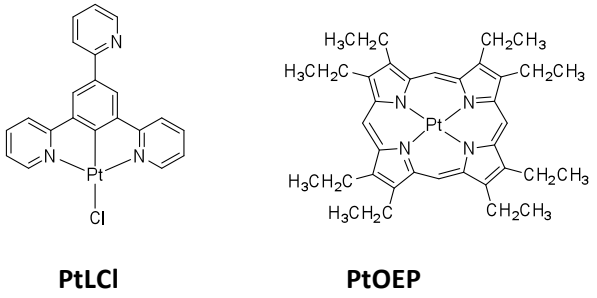
A new combination of lumophores has enhanced O_2 sensitivity with a visual sensor which manifests as a red, yellow, or green glow depending on O_2 concentrations.[1] The first chemical of interest is platinum(II)-1,3,5-tri-(2-pyridyl)benzene, or PtLCl for short. The second acting molecule is platinum ocatethylporphyrin (Platinum(II) 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin), also known as PtOEP (Fig 1). The novelty of the idea is the combination of the action of these two lumophores, which fluoresce at different O_2 concentrations due to drastic differences in emission spectra as complete or partial luminescence quenching of one or both of the sensing molecules occurs.[2] Up until now, most studies of luminescence have focused on obtaining accuracy of O_2 concentrations with a single lumophore. This particular sensor has been referred to as a "traffic light" because it transitions from red at 0-5% O_2, to yellow in the range of 5-10% O_2, and transitions to green in the range of 30-100% O_2. While useful in many different commercial technologies, a specific niche which relies on this assessment of O_2 levels is modified atmosphere packaging (MAP).[3] MAP can greatly extend product shelf-life by encompassing the food with a specified atmosphere.The ratio of 2 mg of lumophore per 1 gram of polymer solution is recommended in commercial sensing applications.[4] Ideally, to prevent bacterial growth, meats are to be maintained under high oxygen pressure of around 60-85%, quickly and easily assessable with integration of this sensor inside the packaging. Both of these molecules offer new benefits in the food industry because neither poses any known health risks.[5]



PtLCl **PtOEP**

Fig 1. The chemical structure of O_2 sensor lumophores.

1 R. C. Evans, et al.(2006). Novel Luminescence-Based Colorimetric OxygenSensor with a "Traffic Light" Response. *Journal of Fluorescence* **16**(2), 201-207

2 P. Douglas and K. Eaton (2002). Response characteristics of thin film oxygen sensors, Pt and Pdoctaethylporphyrins in polymer films, *Sens. Actuators B* **82**(1–3), 1–9.

3 M. Smolander, E. Hurne, andR.Ahvenainen (1997). Leak indicators for modified-atmosphere packages.*Trends Food Sci*. **8**(4), 101–105.

4 R. N. Gillanders,M. C. Tedford, P. J. Crilly, and R. T. Bailey (2004).Thin film dissolved oxygen sensor based on platinum octaethylporphyrin encapsulated in an elastic fluorinated polymer. *Anal.Chim.Acta***502**(1), 1–6.

5 J. A. G. Williams, A. Beeby, E. S. Davies, J. A. Weinstein,and C. Wilson (2003). An alternative route to highly luminescentplatinum(II)complexes: Cyclometalation with NˆCˆNcoordinatingdipyridylbenzene ligands. *Inorg. Chem*. **42**(26),8609–8611.

The 1H and 13C NMR spectra for the two lumophores, including NOESY and COSY, were recorded on a Varian 400- or 500-MHz instrument and referenced to residual protiosolvent resonances (Tables 1,2). Coupling constants are in Hertz. Electrospray ionization (EI) mass spectra of ligands were acquired on a time-of-flight Micromass LCT spectrometer. All solvents used in preparative work were at least Analar grade, and water was purified using a Purite system. Solvents used for optical spectroscopy were high performance liquid chromatography grade.[6] Both lumophores can be excited in the near-UV-blue spectral region but exhibit very different molar extinction coefficients, PtOEP being greater than PtLCl. In the absence of oxygen, independent luminescence from both species is observed indicating that there is no interaction between the lumophores in the two layers (Fig. 2). CIE *xy* colour coordinates were calculated using the secondary standard observer data for the PtOEP/ECPtLCl/EC sensor response at a series of oxygen concentrations and are shown in the *xy* chromaticity diagram (Fig 3).[7] Significant changes in the *xy* coordinates correspond to dramatic changes in colour in the diagram. In the absence of O2, emission from the PtOEP/EC layer is dominant due to its larger molar extinction coefficient in this sensor film and the *xy* coordinates lie in the red domain.

