the optical oxygen sensor.

Most optical oxygen sensors comprise a light source (common, cheap LED's can be used), a light detector (a photocell), and a cheap, disposable, fibre optic with its distal end coated with a transducer which can produce an optical signal which reflects the ambient partial pressure of oxygen, whether it be dissolved or gaseous. The key ingredient in the sensor is the transducer, elegant in its simplicity, consisting of a luminescent compound encapsulated in a gas-permeable polymer film. Suitable polymers, permeable towards oxygen, include PVC, perspex, polystyrene and silicone rubber. The luminescent compound, on the other hand, has to be special; it must be soluble in polymer solutions and photostable and, most important of all, its luminescence must be readily, but not too readily, quenched by oxygen.

The transducer element of such oxygen optical sensors works on the principle that the luminescence (generated by excitation by light from the light source and measured with the photodetector) from the encapsulated compound is quenched by oxygen in a manner which is described by the Stern-Volmer equation, *ie*

$$I_0/I = 1 + K_{SV} \cdot P_{O_2} \quad (1)$$

where I_0 and I are the intensities of luminescence in the absence and presence of oxygen at a partial pressure P_{O_2} , respectively, and K_{SV} is the Stern-Volmer constant which depends directly upon the rate constant for diffusion of oxygen, the solubility of oxygen and the natural lifetime, τ_0 , of the electronically-excited state of the lumophore in the plastic medium. Thus, by using a suitably calibrated device, a simple measurement of I can be easily related to the ambient partial pressure of oxygen. A rough guide to the sensitivity of an optical oxygen sensor is $P_{O_2}(S=1/2)$, the value of the partial pressure of oxygen necessary to reduce the initial (oxygen free) luminescence exhibited by the film by 50%. From Equation 1 it follows that $P_{O_2}(S=1/2) = 1/K_{SV}$.

A wide range of fluorescence quenching-based sensors have been reported (1) but many appear of limited use due to: (i) having either too high or too low an oxygen sensitivity, (ii) the requirement of excitation by UV light, and/or a poor photostability. Thus, until recently the search for suitable luminescent compounds for the transducing element of oxygen optical sensors had uncovered few possibilities. The most popular of these to date are tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) and tris(1,10-phenanthroline)ruthenium(II), $[Ru(dpp)_3]^{2+}$ (1, 2). However, the latter complex, and related bipyridyl complexes, have short natural lifetimes (typically $< 5\mu s$); the shorter τ_0 , the lower is K_{SV} , and the less sensitive the sensor is towards changes in P_{O_2} . In

addition, the latter complexes are very water soluble, and special measures have to be taken in order to incorporate them into the hydrophobic medium of most polymers.

Room temperature phosphorescence (RTP) quenching-based sensors have become the focus of recent attention as they have several advantages over those based on fluorescence. The longer excited-state lifetimes of phosphorescent indicators give rise to a high quenching efficiency by oxygen. In addition, the long excitation and emission wavelengths are more compatible with available optical monitoring technology. Most recently, RTP quenching-based sensors have utilized metal chelates such as tetrakis(pyrophosphito)dipalladium(II) (3) and 8-hydroxy-7-iodo-5-quinoline sulfuric acid (ferron) chelates (4) and a range of modified Pd(II) and Pt(II) porphyrins (5, 6).

It appears that many binuclear and polynuclear gold(I) compounds with close Au...Au contacts exhibit strong visible luminescence when excited in the UV (7-10). More recently, three coordinate mononuclear gold(I) compounds have also been synthesized which luminesce strongly both in the solid state and, in some cases, in solution (11-15). The typically long excited state lifetimes (4 - 200 μ s) (11, 16) and large spectral Stoke's shifts observed for many of these trigonal gold(I) compounds suggest that the emission associated with them is phosphorescence and it has been assigned to the metal-centred triplet to singlet transition $p_z \rightarrow d_\sigma$ (11).