1H NMR of Lumophores	
PtLCl (400 MHz, CDCl3)	**PtOEP** (500 MHz, CDCl3)
8.75 (3H, d, 3*J*) 4.5 Hz, H6), 8.74 (3H, s, H2¢), 7.99 (3H, dd, 3*J*) 7.5 Hz, 4*J*) 1.0 Hz, H3), 7.81 (3H, td, 3*J*) 7.5 Hz, 4*J*) 2.0 Hz, H4), 7.29 (3H, ddd, 3*J*) 7.5 and 4.5 Hz, 4*J*) 1.0 Hz, H5)	8.78 (2H, dd, 3*J*) 5.0 Hz, 4*J*) 1.0 Hz, H6), 8.65 (1H, t, 4*J*) 1.5 Hz, H2¢), 8.40 (2H, d, 4*J*) 1.5 Hz, H4¢), 8.01 (2H, d, 3*J*) 8.0 Hz, H3), 7.89 (4H, m, Ha, H4), 7.73 (2H, d, 3*J*) 8.0 Hz, Hb), 7.67 (2H, dd, 3*J*) 8.0 Hz, 4*J*) 1.0 Hz, Hb¢), 7.48 (2H, t, 3*J*) 8.0 Hz, Ha¢), 7.36 (3H, m, Hc¢, H5).

Table 1.H NMR of the lumophores.

13C NMR of Lumophores	
PtLCl (CDCl3)	**PtOEP** (CDCl3)
157.1 (quat), 149.7 (C2), 140.5 (quat), 137.1 (C4), 126.3 (C6), 122.6 (C5), 121.2 (C3)	156.7, 142.3, 140.8, 140.7, 139.6, 138.0, 129.0 (Ca), 128.0 (Ca), 127.7 (Cb), 127.6 (Cc), 127.2 (Cb), 126.9 (C4), 125.0, 122.9 (C5), 121.6 (C3)

Table 2. C NMR of the lumophores.

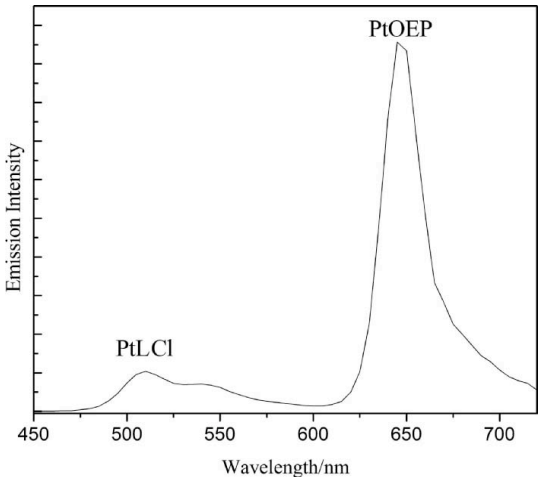


Fig. 2. Emission spectrum of PtOEP/EC-PtLCl/EC dual-lumophore sensors shows absorbances in the absence of oxygen at 295 K.