We have recently (17) synthesised two novel lipophilic, luminescent gold(I) complexes: an eight-membered ring structure containing two gold metal centres, bis{ μ -(bis(diphenylphosphino)octadecylamine-P,P')}diiododigold(I), referred to as JM6277, and a tripod structure containing one gold centre, 1,1,1-tris(2-diphenylphosphinitomethyl)ethanegold(I) chloride, referred to as JM6280. The structures of these two complexes are illustrated in Figures 1(a) and 1(b), along with their observed luminescence responses towards different levels of oxygen when encapsulated in a thin, 20 μ m, polystyrene film. Table 1 summarizes the UV/visible absorption and emission characteristics of JM6277 and JM6280, together with those of the more traditionally used [Ru(dpp)₃]²⁺ complex and the measured values of $P_{O_2}(S = 1/2)$ when these complexes are encapsulated in polystyrene. From the results of this work, it appears that both JM6277 and JM6280 can be used to generate optical oxygen sensors which are more sensitive than a similar [Ru(dpp)₃]²⁺-based sensor. The response and recovery of the two gold

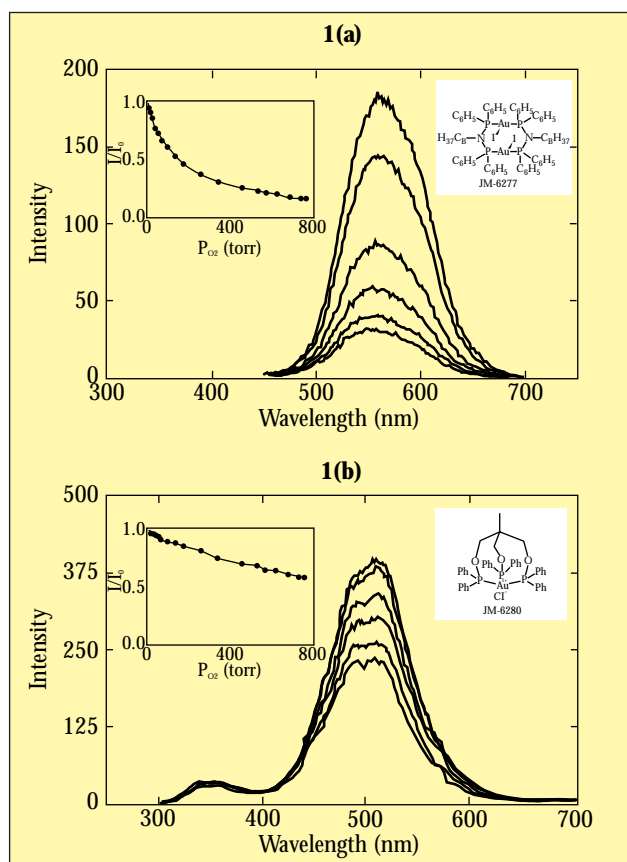


Figure 1 (a) Diagram illustrating the variation in emission spectrum for gold complex JM6277 when exposed to the following P_{O_2} levels (from top to bottom): 0, 34, 160, 319, 555 and 760 torr; the left-hand side insert diagram illustrates the subsequent plot of the data in the form of relative emission intensity (I/I_0) versus P_{O_2} ; the structure of the gold complex is illustrated on the right-hand side of the diagram. (b) Similar diagram as in (a) but for gold complex JM6280.

complex based films, towards a change of P_{O_2} from 0 to 100% O_2 and 100% to 0% O_2 , respectively, are both rapid (26s response and 100s recovery for JM6277 and 23s response and 71s recovery for the less sensitive JM6280) and reversible. The films show no deterioration in response when exposed to alternating atmospheres of oxygen and nitrogen over many hours and can be stored without appreciable deterioration in the dark and in the freezer section of a fridge for many months. It is worth noting at this point that the mechanism for quenching is not known and that other small gaseous molecules, such as NO and SO_2 , also may quench the emission of gold(I) complexes of the type described here.

The measurement of oxygen is essential in many

Table 1 Photochemical characteristics of JM6277, JM6280 and [Ru(dpp)₃]²⁺ encapsulated in polystyrene as optical oxygen sensors

Luminescent compound	τ_o / μ s	λ_{max} (absorption) /nm	λ_{max} (emission) /nm	P _{O₂} (S=1/2) /torr
JM6277	9.8	418	530	187
JM6280	3.1 (12.2)*	283	501	1110
[Ru(dpp) ₃] ²⁺	5.4	460	613, 627	5800

* Exhibits a biexponential

industries, especially those which utilize metabolizing species, such as those based on biotechnology. However, nowhere is the measurement of dissolved oxygen levels more important than in Clinical Analysis and the measurement of P_{O₂} in blood. Optical oxygen sensors offer the possibility of routine cheap, remote and continuous patient bedside monitoring. Indeed, optical sensors in general, offer the possibility of the routine continuous monitoring of many analytes of physiological significance, such as P_{O₂}, pH and P_{CO₂} - a situation which is usually considered the preserve of intensive care, such has been the cost of the instrumentation involved. Only time, and research, will tell if optical oxygen sensors of this type can live up to their initial promise. If so, precious metal complexes, including gold based complexes, will be a key component (1).

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