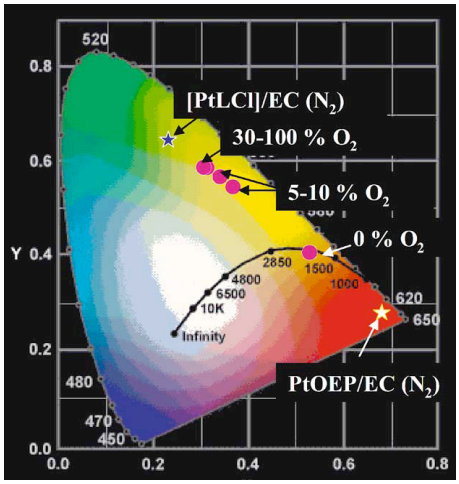
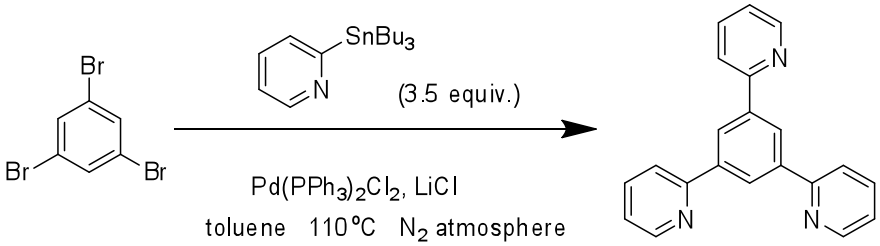


Fig. 3. CIE *xy* colour coordinates of the PtOEP/EC-PtLCl/EC dual-lumophore shows different sensor responses at different oxygen concentrations.

[6] Milgrom, L.R (1985). 1H and 13C NMR of platinum porphyrins-II. Platinum complexes of meso-tetrakis(3,5-di-t-butyl-4-hydroxyphenyl) porphyrin and 2,3,7,8,12,13,17,18-octaethylporphyrin. *Polyhedron*, **4** (7), pp. 1279-1282.

[7] Y. Le Grand (1957). Light, Colour and Vision, Chapman and Hall, London.

While there are numerous ways to generate the lumophores, the sensor undergoes a novel polymerization pathway in which to generate a functional oxygen sensor.[89] To generate the lumophore, toluene (15 mL) was added to a mixture of tbb(0.87 g, 2.76 mmol), 2-(tri-*n*-butylstannyl)pyridine (4.34 g of 81% purity, equivalent to 9.55 mmol, remainder mostly tetra-*n*-butyltin), lithium chloride (1.21 g, 38.6 mmol), and bis(triphenylphosphine)- palladium(II) chloride (154 mg, 0.22 mmol) contained in an ovendriedSchlenk tube. The mixture was degassed via five freezepump- thaw cycles and then heated at reflux under an atmosphere of dinitrogen for 20 h (Scheme 1). PtOEP was obtained from Porphyrin Products Ltd. O2 and N2 were BOC "high purity" gases and were used as received. Oxygen sensors were prepared by dissolving 2mg of lumophore in 2 ml THF and adding 0.4 ml of this solution to 1.0 g of a polymer solution, prepared by dissolving the polymer in an appropriate solvent to give solutions of similar viscosity as follows: EC in 10% (w/v) 80:20 toluene:ethanol and CAB in 20% (w/v) acetone.[1,10] Sensor films were prepared by spin coating these solutions on glass slides. The dual lumophore sensor was prepared by casting PtOEP-EC and PtLCl-EC as separate layers on the same glass support.[11] 11The PtOEP-EC layer was allowed to dry completely before casting the PtLCl-EC layer above it. For the dual-lumophore sensor, both PtLCl and PtOEP are quenched to some degree at all oxygen concentrations and correspondingly generate luminescence proportional to oxygen concentration.[12]



Scheme 1. One step synthesis of PtLCl ligand.

[8] S. J. Farley, D. L. Rochester, A. L. Thompson, J. A. K. Howard, and J. A. G. Williams (2005). Controlling emission energy, selfquenching and excimer formation in highly luminescent N^C^N coordinated platinum(II) complexes, Inorg. Chem.In press.

[9] K. Kalyanasundaram (1992). Photochemistry of Polypyridine and Porphyrin Complexes, Academic Press, New York, 500.

[10] D. B. Judd and G.Wyszecki (1962). Color in Business, Science and Industry, Wiley, New York.

[11] J. A. G. Williams, A. Beeby, E. S. Davies, J. A. Weinstein, and C. Wilson (2003). An alternative route to highly luminescent platinum(II) complexes: Cyclometalation with N^C^N coordinating dipyridylbenzene ligands. *Inorg. Chem.* **42**(26), 8609–8611.

[12] R. C. Evans and, P. Douglas (2006).Controlling the Color Space Response of Colorimetric Luminescent Oxygen Sensors.*Analytical Chemistry,* **78**(16), 645-5652